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ABSTRACT

Rippy, Janet Fairbanks Miles. Factors Affecting pH Establishment and Maintenance in Peat Moss-Based Substrates. (Under the direction of Paul V. Nelson)

Problems of inconsistent initial pH in peat moss substrates created using standard formulas for agricultural limestone additions, and substrate pH drift from the initial target may result from variations in the neutralization capacity of limestone and in the neutralization requirement of peat moss. This research was conducted to evaluate physical and chemical properties of limestone that may influence neutralization capacity, and properties of peat moss that may influence neutralization requirement. Limestones from twenty North American quarries were wet-sieved into eight particle diameter fractions (600 to < 38 µm). Specific surface of limestone particles was measured for each fraction. Reaction times were determined on three limestone particle size fractions. Particle size distribution, $CaCO_3$ and $MgCO_3$ contents, internal porosity, hardness, soundness, specific gravity, and specific surface were analyzed in multiple regressions with particle size included and also held constant at three size fractions to evaluate effects on limestone neutralization capacity. Peat moss samples were selected from Alberta, Canada bogs to represent the maximum range of species composition and the decomposition range (H1.5 to H4.0) used for commercial horticulture. Peat moss cation exchange capacity, base and iron saturation, inherent pH, buffer capacity and neutralization requirement were measured. These properties were analyzed in a multiple regression along with species composition, degree of decomposition, and detritus to determine effects on peat moss neutralization requirement. Limestones differed significantly in specific surface for each particle diameter fraction and in reaction times. There were significant variations in cation exchange capacity, base saturation, inherent pH, buffer capacity and neutralization requirement of peat mosses. Neutralization requirement was negatively correlated with base saturation, inherent pH, decomposition, [Fe^{2+}], and sedge; and was positively correlated with *S. angustifolium*. *Sphagnum* species influenced cation exchange capacity, base saturation, and inherent pH. Inherent pH was most influenced by base saturation. Peat moss samples containing large amounts of *S. fuscum* had high

cation exchange capacity and base saturation, and low degrees of decomposition. Adding specific surface measurements to those of particle size distribution and $CaCO_3$ content will further characterize limestone neutralization capacity; however, the problem of inconsistent initial pH can be better managed by understanding the inherent pH and base saturation of the peat mosses in the substrate. The problem of pH drift from the target can be controlled by ensuring an adequate amount of *S. fuscum* in the substrate.

Factors Affecting pH Establishment and Maintenance in Peat Moss-Based Substrates

by
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Dedication

The research embodied in this dissertation is dedicated to my devoted and loving husband. His willingness to accept my rightful role during the last few years of difficult family transitions made it possible for me to complete this work. His support was offered selflessly and without complaint. He was determined that I would see this endeavor to completion.

Aside from taking on my family responsibilities, he was always available with an open ear, an open mind, and a strong shoulder. Always picking up my pieces and keeping life on even footing. On top of all that, he was also a great lab assistant! He is an exceptional human being.

Biography

Janet Fairbanks Miles Rippy is a native of Saginaw, Michigan. The summers of her youth were spent on the shores of Lake Michigan where she learned a strong sense of community with and appreciation for natural environments. She completed two years of undergraduate study in the field of the performing arts, majoring in Dance, at Southern Methodist University. She then returned to Michigan where she was married for 18 years. During the course of her marriage, Janet raised two children, taught dance and ski lessons, and volunteered her time to enhance the quality of life in her community. She was a member of the Board of Directors of the Saginaw Symphony, the Saginaw Art Museum and The Junior League of Saginaw, as well as being a member of the choir and the Board of Directors (Vestry) of St. John's Episcopal Church and being the leader of that church's Youth programs. When her children were in high school, Janet resumed her academic career and obtained a Bachelor of Science in Horticulture/Floriculture degree at Michigan State University, where she graduated with High Honors. Janet obtained a Master of Science degree in Horticultural Science at North Carolina State University where she focused on developing an organic growing system for greenhouse tomatoes as well as studied the use of biological methods for controlling whiteflies. Janet, who now resides in Bluffton, South Carolina, is currently pursuing a Ph.D. degree, also from North Carolina State University. Her doctoral research involves discernment and evaluation of factors affecting the establishment and maintenance of pH in peat moss-based growing substrates. Her lifelong goal is to own a farm which will integrate plants and animals (mainly horses) using sustainable practices, and which will provide a venue for sustainable research and community education of such.

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Introduction

Factors Affecting pH Establishment and Control in Peat Moss Based Substrates

The Problem:

Nearly all greenhouse crops, about 60 percent of landscape nursery crops, most seedlings for horticultural, forestry, and agronomic crops, and all house plants are grown in container substrates. An additional quantity of container substrate is used for amending gardens and filling planters. These substrates are mixtures of materials that only infrequently include soil. Because horticultural substrates are high in organic matter content, they should be well buffered against pH shifts (Sims, 1996). The basis for most of these substrates is peat moss, pine bark, or coir coconut fiber. All of these start out as acidic mixes and continue to acidify and buffer during crop production; consequently, limestone is incorporated into them during formulation to raise the substrate pH.

Growers who formulate their own substrates and formulation companies that sell ready-mixed substrates are faced with two problems. First, there is difficulty in attaining consistently initial substrate pH using standard formulas for limestone additions. The second problem arises when substrate pH drifts away from the initial target over the course of production.

The amount of limestone needed to raise the substrate pH to the commonly used range of 6.0 to 6.5 is determined through preliminary lime rate tests. However, these rates do not work consistently over time. As successive batches of substrate are produced, initial pH varies unacceptably, both upward and downward. Substrate formulators with a pH target of 6.0 experience differences from batch to batch as wide as 5.2 to 7.0. The problem does not stop with the initial pH level. During the course of crop production, some batches of substrate will tend to hold pH levels within recommended ranges while others rapidly rise or decline to injurious levels. Lower and higher levels radically upset plant nutrition and can be detrimental to crops. The perennial statement made at grower conferences is, "if substrate pH could be controlled, 50 to 75 percent of all nutritional problems would be avoided." The variations in substrate pH result in increases in managerial, labor, and materials costs to the growers, as well as reductions in crop quality and sometimes crop losses.

Often growers engage substrate formulators in litigation. Thus both growers and substrate formulators end up suffering economic losses.

Aside from greenhouse crop management practices, such as use of the wrong quantity of limestone in the substrate mix or use of fertilizers with the wrong pH reaction, substrate pH variations can stem from two major sources. First, limestones across and within quarries can differ greatly in capacity to neutralize acid in peat moss substrates – the **"neutralization capacity".** Similarly, within or among bogs, peat moss may vary in the amount of inherent acidity that must be neutralized – the **"neutralization requirement"**.

Neutralization Capacity of Limestones:

In a review of early limestone research, there is well-documented consensus that particle size influences dissolution rates of limestone, hence its value for neutralizing substrate acidity. The general conclusions are that small limestone particles have a short-term, immediate effect, whereas larger particles are slower to react, but are effective for a longer period of time (Barber, 1984). From a horticultural perspective, Leda and Wright (1991) concluded that fine limestone grades were more effective than coarser grades in raising container media pH in which boxwoods were grown. This conclusion was substantiated in more recent studies by Argo and Biernbaum (1996a and 1996b), in which they state that the extremely fine particles of hydrated lime were completely reacted within four weeks as opposed to the coarser, carbonate lime which continued to react for the entirety of the seventeen week study. In this study, the conclusions are undoubtedly true as concerns the reactivity of the two liming materials. However, correlations between reactivity and particle size cannot be drawn since the liming materials studied have very different chemical and physical composition.

Although it is commonly accepted that the size of limestone particles affects neutralization capacity, the results of these studies vary greatly when considering the amount of acidity that is neutralized by a specific particle size. Barber (1984) reviewed research on crop response, hence "effectiveness" of limestone particle size fractions. In order to summarize the results of several studies, he found it necessary to create relative effectiveness values due to great variability in crop response. He later states that no distinct mesh size separates effective from ineffective limestones, indicating that there is most likely an overlap in crop response among particle sizes. Such variation, along with growers' and substrate formulators' experiences mentioned above, give rise to the idea that particle size may not be the only factor, or possibly even the greatest factor, contributing to the neutralizing capacity of limestone particles.

Discrepancies could exist, in part, due to error in the underlying assumptions upon which much of the early research was based. Many studies on limestone dissolution and limestone reactions with soil incorporate the hypothesis that the rate of reduction in limestone particle diameter is the same for all particle sizes (Kriege, 1929; Bear and Allen, 1932; Salter and Schollenberger, 1940; Schollenberger and Salter, 1943; and Schollenberger and Whittaker, 1962). Schwartzendruber and Barber (1965) derived a dissolution equation from this equal rate reduction hypothesis based on the assumptions that (i) the initial mass of limestone was present as spheres with uniform density, size and composition, and (ii) the rate of loss of mass was directly proportional to the instantaneous surface area of the spheres. They were aware that limestone particles are not spherical, but reasoned that the difference in shape would be the same for all particle sizes, thus errors would be cancelled when making comparisons among sizes. Although the dissolution equation should have produced linear relationships between reduction of particle diameter and time, when applied to data from various studies, the reduction in diameter of finer particles departed from linearity. Barber (1984) concluded that limestone dissolution was not only a function of particle diameter. He also stated that the rate of reaction of limestone with soil depends on both fineness and the chemical and physical composition of the particles.

Throughout the last century, several researchers have investigated aspects of limestone in conjunction with particle size that might be more pertinent to the characterization of neutralizing value. Morgan and Salter (1923) investigated the effect of hardness, porosity, specific gravity, crystalline composition, and chemical analysis on limestone dissolution and concluded that only calcium (Ca) and magnesium (Mg) had a large effect on the rate of dissolution. Elphick (1954) found that in 20-40 mesh separates, there was a wide range in relative surface, as measured by the limestone reaction with oxalate. Also in 1954, Love and Whittaker used adsorption of krypton (Kr) to measure limestone surface area. They discovered that limestones of the same size but different sources varied widely in measured specific surface. They also found that surface area measured was much greater than surface area calculated. They stated this phenomenon was indicative of considerable internal porosity. Stukenholtz (1958) compared same-size Nebraska limestones from the Cretaceous, Pennsylvanian, and Permian formations and found the Cretaceous limestones to react most rapidly. Bussieres (1978) conducted research in which shape and surface area of limestone particles, as well as marine and terrestrial sources of limestone were the factors taken into consideration. He deduced that marine limestone particles are cylindrical in shape and have a cellular structure which may lead to underestimation of reactive surface. He also concluded that flat particles are likely to release Ca at a constant rate.

In another application, limestone quarriers have found that, in addition to particle size, particle hardness, internal porosity, resistance to weathering, specific gravity and the calcium/magnesium ratio are of significant importance in the durability of construction materials. These physical/chemical properties may also have a significant affect on the dissolution rates of limestones, hence their neutralization capacity.

It is possible that the difficulties with horticultural substrate pH management arise from the application of agricultural precepts to horticultural endeavors. The vast majority of limestone research has been conducted on agronomic crops grown in field soils. Consequently, the specifications for agricultural limestone have been designed with the goals of reducing input costs and enhancing production of these crops. To these ends, it is expected that an agricultural limestone will raise soil pH to a given level within three or four months and provide residual neutralization for up to three years. Barber (1984) states that it is generally desirable to use lime that reacts almost completely within a two to three year period. Although researchers have identified and documented many factors that affect the neutralization capacity of limestones, it was apparently not considered to be economical or necessary to define limestone beyond particle size distribution for agronomic purposes.

Horticultural cropping systems are inherently different from agronomic systems. The acidity in horticultural substrates arises largely from organic compounds, as opposed to the mineral sources of acidity present in field soils. This could explain why Jorgenson (1957) found that the limestone reaction rates were faster on peat soils than on sandy loam soils of equal acidity. Production time for containerized crops is much shorter than for agronomic crops. Container substrate pH must be at target in three to four days and residual neutralization is only needed for four to six months for most crops. Thus, the initial and short-term reactivity of limestone are of interest for horticultural purposes, whereas the long-term, residual activity is of greater importance for agronomic applications. Furthermore, most containerized crops are grown in containers causing a preponderance of root mass to that of substrate. In light of the inherent differences in cropping systems, it seems reasonable to suppose that the specifications for agricultural limestone are not adequate for horticultural uses.

Neutralization Requirement of Peat Moss:

Factors that may affect the neutralization requirement of peat moss among batches are cation exchange capacity (CEC), base saturation [proportion of CEC neutralized by basic cations: calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+)] , bulk density, degree of decomposition, and inherent pH. It is possible that some or all of these properties are related to the composition of plant species in each batch of peat. Although some references have been made regarding the differences in physical and chemical properties among reed sedge, hypnum and sphagnum peat mosses (Argo and Biernbaum, 1997; Nelson, 2002; Bunt, 1988; and Puustjarvi and Robertson, 1975), the species of *Sphagnum* that are used for horticultural purposes have been thought to be highly consistent from batch to batch, as well as over time. In a review of the botanical literature regarding the occurrence and growth habits of *Sphagnum* species, it becomes apparent that variations may indeed exist.

The type of peat moss most commonly used for containerized substrates in North America is of the genus *Sphagnum* and is obtained largely from mires in Canada. There are three environmental gradients considered to be of primary importance in relation to vegetation that exists in mires (wet, spongy earth): ombrotrophic (derives moisture from precipitation only) to minerotrophic (derives moisture from water in contact with mineral soils), wet to dry, and mire margin to mire expanse (Sjörs, 1948, 1950).

Du Rietz (1949, 1954) described the relationship between trophic status and vegetation. He distinguished between fens and bogs. Fens are differentiated from bogs when pH, cation concentrations, and electrical conductivity (EC) readings indicate water contact with mineral soil water (Horton et al., 1979). Vegetation in bogs is not influenced by water which is in contact with mineral soils (geogenous). Rather, the moisture in a bog is derived solely from precipitation (ombrogenous) (Horton et al., 1979). Du Rietz (1949, 1954) further divided fens into rich fens and poor fens. He stated that pH and conductivity are higher throughout rich fens than in poor fens. Intermediate fens are mentioned by Sjörs (1952). These include some less exclusive species of both rich and poor fens (Horton et al., 1979). The water of intermediate fens is characterized by higher pH – similar to rich fens – but lower cation concentrations - similar to poor fens (Sonesson, 1966).

Therefore, across Canada, trophic gradients range from ombrotrophic conditions in the treed-tundra, where vegetation is elevated above the water table by permafrost, to very poorly minerotrophic conditions in thaw-pockets (isolated areas of thawed ground) characterized by [Ca^{2+}] of 0.4-5.5 ppm, [Mg^{2+}] of 0.01-0.3 ppm, and EC of 19.2-36.1 μmho/cm (1 μmho = 1 μS), to more highly minerotrophic conditions along streams in which pH ranges from 4.8-5.1, [Ca^{2+}] of 6.3-6.5 ppm, [Mg^{2+}] of 0.2-0.3 ppm, and EC of 35.6-41.9 μmho/cm (Horton et al., 1979).

Along the moisture gradient, Sjörs (1948) divides Scandinavian mire vegetation into hummock, lawn, carpet, and mud-bottom communities (Horton et al., 1979). This series is related to water level, but also to the amplitude of variation and duration of the water at a particular level (Persson, 1961). The firmness and aeration of the peat (which are affected by the water level) are also important considerations (Sjörs, 1948).

Hummocks are the highest and driest (Sjörs, 1950), and are usually located above the maximum water level (Sonesson, 1970). Hollow communities rarely exist in bogs which, by definition, cannot be in contact with mineral soil water. Lawns are a firm vegetation (like hummock communities), but they are situated closer to the subsoil water level (Sjörs, 1948). Sonesson (1970) states that lawn communities are situated below the maximum water level.

Carpets occur in aquatic habitats which are a part of a terrestrial system (Sjörs, 1950). In carpets, the vegetation is loosely associated and comprises a floating mat which is immersed to emergent (Horton et al., 1979). Mud-bottom communities exist at the same level relative to subsoil water as carpets, but may be periodically dry (Sjörs, 1950). They are primarily differentiated from carpet communities by the paucity of bryophytes and a predominance of algae (Horton et al., 1979).

Vitt et al., (1975a) describe a similar sequence of vegetation relative to water level for North American mires and refer to it as the hummock to hollow series. Instead of different terms for the intermediate stages between hummock and hollow, the vegetation is referred to its position along a gradient relative to other plants. In thaw pockets, mounds are drier and more stable than the floating carpets. Extensive *Sphagnum* lawns occur along the edges of streams and these are firmer than the carpets in the thaw pockets. The hummocks are at the driest end of the spectrum (Horton et al., 1979).

The mire margin to mire expanse gradient applies mainly to fens because bog vegetation is independent of the chemical influences of the mineral soil. Consequently, the variations between margin and expanse vegetation are not as prevalent in bogs as in fens (Sjörs, 1950).

The position of a fen community in this gradient is determined from its composition, NOT its location in relation to mineral soil (Sjörs, 1950). Consequently, mire margin vegetation may occur along streams or springs which are far from the actual margin of the mire (Persson, 1961; and Pakarinen and Ruuhijärvi, 1978). Trees and/or shrubs are the prominent physiognomic feature of margin communities (Sjörs, 1950; Persson, 1961; and Malmer, 1962). Mire expanses are central open areas (Sjörs, 1950) comprised mainly of "real mire" plants (Persson, 1961). This gradient has not been included in North American studies, however, Vitt and Slack (1975) describe changes in vegetation along a shade-exposure gradient.

In the Canadian mires, there are three dominant *Sphagnum* species: *S. fuscum* (Schimp.) Klingrr., *S. magellanicum* Brid., and *S. angustifolium* (Russow) C. Jens. Differences in vegetation correlate, to some extent, with differences in pH and cation concentration (Du Rietz, 1949, 1954). Gignac and Vitt (1990) state that *Sphagna* species groups and stand dispersal (in western Canada) are determined by climate and surface water chemistry, especially EC and concentrations of Ca^{2+} and Mg^{2+}. More recently, Bragazza and Gerdol (1999) found that in a mire in the Bolzana Province of northern Italy, species distribution was more strongly influenced by water table position and flow rate of surface water than by surface water chemistry. Mulligan and Gignac (2001) concur with this finding, stating that (in northern Alberta, Canada) depth to water was the most important factor for all species except *S. fuscum*. Although Gignac and Vitt (1990) conclude that *Sphagna* species are limited to mires having low cationic concentrations and EC, the species of *Sphagna* are discriminative indicators of subtle changes in the environmental gradients of moisture, trophic status, and exposure (Horton et al., 1979).

Sphagnum angustifolium:

Although many niche overlaps occur, the fourteen species of *Sphagna* can be divided into wet stands" and "dry stands". *Sphagnum angustifolium* and *S. magellanicum* occur in fairly dry stands (Dunhofen, 1999). *Sphagnum angustifolium* exhibits continental tendencies and is a dominant species in poor fens (Vitt and Andrus, 1977). *Sphagnum angustifolium* is fairly abundant and widespread in the province of Alberta, Canada; however, it becomes sporadic and scarce in calcareous regions. *Sphagnum angustifolium* typically forms lawns, or occurs in hollows below *S. magellanicum* in weakly to moderately minerotropohic habitats (Vitt and Andrus, 1977).

Sphagnum angustifolium has a narrow range of tolerance with respect to water depth. (Horton et al., 1979). Where the vertical drop is sharp on the up-slope side (relative to water flow) of depressions, the zone of *S. angustifolium* is narrow, whereas on the down-slope side where the drop is gradual, *S. angustifolium* exists in a broad zone (Vitt et al., 1975b).

In the Caribou Mountains, *S. angustifolium* was abundant in the thaw-pockets and also occurred along shrub-bordered streams. Thus, it was subjected to a broad range of trophic conditions {pH 3.5-4.8, [Ca^{2+}] of 0.01-0.16 $mol{\cdot}L^{-1}$, [Mg^{2+}] of 0.004-0.012 $mol{\cdot}L^{-1}$, and conductivity of 35.4-63.1 µmho/cm (in all cases, the lower values refer to thaw-pockets and the larger values refer to the streams)}. In thaw-pockets, *S. angustifolium* formed low mounds on top of somewhat consolidated floating carpets and so, was not submerged. In such thaw pockets, this species was most abundant in the areas transitioning from thaw-pocket to treed-tundra where there existed a higher proportion of drier micro sites. In streams, *S. angustifolium* existed in lawns where they remained moist but not submerged (Horton et al., 1979).

Sphagnum angustifolium has broad tolerances in the mire margin-mire expanse gradient. Andrus (1974) reported this species to occur in both open mats and shaded forests. However, it has been noted the *S. angustifolium* is dominant in shaded habitats whereas *S. magellanicum* is dominant in open habitats (Katz, 1926; and Vitt and Slack, 1975). In the Caribou Mountains, Horton et al. (1979) found *S. magellanicum* to be the only consistent associate of *S. angustifolium*.

Sphagnum fuscum:

S. fuscum most frequently forms islands of ombrotrophic vegetation in a surrounding rich fen (Horton et al., 1979). In rich fens, where ground water is calcareous, *Sphagnum fuscum* and *S. warnstorfii* are the only species commonly encountered. In these areas, *S. fuscum* occurs on hummocks above *S. warnstorfii*. In more acidic areas, it occurs on hummocks above *S. magellanicum* and *S. angustifolium* (Vitt and Andrus, 1977).

S. fuscum dominates the nutrient poor sites where permafrost exists (Vitt and Andrus, 1977). The hummocks are varied from 30-50 cm in height and are elevated above the level of groundwater, on permafrost, thus making them ombrotrophic (Horton et al., 1979). Consequently, this species is not limited by surface water chemistry (Gignac and Vitt, 1990).

In the Caribou Mountains, the *S. fuscum* hummocks were the most extensive and highest species of *Sphagnum*, thus representing the extreme end of the wet-dry gradient (Horton et al., 1979). Likewise, Damman (1977) reports that in the domed and plateau bogs along the coasts of Maine and New Brunswick, *S. fuscum* dominated the driest areas.

Although *S. fuscum* exhibits continental tendencies (Vitt and Andrus, 1977) it is the most widespread of all *Sphagna* species, occurring in habitats irrelevant of climate (Gignac and Vitt, 1990). Also, it is the dominant species in the forested muskegs (Vitt and Andrus, 1977). In a more recent study conducted to measure the ability of some bryophytes to live in each others' habitats, Mulligan and Gignac (2001) discovered that *S. fuscum* was able to grow in all habitats and its distribution was not limited to any of the traditionally measured habitat factors.

S. fuscum forms hummocks in open and semishaded habitats (Vitt and Andrus, 1977; and Horton et al., 1979). The small size and high density of the shoots give it a superior ability to raise capillary water, which enables it to continue upward growth at a considerable distance from the water table. This characteristic allows *S. fuscum* to play a major role in the formation of hummocks on a raised bog (Lindholm, 1990).

Although *S. fuscum* grows in drier microhabitats than the aquatic *Sphagna*, it is not a particularly xerophytic species. It is characterized by a compact growth form which promotes moisture retention (Horton et al., 1979)

Sphagnum magellanicum:

S. magellanicum has widespread tendencies within Alberta (Vitt and Andrus, 1977); however, it is never a very dominant or even a prevalent component of mire vegetation there (Horton et al., 1979). Like *S. angustifolium* and *S. fuscum*, it grows in acidic habitats, but is limited in Western Alberta by the calcareous nature of the substrate (Vitt and Andrus, 1977).

In general, *S. magellanicum* forms small hummocks or occurs on the sides of larger hummocks in poor fens (Vitt and Andrus, 1977). Kulczyńsky (1949) noted that *S. magellanicum* grows in very mesic habitats but cannot tolerate flooding. This species tolerates moisture conditions that are similar to but somewhat drier than those tolerated by *S. angustifolium* (Horton et al., 1979). In accordance with these observations, Horton et al. (1979) found that in the Caribou Mountains, *S.*

magellanicum occurred in the shallower parts of thaw pockets where the transition to treed-tundra was gradual, and it was found only on the better developed mounds of *S. angustifolium* (Horton et al., 1979).

Jeglum (1971) reports that *S. magellanicum* tolerates a narrower pH range than *S. angustifolium*, and in the Caribou Mountains, it did not exist in the more minerotrophic habitats along streams, where *S. angustifolium* did occur (Horton et al., 1979). The water where *S. magellanicum* grows characteristically has pH 3.4, [Ca^{2+}] 0.8 $mol{\cdot}L^{-1}$, [Mg^{2+}] of 0.004 $mol{\cdot}L^{-1}$, and conductivity of 23.2 μmho/cm (Horton et al., 1979).

The three species of *Sphagnum* just described are the most commonly used for horticultural purposes. They exist in three distinct strata with respect to the water table (MacDonald, J. Botanist, Highland Grey Co. Alberta, Canada - personal communication, 2003). In thaw-pockets and depressions of treed tundra, where the vegetation mat is somewhat firm and conditions are poorly minerotrophic, *S. angustifolium* forms low mounds just above the water level. *S. magellanicum* grows on top of the larger mounds of *S. angustifolium* in the thaw-pockets. In the treed-tundra, *S. magellanicum* forms low hummocks. Ombrotrophic conditions of the treed-tundra give rise to the largest hummocks which are comprised of *S. fuscum* (Horton et al., 1979).

Substrate inherent pH and base saturation are key considerations when determining the neutralization requirement for use as a horticultural growing medium. These factors also have the potential to influence nutrient availability to plants grown in peat-based substrates. Consequently, understanding the natural habitat of the *Sphagnum* species used in horticultural substrates provides insight for effective substrate pH and fertilizer management.

As vegetation gets farther removed from the geogenous water, there is a decrease in pH and cation concentration of the water associated with each stratum. Hummock species (*S. fuscum*) have more uronic acid functional groups than hollow species (*S. angustifolium*). Uronic acids are any of a class of compounds containing the chemical structure HOOC(CHOH)(N)CHO and include both carboxylic and aldehydic groups. These uronic acid reaction sites are protonated [loaded with readily exchangeable hydrogen ions (H^+)]. The differences in the number of uronic acid sites among

Sphagnum species may cause variation in the neutralization requirement of peat moss. In natural situations, the uronic acid sites are only about 20% saturated with bases, simply because there are very few bases available in ombrotrophic habitats (Vitt, D. Department of Botany, Southern Illinois University – personal communication, 2002). Such conditions may cause *S. fuscum* to be inherently very acidic. Likewise, *S. angustifolium*, and to a lesser degree *S. magellanicum* have greater contact with mineral soil water making it plausible that these species could have a greater percent base saturation, leading to a higher inherent pH.

Project Objectives and Methods:

The objectives of this research project were two-fold. The first area of focus was to evaluate, from a horticultural perspective, the physical and chemical properties of limestone that influence neutralization capacity. The second objective is to characterize the physical and chemical properties of peat moss that influence neutralization requirement.

From reviewing the literature and from conversations with a limestone supplier (David Jahn, Martin Marietta Technologies, Inc., Mason, Ohio – personal communication - 2001) as well as physical and chemical soil scientists and microbiologists at North Carolina State University, seven characteristics of limestone that might significantly impact neutralizing value have been determined. They include: 1. particle size (PS), 2. specific surface of limestone particles (SS), 3. particle hardness (H), 4. soundness [(SD) resistance of particles to degradation], 5. the amount of internal porosity (P), 6. the calcium (Ca) and magnesium (Mg) content (C and M, respectively), and 7. specific gravity. It is possible that several of these physical properties may be interrelated (for example: Ca and Mg content and/or particle size may relate to surface area).

In order to achieve the first objective, twenty limestone samples were selected from quarries across North America to represent a broad range of H, SD, P, C, and M. Each was wet-sieved into eight particle-size fractions. In addition to these tests, SS and reaction times were determined on limestone samples from each quarry. The physical and chemical properties exerting the greatest influence on neutralization capacity were statistically evaluated by regressing them against the reactivity rate, as well as each other.

To achieve the second objective, a set of 480 samples of peat moss were taken from bogs across Alberta, Canada. Sixty-four of these samples were selected for testing. The selected samples represented a broad range of species distribution (SD) and degree of decomposition (DD). Inherent pH, CEC, BS were measured for each of these samples. Additionally, the acid neutralization requirements were determined. As for the limestone data from the first objective, a multiple regression was conducted on the peat moss data in order to determine the physical and chemical properties that exert the greatest influence on the neutralization requirement of the peat moss.

Factors affecting the neutralization capacity of limestones, from a horticultural perspective, and factors influencing the neutralization requirement of peat moss determined in this study, make it possible to generate a formula for the attainment and maintenance of a target pH in a peat-based substrate.

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Chapter 1

Soilless Root Substrate pH Measurement Technique for Titration

Abstract:

Measurement of substrate pH entails procurement of the substrate solution and measurement of the solution pH. Acid/base reactions are completed at the time of testing. Determination of substrate pH during development of a titration curve is more complex because it involves initially the reaction of a base with the substrate. Five factors that can influence the resulting pH values were investigated in this study and include: amount of water added to substrate, method to procure substrate solution for pH determination, chemical form of base used, time allowed for acid/base reaction and the addition of $CaSO_4$. Substrate in this study consisted of sphagnum peat moss and perlite (3:1 v/v) amended with wetting agent. Dolomitic limestone (6 $g \cdot L^{-1}$ substrate) was added to substrate for the water amount and solution procurement method experiments. Except for the water amount experiment, deionized water was added by weight to achieve 95% container capacity. Dishes were incubated at 20° C for specified times. To identify the minimal level of water necessary to assure complete contact between base and substrate for neutralization, additions equivalent to 95%, 100%, 120%, and 150% container capacity were tested. The 95% level proved adequate. The saturated media extraction and pour-through bulk solution displacement methods for pH determination resulted in higher pH values in the incubated substrate than the squeeze bulk solution displacement method. This indicated that the former two methods diluted the soil solution. The squeeze method was deemed most effective. NaOH resulted in higher pH endpoints than $Ca(OH)_2$. This was apparently due to a higher affinity of Ca^{2+} for peat moss exchange sites. Since Ca^{2+} is the predominant cation associated with liming materials for soilless substrates, $Ca(OH)_2$ is more appropriate for titration. From the tested incubation times of 0, 2, 4, 8, 24, 48, and 96 hours, the duration of 24 hours was found to be adequate to allow complete reaction of base with substrate acidity. The best procedure for determining pH in a substrate titration situation included a water level

of 95% container capacity, $Ca(OH)_2$ base, an incubation time of 24 hours and the squeeze solution displacement method. The additional $CaSO_4$ was not necessary.

Chemical names: calcium hydroxide [$Ca(OH)_2$], calcium ion (Ca^{2+}), calcium sulfate ($CaSO_4$), sodium hydroxide ($NaOH$)

Introduction

A titration curve showing pH as a function of added amounts of base applied is a useful tool for comparing the neutralization requirements of various substrates or substrate components and neutralization capacities of different liming materials. The relationship between substrate solution pH and milliequivalents of base added to a soilless root substrate for the development of a titration curve is dependent on several factors. These include amount of water added to substrate, type of base used for titration, substrate solution procurement method, time allowed for acid/base reaction and the addition of calcium sulfate ($CaSO_4$).

The ratio of water to soil in the test suspension has the effect of increasing pH as the water to soil ratio increases (Thomas, 1996; and Shaw, 1960). However, in soil suspensions, this is not a 1:1 effect. For instance, increasing the water content by ten times does not result in an increase in pH of one unit. Rather, pH will increase by 0.4 units (Davis, 1943). The pH value is a measure of hydrogen ion (H^+) activity in a solution. The addition of water dilutes the concentration of H^+. However, in soil suspensions, additional water also increases the dissociation of H^+ from substrate particles (Thomas, 1996). An additional concern of special importance for studies in which substrate, base, and water are incubated is the possible creation of anaerobic conditions which can impact substrate solution pH. Thus, while it is important to provide sufficient water to bring base into contact with the hydrogen ions (H^+) on the substrate exchange sites, anaerobic conditions caused by prolonged saturation with water must be avoided.

Various methods are used to extract or displace substrate solutions for measurement of pH. Those methods that entail the addition of water above the level of container capacity can result in elevated pH values (Reddy, 2001) due to the dilution effect previously mentioned. Those methods that utilize shaking or stirring result in lowering pH measurements. This lowering effect is caused by mixing carbon dioxide (CO_2) from the air with the water in the solution, producing carbonic acid. The CO_2 effect can be highly significant, especially in substrates containing calcium carbonate ($CaCO_3$) (Thomas, 1996).

There are three similar procedures frequently employed by the horticulture industry for extracting or displacing substrate solutions. The saturated media extract (SME) method (Warncke and Krauskopf, 1983) involves adding water to the substrate until it is just glistening on the surface. After reaching equilibrium, the solution is squeezed through cheesecloth. While the amount of water added is a subjective decision, the SME method provides fairly stable and reproducible pH measurements. In the pour-through (PT) method, the substrate solution is removed from the substrate for testing by displacement, rather than extraction (Faber and Nelson, 1984). In this method, an amount of water moderately less than that held in a containerized substrate is poured over the substrate surface one hour after a fertilization or irrigation event, thus displacing the substrate solution which is collected as it leaches form the bottom of the container (Wright, 1986). The squeeze (SQ) method (Scoggins et al., 2001) involves simply squeezing the solution out of the substrate sample through cheesecloth. The PT and SQ methods provide an unaltered displaced solution sample for testing. The SME method does alter the solution to some extent by adding more water than exists at container capacity. Thus, the resulting pH is higher than in unaltered soil solutions and nutrient levels are lower.

Measured pH levels can also vary significantly depending on the type of base used to titrate substrate acidity. This effect is due, in part, to the strength of the base. Strong bases dissociate completely and quickly, whereas weak bases require more time to react completely. Additionally, the valency of the associated basic cations dictates differences in affinity for binding (exchange) sites on the substrate. Sodium (Na^+), being monovalent, does not have as great an affinity for exchange sites as does calcium (Ca^{2+}). Therefore, the number of H^+ dissociated from the substrate will be greater (causing lower pH) when Ca^{2+} is the exchanging cation than when Na^+ is used.

In incubation studies, the amount of time allowed for the reactions to occur can have an effect of the resulting pH values. This is particularly important when using a weak base which takes time to dissociate completely. It is possible that the time required for a complete reaction is long enough to allow secondary, biological reactions, such as decomposition to begin, causing variation in results. Sometimes, an amendment such as $CaSO_4$ is combined with the substrate. This addition can stabilize the acid/base reactions over time (Argo. W.R. 2003. Blackmore Company, Inc. Belleville, MI. Personal Communication). The Ca^{2+} background this amendment provides can enhance the dissociation of H^+ from exchange sites in organic materials. $CaSO_4$ is also incorporated occasionally into greenhouse substrates for fertilizer.

The first objective of this study was evaluate the effects of water amount (W), solution procurement method (SP), type of base (B), time allowed (T) and the addition of $CaSO_4$ to develop a protocol for titrating soilless substrates. The second objective was to develop a titration curve for sphagnum peat moss that could be used to determine the amount of lime required to achieve a specified pH level (neutralization requirement).

Methods and Materials

For all experiments, the substrate consisted of sphagnum peat moss and perlite (Sun Gro Horticulture, Bellevue, Wash.) in a volume ratio of 3:1 and amended with the proprietary wetting agent used by Sun Gro in their commercial soilless substrates. All experiments were a complete random design (CRD) with 10 replications. The experimental unit for each study consisted of 50 g substrate placed in a lidded, plastic seed germination dish (10.2 cm X 10.2 cm X 2.6 cm). Substrate was amended with specified amounts of deionized water and bases and the dishes were incubated at 20° C for specified amounts of time.

Moisture content (MC) is the amount of water contained in fresh substrate. MC was determined on a weight basis by filling three, 500 mL beakers with substrate. The filled beakers were weighed to obtain a fresh weight (FW), placed in a laminar flow oven at 105° C for 48 hours and then weighed a final time to obtain the oven-dry weight (ODW). MC was calculated by subtracting ODW from FW.

Container capacity (CC) is the amount of water that can be held by the substrate against gravitational forces. CC was also determined on a weight basis by filling ten, weighed incubation dishes with 50 g (FW) substrate, each. Water was added until it was just glistening on the substrate surface. The dishes were allowed to stand for 1 h, to ensure that all the substrate pore spaces had become water-filled. During this time, additional water was added, as needed, to maintain its level at the substrate surface. After 1 h, the dishes were covered with lids in which nine, evenly spaced holes (0.48 cm diameter) had been drilled. Dishes were flipped upside down, on racks, and were allowed to drain for thirty minutes. After draining, the lids were removed and the dishes and contents were weighed to obtain the drained weight (DW). Retained water weight was calculated by subtracting the dish weight-plus-substrate FW from DW. MC was added to water weight to obtain CC of oven-dry substrate by weight.

Solution pH for all studies was measured using a glass electrode and pH meter (Extech Instruments, Waltham, Mass.). The meter was calibrated with a pH 7.0 and 4.0 standard before the first measurement and after every 10 subsequent measurements.

Data for the W, SP, B, and T± $CaSO_4$ experiments were analyzed using analysis of variance and means were separated by Tukey's HSD (PROC GLM, SAS Institute, Cary, NC). The titration curve was generated with and without $CaSO_4$ by regressing pH against milliequivalents of base (Microsoft Excel, Microsoft Corporation).

Water Amount (W):

For W, dolomitic limestone was added to the substrate at a rate of 6 $g \cdot L^{-1}$. Dishes were filled with 50 g substrate (FW) and water was added to achieve either 95%, 100%, 120%, or 150% CC, by weight. Dishes were incubated for either 5 h or 14 d. Funnels were lined with a double layer of cheesecloth and were then placed in beakers. After incubation, the entire contents of each dish were scraped into the cheesecloth-lined funnels and the solution was squeezed through the cheesecloth and pH was measured.

Solution Procurement Method (SP):

The effects of three solution procurement methods on solution pH were evaluated: squeeze (SQ), pour-through (PT), and saturated media extract (SME). For all three, dolomitic limestone was added to the substrate at a rate of 6 $g \cdot L^{-1}$. Fifty g substrate (FW) was added to each incubation dish and water was pipetted in to obtain 95% CC. The dishes were incubated for either 5 h or 14 d.

For SQ, solution was extracted through cheesecloth-lined funnels as described for W (above) and solution pH was measured. For PT, the contents of each dish were scraped into cheesecloth-lined funnels. Then, an amount of deionized water equal to 95% CC, by weight, was poured over the surface to displace the substrate solution. The leachate was collected and pH determined. For SME, after incubation, water was added until the contents were just glistening. The dishes were allowed to stand for 30 minutes so equilibrium could be attained between substrate and solution. Then, solution was procured as for SQ and pH was measured.

Type of Base (B):

The effects of sodium hydroxide (NaOH) and calcium hydroxide [$Ca(OH)_2$] on solution pH were studied in B. Since NaOH is highly soluble, it was added to deionized water to make a basic solution that provided 2 meq alkalinity. $Ca(OH)_2$, being less soluble, was incorporated into the substrate, also to provide 2 meq alkalinity, as each dish was filled. The basic solution or deionized water [for the $Ca(OH)_2$ treatments] was added to achieve 95% CC. Substrate solution pH was procured using SQ and pH measured after 0, 2, 4, 8, 24, 48, and 96 hours incubation.

Incubation Time (T) with and without $CaSO_4$:

$CaSO_4$ is frequently used by growers as a sulfur (S) fertilizer, since S deficiency is known to occur in some areas of the country. $CaSO_4$ is also thought to help stabilize the acid/base reactions between peat moss substrates and liming materials (Argo. W.R. 2003. Blackmore Company, Inc. Belleville, MI. Personal Communication). In T, $Ca(OH)_2$ was incorporated with substrate in each dish to provide 6 meq alkalinity and was tested with and without $CaSO_4$ added at a rate of 1 $g \cdot L^{-1}$ (253 mg/dish). Deionized water was pipetted into the dishes to achieve 95% CC. Solution was procured using SQ, and pH was measured after 0, 1, 2, 4, 24, 48, and 96 hours incubation.

Titration Curve:

The substrate was titrated with and without $CaSO_4$ at the same rate as in T. The titrating base used was $Ca(OH)_2$, which was incorporated with the substrate to provide 0 – 24 meq alkalinity in 1 meq increments. Water was added to achieve 95% CC. The dishes were incubated for 24 hours. Solution was procured via SQ and pH was measured. There were seven replications.

Results and Discussion

Water Amount (W):

A stable and equal pH reading was seen in the 95% CC and 100% CC water treatments at 5 h ($P = 0.3725$) and 95% CC at 14 d ($P = 0.0404$), as shown in Table 1.1. After 5 h of incubation, solution pH decreased as water amount increased. Conversely, after incubation for 14 d, solution pH increased with increasing water. The former phenomenon may be explained by the previously mentioned theory of Davis (1943), in which the greater amounts of water enhanced the dissociation of H^+ from the substrate exchange sites. At 5 h, the short period of time was possibly not long enough for the limestone to dissolve sufficiently to neutralize the additional H^+ released. However, after 14 d, the limestone may have been dissociated completely and the H^+ concentrations had reached equilibrium between the substrate and the solution, thus producing the well-documented dilution effect. Our goal was to supply enough water to ensure complete contact of bases with substrate while avoiding the dissociation or dilution of H^+ in the measuring solution. Consequently, the best overall level of water addition for the purposes of this study was 95% of CC.

Solution Procurement Method (SP):

Only the SQ method provided consistent results at both 5 h and 14 d (Table 1.2). This is fortuitous because SQ yields unaltered substrate solution, hence the actual pH condition, in the substrate. The SME and PT methods resulted in higher pH levels at 5 h, and PT did so at 14 d indicative of water dilution. This was anticipated in the SME procedure as explained earlier, but not in PT. In the laboratory, the transfer of substrate from germination dishes to funnels in the PT method created macro pore channels. These channels allowed the added deionized water to pour freely through the substrate instead of displacing the substrate solution.

Type of Base (B):

NaOH produced higher pH values at all times ($P < 0.0001$) than $Ca(OH)_2$ as shown in Figure 1.1. This result was expected due to the higher affinity of the divalent cation Ca^{2+} for substrate exchange sites than the monovalent Na^+. This greater affinity allowed Ca^{2+} to displace more H^+ than Na^+, creating a more acidic solution. These data were collected in a system where only 2 meq base were applied to 50 g peat moss resulting in pH levels mostly between 4.5 and 5.0.

Incubation Time with and without $CaSO_4$:

The addition of $CaSO_4$ resulted in significantly lower pH values at all times (0, 24, and 48 hours, $P = 0.0028$; 1, 2, and 96hours, $P < 0.0001$; 4 hours, $P = 0.0030$; Figure 1.2). At this low level of alkalinity, it is possible that the additional Ca^{2+} displaced H^+ on the substrate exchange sites in excess of the amount of base available to neutralize them. $CaSO_4$ did not consistently reduce the variability of the pH measurements, but did hasten the acid/base reaction to completion. Regardless of the presence or absence of $CaSO_4$, the acid had been completely neutralized when the dishes were incubated for 24 h.

Titration Curve:

When alkalinity is provided to result in solution pH measurements ranging from ~ 4.0 to 8.0, it is clear that the addition of $CaSO_4$ exerts the greatest influence in the low pH range (Figure 1.3). Significant differences occurred between the two curves at and below pH 5.0. In the pH range in which plants are grown, there was no effect of $CaSO_4$. Since there are many experimental factors that can significantly influence pH measurements, care must be taken when developing a titration curve relating solution pH to added amounts of base. If the information provided from such a titration curve is to be used as a means of comparison, it is necessary to match the experimental methods used for creating the curve to the systems to which the resulting information will be applied.

Conclusions

The titration curve developed here will subsequently be used to compare the neutralization requirements of various sphagnum peat moss samples, and also to determine and compare the neutralization capacities of various limestones. From the results of these studies, incorporating $Ca(OH)_2$ into the substrate, adding water to achieve 95% CC, incubating for 24 h at 20°C, and procuring solution for pH measurement using SQ represent the most appropriate protocol for developing a titration curve for the intended purpose. In addition, it is not necessary to incorporate $CaSO_4$ into the procedure unless one is considering a crop grown at pH 5.0 or lower and preplant Ca in addition to that supplied by limestone is used.

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Table 1.1. Effects of the amount of water added to peat moss:perlite substrate (3:1 v/v + dolomitic limestone at a rate of 6 $g \cdot L^{-1}$) and incubation duration on resulting pH measurements.

Incubation time	**Water added (% CC)**	**Average pH**	**Standard Deviation**
5 hours	95	6.23 b[z]	0.10
	100	6.22 b	0.07
	120	6.10 a	0.06
	150	6.03 a	0.07
14 days	95	6.29 b	0.05
	100	6.42 c	0.03
	120	6.44 c	0.07
	150	6.55 d	0.04
	Tukey's $HSD_{0.05}$	0.09	

[z] Different letters denote significant differences at alpha = 0.05.

Table 1.2. Effects of solution procurement methods and incubation duration on solution pH.

Incubation Time	**Solution Procurement Method**	**Average pH**	**Standard Deviation**
5 hours	Squeeze	6.27 a	0.17
	Saturated Media Extraction	6.52 c, d	0.04
	Pour Through	6.61 d	0.04
14 days	Squeeze	6.25 a	0.12
	Saturated Media Extraction	6.34 a, b	0.04
	Pour Through	6.44 b, c	0.03
	Tukey's $HSD_{0.05}$	0.11	

[z] Different letters denote significant differences at alpha = 0.05.

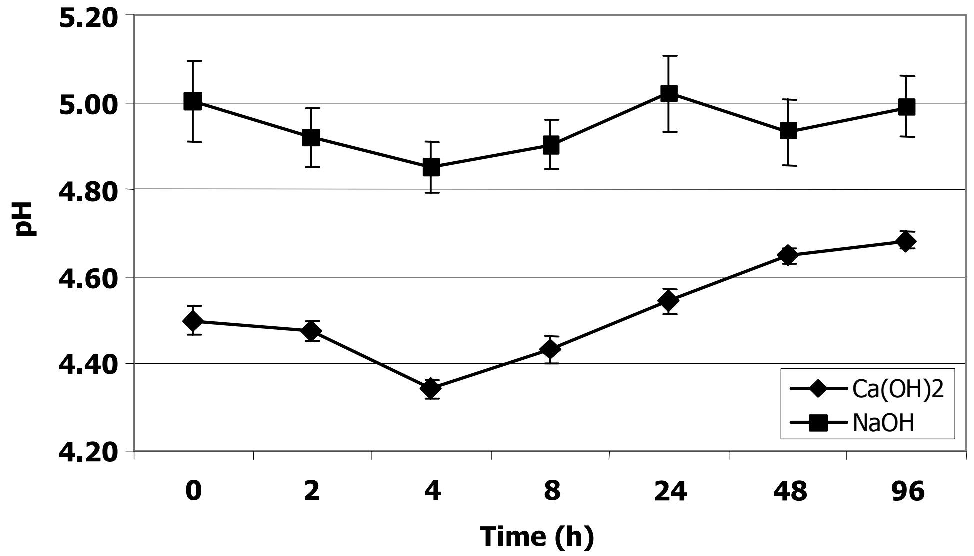

Figure 1.1. The effects of 2 meq NaOH and $Ca(OH)_2$ in 50 g substrate on substrate solution pH over time.

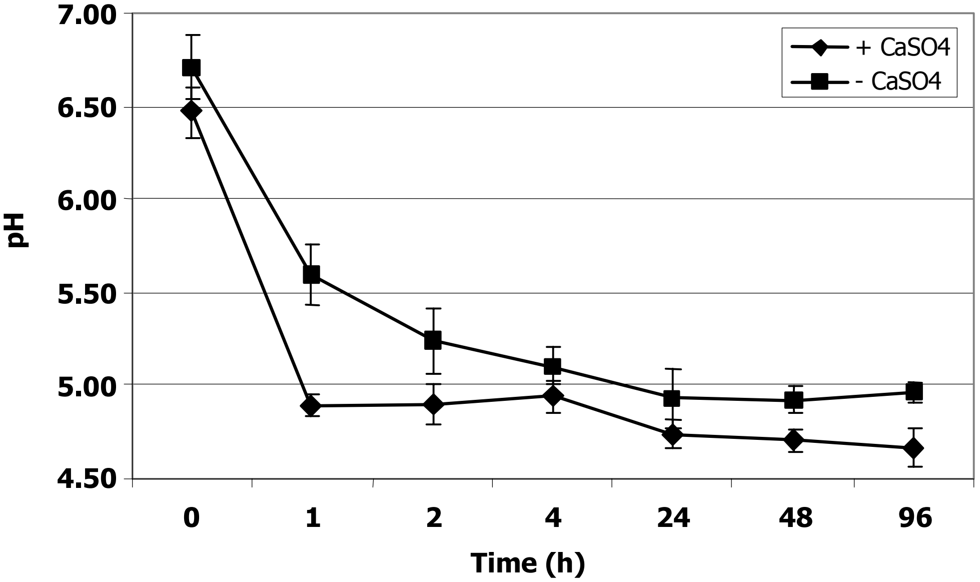

Figure 1.2. The effects of 6 meq $Ca(OH)_2$ with and without $CaSO_4$ on substrate solution pH over time.

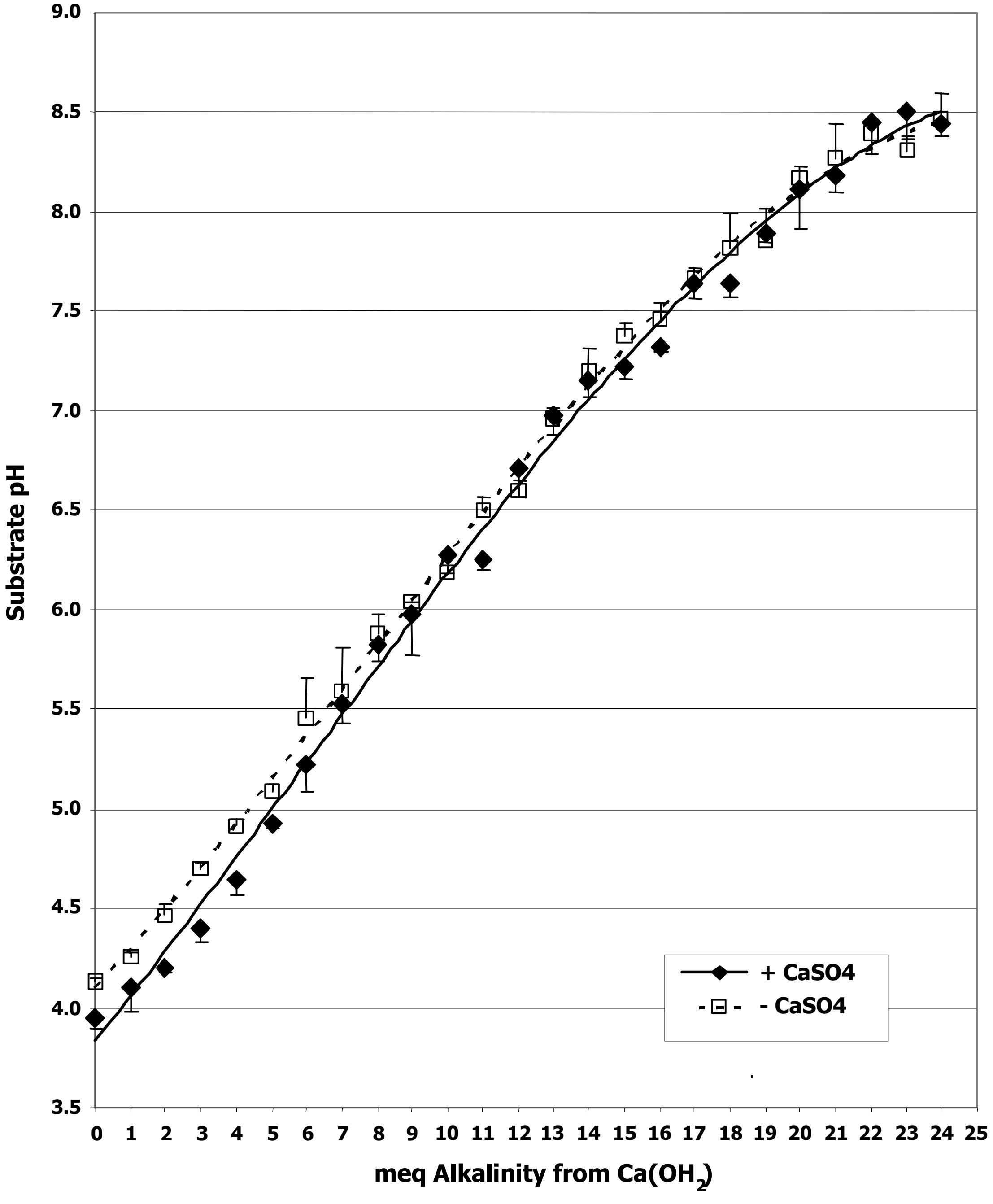

Figure 1.3. Titration of peat moss - perlite (3:1 by volume) substrate with $Ca(OH)_2$, with and without $CaSO_4$.

Regression equation for + $CaSO_4$: $y = -0.0002x^3 + 0.003x^2 + 0.2223x + 3.8295$ $r^2 = 0.9962$.

Regression equation for - $CaSO_4$: $y = -0.0002x^3 + 0.005x^2 + 0.189x + 4.0962$ $r^2 = 0.9983$.

Chapter 2

Limestone Specific Surface Versus Particle Size

Abstract:

Agricultural limestone is classified based on particle-size distribution, a key factor influencing its neutralization capacity. This property is an effective basis for liming recommendations for agronomic purposes which target gradual rise in soil pH and residual neutralization for three years. Inconsistencies are prevalent when agricultural limestone is used for horticultural applications which require rapid attainment of target pH and residual neutralization for only four months. Variations in pH among batches of substrate produced with the same limestone rate and pH drift from the same initial pH during crop production infer that factors other than particle diameter also influence limestone neutralization capacity. In this study the relationship between specific surface and diameter of limestone particles was examined. Limestones obtained from twenty North American quarries were analyzed for $CaCO_3$ and $MgCO_3$ content and wet-sieved into eight particle diameter fractions from 600 to < 38 μm (passing 30 to 400 mesh U.S. Standard screens). Specific surface ($m^2 \cdot g^{-1}$) of particles was measured in three replications for each fraction following the BET method with N_2, which assumes condensation of N_2 in a continuous mono-molecular layer on all particle surfaces. At each particle diameter fraction, specific surface varied significantly among quarries. Large specific surface may indicate many reactive interfaces with acids, hence high neutralization capacity. In containerized production, typical to horticulture, preponderance of root over substrate mass and short crop duration dictate narrower characterization of limestone than is currently used. Specific surface may describe limestone neutralization capacity more finely than does particle diameter.

Chemical names: Dinitrogen gas (N_2), calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$)

Introduction

There is well-documented consensus that particle size influences dissolution rates of limestone, hence its value for neutralizing substrate acidity. The general conclusions are that small limestone particles have a short-term, immediate effect, whereas larger particles are slower to react, but are effective for a longer period of time (Barber, 1984). From a horticultural perspective, Leda and Wright (1991) concluded that fine limestone grades were more effective than coarser grades in raising container media pH in which boxwoods were grown. This conclusion was substantiated in more recent studies by Argo and Biernbaum (1996a and 1996b), in which they state that the extremely fine particles of hydrated lime were completely reacted within four weeks as opposed to the coarser, carbonate lime which continued to react for the entirety of the seventeen week study.

Growers who formulate their own substrates and formulation companies that sell ready-mixed substrates determine the amount of limestone needed to raise the substrate pH to the target range through preliminary lime rate tests. Problems frequently arise when, as successive batches of substrate are produced, the initial pH varies unacceptably, both upward and downward. The problems do not stop with initial pH level. Subsequently, some batches of substrate will tend to hold pH levels within recommended ranges while others rapidly decline to injurious levels. These variations result in increases in managerial, labor, and materials costs needed for compensation as well as reductions in crop quality and sometimes crop losses. Often growers engage formulators in litigation. Thus both growers and substrate formulators end up suffering economic losses.

Variations in pH levels across batches of substrate are undoubtedly due, in part, to shifts in the neutralization capacity of limestone from lot to lot. Limestones across and within quarries can differ greatly in capacity to neutralize acid**.**

Although it is commonly accepted that the size of limestone particles affects neutralization capacity, the results of numerous studies vary greatly when considering the amount of acidity neutralized by a specific particle size. In reviewing research on crop response, hence "effectiveness" of limestone particle size fractions, Barber (1984) found it necessary to create relative effectiveness values in order to summarize the results of several studies due to great variability in results. He later states that no distinct mesh size separates effective from ineffective limestones, indicating that there is most likely an overlap in crop response among particle sizes. Such variation, along with growers' and substrate formulators' experiences mentioned above, give rise to the idea that particle size may not be the only factor, or possibly even the greatest factor, contributing to the neutralizing value of limestone particles.

Discrepancies could exist due to variation in the specific surface of the limestone particles. Barber (1984) states that the reactivity of limestone should be related to its exposed surface area. Elphick (1954) found that in 20-40 mesh separates, there was a wide range in relative surface, as measured by the limestone reaction with oxalate. Also in 1954, Love and Whittaker used adsorption of krypton (Kr) to measure limestone surface area. They discovered that limestones of the same size but different sources varied widely in measured surface. They also found that measured surface area was much greater than that calculated. Shaw (1960) concluded that increased fineness of limestone particles caused a more complete reaction because of the increased amount of surface area. Bussieres (1978) conducted research in which shape and surface area of limestone particles, as well as marine and terrestrial sources of limestone were the factors taken into consideration. He deduced that marine limestone particles are cylindrical in shape and have a cellular, somewhat porous structure which led to underestimation of reactive surface calculated from particle size.

The vast majority of limestone research has been conducted with the goal of reducing input costs and enhancing production of agronomic crops grown in field soils. In agricultural settings, limestone applications are expected to raise soil pH to target levels within 3-4 months and continue neutralizing the soil acidity for up to three years. Although researchers have documented variation in surface area among limestone sources with particle size held constant, it was apparently not considered to be economical or necessary to define limestone beyond particle size distribution for agronomic purposes.

Horticultural substrates are comprised mainly of peat moss or pine bark, both of which are highly acidic materials. The acidity in these substrate materials arises from organic compounds, as opposed to mineral sources in soils. In order to be effective for plant growth, these substrates must be neutralized to a pH of 6.0-6.5. For horticultural applications, it is important to reach the target pH within a few days. Furthermore, residual neutralization activity is only required for 4-6 months for most horticultural crops. Additionally, horticultural crops have a preponderance of shoot over root mass as well as a preponderance of root mass to substrate as compared to field-grown crops. Thus, the neutralization capacity of limestones is far more critical for horticultural uses than it is for agricultural purposes.

From a horticultural perspective, it now becomes feasible to revisit factors that might define more acutely the neutralization capacity of limestones. In keeping with the theory of Barber (1984) mentioned above - that the capacity of limestone to neutralize acidity should be related to the specific surface of the limestone particles – and in light of a need for narrower characterization of the neutralization capacity for horticultural applications, the objective of this research was to determine the relationship between specific surface and particle diameter of limestones.

Methods and Materials

Limestone samples were obtained from twenty North American quarries. The $CaCO_3$ and $MgCO_3$ content of the limestones were determined at the individual quarries. Each sample was wet-sieved (see Appendix I) into eight particle diameter fractions making a total of 160 samples. The fractions ranged in diameter from 600 to < 38 µm (passing through 30 to 400 mesh U. S. Standard screens). Limestone samples were arranged in a complete random design with three replications for each particle diameter fraction.

The surface area of each fraction was measured using a Monosorb Surface Area Analyzer (Quantachrome, Corp., Boynton Beach, FL). This instrument utilizes the BET theories (Brunauer et al., 1938; and Carter et al., 1986) to determine surface area by measuring the amount of gas adsorbed to the particle surfaces under conditions of controlled temperature and partial pressure of the adsorbate. Dinitrogen gas (N_2) was the adsorbate used because it is assumed to form a single molecular layer on all available surfaces. The instrument quantifies the number of N_2 molecules needed for monolayer coverage of the surfaces of the limestone samples. It then calculates the surface area using the known cross-sectional area of the N_2 molecules (3.15 Å) and the linear form of the BET equation for adsorption.

Sample cells for the Monosorb instrument were stored in a laminar flow oven at 110°C. They were cooled in a dessicater to avoid the deposition of moisture. They were weighed, filled with the limestone samples, and returned to the oven for 24 hours to remove any sample moisture that may have accumulated. The sample cells were outgassed for twenty minutes to provide a N_2 background just prior to the surface area determination process. The sample cells were returned to the oven for 24 hours after surface area analysis to remove any condensation that may have occurred on the limestone, and then weighed again. The initial weight of the sample cell was subtracted from the final weight to determine the weight of the limestone sample on which the surface area was measured. Specific surface was calculated by dividing the surface area by the weight of the limestone sample. Specific surface is expressed as square meters of surface area per gram of limestone ($m^2 \cdot g^{-1}$).

The specific surface measurements for the limestone samples were compared with an analysis of variance (SAS Institute, Cary, NC) among reps and limestone sources for each particle diameter. The treatment means were separated using Tukey's HSD (SAS Institute, Cary, NC).

Additionally, images were obtained of several limestone particles at the Cellular and Molecular Imaging Facility in the Department of Botany at North Carolina State University (NCSU). A Zeiss Axiophot upright microscope, fitted with a polarized lens was used. The images presented here were magnified by 40X.

Results and Discussion

Specific surface values for eight particle diameter fractions from twenty sources of limestone are listed in Table 2.1. As was expected, for all limestone sources the coarsest particles had smaller specific surface than the finest particles. Accordingly, eight of the twenty sources: III, V, VII, X, XV, XVI, XVII, and XIX, had increasingly larger specific surface as particle diameter decreased (slight discrepencies appearing in sources VII, XV, XVI, and XVII were not significant at α=0.05).

Most of the remaining sources exhibited a decrease in specific surface from the coarsest particles to around the 170-200 mesh screen size particle fraction. This decrease occurred either gradually or suddenly. Beyond this particle size fraction, as particle diameter decreased the specific surface increased. It is possible that the larger limestone particles contained internal pores that were accessible to N_2. In this case, measurements of the internal pore surfaces would have been included in the total specific surface. The smaller limestone particles may have occurred due to breakage along the axes of these internal pores causing not only a reduction in particle size, but also a reduction in exposed surfaces.

The last row of the table shows the amount of variation between the lowest and highest specific surface for each particle diameter fraction. For instance, there was a 74-fold difference in the coarsest particles. The differences between lowest and highest specific surface decreased with particle diameter, but even for the finest particles, there was still a large, 20-fold difference.

Specific surface is a measure of the amount of N_2 accessible surface per gram of material. It is assumed that H^+ and water (H_2O) can access the same surfaces. Large specific surface may indicate many reactive interfaces with acids. Since the reactivity of limestone is dependent on the number of exposed reaction sites, it seems plausible that this tremendous variation in specific surface may have a great influence on the neutralization capacity of a limestone.

The neutralizing value of limestones is currently defined by the $CaCO_3$ equivalent. The limestone sources in Table 2.1 are listed in order of increasing $CaCO_3$ content. The first seven sources also contained from 20-50% $MgCO_3$, thus are labeled as being dolomitic. The lowest specific surface was evident in dolomitic limestones; however, in the 30-50 and the 325-400 mesh screen fractions, dolomitic limestones also accounted for the largest specific surface. Additionally, there were eight calcitic limestones that had lower specific surface than the dolomitic limestones with the two highest specific surfaces, regardless of particle diameter fraction. These results suggest that the variation in limestone specific surface is not strictly related to the $CaCO_3$ or $MgCO_3$ content.

Figure 2.1 depicts limestone particles from four different quarries. Each image presented is a representative particle from the 325-400 mesh screen size fraction. Dolomitic limestones appear to be somewhat cube-shaped, with few angles or edges. Calcitic limestones are irregular and do not exhibit a characteristic shape. The limestones with low specific surface appear to have smooth, hard surfaces which are somewhat planar. Those with high specific surface have rough surfaces with numerous invaginations. Limestones with high specific surface contain many more exposed surfaces, hence reaction sites, than those with low specific surface.

Specific surface appears to be a characteristic measurement for limestones. The ranking of specific surface, from low to high (evidenced by the letters indicating signifcant differences), tends to be fairly constant across particle diameter fractions.

Conclusions

Although limestone specific surface increases as particle diameter decreases, there is a tremendous variation in the specific surface of limestones for any given particle diameter fraction. This variation does not appear to be very strongly related to the $CaCO_3$ or $MgCO_3$ content of the limestones. Furthermore, the specific surface measurements of a limestone, relative to other limestones, are consistent, regardless of particle diameter. While particle diameter and $CaCO_3$ equivalent may be the only measurements that are necessary or economically feasible for agronomic purposes, it is probable that specific surface could provide much of the additional information that is needed to define more narrowly the neutralization capacity of limestones for horticultural purposes.

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Table 2.1. Specific surface ($m^2 \cdot g^{-1}$) for eight particle-diameter fractions from twenty sources (quarries) across North America. Sources are listed in order of increasing calcium content.

Source	**Type**	**Particle Diameter Fractions[z] (U.S. Standard screens)**							
		30-50	**50-100**	**100-170**	**170-200**	**200-270**	**270-325**	**325-400**	**> 400**
I	D[y]	1.501 d[x]	1.761 d, e	1.715 e, f	1.481 e	1.229 f	1.094 e, f	1.089 e, f	3.997 c
II	D	0.725 f	0.629 g, h	0.530 g, h, i	0.514 h, i, j, k	0.518 h	0.635 g, h, i	0.659 g, h, i	1.847 e, f, g
III	D	0.205 j, k	0.217 i, j	0.268 g, h, i	0.293 k, l	0.390 h, i, j	0.402 i, j, k	0.420 i, j	1.474 g, h, i
IV	D	5.110 a	5.035 b	4.560 b	5.160 b	5.761 b	5.847 a	6.247 a	6.940 b
V	D	0.069 k	0.075 j	0.099 i	0.106 l	0.130 j	0.168 k	0.190 j	0.847 i, j
VI	D	1.685 c	1.499 e, f	1.371 e, f	1.282 e, f	1.338 f	1.359 d, e	1.360 e	3.433 c, d
VII	D	0.681 f, g	0.701 g	0.740 g	0.763 g, h	0.805 g	0.749 g, h	0.789 g, h	1.723 e, f, g, h
VIII	D	0.294 i, j	0.276 i, j	0.184 h, i	0.131 l	0.170 i, j	0.182 k	0.205 j	0.460 j
IX	C	1.612 c, d	2.071 d	2.580 d	1.888 d	2.680 d	1.911 c	2.464 d	6.516 b
X	C	1.220 e	1.260 f	1.333 e, f	1.314 e	1.306 f	1.291 d, e	1.309 e	3.020 d
XI	C	0.185 j, k	0.233 i, j	0.305 g, h, i	0.359 j, k, l	0.425 h, i	0.506 g, h, i, j	0.512 h, i	1.248 g, h, i
XII	C	3.402 b	5.670 a	6.555 a	6.954 a	6.239 a	6.007 a	5.882 b	9.240 a
XIII	C	3.344 b	3.701 c	3.072 c	2.972 c	3.181 c	3.133 b	3.035 c	3.861 c
XIV	C	0.426 h, i	0.391 g, h, i, j	0.454 g, h, i	0.490 i, j, k	0.534 g, h	0.591 g, h, i	0.602 h, i	1.576 f, g, h
XV	C	0.366 i	0.514 g, h, i	1.241 f	1.017 f, g	1.347 f	1.455 d	0.928 f, g	1.372 g, h, i
XVI	C	0.537 g, h	0.605 g, h	0.737 g	0.710 h, i	0.813 g	0.863 f, g	0.918 f, g	2.377 e
XVII	C	1.690 c	1.592 g	1.780 e	2.025 d	2.143 e	2.214 c	2.194 d	3.077 d
XVIII	C	0.433 h, i	0.440 g, h, i	0.590 g, h, i	0.532 h, i, j, k	0.639 g, h	0.674 g, h, i	0.767 g, h	2.179 e, f
XIX	C	0.768 f	0.693 g	0.597 g, h	0.595 h, i, j	0.578 g, h	0.626 g, h, i	0.644 g, h, i	1.245 g, h, i
XX	C	0.331 i, j	0.344 h, i, j	0.408 g, h, i	0.469 i, j, k	0.514 h	0.540 g, h, i	0.574 h, i	1.191 h, i
Tukey's $HSD_{0.05}$		0.159	0.326	0.489	0.270	0.283	0.332	0.298	0.638
Low-High		74.1 x	75.6 x	66.2 x	65.6 x	47.9 x	35.8 x	32.9 x	20.1 x

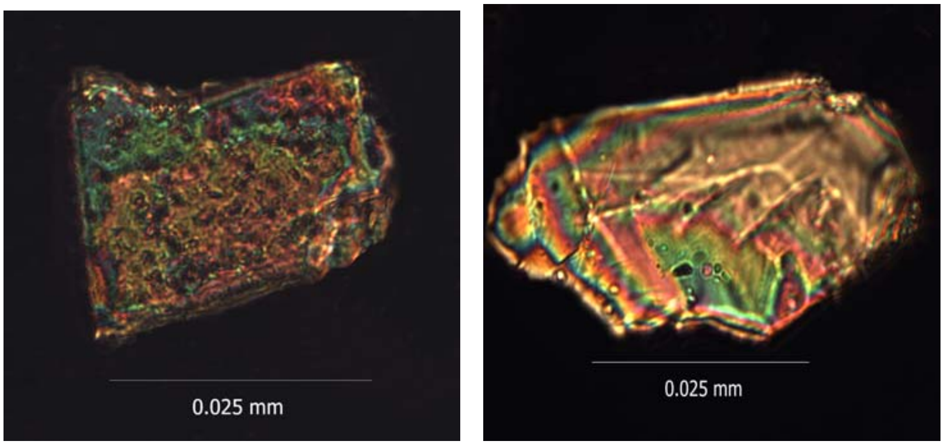
[z] Limestone particles were wet-sieved through U.S. Standard screens. The first number represents the screen mesh size that particles passed through. The second number represents the screen mesh size upon which particles were retained.

[y] Type of limestone based on calcium or magnesium content: D = dolomitic, 20-50% $MgCO_3$, C = calcitic, 70-100% $CaCO_3$.

[x] Different letters denote significant differences among sources at $\alpha = 0.05$.

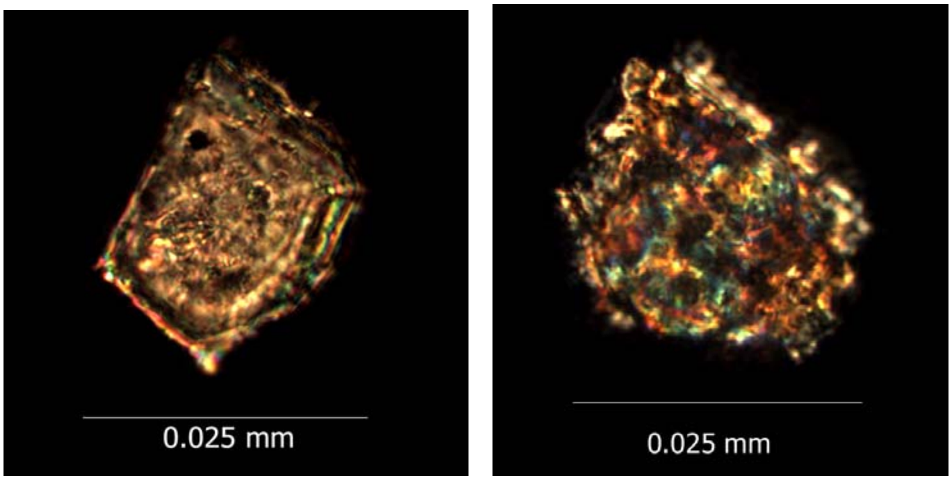
Specific	Limestone Type	
Surface	Dolomitic	Calcitic

Low



Images by Yue Xu, Cellular and Molecular Imaging Facility, NCSU

High



Images by Yue Xu, Cellular and Molecular Imaging Facility, NCSU

Figure 2.1. Digital images of 325-400 mesh particles of dolomitic and calcitic limestones, with low and high specific surfaces. Images were obtained using a Zeiss Axiophot upright microscope with a polarized lens and a 40x objective.

Chapter 3

Reaction Times of Twenty Limestones

Abstract:

Agricultural limestone is classified based on particle-size distribution and calcium carbonate equivalent, key factors influencing neutralization capacity. Inconsistencies are prevalent when agricultural limestone is used for horticultural applications. Variations in pH among batches of substrate produced with the same limestone rate and pH drift from the same initial pH during crop production infer that there are other important factors affecting limestone neutralization capacity. Horticultural uses for limestone may require more detailed characterization of neutralization capacity than is provided in agricultural limestones. In this study, reaction times of twenty limestones containing a broad range of $CaCO_3$ were compared. Limestones were wet-sieved into three particle diameter fractions: coarse (600-300 µm or 30-50 mesh U.S. Standard screen), mid-size (90-75 µm or 170-200 mesh screen), and fine (45-38 µm or 325-400 mesh screen). Reaction times were obtained by reacting 10 mL of $5N$ NH_4Cl with 100 mg of limestone in the presence of steam. The evolved NH_3 was cooled and condensed as NH_4OH, which was collected in a beaker containing 1 meq H^+ from $1N$ H_2SO_4 and bromcresol green dye which turns blue at $pH > 5.3$. Time was recorded from the first evolution of steam from the reaction vessel until the first appearance of blue color in the collection beaker. Neutralization reaction times were measured in a complete random design with three replications and are expressed as seconds required for 1 mg limestone to neutralize 1 meq H^+ ($s \cdot mg^{-1}$ per 1 meq H^+). Data were analyzed by ANOVA and means separated by Tukey's HSD. Fine limestone particles reacted faster than coarse particles; however there is a point beyond which degree of fineness no longer affected reactivity in calcitic limestones. Dolomitic limestones were slower reacting than calcitic limestones with the degree of difference being much greater than previously reported. Reaction times of all particle sizes of dolomitic, and coarse calcitic limestones varied significantly. These departures from results reported previously indicate that particle diameter and calcium

carbonate equivalent may not be the only important factors influencing limestone neutralization capacity.

Chemical names: calcium carbonate ($CaCO_3$), ammonium chloride (NH_4Cl), ammonia (NH_3), ammonium hydroxide (NH_4OH), hydrogen ions (H^+), sulfuric acid (H_2SO_4)

Introduction

Nearly all greenhouse crops, about 60 percent of landscape nursery crops, most seedlings for horticultural, forestry, and agronomic crops, and all house plants are grown in container substrates. The basis for most of these substrates is peat moss, pine bark, or coir coconut fiber. All of these start out as acidic mixes and continue to acidify during crop production. To date, agricultural limestone has been used to neutralize the acidity of horticultural substrates.

Two measures which have been deemed acceptable for characterization of agricultural limestones are particle size distribution (Barber, 1984; Perkins, 1961; Motto and Melstead, 1960; Jorgenson, 1957; Elphick, 1955; Beacher et al., 1952; Hoyert and Axley, 1952; Meyer and Volk, 1952; Lyon, 1931; Rost and Fieger, 1927; Frear, 1921; Kopeloff, 1917; White, 1917; and Thomas and Frear, 1915) and calcium carbonate equivalent (CCE) (Thomas and Hargrove, 1984). Indeed, these two measures are adequate to describe the reactions of limestones with acid soils for producing successful agronomic crops. However, difficulties have arisen when agricultural limestone has been used for horticultural applications.

Growers who formulate their own horticultural substrates and formulation companies that sell ready-mixed substrates to growers are faced with two problems. First, there is difficulty in attaining consistently the initial target pH of the substrate using standard formulas for limestone additions. The second problem arises when substrate pH drifts away from the initial target over the course of production. These variations result in increases in managerial, labor, and materials costs, as well as reductions in crop quality and sometimes crop losses. Often growers engage formulators in litigation. Thus both growers and substrate formulators end up suffering economic losses. This indicates that the measures used to define agricultural limestones are not explicit enough for horticultural purposes.

There appears to be great variability in the rate at which limestones react with, and consequently, neutralize the substrate acidity. Thomas and Hargrove (1984) state that the rate of neutralization strongly depends on the rate of dissolution and hydrolysis of calcium carbonate ($CaCO_3$) to form hydroxide ions (OH^-). The rate of dissolution and hydrolysis may vary among limestones from different quarries. In this study, the reactivity rates of three particle size fractions of twenty limestones spanning a broad range of $CaCO_3$ and magnesium carbonate ($MgCO_3$) content were obtained in order to determine whether or not variations in reactivity rates exist regardless of particle size or calcium content.

Methods and Materials

Limestone samples were obtained from twenty quarries across North America. The contents of $CaCO_3$ and $MgCO_3$ in the limestones were determined at the individual quarries. Limestones containing 20% - 50% $MgCO_3$ were labeled "dolomitic", and those containing 70% - 100% $CaCO_3$ were considered "calcitic". The samples were wet-sieved into eight particle size fractions. For this study, three particle size fractions were used. The "coarse" particles passed through a 30- and were retained on a 50-mesh screen (600-300 µm). The "mid-size" particles passed through a 170- and were retained on a 200-mesh screen (90-75 µm). Particles that passed a 325- and were retained on a 400-mesh screen (45-38 µm) comprised the "fine" particles. U.S. Standard screens were used for the limestone fractionation.

Reaction times were determined according to a procedure (see Appendix I.B.) originally described by Gleria (1929) and later improved upon by Shaw and Robinson (1959). In this procedure, 10 mL of 5N ammonium chloride (5N NH_4Cl) were placed in a vessel with 100 mg of a limestone sample. Steam was added to the reactants which resulted in the volatilization of ammonia (NH_3). The NH_3 was cooled and condensed as NH_4OH, which was collected in a beaker containing 1 meq hydrogen ions (H^+) from 1N sulfuric acid (1N H_2SO_4) and bromcresol green indicator dye. This dye is yellow at pH < 3.7, green from pH 3.7 - 5.3, and blue at pH > 5.3. Time was recorded from the first evolution of steam from the reaction vessel until the first appearance of blue color in the collection beaker. Reaction times were expressed as time (in seconds) required for 1 mg limestone to neutralize 1 meq H^+ ($s \cdot mg^{-1}$ per 1 meq H^+) to pH 5.3.

The experiment was conducted in a complete random design (CRD) with three replications. The data were analyzed using an analysis of variance (ANOVA) and means were separated by Tukey's HSD at $\alpha = 0.05$. There were three replications of each particle size fraction for all twenty limestone sources.

Results and Discussion

Listed in Table 3.1 are the reaction times of three particle size fractions from twenty limestone sources averaged over three replications. As was expected, the amount of time required for each limestone source to neutralize 1 meq H^+ to pH 5.3 decreased with the decrease in particle diameter, regardless of whether they were dolomitic or calcitic limestones. There were two exceptions, sources VII and XX, where the reaction times for the mid-size and fine particles from these two sources were not significantly different.

There has been research that leads to the idea that there may be a limit beyond which the degree of particle fineness ceases to influence the effectiveness of limestones in neutralizing acid. The general consensus has been that limestone with 100% passing a 60 mesh screen is no more effective than limestone with only 50% passing the same screen size (Barber, 1984; Perkins, 1961; Jorgenson, 1957; Beacher et al., 1952; Meyer and Volk, 1952; Kopeloff, 1917; White, 1917; and Thomas and Frear, 1915). Likewise, Adams (1979) determined that material passing a 60 mesh screen was as reactive as that passing a 100 mesh sieve. The reaction times for the calcitic limestones used in this study are in accordance with this consensus. For these limestones, there were no significant differences in reaction times between the mid-size (90-75 µm) and fine (45-38 µm) particles. In contrast, five of the eight dolomitic limestones had significantly different reaction times between the mid-size and fine particles. The coarse particles (600-300 µm) took significantly more time to react (had higher reactivity rates) than the other two particle size fractions for all limestone sources.

Dolomitic limestone reacts more slowly than calcitic because it is less soluble (Thomas and Hargrove, 1984). In this study, the average reaction times for the dolomitic limestones were approximately 2.5x - 4.5x greater than the average times for the calcitic limestones. Hence, these results are in agreement with previous studies. Additionally, in a review of previous literature, Barber (1984) concludes that for an equal reaction, dolomitic limestones need to average about half the diameter of calcitic limestones. His conclusion was not upheld by this study, in which the fine particles were approximately half the diameter of the mid-size particles. The average reaction time for the fine, dolomitic limestones was more than double that for the mid-size, calcitic limestones. Thus, while the results of this study agree with the former statement - dolomitic limestones did react more slowly than the calcitic limestones - the degree of difference in the reaction times between the two types of limestones was much greater in this experiment than that reported previously.

Several researchers have concluded that the difference in effectiveness between $MgCO_3$ and $CaCO_3$ was reduced as particle size decreased (Perkins, 1961; Jorgensen, 1957; Beacher et al., 1952; Meyer and Volk, 1952; Kopeloff, 1917; White, 1917; and Thomas and Frear, 1915). In this study, the reaction time averaged over all mid-size dolomitic limestones was 4.2x greater than that for the calcitic limestones while the average overall reaction time for the fine dolomitic particles was reduced to 3.2x greater than for the calcitic limestones. For these two particle size fractions the difference in effectiveness did decrease; however, both particle size fractions had a greater difference in average reaction time than the coarsest particles, for which the average reaction time for dolomitic limestones was only 2.5x greater than that for the calcitic limestones.

The results pertaining to the calcitic limestones used in this study are in accord with conclusions drawn in previous experiments; however, when the relationship between dolomitic and calcitic limestones is considered, this experiment resulted in much greater differences in effectiveness between the two types of limestone than the conclusions that have been reported to date. In many of the studies mentioned above, the “effectiveness” of limestones has been evaluated by measuring crop response. In such studies, the Mg supplied to plants from the dolomitic limestones may have contributed to the overall growth and development of the crops; consequently enhancing the perceived effectiveness of these limestones.

This experiment resulted in tremendous, significant variation in reaction times among dolomitic limestone sources for any given particle size fraction, but very little (coarse particles) or no (mid-size and fine particles) significant difference among the calcitic limestones. Table 3.1 lists limestone sources in order of increasing $CaCO_3$ content, which, for the dolomitic limestones, is equivalent to decreasing $MgCO_3$ content. For the dolomitic limestones, and, to some extent for the coarse calcitic limestones, the $CaCO_3$ (or $MgCO_3$) content does not appear to be the only important factor, aside from particle size, that exerts influence on the rate at which limestones neutralize acid.

Conclusions

Finer particles neutralize acid faster than coarse particles; however, for the calcitic limestones used in this study, there appears to be a particle size between 300 and 90 µm beyond which reduced particle size no longer affects reaction times. This "point of no return" did not appear to exist in the particle size fractions of dolomitic limestones used for this study, although it may occur in finer particles.

Dolomitic limestones were slower to react than calcitic limestones. The relative rates of reactivity of dolomitic and calcitic limestones varied with particle size.

Tremendous, significant variation in reaction times among dolomitic limestones and slight, but significant variation in reaction times of the coarsest, calcitic limestones give rise to the idea that there may be factors other than particle size or $CaCO_3$ content that influence limestone reactivity rates. It is possible that the agricultural limestone standards that are currently used are explicit enough to characterize calcitic limestones for horticultural use; however dolomitic limestone may require additional analyses to be described accurately enough for horticultural purposes.

These data were obtained in a lab, where the limestones were not subjected to variations in moisture or temperature, factors which may influence reaction times. It remains to be seen how results from this study correlate to limestone reactions in containerized substrates in a greenhouse setting.

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Table 3.1. Reaction times [seconds required for 1 mg limestone to neutralize 1 meq H^+ ($s \cdot mg^{-1}$ per1 meq H^+)] to a bromcresol green endpoint (pH 5.3) of limestones from twenty sources (quarries). Sources are listed in order of increasing calcium content.

Limestone			**Particle Diameter Fractions (µm)**			**Tukey's**
Source	**Type**[z]	**% $CaCO_3$**	**600 - 300**	**90 – 75**	**45 – 38**	**HSD $_{0.05}$**
I	D	51.0	11.02 a, b[y]	1.90 c*	1.19 c*	0.20
II	D	52.3	9.38 b, c	2.61 b*	1.62 b*	0.76
III	D	54.1	10.40 b, c	3.50 a	2.28 a	nsd[x]
IV	D	54.1	0.51 i	0.23 d	0.17 e	nsd
V	D	55.0	11.92 a	3.92 a*	2.10 a*	1.00
VI	D	58.9	8.88 d	1.87 c*	1.00 c, d*	0.41
VII	D	67.3	2.62 h	0.58 d	0.82 d	nsd
VIII	D	68.2	6.40 e	2.30 b, c*	1.72 e*	0.55
Average Times			7.64	2.12	1.36	
IX	C	78.9	2.98 h	0.48 d	0.43 e	nsd
X	C	83.5	4.42 f, g	0.57 d	0.473 e	nsd
XI	C	90.6	3.13 f, g	0.433 d	0.34 e	nsd
XII	C	90.9	4.47 f	0.55 d	0.47 e	nsd
XIII	C	91.5	3.04 g, h	0.45 d	0.41 e	nsd
XIV	C	95.6	2.74 h	0.41 d	0.41 e	nsd
XV	C	96.0	2.56 h	0.38 d	0.38 e	nsd
XVI	C	96.1	2.35 h	0.57 d	0.40 e	nsd
XVII	C	96.9	3.28 f, g, h	0.51 d	0.45 e	nsd
XVIII	C	97.4	2.89 h	0.43 d	0.38 e	nsd
XIX	C	98.0	2.14 h	0.78 d	0.47 e	nsd
XX	C	98.1	2.83 h	0.44 d	0.47 e	nsd
Average Times			3.07	0.50	0.42	
Tukey's HSD$_{0.05}$			1.40	0.57	0.33	

[z] Type of limestone is based on calcium or magnesium content: D = dolomitic which contains 20-50% $MgCO_3$, C = calcitic which contains 70-100% $CaCO_3$.

[y] Different letters denote significant differences at $\alpha = 0.05$ in reaction times within a particle size fraction.

[x] no significant differencebetween mid-size and fine particle size fractions.

* Denotes a significant difference in reactivity rates between the two finest particle size fractions.

Chapter 4

Evaluation of Limestone Physical and Chemical Properties on Neutralization Capacity

Abstract:

Although several physical and chemical properties of limestone have been shown to affect limestone neutralization capacity, particle size distribution and $CaCO_3$ content have been deemed adequate measures to classify agricultural limestones. When using agricultural limestone to neutralize substrate acidity in horticultural endeavors, problems of inconsistent initial pH in substrates that are created using standard formulas for limestone additions, and pH drift from the initial target in those substrates, occur. This study was conducted to evaluate the effects particle size, $CaCO_3$ and $MgCO_3$ content, internal porosity, hardness, soundness, specific gravity, and specific surface of several limestones from twenty quarries selected to maximize differences in properties on limestone reactivity in order to determine the degree of influence of these factors on the neutralization capacity of the limestones. Data for all these physical/chemical properties were analyzed in multiple regressions with particle size included and with particle size held constant at coarse [30-50 mesh (600-300 μm)], medium [170-200 mesh (90-75 μm)], and fine [325-400 mesh (45-38 μm)] fractions. Particle size accounted for slightly more than half of the neutralization capacity of the limestones. With particle size held constant, $CaCO_3$ or $MgCO_3$ had the greatest impact on limestone reactivity, accounting for about 50% of the reactivity. Specific surface did not correlate significantly to particle size, thus addressed an additional aspect of limestone reactivity. Porosity, hardness and bulk density were highly correlated to each other, thus measured the same aspect of limestone reactivity. Soundness had little influence on reactivity. Adding specific surface measurements to particle size and $CaCO_3$ content increased the power of the reactivity prediction model to 82% of the reactivity. The addition of a fourth measurement; either porosity, hardness or bulk density, increased the model strength to only 88%. It may be useful to include specific surface measurements to the description of limestones used for horticultural purposes.

Chemical names: calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$)

Introduction

Researchers have attempted to characterize the neutralization capacity of limestones for more than a century. Barber (1984) provided a comprehensive review of the literature. This has been a difficult and inconclusive task which gives rise to the idea that there may be great variability in the rate at which limestones react with, and consequently neutralize the substrate acidity. Barber (1984) states that the chemical and physical composition of limestone influences its rate of reaction with the soil. Thomas and Hargrove (1984) state that the rate of [limestone] neutralization strongly depends on the rate of dissolution and hydrolysis of calcium carbonate ($CaCO_3$) to form hydroxide ions (OH^-) and the rate at which the OH^- are removed from the system. The two obvious factors that affect the dissolution of $CaCO_3$ are particle size (large particles provide fewer reaction sites per unit mass than small particles) and the amount of $CaCO_3$ in any given limestone [expressed as the calcium carbonate equivalent (CCE)].

Additionally, there are several other factors that may influence the rate of $CaCO_3$ dissolution. Love and Whitakker (1954) hypothesized that the reactivity of limestone should be related to its exposed surface area and used adsorbed krypton (Kr) to measure surface area. They found considerable variation in the measured surface regardless of particle diameter. These results were later supported by Rippy et al. (2005) who used dinitrogen (N_2) gas as the adsorbate with the same results. The latter also found that the specific surface measurements did not appear to be related to the calcium (Ca) or magnesium (Mg) content of the limestones.

When measured surface area was much greater than that calculated from geometric surface, Love and Whitakker (1954) suggested this to be evidence of internal surfaces. Later, Bussieres (1978) conducted research in which shape and surface area of limestone particles, as well as marine and terrestrial sources of limestone were the factors taken into consideration. He deduced that marine limestone particles are cylindrical in shape and have a cellular, somewhat porous structure which led to underestimation of reactive surface calculated from particle size.

Porosity was earlier investigated by Morgan and Salter (1923) along with the effects of hardness, specific gravity (bulk density), crystalline composition, and chemical analysis on the rate of dissolution of limestone particles. These researchers determined that although Ca and Mg content had the greatest effect on limestone dissolution rates, all factors had a certain degree of influence.

Around the middle of the Twentieth Century, researchers turned their attention away from trying to characterize the limestone reactions, specifically; and started describing these reactions as they occur in various applications. It has been determined that taken together, both particle size distribution and CCE provide an acceptable and economically feasible description of the neutralization capacity of limestones for agricultural applications (Barber, 1984). Indeed, the reactions of limestones with acid soils that are described by these two measures are adequate for producing successfully agronomic crops.

Since the advent of horticulture, agricultural limestone has been used extensively to neutralize the acidity of horticultural substrates with inconsistent results. There is difficulty in attaining consistently the initial substrate pH using standard formulas for limestone additions. Furthermore, problems arise when substrate pH drifts away from the initial target over the course of production.

Substrate pH has a significant effect on the availability of nutrients to plants. This effect is especially pronounced for horticultural crops grown in containers. Substrates for these crops provide little pH buffering capacity due to the preponderance of root mass to substrate. This effect increases as container size decreases. Also, containerized plants have a very large shoot to root ratio, which makes nutrient management a critical factor in crop production.

Although particle size distribution and CCE describe sufficiently the neutralization capacity of limestones for agricultural applications, it is possible that horticultural endeavors require additional classification. The objective of this study was to evaluate the effects of several limestone physical and chemical properties on limestone reactivity in order to determine the degree of influence of these factors on the neutralization capacity of the limestones.

Methods and Materials

Limestone samples were collected from twenty sources (quarries) across North America where they had been analyzed for hardness (H), soundness (SD), internal porosity (P), bulk density (BD), $CaCO_3$ content (C), and magnesium carbonate ($MgCO_3$) content (M). The limestones were wet-sieved into eight particle size (PS) fractions (Martin Marietta Technologies, Inc., Mason, Ohio).

Specific surface (SS) was measured on three replications of each particle size fraction from each limestone source following the BET theory that dinitrogen gas (N_2) will form a monomolecular layer on all surfaces (Rippy et al., 2005). Reaction times (RT) for 100 mg limestone to neutralize 1 meq H^+ from 1N sulfuric acid (1N H_2SO_4) to pH 5.3 were determined on three replications of coarse [30-50 mesh (600-300 μm)], medium [170-200 mesh (90-75 μm)], and fine [325-400 mesh (45-38 μm)] particles from each source (Rippy and Nelson, 2005). RT was considered to represent limestone reactivity or neutralization capacity.

A multiple regression (SAS Institute, Cary, NC) was conducted to evaluate the relationships of PS, H, SD, P, BD, C, M, and SS to RT. Since it has long been accepted that particle size has the greatest influence on limestone reactivity rates, a multiple regression was also conducted for each of three particle size fractions (same as were used for RT mentioned above) individually. This regression, conducted for each particle size fraction, was done to elucidate not only the relationships among each of the physical/chemical properties, but also, their relative influence on limestone RT. Three particle size fractions were used in order to determine whether or not the relationships among the physical/chemical properties were consistent regardless of particle size.

Physical and chemical properties were then eliminated one at a time, starting with the property having the least significant correlation to RT. After a property was eliminated from the model, significance was recalculated on those remaining using an analysis of variance [ANOVA (SAS Institute, Cary, NC)]. This process continued until only those properties having a significant influence on RT at $\alpha=0.05$ remained.

In the final step, r^2 values were generated for each physical/chemical property individually and then for all possible combinations of the properties when two, and up to all seven, properties were included. The r^2 values indicate the degree to which RT is explained by each property or combination of properties.

Results and Discussion

The results of the multiple regressions, the step-by-step elimination ANOVAs and the r^2 values with PS included in the model, as well as with PS held constant are presented in their entirety in Appendix II.A. Only the key elements from these results are presented in this text.

When particle size (PS) was included in the model containing all of the physical and chemical properties, 62% of the variation in reaction times (RT) was explained. Particle size accounted for 35%, slightly more than half, of this variation. Although this was significant and indeed the greatest factor influencing RT, other factors were exerting significant influence as well.

The relationships among all the physical and chemical properties studied, as well as their influence on limestone neutralization capacity, with particle size held constant at three different size range fractions, are presented in Table 4.1. It is helpful to visualize the neutralization capacity of limestone as a multi-faceted question, with each of the properties explaining individual phenomena, or segments of the question. When properties are highly correlated to others, aside from RT, they are explaining the same realm of phenomena.

RT was significantly correlated to all of the properties studied with the exception of hardness (H), but this discrepancy was apparent only in the finest particle size fraction. Hardness was highly correlated to both bulk density (BD) and porosity (P), meaning all three were providing the same type of information. The correlation of RT with all three of these properties weakened as particle size was reduced.

Bulk density is reduced with the occurrence of more and larger air spaces within the limestone particles. Similarly, particles with greater P will crumble into smaller particles more easily (measured by H) than will particles with few internal spaces. It is plausible that breakage occurs along the axes formed by the pores. Thus, the finest particles may contain no, or few, internal pores. Since H is most highly correlated to P, it has little influence on limestone reactivity when internal pores are not present.

Although the influences of P and BD on limestone neutralization capacity weakened as PS decreased, they remained significant in the finest particles. It has been established that H, P, and BD affect the same sphere of influence exerted on neutralization capacity. Outside this realm, the influence of H on RT is reasonably related to that of soundness (SD) and is not significantly related to specific surface (SS). Conversely, the effects of P and BD on RT are significantly related to SS and are not significant to those of SD. In this case, the relationships outside the sphere of strong influence have a certain amount of impact on the neutralization capacity of limestone.

In this study, SD had a reasonable correlation to H but was not strongly correlated to any of the other properties. Finally, it was only poorly correlated to limestone reactivity. SD is a measure used by various construction industries to determine the degree to which limestone particles withstand degradation due to freeze/thaw cycles. Limestone was not subjected to temperature variations during determination of RT in the lab, nor would it be in a greenhouse setting. While this measure may be very important when considering limestone materials to be used for concrete or asphalt, it does not appear to have much influence on the neutralization capacity of limestone in regards to horticultural applications.

As was expected, with particle size held constant, $CaCO_3$ content (C) and $MgCO_3$ content (M) had the greatest impact on limestone neutralization capacity. These two measures are highly correlated to each other, which is not surprising. They are, to some extent, a replacement series. All limestones contain at least 50% $CaCO_3$. Beyond that, as the amount of $MgCO_3$ increases, the amount of $CaCO_3$ must decrease.

In this study, specific surface (SS) did not correlate significantly to particle size [(PS (r = 0.0809, p = 0.3204)]. A strong correlation to PS would imply that most of the exposed surface is on the exterior of the particles; however, limestones contain varying amounts of internal pore spaces, hence exposed internal surfaces.

In the coarsest particles, SS had a weaker affect on reaction times (RT) than did P, H, or BD. The opposite was true in the finest particle size fraction, supporting the earlier mentioned theory that internal pores exist in coarse, but are scarce in fine, particles. Limestone rate of neutralization depends not only on the rate of dissolution and hydrolysis of $CaCO_3$, but also on the rate at which OH^- are removed from the reaction sites (Sparks, 2003). The transport rate of OH^- out of pores would be much slower than that for OH^- formed from external reactions. Furthermore, the OH^- may exert a sphere of influence within the pores (DeTurk, 1939). By causing temporarily high pH within the pores the reaction rate would be slowed. Most probably, SS has a stronger influence on RT in the fine particle size fraction than in the coarse, because of the reduced internal porosity.

The stepwise elimination ANOVA results are presented in Table 4.2, which lists the limestone physical/chemical properties, other than PS, that had a significant influence on neutralization capacity. For all particle size fractions, C and SS had the greatest impact. P, H, or both along with BD, were also significantly related to limestone neutralization capacity in the coarse, medium, and fine particle size fractions, respectively.

The r^2 values showing the contribution of limestone physical/chemical properties individually, and in some combinations, to neutralization capacity for three particle size fractions are presented in Table 4.3. At the bottom of this table are listed the highest contributions possible, obtained by including all of the properties studied here, for each particle size fraction. As properties are added, the contribution to limestone neutralization capacity increases. The interval of increase is reduced as successive properties are added.

Within each section of Table 4.3, four combinations of properties with the highest contribution to neutralization capacity are listed in order of greatest to least contribution. Combinations having r^2 values that are close to each other may be used interchangeably, because they are accounting for the same phenomena of the neutralization capacity question.

For instance, with two properties in the model, the combination of C and SS provide the greatest contribution to limestone neutralization; however, M and SS may also be used with reasonably similar results. Likewise, if it were desired to add a third property to the model, either P, H, or BD may be combined with C and SS to achieve a similar contribution.

The highest possible r^2 value obtained in this study was 0.8514. The content of $CaCO_3$ and $MgCO_3$, as a weight percentage of the total limestone weight, for the twenty limestones used in this study are shown in Figure 4.1. Five of the twenty limestones contained greater than 10% material other than C or M. This material may have influenced the extent to which the physical properties impacted RT. At this time, it is neither known what that other material is, nor its impact on limestone neutralization. The fact that only one of these limestones was made up entirely of reactive material accounts for the r^2 value being less than 1.0.

Conclusions

Of course, it is desirous to account for the total contribution to limestone reactivity. Considering that the tests required to obtain data for each of these physical/chemical properties consume time and money, the type and number of properties to include in the neutralization model becomes dependent upon financial feasibility, ease of acquiring data, and the degree to which limestone neutralization capacity must be characterized.

Particle size (PS) and $CaCO_3$ equivalent (CCE) are already being used to characterize limestone neutralization capacity well enough for agronomic purposes, but containerized crop production systems require a more complete definition. Specific surface (SS) addresses a realm of the limestone neutralization capacity question that is not answered well by PS or CCE. In combination with PS and CCE, SS exerts the greatest influence on limestone neutralization capacity. If additional characterization of limestone reactivity is required, either porosity, hardness, or bulk density may be added interchangeably.

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Table 4.1. Pearson correlation coefficients for relationships of each limestone physical/chemical property to every other property for three particle size fractions. Absolute values of coefficients range from 0 to 1 with 1 indicating the strongest possible relationship. Physical/chemical properties were obtained from limestones from twenty quarries selected to encompass a broad range for each variable.

	Reaction Time (RT)	**Hardness (H)**	**Soundness (SD)**	**Porosity (P)**	**$CaCO_3$ (C)**	**$MgCO_3$ (M)**	**Bulk Density (BD)**	**Specific Surface (SS)**
				30-50 mesh screen size				
RT	1.0000	-0.4065	-0.2926	-0.3198	-0.7646	0.7120	0.4565	-0.3220
H	-0.4065	1.0000	0.4140	0.8001	0.5243	-0.4493	-0.7646	0.2159*
SD	-0.2926	0.4140	1.0000	0.1783*	0.3882	-0.3676	-0.2341*	0.1097*
P	-0.3198	0.8001	0.1783*	1.0000	0.4762	-0.4547	-0.9560	0.3132
C	-0.7646	0.5243	0.3882	0.4762	1.0000	-0.9650	-0.5847	-0.1254*
M	0.7120	-0.4493	-0.3676	-0.4547	-0.9650	1.0000	0.5616	0.1342*
BD	0.4565	-0.7646	-0.2341	-0.9560	-0.5847	0.5615	1.0000	-0.3295
SS	-0.3220	0.2159*	0.1097*	0.3132	-0.1254*	0.1342*	-0.3295	1.0000
				170-200 mesh screen size				
RT	1.0000	-0.3037	-0.3442	-0.3190	-0.7477	0.7284	0.4352	-0.3601
H	-0.3037	1.0000	0.4140	0.8001	0.5243	-0.4493	-0.7646	0.2880
SD	-0.3442	0.4140	1.0000	0.1783*	0.3882	-0.3676	-0.2341*	0.1379*
P	-0.3190	0.8001	0.1783*	1.0000	0.4762	-0.4547	-0.9560	0.3253
C	-0.7477	0.5243	0.3882	0.4762	1.0000	-0.9650	-0.5847	0.0113*
M	0.7284	-0.4493	-0.3676	-0.4547	-0.9650	1.0000	0.5616	-0.0119*
BD	0.4352	-0.7646	-0.2341	-0.9560	-0.5847	0.5615	1.0000	-0.3808
SS	-0.3601	0.2880	0.1379*	0.3253	0.0113*	-0.0119*	-0.3808	1.0000
				325-400 mesh screen size				
RT	1.0000	-0.2676*	-0.2995	-0.3055	-0.7217	0.7025	0.4054	-0.4065
H	-0.2676*	1.0000	0.4140	0.8001	0.5243	-0.4493	-0.7646	0.2866
SD	-0.3055	0.4140	1.0000	0.1783*	0.3882	-0.3676	-0.2341*	0.1047*
P	-0.2995	0.8001	0.1783*	1.0000	0.4762	-0.4547	-0.9560	0.2828
C	-0.7217	0.5243	0.3882	0.4762	1.0000	-0.9650	-0.5847	-0.0212*
M	0.7025	-0.4493	-0.3676	-0.4547	-0.9650	1.0000	0.5616	0.0290*
BD	0.4054	-0.7646	-0.2341*	-0.9560	-0.5847	0.5615	1.0000	-0.3325
SS	-0.4065	0.2866	0.1047*	0.2828	-0.0212*	0.0290*	-0.3325	1.0000

* Denotes property relationships that were NOT significantly correlated. All other correlations were significant at $\alpha = 0.05$.

Table 4.2. Stepwise elimination ANOVA results listing limestone physical or chemical properties that were significantly correlated to reaction times at α=0.05.

Particle Size Fraction (U.S. Standard Screens)					
30-50 mesh		**170-200 mesh**		**325-400 mesh**	
Property	***p*-value**	**Property**	***p*-value**	**Property**	***p*-value**
$CaCO_3$	<0.0001	$CaCO_3$	<0.0001	$CaCO_3$	<0.0001
Sp. Surface	<0.0001	Sp. Surface	<0.0001	Sp. Surface	<0.0001
Porosity	0.0001	Hardness	0.0031	Hardness	0.0002
				Bulk Density	0.0098
				Porosity	0.0130

Table 4.3. Correlation (r^2 values) of limestone physical/chemical properties with limestone reaction times for three particle size fractions. Values are listed for each property individually, and then for the four highest ranking correlation combinations for up to four properties.

Variables are coded as follows: BD= Bulk density, C=% $CaCO_3$, H=Hardness, M=% $MgCO_3$, P= Porosity, SD=Soundness, SS=Specific surface.

Limestone Particle Diameter Ranges (µm)					
600-300 mesh		90-75 mesh		45-38 mesh	
Property	r^2 value	Property	r^2 value	Property	r^2 value
1 property in the model					
C	0.5845	C	0.5590	C	0.5208
M	0.5070	M	0.5305	M	0.4935
BD	0.2084	BD	0.1894	SS	0.1653
H	0.1652	SS	0.1296	BD	0.1643
SS	0.1037	SD	0.1185	P	0.0933
P	0.1023	P	0.1017	SD	0.0897
SD	0.0856	H	0.0922	H	0.0716
2 properties in the model					
C, SS[z]	0.7620	C, SS	0.6827	C, SS	0.6988
M, SS	0.6846	M, SS	0.6540	M, SS	0.6759
C, M	0.5942	C, H	0.5698	C, H	0.5377
C, P	0.5871	C, SD	0.5624	C, M	0.5227
3 properties in the model					
C, P, SS	0.8269	C, H, SS	0.7371	C, H, SS	0.7866
BD, C, SS	0.8148	BD, C, SS	0.7171	BD, C, SS	0.7475
C, H, SS	0.7821	C, P, SS	0.7160	C, P, SS	0.7369
C, SD, SS	0.7682	C, M, SS	0.6833	H, M, SS	0.7197
4 properties in the model					
C, P, SD, SS	0.8374	C, H, SD, SS	0.7413	BD, C, H, SS	0.7893
C, M, P, SS	0.8327	BD, C, H, SS	0.7401	C, H, SD, SS	0.7884
C, H, P, SS	0.8292	C, H, M, SS	0.7388	C, H, M, SS	0.7883
BD, C, P, SS	0.8276	C, H, P, SS	0.7379	C, H, P, SS	0.7869
All properties	0.8514	All properties	0.7501	All properties	0.8260

[z] Where there are more properties than one in the model, properties are listed in alphabetical order. The arrangement of properties within a row does NOT indicate relative strength of correlation.

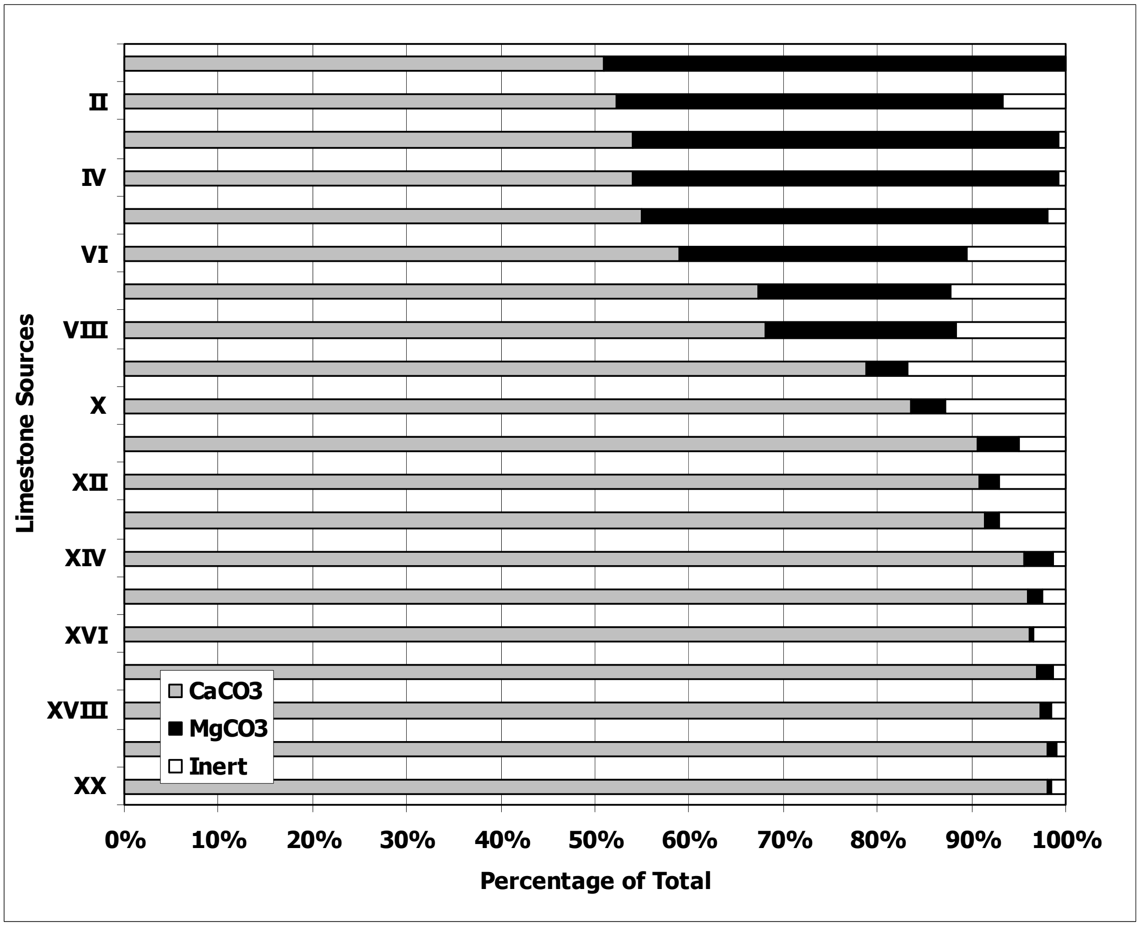

Figure 4.1. The percentages of CaCO3 and MgCO3 in limestones from twenty sources (quarries).

Chapter 5

Cation Exchange Capacity and Base Saturation Variation Across Alberta, Canada Peat Moss

Abstract:

Problems of inconsistent initial pH in peat moss-based substrates that are created using standard formulas for limestone additions, and pH drift from the target in those substrates may be due to variations in the CEC and BS of peat moss. This study was conducted to determine the extent to which such variation exists. Sixty-four peat moss samples were selected from several bogs across Alberta, Canada to represent maximum gradients in plant species composition and to encompass degrees of decomposition that are commonly found in *Sphagnum* peat mosses used for commercial soilless substrates. Adsorbed cations on each peat moss sample were displaced with HCl, and flushed out with three deionized water washes. The displacing/flushing solution was collected and later analyzed for concentration of bases ([Ca^{2+}], [Mg^{2+}], [K^+], and [Na^+]). After cations were removed, the peat moss exchange sites were saturated with $Ba(OAc)_2$ to displace the H^+ which were then collected by a second flushing with deionized water. This second displacing/flushing solution was titrated with measured amounts of NaOH to a phenolphthalein end point (pH ~8.0). Base saturation and CEC were calculated. There were significant variations in CEC (108-162 $cmol{\cdot}kg^{-1}$) and BS (15-71% of CEC) among the peat moss samples. Calcium accounted for 68% of the BS. It would be anticipated that high CEC peat mosses would have a greater buffering capacity than those with low CEC, which should result in less pH drift. Further, peat mosses with the higher BS should have a lower neutralization requirement to achieve a target pH.

Chemical names: barium acetate [$Ba(OAc)_2$], calcium (Ca^{2+}), hydrochloric acid HCl, hydrogen ions (H^+), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+),.

Introduction

Growers who formulate their own soilless substrates and companies that sell ready-mixed soilless substrates are faced with two problems. First, there is difficulty in attaining consistently initial substrate pH targets using standard formulas for limestone additions. The second problem arises when substrate pH drifts away from the initial target over the course of production. It is possible that within or among mires, there may be variation in the "neutralization requirement" of peat mosses.

Two factors that may affect the neutralization requirement of peat moss among batches are cation exchange capacity and base saturation [fractional calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), and sodium (Na^{+})]. These properties may be related to the composition of plant species in each batch of peat. Some references have been made regarding the differences in physical and chemical properties among the three types of peat that may be commonly found in horticultural substrates: reed sedge, hypnum, and *Sphagnum* peat mosses (Nelson, 2002; Argo and Biernbaum, 1997; Bunt, 1988; and Puustjarvi and Robertson, 1975). Of these three types of peat, *Sphagnum* is used most extensively and has been thought to be highly consistent from batch to batch, as well as over time.

There are fourteen species of *Sphagnum* but only three are used in commercial container substrates: *S. angustifolium* (Russow) C. Jens, *S. fuscum* (Schimp.) Klingrr., and *S. magellanicum* Brid. In a review of the botanical literature regarding the occurrence and growth habits of these *Sphagnum* species, it becomes apparent that variations may indeed exist.

Du Rietz (1949, 1954) described the relationship between trophic status and vegetation, and distinguished between fens and bogs. Fens are differentiated from bogs when pH, cation concentrations, and electrical conductivity (EC) indicate water contact with mineral soil water (Horton et al., 1979). Therefore, fen vegetation is considered to be minerotrophic. By definition, bogs are not influenced by water that is in contact with mineral soils. Rather, the moisture in a bog is derived solely from precipitation, thus, bog vegetation is ombrogenous (Horton et al., 1979).

Across Canada, trophic gradients range from ombrotrophic conditions in the treed-tundra, where vegetation is elevated above the water table by permafrost, to very poorly minerotrophic conditions in thaw-pockets (isolated areas of thawed ground) characterized by [Ca^{2+}] from 0.01-0.14 $mol{\cdot}L^{-1}$, [Mg^{2+}] from 0.0004-0.0123 $mol{\cdot}L^{-1}$, and EC from 9.2-36.1 $\mu mho{\cdot}cm^{-1}$ (1 μmho = 1 μS), to more highly minerotrophic conditions along streams in which pH ranges from 4.8-5.1, [Ca^{2+}] from 0.157-0.162 $mol{\cdot}L^{-1}$, [Mg^{2+}] from 0.008-0.012 $mol{\cdot}L^{-1}$, and EC from 35.6-41.9 $\mu mho{\cdot}cm^{-1}$ (Horton et al., 1979).

The three species of *Sphagnum* used for horticultural purposes exist in distinct strata with respect to the water table (Mulligan and Gignac, 2001; and Bragazza and Gerdol, 1999). *Sphagnum angustifolium* is a dominant species in poor (slightly minerotrophic) fens; however, it becomes sporadic and scarce in calcareous regions. It typically occurs in hollows below *S. magellanicum* in weakly to moderately minerotropohic habitats (Vitt and Andrus, 1977). *Sphagnum magellanicum* grows in moist habitats but cannot tolerate flooding (Kulczyńsky, 1949). It occurs in the shallower parts of thaw pockets and is found only on the better developed mounds of *S. angustifolium* (Horton et al., 1979). *Sphagnum fuscum* most frequently forms islands of ombrotrophic vegetation, occurring on bogs above *S. magellanicum* and *S. angustifolium* (Vitt and Andrus, 1977).

The distinct variation in the pH of the water among the strata in which these *Sphagnum* species are found may cause them to differ in base saturation (BS) and cation exchange capacity (CEC) which is influenced by the pH dependent exchange of cations and hydrogen ions (H^+) from organic acid fundamental groups (Argo and Biernbaum, 1997, Sumner and Miller, 1996, and Helling et al., 1964). Since peat is harvested across bogs without respect to speciation, these differences may affect the CEC abd BS, hence, the neutralization requirement of the peat moss used for container substrates among batches. This study was conducted to examine the extent to which variation in CEC and BS exists among peat mosses across Alberta, Canada.

Methods and Materials

Much of the peat moss used for commercial soilless substrates in the United States comes from Canadian mires. These bogs are harvested during June, July and August. The harvested peat moss is stockpiled in windrows at the edges of the bogs until it is used. In September, 2002, 465 samples were collected from three Alberta, Canada mires; one from each pile of harvested peat moss, and were analyzed for degree of decomposition according to the von Post (1935) scale [later modified by Puustjarvi and Robertson (1975)] and species composition by Jean MacDonald (Botanist, Highland Grey Co. Alberta, Canada). Of these samples, 64 were selected to represent a broad range of the three *Sphagnum* species and sedge composition within each of six decomposition stages: H1.5 – almost no decomposition, to H4 – slightly decomposed. Peat moss that is more highly decomposed than H4 is not used for commercial horticultural purposes.

Cation exchange capacity was measured on approximately 2 g of air-dry, ground peat moss in a complete random design (CRD) with three replications using a protocol described by Thorpe (1973). In this procedure, peat moss was soaked in 100 mL half-normal hydrochloric acid (0.5N HCl) to displace the adsorbed cations and saturate the peat moss exchange sites H^+. The suspension was filtered through coarse, fast filter paper and the displaced cations were removed with three successive washes of deionized water (100 mL each). The filtrate + washes solution was collected for later analysis of cation concentration. After the third wash, the peat moss was soaked in 100 mL barium acetate [0.5N $Ba(OAc)_2$], which displaced the H^+ by saturating the exchange sites with barium (Ba^{2+}). This suspension was filtered and the peat moss was washed three more times with 100 mL deionized water for each wash to remove the displaced H^+. This second filtrate + washes solution was collected and titrated with sodium hydroxide (0.1N NaOH) to a phenolphthalein endpoint (pH ~8.0). Cation exchange capacity was calculated from the amount of titrant used and expressed as $cmol \cdot kg^{-1}$.

The first solution was analyzed for concentrations of Ca^{2+}, Mg^{2+}, K^+ and Na^+ using atomic absorption spectrometry. Standard curves were generated to convert absorbance readings to $mg \cdot L^{-1}$. Measured cation concentrations were calculated and expressed as $cmol \cdot kg^{-1}$. Base saturation as a percentage of CEC was calculated by dividing the sum of the cation concentrations by the CEC and multiplying by 100. Moisture content of the air-dry peat moss samples was determined at the time CEC was measured. All data was standardized to an oven-dry basis.

Cation exchange capacity and BS data were analyzed by an analysis of variance (SAS Institute, Cary, NC) for differences among the 64 peat moss samples at $\alpha = 0.05$. Degree of decomposition, species distribution, and measured cation concentrations ($\text{cmol}\cdot\text{kg}^{-1}$) were included in a multiple regression to determine the extent to which they were related to CEC and BS.

Results and Discussion

Averaged over three replications, CEC ranged from 108 ± 7 to 162 ± 23 $\text{cmol}\cdot\text{kg}^{-1}$, with the mean value of all 64 samples being 139 ± 15 $\text{cmol}\cdot\text{kg}^{-1}$. Inherent base saturation for the peat mosses ranged from 15 ± 4% - 71 ± 6% of CEC. The mean BS was 30 ± 11% CEC. The CEC values with BS as a percentage of CEC for 64 peat moss samples are depicted in Figure 5.1. There was a significant difference between both CEC and BS of peat mosses with the lowest and the highest values; however, there was considerable overlap among both measurements of the remaining peat moss samples.

Puustjarvi and Robertson (1975) reported a range of CEC values in relation to degree of decomposition from 100 $\text{cmol}\cdot\text{kg}^{-1}$ for H1 peat mosses to 124 $\text{cmol}\cdot\text{kg}^{-1}$ for H5 peat mosses. Cowan (2005) described organic soils as those which are mostly comprised of peat moss. He provided a CEC range from 150 - 200 $\text{cmol}\cdot\text{kg}^{-1}$ in newly formed organic soils. Although there is some variation in the published CEC values, those obtained in this study are in accordance with the literature. Base saturation values are in keeping with Cowan (2005), who states that peat soils can be up to 50% base saturated.

The basic cation concentrations as a percentage of BS are presented in Figure 5.2. All were within previously reported ranges except [Na^+], which was only slightly higher. Calcium accounted for the largest portion of BS. Bunt (1988) states that the high CEC of peat (as opposed to mineral soils) indicates the potential for greater adsorption of divalent cations (Ca^{2+} and Mg^{2+}) while most of the monovalent cations (K^+ and Na^+) remain water soluble. One divalent cation will displace two H^+. Thus, divalent basic cations will neutralize acid more efficiently than monovalent cations.

Additionally, Ca^{2+} and Mg^{2+} are weakly complexed with carboxyl groups, making them readily exchangeable with H^+ (Broadbent and Ott, 1957).

In comparing BS and CEC (Figure 5.1), the peat moss samples with lower CEC values appear to be situated among the group of peat moss samples with high BS values, and those with the lowest BS have moderately high CEC. While peat moss samples varied in the amount of exchange sites, they also varied in the amount of associated bases. These variations are due to the composition of *Sphagnum* species in the peat moss samples. The CEC of peat moss samples with varying composition of the three *Sphagnum* species are depicted in Figure 5.3. Peat moss samples with high CEC contained larger amounts of *S. fuscum* than samples with low CEC.

In Table 5.1, the Pearson correlation coefficients for the relationships of CEC, BS, degree of decomposition, species composition, and measured cation concentrations are listed along with associated *p*-values. From this table, CEC was significantly correlated to *S. fuscum*; however, BS was most highly correlated to sedge. *Sphagnum fuscum* is ombrotrophic vegetation having no contact with soil surface water; thus, would have few associated cations other than H^+.

As mentioned earlier, Puustjarvi and Robertson (1975) found CEC to vary with degree of decomposition. It seems reasonable that as the peat moss decomposes, there would be more ionizable organic acid functional groups exposed; however, in this study, there was no significant correlation between CEC and decomposition.

Because of the minerotrophic habitats of *S. angustifolium* and *S. magellanicum*, it may be intuitive to presume that greater extractable [Ca^{2+}] and [Mg^{2+}] would be associated with these species than with ombrotrophic *S. fuscum*. In this study, although the correlation is not strong, extractable [Ca^{2+}] and [Mg^{2+}] are positively correlated to *S. fuscum* and negatively correlated to the other two *Sphagnum* species. In light of the positive correlation between *S. fuscum* and CEC, this unexpected relationship of bases to the three *Sphagnum* species studied leads to the idea that the CEC must be much higher in *S. fuscum* than in the other two species; consequently, allowing the bases to be present in greater quantity on this species.

Although *S. fuscum* is found in ombrotrophic, rather than minerotrophic habitats, the samples examined here were taken from stockpiles of harvested peat. The cations other than H^+ associated with *S. fuscum* were probably exchanged from other species with lower CEC. Since [Ca^{2+}] exerts a significant, positive influence on CEC, and BS, it may be interesting to study these relationships with greater depth than was feasible in this study.

Conclusions

Peat moss samples varied significantly in CEC and BS. The variation was due to the species composition of the peat moss samples. Cation exchange capacity appears to be a fixed value that is fundamental to the peat moss and varies by species. The influence of species on BS appears to be related to [Ca^{2+}] and [Mg^{2+}] associated with the peat mosses. Cation exchange capacity and BS are independent properties, but they both are highly influenced by [Ca^{2+}].

Since Ca^{2+}, a basic cation, comprises the majority of BS, it is reasonable to assume that peat mosses with a high BS will have a lower neutralization requirement than those with a low BS. Peat mosses with a high CEC have a greater ability to exchange cations with H^+, allowing for a greater buffering capacity than those with low CEC. Greater buffering capacity may result in less pH drift.

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Table 5.1. Pearson correlation coefficients for the relationships among cation exchange capacity (CEC), base saturation (BS), degree of decomposition, peat moss species and measured cation concentrations (meq·100g^{-1} oven-dry peat moss). Absolute values of coefficients range from 0 to 1 with 1 indicating the strongest possible relationship. For each number pair, the top number is the coefficient and the bottom number is the associated p-value.

				***Sphagnum* species**							
	CEC	**BS**	**decom-position**	**fuscum**	**angust-folium**	**magell-anicum**	**sedge**	**[Ca]**	**[Mg]**	**[K]**	**[Na]**
CEC	1.00000	0.02367	0.00198	0.22272	-0.04927	-0.23581	-0.08462	0.25483	0.31595	-0.04133	0.22133
		0.7445	0.9782	0.0019	0.4973	0.0010	0.2432	0.0004	<.0001	0.5692	0.0020
BS	0.02367	1.00000	0.07827	0.14124	-0.33498	-0.15886	0.27744	0.95122	0.69705	0.27240	0.14106
	0.7445		0.2806	0.0507	<.0001	0.0277	<.0001	<.0001	<.0001	0.0001	0.0510
decomp	0.00198	0.07827	1.00000	-0.23922	-0.11767	-0.10291	0.18928	0.10105	-0.07213	0.10526	-0.08675
	0.9782	0.2806		0.0008	0.1040	0.1555	0.0086	0.1631	0.3201	0.1462	0.2315
fuscum	0.22272	0.14124	-0.23922	1.00000	-0.52097	-0.31724	-0.36107	0.17467	0.35257	-0.01055	-0.01890
	0.0019	0.0507	0.0008		<.0001	<.0001	<.0001	0.0154	<.0001	0.8846	0.7947
angust	-0.04927	-0.33498	-0.11767	-0.52097	1.00000	-0.00193	-0.42477	-0.32014	-0.30135	0.11409	0.04064
	0.4973	<.0001	0.1040	<.0001		0.9788	<.0001	<.0001	<.0001	0.1151	0.5757
magell	-0.23581	-0.15886	-0.10291	-0.31724	-0.00193	1.00000	-0.17929	-0.23305	-0.21674	-0.00492	-0.04239
	0.0010	0.0277	0.1555	<.0001	0.9788		0.0128	0.0011	0.0025	0.9461	0.5594
sedge	-0.08462	0.27744	0.18928	-0.36107	-0.42477	-0.17929	1.00000	0.25295	0.06480	-0.17770	0.03322
	0.2432	<.0001	0.0086	<.0001	<.0001	0.0128		0.0004	0.3718	0.0137	0.6474
[Ca]	0.25483	0.95122	0.10105	0.17467	-0.32014	-0.23305	0.25295	1.00000	0.68592	0.27352	0.09768
	0.0004	<.0001	0.1631	0.0154	<.0001	0.0011	0.0004		<.0001	0.0001	0.1777
[Mg]	0.31595	0.69705	-0.07213	0.35257	-0.30135	-0.21674	0.06480	0.68592	1.00000	0.01856	0.26509
	<.0001	<.0001	0.3201	<.0001	<.0001	0.0025	0.3718	<.0001		0.7984	0.0002
[K]	-0.04133	0.27240	0.10526	-0.01055	0.11409	-0.00492	-0.17770	0.27352	0.01856	1.00000	-0.08419
	0.5692	0.0001	0.1462	0.8846	0.1151	0.9461	0.0137	0.0001	0.7984		0.2457
[Na]	0.22133	0.14106	-0.08675	-0.01890	0.04064	-0.04239	0.03322	0.09768	0.26509	-0.084190	1.0000
	0.0020	0.0510	0.2315	0.7947	0.5757	0.5594	0.6474	0.1777	0.0002	0.2457	

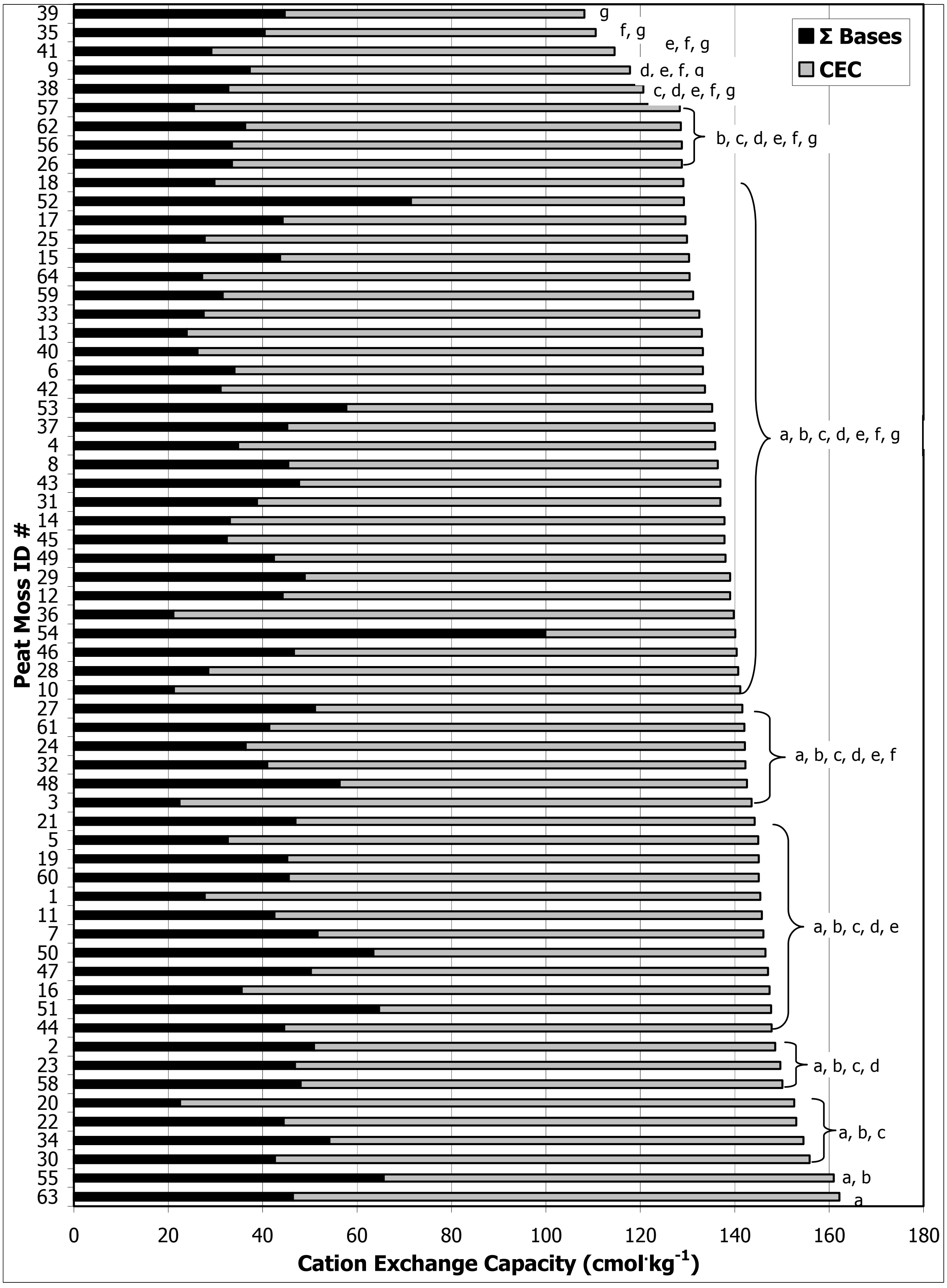

Figure 5.1 Cation exchange capacities (CEC) and the sum of the basic cations Ca, Mg, K, and Na. Significant differences in CEC are denoted by different letters. Tukey's $HSD_{0.05}$ = 33.19

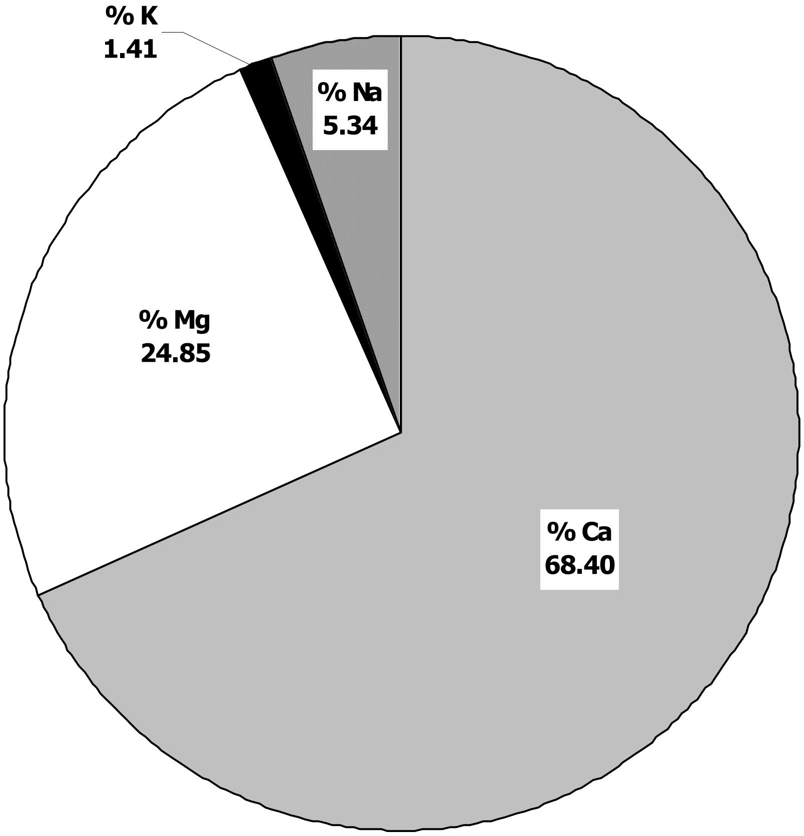

Figure 5.2. Basic cations as a percentage of the base saturation, averaged over 64 peat mosses.

Ranges of bases: Ca 69.07-88.10, Mg 7.35-23.60, K 0.30-6.16, Na 1.85-12.55.

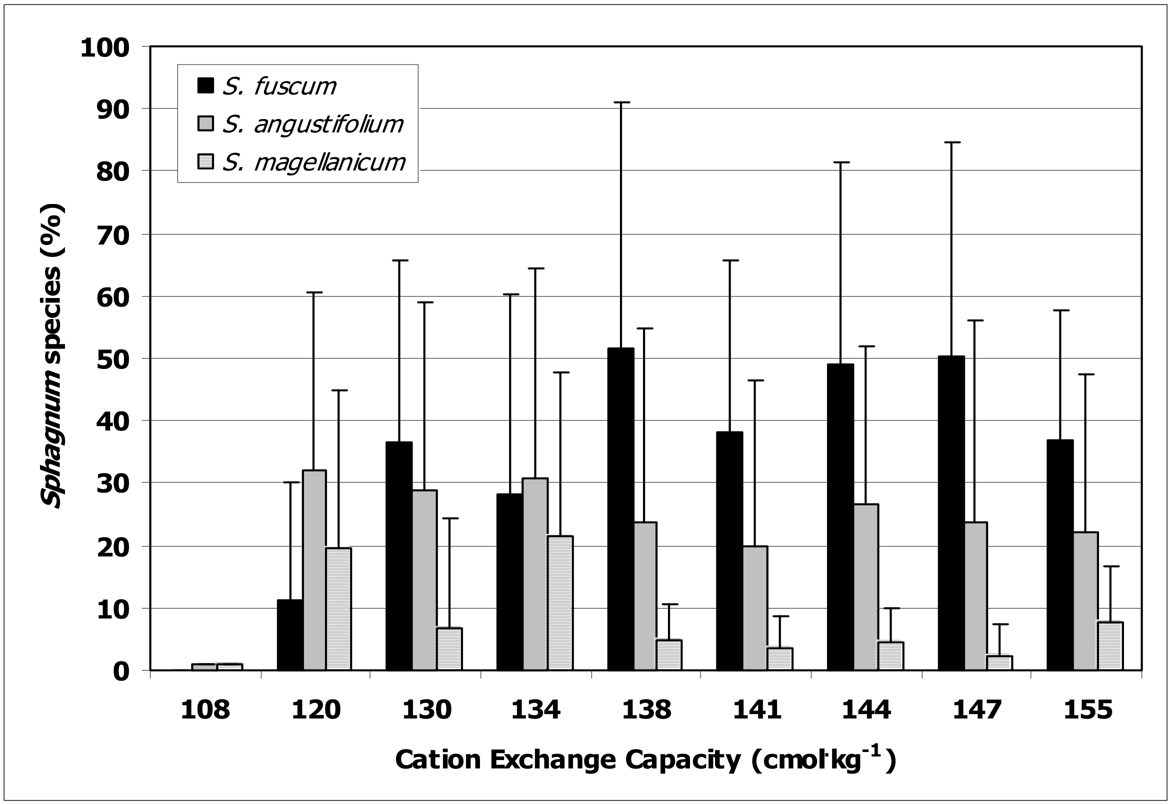

Figure 5.3. Cation exchange capacities [(CEC) cmol·kg^{-1}] of peat moss samples with varying amounts of three *Sphagnum* species. A total of 64 peat moss samples were evaluated. Depicted here is the sample with the lowest CEC and then the average of groups of eight samples ordered sequentially by increasing CEC.

Chapter 6

Neutralization Requirement, Inherent pH, and Buffering Capacity of Peat Moss

Abstract:

Peat moss-based substrates are acidic and are generally neutralized with limestone. The acidity is thought to be exchangeable or soluble H^+ arising from carboxylic and phenolic acids. Problems of inconsistent initial pH in peat moss-based horticultural substrates created using standard formulas for limestone additions, and pH drift from the initial pH occur and may be due to variations in the physical and chemical properties which affect peat moss neutralization requirements. This study was conducted to determine the extent to which variations exist in peat moss neutralization requirement, inherent pH, and buffer capacity, and to examine the relationship of inherent pH and buffer capacity to neutralization requirement. Sixty-four peat mosses from Alberta, Canada were incubated with $Ca(OH)_2$ in a complete random design with three replications to provide 0, 0.81, 1.21, 1.62, 1.89, 2.16, 2.56, and 2.97 mmol base and water at 95% CC at 20°C for 24 h. Solution pH was measured. Base titration curves and were generated to calculate acid neutralization requirement [base used per unit pH change from inherent (original) pH to 5.8] and pH buffer capacity (base used from pH 5.4-6.2). Peat mosses differed significantly in neutralization requirement (range: 0.15 ± 0.07 to 0.48 ± 0.04, mean: 0.35 ± 0.06 $mol \cdot kg^{-1}$ per unit pH), inherent pH (range: pH 3.2 ± 0.03 to 5.2 ± 0.02, mean: 3.7 ± 0.3), and buffer capacity (range: 0.05 ± 0.02 to 0.20 ± 0.03, mean: 0.11 ± 0.03 $mol \cdot kg^{-1}$). Inherent pH and buffer capacity were regressed against neutralization requirement and were positively related, indicating the possibility of buffer zones at low pH and the existence of a source of acidity other than H^+, such as Fe^{3+}. Variations in neutralization requirement dictate adjustment to standard liming formulas. Variations in buffer capacity may offer explanation for the drift from initial pH in peat moss-based substrates.

Chemical names: calcium hydroxide [$Ca(OH)_2$], hydrogen ions (H^+), iron ions (Fe^{2+})

Introduction

Sphagnum peat moss is commonly used as a major component of many commercial horticultural substrates. Substrates made from this material are naturally acidic and are frequently neutralized with limestone. The general purpose for amending any substrate with limestone is to neutralize enough of the total acidity in a specified volume of substrate to increase the pH to a desired value (Sims, 1996). The dominant source of acidity in peat moss is ionizable hydrogen ions (H^+) that originate from carboxylic or phenolic acid functional groups (Thomas and Hargrove, 1984). This type of acidity is termed "exchangeable" or "salt-replaceable" because the H^+ are easily exchanged with other cations (Brady, 1990). The other acid source in peat moss substrates is soluble, or dissociated, H^+ that may result from precipitation, soluble organic acids, oxidation of ammonium (NH_4^+)-based fertilizers, or hydrolysis of monocalcium phosphate fertilizers (Thomas and Hargrove, 1984). This type of acidity is termed "active". The amount of active acidity is small compared to that of exchangeable acidity (Brady, 1990.) When substrates are maintained at or above pH 5.5, as is the case in most horticultural production regimes, all of the acidity is pH-dependent, regardless of whether it is active or exchangeable (Sims, 1996; and Helling et al., 1964). As pH increases, H^+ saturation decreases (Lucas et al, 1975; and Puustjarvi and Robertson, 1975), allowing for the adsorption of basic cations.

The peat moss used for commercial horticultural endeavors has been thought to be highly consistent among batches; however, growers who formulate their own substrates and formulation companies that sell ready-mixed peat moss-based substrates have been faced with two problems. First, there is difficulty in attaining consistently the initial target pH using standard formulas for limestone additions. The second problem arises when substrate pH drifts away from the initial target over the course of production. These problems may arise from variations in the neutralization requirement of peat mosses harvested within or among bogs.

Two factors that have the potential to affect the neutralization requirement of peat mosses are inherent pH and buffering capacity. Inherent pH is considered here to be the pH of the peat moss before it has been subjected to neutralization. Buffering capacity is the inherent tendency of the peat moss to resist a change in pH (Sims, 1996). Both properties are thought to be fundamental to the peat moss itself. The objectives of this study were to determine the extent to which variations in the neutralization requirement, inherent pH and buffering capacity of peat moss exist, and to evaluate the effects of inherent pH and buffering capacity on peat moss neutralization requirement.

Methods and Materials

Sixty-four peat moss samples, collected from various bogs in Alberta, Canada, were titrated following the procedure described by Rippy and Nelson (2005). In this procedure, an amount of peat moss equivalent to 2 g oven dry, was mixed thoroughly with reagent grade $Ca(OH)_2$ at a rate of 0, 30, 45, 60, 70, 80, 95, and 110 mg base per gram of peat moss (to provide 0, 0.81, 1.21, 1.62, 1.89, 2.16, 2.56, and 2.97 mmol alkalinity, respectively). The base increments were selected from a preliminary study to ensure that the peat moss samples would be titrated to at least pH 7.0. Deionized water was added to achieve 95% CC. The dishes were incubated for 24 h at 20°C. The substrate solution was procured using the squeeze method (Scoggins et al., 2001). The solution pH was measured using an ion sensitive electrode and pH meter (Extech Instruments, Waltham, Mass.). The meter was calibrated with pH 7.0 and pH 4.0 standards before the first measurement and after every 10 subsequent measurements. The peat moss titrations were conducted in a complete random design with three replications. Titration curves relating pH to added base from $Ca(OH)_2$ were generated for all peat moss samples along with their associated equations and r^2 values (Microsoft Excel, Microsoft Corporation).

The inherent pH of the peat moss was the pH value obtained from 0 meq alkalinity. Neutralization requirement ($mol \cdot kg^{-1}$) was determined by calculating the amount of base that was required to raise the peat moss from inherent pH to pH 5.8, using the titration curve equations. To account for variations in inherent pH, these calculated values were divided by the pH range (pH 5.8 - inherent pH). Thus, neutralization requirement was the amount of base required ($mol \cdot Kg^{-1}$) per unit increase of pH. This study focused on the buffering capacity of peat mosses within the pH range in which most horticultural crops are grown. To this end, buffering capacity ($mol \cdot kg^{-1}$) was calculated as the amount of base required to raise peat moss pH from 5.4 to pH 6.2.

These data were analyzed for differences in neutralization requirement, inherent pH, and buffering capacity by analysis of variance with means compared by Tukey's HSD at $\alpha = 0.05$ (SAS Institute, Cary, NC). Additionally, inherent pH and buffering capacity were regressed against neutralization requirement (Microsoft Excel, Microsoft Corporation).

Results and Discussion

There was a significant difference between peat mosses having the highest and lowest neutralization requirements ($p < 0.0001$). The range of neutralization requirement values across the 64 peat moss samples is depicted in Figure 6.1. Although significant differences were present among many of the peat mosses, considerable overlap in significance existed. Neutralization requirement values ranged from 0.15 ± 0.07 to 0.48 ± 0.04 $mol \cdot Kg^{-1}$ per unit pH. Averaged over all 64 peat mosses, the mean neutralization requirement was 0.35 ± 0.06 $mol \cdot kg^{-1}$ per unit pH.

Peat mosses differed significantly in inherent pH ($p < 0.0001$). Peat mosses having the two highest inherent pH values differed significantly from each other, as well as from all other peat mosses (Figure 6.2). Similarly, the peat moss with the lowest inherent pH value, while not being significantly different from the peat moss with the second lowest inherent pH, did differ significantly from all other peat mosses. The mean inherent pH for all peat mosses was pH 3.7 ± 0.3; however inherent pH values for individual samples ranged from pH 3.2 ± 0.03 to pH 5.2 ± 0.02.

The peat moss having the greatest pH buffering capacity was significantly different from that with the least buffering capacity ($p = 0.0213$). There were no other significant differences among the remaining peat mosses. Buffering capacity ranged from 0.05 ± 0.02 to 0.20 ± 0.03 $mol \cdot kg^{-1}$. The mean buffering capacity was 0.11 ± 0.03 $mol \cdot kg^{-1}$. Titration curves were generated from the three-replication averages of the peat moss with the greatest and least buffering capacity, and are depicted in Figure 6.3.

In acid/base titrations, pH does not always increase consistently with added increments of base. Areas on the titration curve where added base does not result in a significant change in pH are called "buffer zones". The evaluation of buffer zones is rather subjective; however for the purposes of this study, buffer zones were determined to exist when an added increment of base produced a rise in pH of < 0.05 units.

Of the 64 peat moss samples studied here, seven had no buffer zone (pH increased linearly with added base), 26 had one buffer zone, 27 had two buffer zones, and four had three buffer zones. In addition to the variation in the number of buffer zones that existed in the peat moss samples, the pH range over which the buffer zones occurred also varied. Titration curves for three peat moss samples, each containing one buffer zone, are presented in Figure 6.4 to show the variation in buffer zone pH.

Peat mosses with a lower inherent pH could be expected to require a greater amount of base to reach the target pH than peat mosses with a high inherent pH; however, inherent pH alone may not be the only factor that affects neutralization requirement. Peat moss samples that have buffer zones in the low pH range would have a greater neutralization requirement than those having a linear pH response to added base, regardless of inherent pH.

Sims (1996) states that the amount of lime required to attain the target pH depends greatly on the physical and chemical properties which contribute to the buffering capacity. As buffering capacity increased, so does neutralization requirement. This is a logical result. Peat mosses with a low buffering capacity would offer little resistance to changes in pH; consequently, would require less lime to effect pH changes than would peat mosses with high buffering capacities.

In another study (Chapter 5), cations were displaced from sub-samples of the same 64 peat mosses used for this study, in order to determine base saturation. The displacing solution was measured for concentrations of bases via atomic absorption spectrometry. At the same time, iron concentrations ($[Fe^{2+}]$) were measured. The range of $[Fe^{2+}]$ on these peat mosses ranged from 0.31 - 3.88 $cmol{\cdot}kg^{-1}$, with a mean value of 1.0 $cmol{\cdot}kg^{-1}$. Although it has been reported (mentioned above) that H^+, whether exchangeable or soluble, are the only source of acidity in peat moss-based substrates, Fe^{2+} has been found to be present. The mires in Alberta, Canada exist on the lee side of the Caribou Mountains, from which iron is mined. It would not be unusual to suppose that iron may be present in the peat moss habitats of this region. Considering the low inherent pH that is characteristic of peat moss, it is quite possible that Fe^{2+} is another source of acidity that should be considered when determining peat moss neutralization requirements.

Conclusions

Peat mosses differed significantly in neutralization requirement and inherent pH, which explain, in part, the difficulties that have been encountered in establishing consistently an initial target pH in horticultural substrates using standard formulas for limestone additions. Variations in neutralization requirement may be caused, in part, by the presence or absence of, and the intensity of, buffer zones in the lower pH ranges. Variations in inherent pH may be due to varying amounts of associated Fe^{2+}. Peat mosses also differed significantly in buffering capacity in the pH range of 5.4 - 6.2. These variations, in the pH range in which most horticultural crops are grown, could explain the problem of substrate pH drift during the course of crop production.

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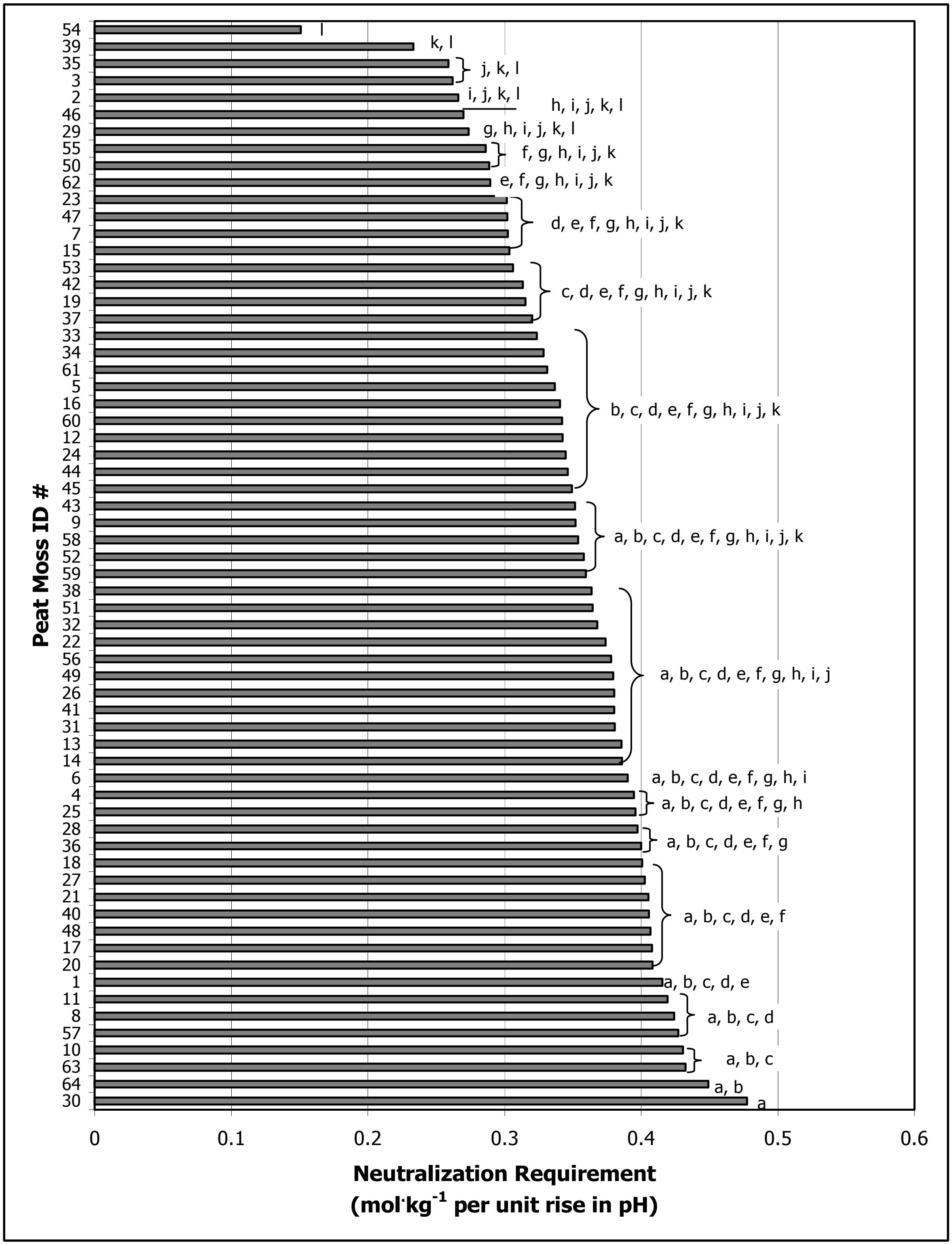

Figure 6.1. Neutralization requirements (base needed to pH from original to 5.8) of peat mosses from three Alberta, Canada mires. Significant differences are denoted by different letters. Tukey's $HSD_{0.05}$ = 0.013.

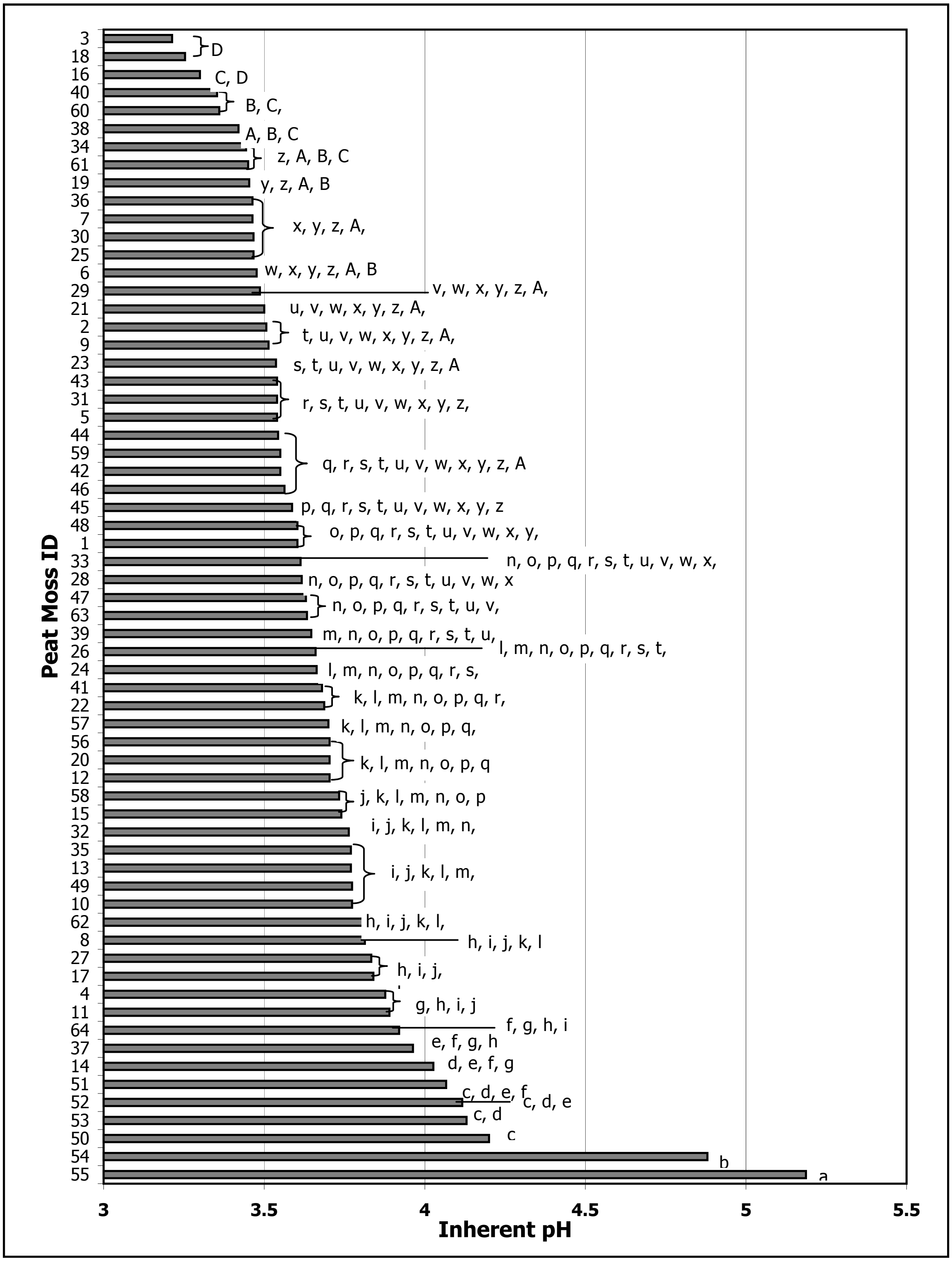

Figure 6.2. Inherent pH of 64 peat mosses from bogs across Alberta, Canada. Significant differences are denoted by different letters. Tukey's $HSD_{0.05}$ = 0.1617.

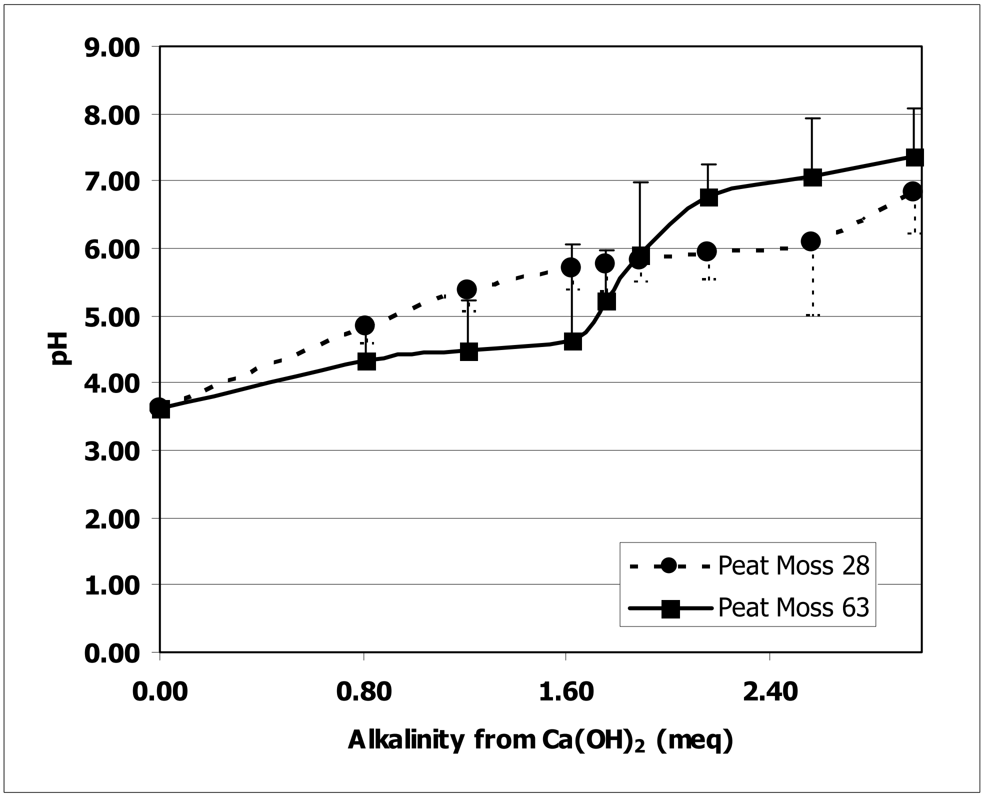

Figure 6.3. Titration curves of peat mosses with the greatest (peat moss 28) and least (peat moss 63) buffering capacity in a range which includes pH 5.4 - 6.2, the range in which most horticultural crops are grown. The two were significantly different with $p=0.0213$ at $\alpha = 0.05$.

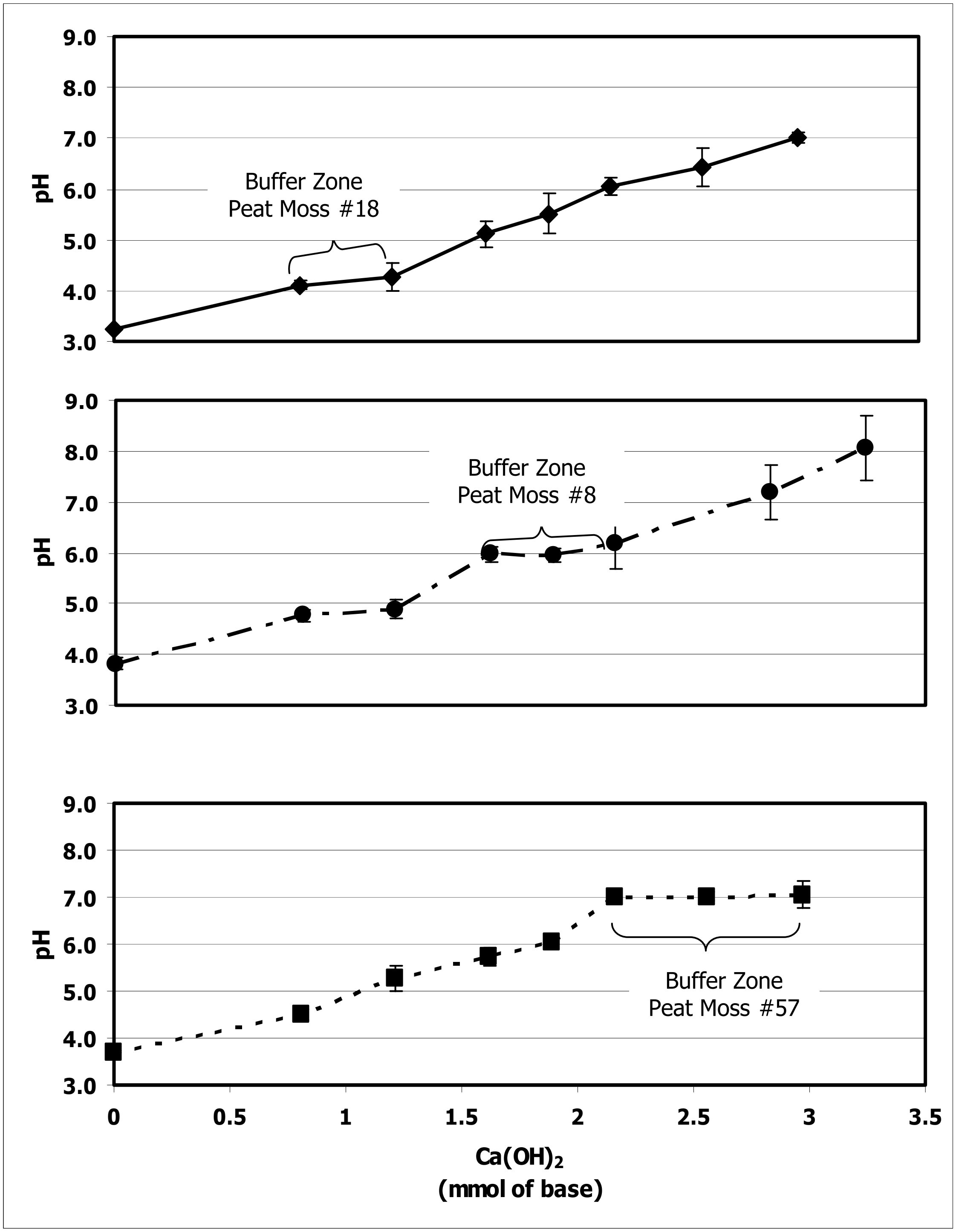

Figure 6.4. Titration curves with standard error bars averaged over three replications, for three peat mosses depicting the variation in range of pH over which the buffer zones may occur.

Chapter 7

Evaluation of Properties Influencing Neutralization Requirement of Peat Moss

Abstract:

Horticultural substrates are naturally acidic and are frequently amended with limestone to raise pH. Difficulties encountered in attaining consistently an initial target pH using standard formulas for limestone additions may be due to variations in the neutralization requirement of peat moss among batches. The objectives of this study were to examine the relationships among several physical/chemical properties of peat moss and to determine the extent to which they influence neutralization requirement. Peat moss samples were collected from stockpiles of recently harvested bogs in Alberta, Canada and analyzed for composition of three *Sphagnum* species, as well as sedge and degree of decomposition. Cation exchange capacity, base saturation, inherent pH, buffer capacity, [Fe^{2+}], and peat moss neutralization requirement were measured on 64 of these peat samples, which were selected to maximize a range of species distribution and decomposition within the range acceptable for commercial horticulture. Data for these physical/chemical properties were analyzed in a multiple regression to elucidate interrelationships and determine the extent to which they influence neutralization requirement. Neutralization requirement was inversely related to base saturation (r = -0.4017, p<0.0001), inherent pH (r = -0.2112, p=0.0033), [Fe^{2+}] (r = -0.1495, p=0.0384), degree of decomposition (r = -0.2717, p=0.0001), and sedge (r = -0.2314, p=0.0012); and positively correlated to *S. angustifolium* (r=0.1503, p=0.0374). Neutralization requirement was strongly influenced by base saturation and degree of decomposition. As both of these properties increased, neutralization requirement decreased. Taken together, they account for 84% of the influence of this model on neutralization requirement.

Chemical names: iron ion (Fe^{2+})

Introduction

Nearly all horticultural greenhouse crops are grown in container substrates which are comprised largely of peat materials. Three types of peat commonly found in horticultural substrates are reed sedge, hypnum, and *Sphagnum* peat mosses (Nelson, 2002; Argo and Biernbaum, 1997; Bunt, 1988; and Puustjarvi and Robertson, 1975). Of these three types of peat, *Sphagnum* peats are used most extensively.

Horticultural substrates are naturally acidic. The dominant source of acidity in peat moss is hydrogen ions (H^+) that originate from carboxylic or phenolic acid functional groups (Thomas and Hargrove, 1984). It is necessary to neutralize the acidity to a target pH range of ~5.4 – 6.2 for these substrates to be useful media for most plant growth. To this end, horticultural substrates are frequently amended with agricultural limestone according to standard formulas. Although peat moss has been thought to be highly consistent among batches, difficulties have been encountered in attaining consistently an initial target substrate pH using these formulas for limestone additions.

It was shown in Chapter 4 that variations in the neutralization capacity of agricultural limestone could be reduced for horticultural applications by means of including a measurement of specific surface in addition to particle diameter and calcium carbonate equivalent to further describe that capacity. Aside from these limestone effects, the problem of consistent attainment of target substrate pH may be due to variations in the neutralization requirement of peat moss among batches.

Significant variations in the neutralization requirement (NR), inherent pH (pH_{inh}), and buffering capacity (BC) of peat mosses were discovered and discussed in Chapter 6. When plotted against NR, both pH_{inh} and BC appeared to have a positive influence on neutralization requirement.

Of the fourteen species of *Sphagnum*, only three are used in commercial horticultural substrates. They are *S. angustifolium* (Russow) C. Jens, *S. fuscum* (Schimp.) Klingrr., and *S. magellanicum* Brid. They exist in distinct strata with respect to the water table (Mulligan and Gignac, 2001; and Bragazza and Gerdol, 1999). In Chapter 5, the significant relationship of species, most notably *S. fuscum*, to cation exchange capacity (CEC) was determined. Additionally, *S. magellanicum* and *S. angustifolium* were found to have significant influence on base saturation (BS). The neutralization requirement of peat moss may be related to both CEC and BS.

Sims (1996) states that the lime required to attain the target pH depends greatly on the physical and chemical properties which contribute to the buffering capacity [of the substrate]. Puustjarvi and Robertson (1975) state that botanical origin [of peat moss] largely determines secondary characteristics. The objectives of this study were to evaluate the relationships among several physical and chemical properties of peat moss and to determine the extent to which they influence neutralization requirement.

Methods and Materials

Much of the peat moss used for commercial soilless substrates in the United States comes from Canadian mires. These mires are harvested during June, July and August. The harvested peat moss is stockpiled in windrows at the edges of the bogs until it is used. In September, 2002, 465 samples were collected; one from each pile of peat moss harvested from three mires. The samples were analyzed for degree of decomposition according to the von Post (1935) scale [later modified by Puustjarvi and Robertson (1975)] and species composition by Jean MacDonald (Botanist, Highland Grey Co. Alberta, Canada). Of these samples, 64 were selected to represent a broad range of *Sphagnum* species and sedge composition within each of six decomposition stages: H1.5 – almost no decomposition, to H4 – slightly decomposed (von Post, 1937).

Cation exchange capacity (CEC) and base saturation (BS) of the 64 peat moss samples were measured in a CRD with three replications (Chapter 5). In addition to the basic cations, concentrations of iron ([Fe^{2+}]) were also measured. A multiple regression was conducted on CEC, BS, degree of decomposition, species distribution, and measured concentrations of the basic cations ($cmol \cdot kg^{-1}$) to determine the extent to which each of these properties influenced the others.

The peat moss samples were titrated with $Ca(OH)_2$. Neutralization requirement (NR) and buffering capacity (BC) were calculated from titration curve equations. Inherent pH (pH_{inh}) was also obtained from these titrations (Chapter 6).

The CEC and BS data from Chapter 5, and the NR, pH_{inh}, and BC data from Chapter 6 were analyzed in a multiple regression (SAS Institute, Cary, NC) along with $[Fe^{2+}]$, degree of decomposition, *Sphagnum* species and sedge composition, and detritus (that portion of the peat moss samples that was not *Sphagnum* species, sedge, grass, or wood). The measured concentrations of basic cations were not included because their effects are incorporated in the effects of base saturation. Although the correlation coefficients for degree of decomposition, and species composition are presented in Chapter 5 to determine relationships with CEC and BS, they are also included here to evaluate their influence on NR, pH_{inh}, and BC.

The physical properties and $[Fe^{2+}]$ were then eliminated one at a time, starting with the property having the least significant correlation to NR. After a property was eliminated from the model, significance was recalculated on those remaining using an analysis of variance [ANOVA (SAS Institute, Cary, NC)]. This process continued until only those properties having a significant influence on NR at $\alpha=0.05$ remained.

In the final step, r^2 values were generated for each physical property and $[Fe^{2+}]$ individually and then for all possible combinations of these properties when two, and up to all eleven, properties were included. The r^2 values indicate the degree to which NR is explained by each property or combination of properties.

Results and Discussion

The results of the multiple regressions, the step-by-step elimination ANOVAs and the r^2 values are presented in their entirety in Appendix II.B. Only the key elements from these results are presented in this text.

The relationships among all the physical properties and $[Fe^{2+}]$ studied, as well as their influence on peat moss neutralization requirement are presented in Table 7.1. Peat moss neutralization requirement (NR) was inversely related to base saturation (BS), inherent pH (pH_{inh}), $[Fe^{2+}]$, degree of decomposition, and sedge. The presence of bases reduces the amount of acidity to be neutralized. NR was positively correlated to *S. angustifolium*. The positive correlation of *S.*

angustifolium and the negative correlation between sedge and NR are presumed to be due to their association with BS (Chapter 5).

From the correlation study (Table 7.1), the influence of pH_{inh} on NR appears to be mainly due to its positive correlation to BS. Since BS is strongly affected by the basic cations (Chapter 5), indeed, is derived from them, it stands to reason that as the concentrations of bases increase, the peat moss neutralization requirement would decrease. Aside from the relationship to BS, pH_{inh} is positively correlated to degree of decomposition.

Decomposition was strongly related to detritus, which was also positively correlated to pH_{inh}. Remember that according to the von Post (1935) classification, the decomposition values increase with increasing stages of decomposition. Peat moss samples that were more decomposed had higher pH_{inh} than less decomposed samples. This relationship explains the negative influence of decomposition on NR.

It has been reported (above) that the acidity associated with peat moss-based substrates arises from soluble or exchangeable H^+. Presumably, this theory has been supported because it is desirable to maintain a pH range of 5.4-6.2 in horticultural substrates. In this range, acidity is, indeed due to exchangeable H^+. Iron (Fe) is a source of acidity in mineral soils of low pH because it strongly bonds with hydroxide ions (OH^-) in water, leaving acidic H^+ in solution. Measurable $[Fe^{2+}]$ have been found to be present on several of the peat moss samples studied here. In order to accurately measure neutralization requirements, the neutralization sequence must be considered (Sims, 1996). The neutralization sequence refers to the different types of acidity, such as that caused by Fe, that must be neutralized at low pH ranges, before pH rises to the range in which H^+ are the dominant acidity source. To consistently quantify peat moss neutralization requirements, it may become necessary to determine acidity sources in addition to H^+.

In this study, $[Fe^{2+}]$ was significantly correlated, inversely, to NR. Additionally, there was a positive correlation between $[Fe^{2+}]$ and BS. The negative relationship to NR and the positive association with BS was surprising; however, peat mosses having a capacity to adsorb basic cations could also adsorb any other cations. The relationship between $[Fe^{2+}]$ and *S. angustifolium*, *S.*

magellanicum, and sedge mirrors that of these species to BS. It is possible that the influence of [Fe^{2+}] on NR was "overwhelmed" by the preponderance of basic cations affecting the same realm of neutralization phenomena.

Researchers have suggested a relationship between buffering capacity (BC) and CEC (Sims, 1996; Biernbaum, 1992; and Bunt, 1988); however, no significant correlations to BC were found here. The peat moss BC data used in this study was calculated over a pH range of 5.4-6.2 to determine variations in the pH range common to horticultural growing systems. Since NR in this study was calculated for a pH range from original pH to pH 5.8, it was not expected that BC would influence NR. The lack of significant relationship between BC and any of the other properties indicate that BC is a property that is fundamental to all peat moss. Since BC is a property that is fundamental to peat moss species, it is of significant importance to the formulation of peat moss-based substrates.

Interrelationships among all variables were elucidated by the multiple regression correlations, which aided in the understanding of mechanisms that might be occurring in this model. The backwards elimination procedure, with its associated ANOVAs resulted in a list of properties that had significant impact on NR, specifically. These results are presented in Table 7.2. Peat moss neutralization requirement was significantly influenced by base saturation, degree of decomposition, and all four peat species.

The contributions of each property to the neutralization requirement (NR) of peat moss are described by r^2 values. These values are listed in Table 7.3 for each property, individually, and for combinations of two, three and four properties. The highest contribution possible, obtained by including all of the properties studied here, is listed at the bottom of the table. As properties are added, the contribution to NR increases. The interval of increase is reduced as successive properties are added.

Base saturation (BS), by itself, accounts for 62% of the total contribution possible from factors included in this model. The addition of degree of decomposition to BS increases the contribution of the model to 84% of the total. Adding a third property increases the contribution by 6%, and four properties in the model results in a 5% increase. Regardless of the number of properties that are included in the model, BS and decomposition appear to have the strongest tendency to characterize the neutralization requirement.

The neutralization requirement of peat moss is influenced by many complex and interrelated physical and chemical properties that are difficult to separate and characterize. In order to use neutralization requirement data for horticultural applications, extensive calibration studies must be conducted to relate values predicted from laboratory tests to pH values obtained from actual greenhouse settings.

Conclusions

Neutralization requirements in this study were most strongly influenced by base saturation, inherent pH, and degree of decomposition. Peat mosses that were highly saturated with bases had a high inherent pH and consequently, a low neutralization requirement. Similarly, peat mosses that were highly decomposed also had a low neutralization requirement. Neutralization requirement was also influenced by [Fe^{2+}]. An understanding of these factors, in every batch of peat moss used to formulate peat moss-based substrates, is necessary in order to consistently attain an initial target pH.

Cation exchange capacity and buffering capacity determine the resistance to change in pH. These factors are strongly correlated to the amount of *S. fuscum* in the substrate. Ensuring an appropriate amount of *S. fuscum* in peat moss-based substrates will reduce the problem of pH drift away from the target during the course of containerized crop production.

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Table 7.1. Pearson correlation coefficients for the relationships among peat moss neutralization requirement (NR), cation exchange capacity (CEC), base saturation (BS), inherent pH (pH_{inh}), buffering capacity (BC), iron concentrations ($[Fe^{3+}]$ degree of decomposition, detritus, and species composition. Absolute values of coefficients range from 0 to 1 with 1 indicating the strongest possible relationship. For each number pair, the top number is the coefficient (*r*) and the bottom number is the associated *p*-value.

									***Sphagnum* species**			
	NR	**CEC**	**BS**	**pH_{inh}**	**BC**	**$[Fe^{3+}]$**	**decomposition**	**detritus**	***fuscum***	***angust***	***magell***	**sedge**
NR	1.00000	0.04243	-0.40173	-0.21121	0.10568	-0.14953	-0.27167	-0.13503	0.00978	0.15032	0.13855	-0.23136
		0.5590	<.0001	0.0033	0.1446	0.0384	0.0001	0.0618	0.8929	0.0374	0.0553	0.0012
CEC	0.04243	1.00000	0.02367	0.06647	-0.04390	-0.03098	0.00198	0.01140	0.22272	-0.04927	-0.23581	-0.08462
	0.5590		0.7445	0.3597	0.5455	0.6697	0.9782	0.8753	0.0019	0.4973	0.0010	0.2432
BS	-0.40173	0.02367	1.00000	0.49244	-0.09001	0.35383	0.07827	0.06786	0.14124	-0.33498	-0.15886	0.27744
	<.0001	0.7445		<.0001	0.2144	<.0001	0.2806	0.3497	0.0507	<.0001	0.0277	<.0001
pH_{inh}	-0.21121	0.06647	0.49244	1.00000	0.07457	0.07805	0.14219	0.23744	-0.02677	-0.24203	-0.12876	0.29441
	0.0033	0.3597	<.0001		0.3040	0.2819	0.0491	0.0009	0.7125	0.0007	0.0751	<.0001
BC	0.10568	-0.04390	-0.09001	0.07457	1.00000	-0.00467	-0.12572	-0.06826	0.08199	-0.03311	0.05021	-0.07524
	0.1446	0.5455	0.2144	0.3040		0.9487	0.0823	0.3468	0.2583	0.6484	0.4892	0.2997
$[Fe^{3+}]$	-0.14953	-0.03098	0.35383	0.07805	-0.00467	1.00000	0.11473	0.06685	0.03441	-0.25632	-0.17343	0.33666
	0.0384	0.6697	<.0001	0.2819	0.9487		0.1130	0.3569	0.6356	0.0003	0.0161	<.0001
decomposition	-0.27167	0.00198	0.07827	0.14219	-0.12572	0.11473	1.00000	0.79192	-0.23922	-0.11767	-0.10291	0.18928
	0.0001	0.9782	0.2806	0.0491	0.0823	0.1130		<.0001	0.0008	0.1040	0.1555	0.0086
detritus	-0.13503	0.01140	0.06786	0.23744	-0.06826	0.06685	0.79192	1.00000	-0.30341	-0.12761	-0.15337	0.21929
	0.0618	0.8753	0.3497	0.0009	0.3468	0.3569	<.0001		<.0001	0.0777	0.0337	0.0022
S. fuscum	0.00978	0.22272	0.14124	-0.02677	0.08199	0.03441	-0.23922	-0.30341	1.00000	-0.52097	-0.31724	-0.36107
	0.8929	0.0019	0.0507	0.7125	0.2583	0.6356	0.0008	<.0001		<.0001	<.0001	<.0001
S. angustifolium	0.15032	-0.04927	-0.33498	-0.24203	-0.03311	-0.25632	-0.11767	-0.12761	-0.52097	1.00000	-0.00193	-0.42477
	0.0374	0.4973	<.0001	0.0007	0.6484	0.0003	0.1040	0.0777	<.0001		0.9788	<.0001
S. magellanicum	0.13855	-0.23581	-0.15886	-0.12876	0.05021	-0.17343	-0.10291	-0.15337	-0.31724	-0.00193	1.00000	-0.17929
	0.0553	0.0010	0.0277	0.0751	0.4892	0.0161	0.1555	0.0337	<.0001	0.9788		0.0128
sedge	-0.23136	-0.08462	0.27744	0.29441	-0.07524	0.33666	0.18928	0.21929	-0.36107	-0.42477	-0.17929	1.00000
	0.0012	0.2432	<.0001	<.0001	0.2997	<.0001	0.0086	0.0022	<.0001	<.0001	0.0128	

Table 7.2. Stepwise elimination ANOVA results listing peat moss physical properties that were significantly correlated to peat moss neutralization requirement at α=0.05.

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	6	8349.79306	1391.63218	10.56	<.0001
Error	185	24377.00000	131.76626		
Corrected Total	191	32727.00000			

R-Square = 0.2551 and C(p) = 3.5529

Property	**Parameter Estimate**	**Standard Error**	**Type II SS**	**F Value**	**Pr > F**
Intercept	129.38619	14.32570	10749.00000	81.57	<.0001
BS	-0.48553	0.09280	3606.77862	27.37	<.0001
decomposition	-7.39109	1.75569	2335.20312	17.72	<.0001
S. fuscum	-0.30472	0.12086	837.56201	6.36	0.0125
S. angustifolium	-0.31617	0.12296	871.18820	6.61	0.0109
S. magellanicum	-0.25397	0.12619	533.70085	4.05	0.0456
sedge	-0.36318	0.12912	1042.50137	7.91	0.0054

Table 7.3. Peat moss physical/chemical property r^2 values indicating intensity of influence on neutralization requirement. Values are listed for each property individually, and then for the eleven highest ranking correlation combinations for up to four properties. The highest possible r^2 value (that which included all properties) for this model was 0.2615.

Variables are coded as follows: NR = neutralization requirement, CEC = cation exchange capacity, BS = base saturation, pH = inherent pH, BC = buffering capacity, Fe = iron concentrations, DC = degree of decomposition, DT = detritus, FS = *Sphagnum fuscum*, ANG = *S. angustifolium*, MAG = *S. magellanicum*, and SDG = sedge.

1 Property		**2 Properties**		**3 Properties**		**4 Properties**	
Property	r^2 value	Property	r^2 value	Property	r^2 value	Property	r^2 value
BS	0.1614	BS, DC[z]	0.2195	BS, DC, DT	0.2376	BS, DC, DT, SDG	0.2477
DC	0.0738	BS, SDG	0.1770	BS, DC, SDG	0.2265	BS, DC, DT, MAG	0.2426
SDG	0.0535	BS, DT	0.1731	BS, DC, MAG	0.2223	CEC, BS, DC, DT	0.2401
pH	0.0446	BS, MAG	0.1671	CEC, BS, DC	0.2222	BS, BC, DC, DT	0.2388
ANG	0.0226	BS, BC	0.1663	BS, BC, DC	0.2212	BS, DC, DT, FS	0.2388
Fe	0.0224	BS, FS	0.1659	BS, Fe, DC	0.2197	BS, Fe, DC, DT	0.2381
MAG	0.0192	CEC, BS	0.1641	BS, pH, DC	0.2196	BS, pH, DC, DT	0.2380
DT	0.0182	BS, ANG	0.1617	BS, DC, ANG	0.2195	BS, DC, DT, ANG	0.2376
BC	0.0112	BS, pH	0.1616	BS, DC, FS	0.2195	CEC, BS, DC, SDG	0.2284
CEC	0.0018	BS, Fe	0.1614	BS, DT, SDG	0.1840	BS, DC, MAG, SDG	0.2284
FS	0.0001	DC, SDG	0.1074	BS, BC, SDG	0.1810	BS, DC, ANG, SDG	0.2280

Highest r^2 (all properties included): 0.2615

[z] Where there are more variables than one in the model, variables are listed in alphabetical order. The arrangement of variables within a row does NOT indicate relative strength of correlation.

Chapter 8

Summary

This research was born of a need for a greater understanding of the factors that affect the neutralization of acidity in peat moss-based growing substrates. Many researchers have studied acid neutralization in regards to agronomic crop production in mineral soils. To date, most of the information available regarding horticultural substrate acidity has been inferred from research on mineral soils that are high in organic matter. Horticultural crops are mostly grown in containers which results in a preponderance of root over soil mass, as well as shoot to root mass. Plant nutrient management becomes paramount due to these imbalances. The greatest factor affecting nutrient availability and uptake (assuming adequate nutrients are supplied) is substrate pH. Problems in peat moss-based substrate pH establishment and subsequent maintenance have led to the need to re-address the issues of limestone neutralization capacity and peat moss neutralization requirement from a horticultural perspective.

To this end, several limestones were selected from quarries across North America to represent a broad range of physical and chemical properties that were thought to affect neutralization capacity. The limestones were fractionated and additional properties were examined. Particle size was held constant in a multiple regression which included all the other properties to determine the extent to which other factors influenced neutralization capacity.

A similar protocol was followed with peat moss. A review of botanical literature concerning the growth habits and habitats of peat moss lead to the conception that many of the variations in the physical and chemical properties influencing the neutralization requirement of peat moss may be related to species. Samples were collected from stockpiles of newly harvested peat moss and were analyzed for species composition. Several of these were selected to encompass a broad range of species distribution within the range of decomposition stages that are acceptable for commercial horticultural endeavors. Additional properties were determined and another multiple regression was conducted to elucidate interrelationships as well as the influence of each on peat moss neutralization requirement.

Limestones differed significantly in specific surface for each particle diameter fraction ($p < 0.0001$) and also in reaction times ($p < 0.0001$). The addition of specific surface measurements to particle size and $CaCO_3$ content will further characterize the neutralization capacity of limestone used to amend horticultural substrates.

There were significant differences in cation exchange capacity, base saturation, inherent pH, buffering capacity and neutralization requirement among peat mosses. Cation exchange capacity strongly related to *Sphagnum fuscum*. It was independent of buffering capacity which was weakly correlated to *S. fuscum* but not to any other factors studied in this work. Both of these properties appear to be fundamental to the peat moss species. They had no effect on neutralization requirement.

Iron was associated with some of the peat moss samples, creating a source of acidity in addition to H^+ and increasing the neutralization requirement of the peat moss samples. If Fe is present, aluminum (Al^{3+}) may also exist, but was not studied here.

As base saturation and degree of decomposition increased, neutralization requirement was reduced. Both of these measures, taken together exerted the strongest influence on the neutralization requirement of peat moss. For horticultural applications, measurements of decomposition and base saturation should give a good estimate of neutralization requirement, thereby enhancing the ability to attain a consistent initial target pH when formulating peat moss-based substrates.

Cation exchange capacity and buffering capacity determine the resistance to change in pH. These factors are strongly correlated to the amount of *S. fuscum* in the substrate. Ensuring an appropriate amount of *S. fuscum* in peat moss-based substrates will reduce the problem of pH drift away from the target during the course of containerized crop production.

The information gleaned from these studies has merit for industry applications. Factors have been identified that will make it possible better describe the neutralization capacity of limestone and the neutralization requirement of peat moss, which should alleviate the problems of inconsistent attainment of target substrate pH and subsequent drift away from the target that currently occur.

It is still necessary to conduct calibration studies in the greenhouse to relate neutralization requirement results obtained in the lab to pH values encountered during the course of crop production. From there, dissolution curves could be generated with and without plants to further characterize the neutralization mechanisms. Plant effects on substrate pH could be quantified. Furthermore, this research could provide the backbone for future studies which might include the development of horticultural substrates for acid- or base-"loving" plants, or to counteract effects of acidic or alkaline water. The possibilities are seemingly endless!

Appendices

Appendix I.

Procedures

A. Dry versus Wet Sieving For Measuring Limestone Specific Surface

Particle-size distribution of agricultural limestone may be determined by either dry or wet sieving. There is reportedly very little difference between the two methods for particles larger than those passing through an 80-mesh screen (Barber, 1984). Barber (1984) further states that the use of just the number 60 sieve adequately characterizes the fineness characteristics of most limestones. However, he also continues that an additional, coarser sieve may be useful to prevent incorrect measurement of atypical samples.

In separate studies, Wiese (1956) and Elphick (1954) compared particle-size distribution of limestones resulting from both wet and dry sieving. They both concluded that a higher percentage of fine particles was obtained by wet, rather than dry, sieving. Barber (1984) states that wet-sieving is preferable if an accurate measure of the finest particles is desired.

A study was to be conducted to determine if there were differences in limestone specific surface, regardless of particle size. Since this study would incorporate mainly fine limestone particles, a preliminary study was run to determine whether the limestone samples should be wet or dry sieved.

In the preliminary study, a limestone sample was wet sieved and dry sieved into eight particle-size fractions: 30-50, 50-100, 100-170, 170-200, 200-270, 270-325, 325-400, and 400-635 mesh U.S. Standard screens. Surface areas of all fractions for each sieving method were obtained using the Monosorb Surface Area Analyzer (Quantachrome, Corp., Boynton Beach, FL) (see Chapter Two). Surface area was measured in three replications for each fraction and sieving treatment. Specific surface was calculated by dividing the surface area by the oven-dry weight of each sample, and is expressed as square meters of surface per gram of limestone ($m^2 \cdot g^{-1}$).

Specific surfaces for eight particle size fractions of a limestone that was both wet sieved and dry sieved are depicted in Figure I.A.1.

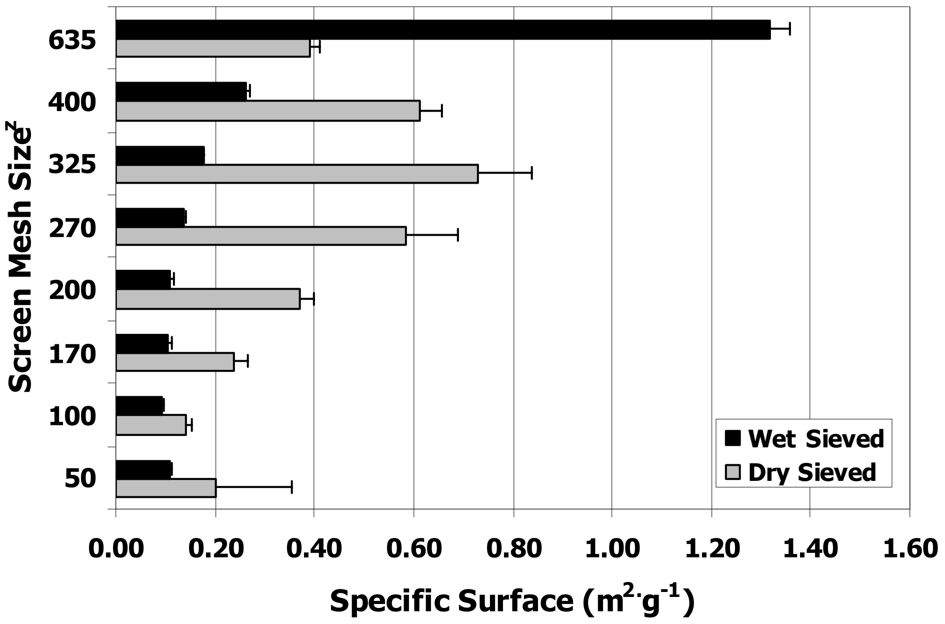

Figure I.A.1. Specific surface for several particle size fractions of a limestone, both wet sieved and dry sieved.

[z] Largest screen mesh size upon which limestone particles were retained.

When the limestone was separated using the dry sieving technique, specific surface did not exhibit the expected indirect relationship with particle size (i.e. increasing specific surface with decreasing particle size). Instead, the largest specific surface occurred in the 270-325 screen mesh size fraction. Furthermore, that fraction, along with the fractions just larger and just smaller than it, all had greater specific surface than the finest particle size fraction. The low specific surface of the finest particles in relation to the other fractions indicates that some fine particles were retained with the larger particle size fractions. This phenomenon is termed “bridging” and it occurs due to electrostatic forces between the coarse and fine particles which arise mainly from the friction created by the dry sieving process (David Jahn, Martin Marietta Technologies, Inc. - personal communication).

The specific surfaces of the limestone that was wet sieved increased as particle size decreased. Additionally, there was very little variation in the data produced with the wet sieving technique. In keeping with the reports of Wiese (1956) and Elphick (1954), the finest particle size fraction exhibited much higher specific surface when wet sieved than when dry sieved.

Irregular specific surface measurements were obtained from the dry sieving method, probably due to bridging of fine limestone particles with coarser particles. Wet sieving produced the expected relationship between specific surface and particle size, as well as less variable specific surface measurements. Since limestone specific surface was to be compared among particle size fractions, it was decided to fractionate the limestone samples using the wet sieving technique.

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B. Obtaining a Single-Value Measurement to Represent Limestone Reactivity

Numerous methods have been devised and employed to evaluate the reactivity of limestones. Balks and Wehrmann (1938) used the oxalate ion, and Barnes (1947) used oxalic acid for measuring the surface reaction of limestone. Beacher and Merkle (1949) studied dilute acetic acid and found a fair correlation between their obtained reactivity values and changes in soil pH after ten weeks incubation. In another study, Thomas and Gross (1952) evaluated numerous solvents including those mentioned above and discovered that none of them were equally effective for both calcitic and dolomitic limestones. Likewise, Webster et al. (1953) found that the oxalic acid method gave excessively high values for dolomitic limestones. Other methods were devised using carbonated water or acetates, as well as acetic acid and failed to show satisfactory correlation between these methods and limestone reactions with soils (Shaw and Robinson, 1959). Gleria (1929) had used ammonium chloride (NH_4Cl) to dissolve calcium carbonate ($CaCO_3$). Shaw and MacIntyre (1935) showed that this reagent will also dissolve magnesium carbonate ($MgCO_3$). Schollenberger and Whittaker (1953) developed a procedure using NH_4Cl, and Shaw and Robinson (1959) found that evaluation of both calcitic and dolomitic limestones with this procedure gave results that were in accord with the reactions of the limestones with acid soils. In ensuing years, the use of ethylenediaminetetracetic acid (EDTA) to describe limestone reactivity has been studied by several researchers but has been found to provide estimates for reactivity that are no more effective than the %$CaCO_3$ (Barber, 1984).

All of these methods produce curves with numerous data points which describe the relationship between limestone dissolution and time. The rate of reactivity of limestones may be dependent on many factors including particle size, chemical composition and physical nature. In order to determine which factors have the greatest effect on reactivity, it was necessary to devise a method for obtaining a single, numerical rating that would characterize the reactivity of limestones. This study was conducted to that end.

Limestone samples were procured from twenty different quarries. For this study, several samples, ranging in calcium content and particle size, were chosen from this set. Since the procedure described by Shaw and Robinson (1959) was found to provide equally effective estimates of both calcitic and dolomitic limestone reactivity which were reflective of limestone reactions in soils, limestone reactivity time curves were generated using an adaptation of this method (see Chapter Three for description).

Regardless of calcium or magnesium content, the point at which 1 meq hydrogen ions (H^+) was neutralized fell within the initial, linear part of the time curve. The linear portion of the time curves obtained from the coarsest particle size fraction [30-50 mesh U.S. Standard screen (600-300 µm)] of a highly calcitic and a highly dolomitic limestone are presented in Figure I.B.1, along with the equations and correlation coefficients showing the soundness of the linear fit.

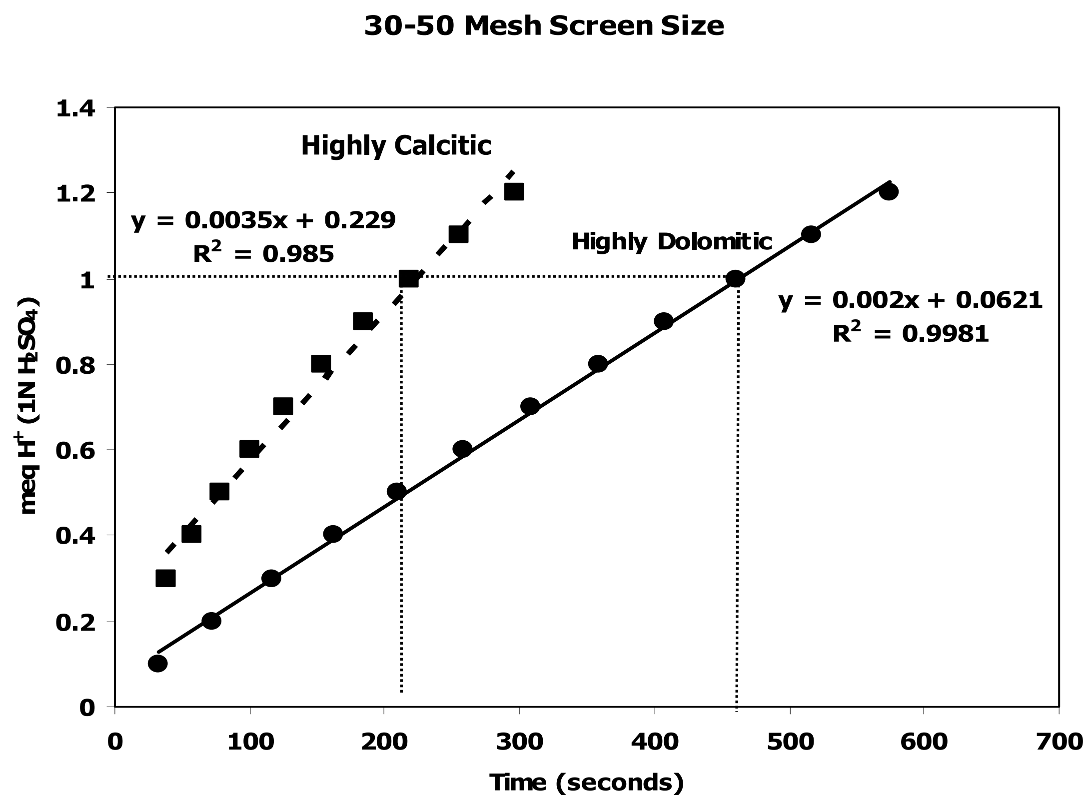

Figure I.B.1. Time required for highly calcitic and highly dolomitic limestones to neutralize 1 meq H^+. The point at which 1 meq H^+ is neutralized occurs within the linear portion of the reactions.

Limestone reactivity time curves were then generated for coarse, mid-size [170-200 mesh screen (90-75 µm)], and fine [325-400 mesh screen (45-38 µm)] limestone particles. Again, 1 meq

H^+ was neutralized within the linear portion of the limestone reactivity curves. The linear portion of these curves derived from three particle size fractions of a calcitic limestone are presented in Figure I.B.2.

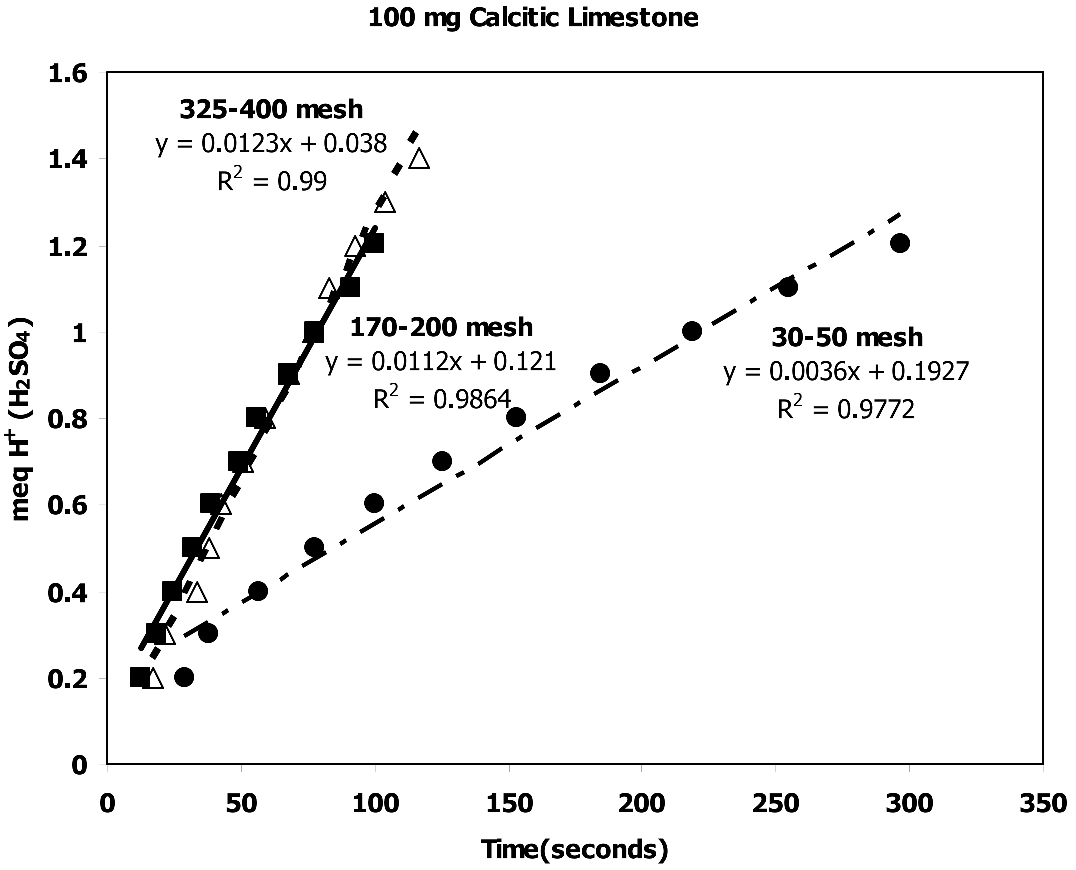

Figure I.B.2. Linear portions of reactivity curves from coarse (30-50 mesh), medium (170-200 mesh), and fine (325-400 mesh) particles of a highly calcitic limestone. Equations and correlation coefficients of the linear fit are included.

From these studies, it was determined that a single value estimation of limestone reactivity could be obtained by using the Shaw and Robinson (1959) procedure and measuring the amount of time, in seconds, required for 100 mg of limestone to neutralize 1 meq H^+ from 1N H_2SO_4 to pH 5.3, as indicated by bromcresol green dye, which turns blue at that pH. The data can then be expressed as seconds per mg limestone per meq H^+ ($s \cdot mg^{-1} \cdot meq^{-1}$).

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Appendix II

A. Properties Affecting Limestone Neutralization Capacity

A. Results of the multiple regression procedures conducted on limestone physical/chemical properties.

1. Results of the correlation procedure to evaluate interrelationships among several limestone physical/chemical properties as well as their impact on limestone reactivity.

   a. Particle size is included in the model.

The CORR Procedure

9 Variables: RT = reactivity times, PS = particle size, H = hardness, SD = soundness, P = internal porosity, C = % $CaCO_3$, M = % $MgCO_3$, BD = bulk density, and SS = specific surface

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
RT	153	2.33529	2.93721	357.3000	0.13000	12.56000
PS	153	175.00000	120.88081	26775.0000	30.00000	325.00000
H	153	31.28235	7.76624	4786.0000	20.00000	52.00000
SD	153	5.73529	6.04012	877.5000	0.40000	26.00000
P	153	2.13529	1.99768	326.7000	0.20000	7.50000
C	153	79.14706	18.84727	12110.0000	51.00000	98.10000
M	153	16.59412	20.02351	2539.0000	0.40000	49.80000
BD	153	2.56865	0.18633	393.0030	2.19000	2.83000
SS	153	1.55417	1.66823	237.7878	0.06450	7.28460

Pearson Correlation Coefficients
N = 153, Prob > |r| under H0: Rho=0

	RT	**PS**	**H**	**SD**	**P**	**C**	**M**	**BD**	**SS**
RT	1.00000	-0.59273 <.0001	-0.22329 0.0055	-0.18479 0.0222	-0.19296 0.0169	-0.45873 <.0001	0.43358 <.0001	0.27059 0.0007	-0.24242 0.0025
PS	-0.59273 <.0001	1.00000	0.00000 1.0000	0.00000 1.0000	0.00000 1.0000	0.00000 1.0000	0.00000 1.0000	0.00000 1.0000	0.08086 0.3204
H	-0.22329 0.0055	0.00000 1.0000	1.00000	0.41395 <.0001	0.80005 <.0001	0.52428 <.0001	-0.44926 <.0001	-0.76459 <.0001	0.26472 0.0009
SD	-0.18479 0.0222	0.00000 1.0000	0.41395 <.0001	1.00000	0.17832 0.0274	0.38820 <.0001	-0.36763 <.0001	-0.23409 0.0036	0.11695 0.1499
P	-0.19296 0.0169	0.00000 1.0000	0.80005 <.0001	0.17832 0.0274	1.00000	0.47618 <.0001	-0.45471 <.0001	-0.95596 <.0001	0.30328 0.0001
C	-0.45873 <.0001	0.00000 1.0000	0.52428 <.0001	0.38820 <.0001	0.47618 <.0001	1.00000	-0.96499 <.0001	-0.58465 <.0001	-0.03742 0.6461
M	0.43358 <.0001	0.00000 1.0000	-0.44926 <.0001	-0.36763 <.0001	-0.45471 <.0001	-0.96499 <.0001	1.00000	0.56161 <.0001	0.04236 0.6031
BD	0.27059 0.0007	0.00000 1.0000	-0.76459 <.0001	-0.23409 0.0036	-0.95596 <.0001	-0.58465 <.0001	0.56161 <.0001	1.00000	-0.34550 <.0001
SS	-0.24242 0.0025	0.08086 0.3204	0.26472 0.0009	0.11695 0.1499	0.30328 0.0001	-0.03742 0.6461	0.04236 0.6031	-0.34550 <.0001	1.00000

b. Particle size was held constant at three size fractions: Coarse (600-300 µm or 30-50 mesh U.S. Standard screen), Medium (90-75 µm or 170-200 mesh screen), and fine (45-38 µm or 325-400 mesh screen).

The CORR Procedure

8 Variables: RT = reactivity times, H = hardness, SD = soundness, P = internal porosity, C = % $CaCO_3$, M = % $MgCO_3$, BD = bulk density, SS = specific surface

-- Size=30-50 mesh--

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
RT	51	5.08098	3.58742	259.1300	0.47000	12.56000
H	51	31.28235	7.81784	1595.0000	20.00000	52.00000
SD	51	5.73529	6.08026	292.5000	0.40000	26.00000
P	51	2.13529	2.01095	108.9000	0.20000	7.50000
C	51	79.14706	18.97250	4037.0000	51.00000	98.10000
M	51	16.59412	20.15656	846.3000	0.40000	49.80000
BD	51	2.56865	0.18757	131.0010	2.19000	2.83000
SS	51	1.36708	1.36661	69.7213	0.06450	5.21670

```
                         Pearson Correlation Coefficients

                       N = 51, Prob > |r| under H0: Rho=0

            RT          H          SD          P           C           M          BD          SS

RT       1.00000    -0.40649    -0.29256    -0.31984    -0.76455     0.71202     0.45651    -0.32202
                     0.0031      0.0372      0.0221     <.0001      <.0001       0.0008      0.0212

H       -0.40649     1.00000     0.41395     0.80005     0.52428    -0.44926    -0.76459     0.21592
         0.0031                  0.0025     <.0001      <.0001       0.0009     <.0001       0.1281

SD      -0.29256     0.41395     1.00000     0.17832     0.38820    -0.36763    -0.23409     0.10973
         0.0372      0.0025                  0.2106      0.0049      0.0080      0.0983      0.4434

P       -0.31984     0.80005     0.17832     1.00000     0.47618    -0.45471    -0.95596     0.31316
         0.0221     <.0001       0.2106                  0.0004      0.0008     <.0001       0.0252

C       -0.76455     0.52428     0.38820     0.47618     1.00000    -0.96499    -0.58465    -0.12538
        <.0001      <.0001       0.0049      0.0004                 <.0001      <.0001       0.3807

M        0.71202    -0.44926    -0.36763    -0.45471    -0.96499     1.00000     0.56161     0.13423
        <.0001       0.0009      0.0080      0.0008     <.0001                  <.0001       0.3477

BD       0.45651    -0.76459    -0.23409    -0.95596    -0.58465     0.56161     1.00000    -0.32946
         0.0008     <.0001       0.0983     <.0001      <.0001      <.0001                   0.0182

SS      -0.32202     0.21592     0.10973     0.31316    -0.12538     0.13423    -0.32946     1.00000
         0.0212      0.1281      0.4434      0.0252      0.3807      0.3477      0.0182


--------------------------------------------------------- Size=170-200 mesh---------------------------------------------------------
```

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
RT	51	1.15627	1.15611	58.9700	0.19000	4.15000
H	51	31.28235	7.81784	1595.0000	20.00000	52.00000
SD	51	5.73529	6.08026	292.5000	0.40000	26.00000
P	51	2.13529	2.01095	108.9000	0.20000	7.50000
C	51	79.14706	18.97250	4037.0000	51.00000	98.10000
M	51	16.59412	20.15656	846.3000	0.40000	49.80000
BD	51	2.56865	0.18757	131.0010	2.19000	2.83000
SS	51	1.59669	1.83142	81.4314	0.10110	7.28460

Pearson Correlation Coefficients

N = 51, Prob > |r| under H0: Rho=0

	RT	H	SD	P	C	M	BD	SS
RT	1.00000	-0.30372 0.0303	-0.34422 0.0134	-0.31896 0.0225	-0.74767 <.0001	0.72836 <.0001	0.43515 0.0014	-0.36006 0.0095
H	-0.30372 0.0303	1.00000	0.41395 0.0025	0.80005 <.0001	0.52428 <.0001	-0.44926 0.0009	-0.76459 <.0001	0.28801 0.0404
SD	-0.34422 0.0134	0.41395 0.0025	1.00000	0.17832 0.2106	0.38820 0.0049	-0.36763 0.0080	-0.23409 0.0983	0.13787 0.3347

P	-0.31896 0.0225	0.80005 <.0001	0.17832 0.2106	1.00000	0.47618 0.0004	-0.45471 0.0008	-0.95596 <.0001	0.32525 0.0199
C	-0.74767 <.0001	0.52428 <.0001	0.38820 0.0049	0.47618 0.0004	1.00000	-0.96499 <.0001	-0.58465 <.0001	0.01127 0.9375
M	0.72836 <.0001	-0.44926 0.0009	-0.36763 0.0080	-0.45471 0.0008	-0.96499 <.0001	1.00000	0.56161 <.0001	-0.01187 0.9341
BD	0.43515 0.0014	-0.76459 <.0001	-0.23409 0.0983	-0.95596 <.0001	-0.58465 <.0001	0.56161 <.0001	1.00000	-0.38082 0.0058
SS	-0.36006 0.0095	0.28801 0.0404	0.13787 0.3347	0.32525 0.0199	0.01127 0.9375	-0.01187 0.9341	-0.38082 0.0058	1.00000

-- Size=325-400 mesh --

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
RT	51	0.76863	0.63996	39.2000	0.13000	2.38000
H	51	31.28235	7.81784	1595.0000	20.00000	52.00000
SD	51	5.73529	6.08026	292.5000	0.40000	26.00000
P	51	2.13529	2.01095	108.9000	0.20000	7.50000
C	51	79.14706	18.97250	4037.0000	51.00000	98.10000
M	51	16.59412	20.15656	846.3000	0.40000	49.80000
BD	51	2.56865	0.18757	131.0010	2.19000	2.83000
SS	51	1.69873	1.78319	86.6351	0.17070	6.44850

Pearson Correlation Coefficients

N = 51, Prob > |r| under H0: Rho=0

	RT	**H**	**SD**	**P**	**C**	**M**	**BD**	**SS**
RT	1.00000	-0.26761	-0.29947	-0.30546	-0.72166	0.70250	0.40539	-0.40653
		0.0576	0.0328	0.0293	<.0001	<.0001	0.0032	0.0031
H	-0.26761	1.00000	0.41395	0.80005	0.52428	-0.44926	-0.76459	0.28661
	0.0576		0.0025	<.0001	<.0001	0.0009	<.0001	0.0414
SD	-0.29947	0.41395	1.00000	0.17832	0.38820	-0.36763	-0.23409	0.10474
	0.0328	0.0025		0.2106	0.0049	0.0080	0.0983	0.4645
P	-0.30546	0.80005	0.17832	1.00000	0.47618	-0.45471	-0.95596	0.28280
	0.0293	<.0001	0.2106		0.0004	0.0008	<.0001	0.0444
C	-0.72166	0.52428	0.38820	0.47618	1.00000	-0.96499	-0.58465	-0.02120
	<.0001	<.0001	0.0049	0.0004		<.0001	<.0001	0.8826
M	0.70250	-0.44926	-0.36763	-0.45471	-0.96499	1.00000	0.56161	0.02901
	<.0001	0.0009	0.0080	0.0008	<.0001		<.0001	0.8399
BD	0.40539	-0.76459	-0.23409	-0.95596	-0.58465	0.56161	1.00000	-0.33250
	0.0032	<.0001	0.0983	<.0001	<.0001	<.0001		0.0171
SS	-0.40653	0.28661	0.10474	0.28280	-0.02120	0.02901	-0.33250	1.00000
	0.0031	0.0414	0.4645	0.0444	0.8826	0.8399	0.0171	

2. Results of the step-by-step backwards elimination ANOVAs which eliminate limestone physical or chemical properties one at a time from the least to most highly correlated to reactivity. Properties are eliminated until all left in the model are significantly correlated at $\alpha=0.05$.

    a. Particle size is included in the model

The STEPWISE Procedure
Model: MODEL1
Dependent Variable: RT

Backward Elimination: Step 0
All Variables Entered: R-Square = 0.6228 and C(p) = 9.0000
Analysis of Variance

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	8	816.70132	102.08766	29.72	<.0001
Error	144	494.63489	3.43496		
Corrected Total	152	1311.33621			

Variable	**Parameter Estimate**	**Standard Error**	**Type II SS**	**F Value**	**Pr > F**
Intercept	12.59678	10.60330	4.84796	1.41	0.2368
PS	-0.01389	0.00125	424.42254	123.56	<.0001
H	0.01907	0.04074	0.75221	0.22	0.6405
SD	0.01105	0.03018	0.46090	0.13	0.7147
P	0.18697	0.33272	1.08466	0.32	0.5750
C	-0.10994	0.03508	33.73274	9.82	0.0021
M	-0.02347	0.03091	1.98004	0.58	0.4490
BD	0.35785	3.52112	0.03548	0.01	0.9192
SS	-0.46228	0.10658	64.61904	18.81	<.0001

Bounds on condition number: 19.55, 665.65

Backward Elimination: Step 1

Variable BD Removed: R-Square = 0.6228 and C(p) = 7.0103

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	816.66584	116.66655	34.20	<.0001
Error	145	494.67037	3.41152		
Corrected Total	152	1311.33621			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	13.63275	2.90898	74.92621	21.96	<.0001
PS	-0.01388	0.00124	424.69872	124.49	<.0001
H	0.02007	0.03939	0.88608	0.26	0.6111
SD	0.01074	0.02992	0.43992	0.13	0.7200
P	0.15637	0.14112	4.18852	1.23	0.2697
C	-0.11086	0.03379	36.70932	10.76	0.0013
M	-0.02366	0.03075	2.02030	0.59	0.4428
SS	-0.46640	0.09823	76.90996	22.54	<.0001

Bounds on condition number: 18.076, 324.33

Backward Elimination: Step 2

Variable SD Removed: R-Square = 0.6224 and C(p) = 5.1384

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	816.22592	136.03765	40.12	<.0001
Error	146	495.11030	3.39117		
Corrected Total	152	1311.33621			

```
               Parameter           Standard
Variable       Estimate            Error           Type II SS           F Value       Pr > F

Intercept      13.60656            2.89938          74.68554              22.02       <.0001
PS             -0.01389            0.00124         425.05082             125.34       <.0001
H               0.02590            0.03578           1.77677               0.52        0.4703
P               0.13853            0.13170           3.75231               1.11        0.2946
C              -0.11134            0.03367          37.09106              10.94        0.0012
M              -0.02510            0.03039           2.31351               0.68        0.4102
SS             -0.46200            0.09717          76.65910              22.61       <.0001

                      Bounds on condition number: 18.047, 260.38
```

Backward Elimination: Step 3

```
                Variable H Removed: R-Square = 0.6211 and C(p) = 3.6557

                                  Analysis of Variance
                                 Sum of               Mean
Source               DF          Squares              Square              F Value            Pr > F

Model                  5         814.44915          162.88983             48.19              <.0001
Error                147         496.88706            3.38018
Corrected Total      152        1311.33621

               Parameter           Standard
Variable       Estimate            Error           Type II SS           F Value       Pr > F

Intercept      13.33309            2.87000          72.95230              21.58       <.0001
PS             -0.01390            0.00124         425.59020             125.91       <.0001
P               0.20717            0.09125          17.42191               5.15        0.0246
C              -0.10125            0.03060          37.02031              10.95        0.0012
M              -0.01736            0.02840           1.26316               0.37        0.5419
SS             -0.45463            0.09648          75.05683              22.20       <.0001

                      Bounds on condition number: 14.952, 165.82
```

Backward Elimination: Step 4

Variable M Removed: R-Square = 0.6201 and C(p) = 2.0234

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	813.18599	203.29650	60.40	<.0001
Error	148	498.15022	3.36588		
Corrected Total	152	1311.33621			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	11.63642	0.72890	857.82935	254.86	<.0001
PS	-0.01389	0.00124	425.52051	126.42	<.0001
P	0.20645	0.09105	17.30383	5.14	0.0248
C	-0.08342	0.00920	276.74608	82.22	<.0001
SS	-0.45566	0.09626	75.42178	22.41	<.0001

Bounds on condition number: 1.494, 20.095

All variables left in the model are significant at the 0.0500 level.

Summary of Backward Elimination

Step	Variable Removed	Number Vars In	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	BD	7	0.0000	0.6228	7.0103	0.01	0.9192
2	SD	6	0.0003	0.6224	5.1384	0.13	0.7200
3	H	5	0.0014	0.6211	3.6557	0.52	0.4703
4	M	4	0.0010	0.6201	2.0234	0.37	0.5419

b. Particle size was held constant at three size fractions: Coarse (600-300 µm or 30-50 mesh U.S. Standard screen), Medium (90-75 µm or 170-200 mesh screen), and fine (45-38 µm or 325-400 mesh screen).

```
------------------------------------------------------------- Size=30-50 mesh------------------------------------------------------------
----

                                   Backward Elimination: Step 0

                     All Variables Entered: R-Square = 0.8514 and C(p) = 8.0000

                                       Analysis of Variance
                                      Sum of                 Mean
Source                 DF             Squares                Square              F Value             Pr > F

Model                   7            547.84497              78.26357             35.19               <.0001
Error                  43             95.63468               2.22406
Corrected Total        50            643.47965


                Parameter              Standard
Variable        Estimate               Error            Type II SS          F Value        Pr > F

Intercept       14.80916               14.45351           2.33486             1.05         0.3113
H               -0.07932                0.05629           4.41547             1.99         0.1660
SD               0.09376                0.04256          10.79432             4.85         0.0330
P                1.10983                0.45225          13.39401             6.02         0.0183
C               -0.21887                0.04855          45.20810            20.33         <.0001
M               -0.03163                0.04312           1.19634             0.54         0.4673
BD               3.76812                4.79727           1.37217             0.62         0.4365
SS              -1.45250                0.18612         135.44784            60.90         <.0001

                         Bounds on condition number: 19.071, 561.16
```

Backward Elimination: Step 1

Variable M Removed: R-Square = 0.8495 and C(p) = 6.5379

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	546.64863	91.10810	41.40	<.0001
Error	44	96.83102	2.20071		
Corrected Total	50	643.47965			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	11.68975	13.74082	1.59275	0.72	0.3995
H	-0.09477	0.05193	7.33076	3.33	0.0748
SD	0.09828	0.04189	12.11503	5.51	0.0235
P	1.16329	0.44398	15.10795	6.87	0.0120
C	-0.18571	0.01757	245.83405	111.71	<.0001
BD	3.89372	4.76897	1.46704	0.67	0.4186
SS	-1.45946	0.18490	137.10555	62.30	<.0001

Bounds on condition number: 18.18, 272.9

Backward Elimination: Step 2

Variable BD Removed: R-Square = 0.8472 and C(p) = 5.1975

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	545.18159	109.03632	49.92	<.0001
Error	45	98.29806	2.18440		

```
Corrected Total        50           643.47965
                       Parameter             Standard
          Variable     Estimate              Error          Type II SS         F Value       Pr > F

          Intercept    22.84025               1.51005       499.75000          228.78        <.0001
          H            -0.08633               0.05070         6.33434            2.90         0.0955
          SD             0.09582             0.04162         11.57650            5.30         0.0260
          P              0.83779             0.19469         40.44876           18.52        <.0001
          C             -0.19375             0.01450        390.13359          178.60        <.0001
          SS            -1.50876             0.17412        164.01341           75.08        <.0001

                            Bounds on condition number: 3.5958, 57.992


                                  Backward Elimination: Step 3

                     Variable H Removed: R-Square = 0.8374 and C(p) = 6.0456

                                      Analysis of Variance
                                    Sum of                Mean
Source                 DF           Squares              Square            F Value                Pr > F

Model                   4           538.84725           134.71181          59.22                  <.0001
Error                  46           104.63240             2.27462
Corrected Total        50           643.47965

                       Parameter             Standard
          Variable     Estimate              Error          Type II SS         F Value       Pr > F

          Intercept    21.00944               1.08202       857.55647          377.01        <.0001
          SD             0.06704              0.03881         6.78486            2.98         0.0909
          P              0.59300              0.13399        44.55472           19.59        <.0001
          C             -0.19632              0.01471       404.95880          178.03        <.0001
          SS            -1.49302              0.17743       161.06239           70.81        <.0001


                            Bounds on condition number: 1.7129, 23.302
```

Backward Elimination: Step 4

Variable SD Removed: R-Square = 0.8269 and C(p) = 7.0963

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	532.06239	177.35413	74.81	<.0001
Error	47	111.41726	2.37058		
Corrected Total	50	643.47965			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	20.56947	1.07356	870.25212	367.11	<.0001
P	0.57166	0.13620	41.76101	17.62	0.0001
C	-0.18636	0.01382	431.12017	181.86	<.0001
SS	-1.43313	0.17764	154.29361	65.09	<.0001

Bounds on condition number: 1.5823, 12.826

All variables left in the model are significant at the 0.0500 level.

Summary of Backward Elimination

Step	Variable Removed	Number Vars In	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	M	6	0.0019	0.8495	6.5379	0.54	0.4673
2	BD	5	0.0023	0.8472	5.1975	0.67	0.4186
3	H	4	0.0098	0.8374	6.0456	2.90	0.0955
4	SD	3	0.0105	0.8269	7.0963	2.98	0.0909

-- Size=170-200 mesh ---

Backward Elimination: Step 0

All Variables Entered: R-Square = 0.7501 and C(p) = 8.0000

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	50.13025	7.16146	18.44	<.0001
Error	43	16.69914	0.38835		
Corrected Total	50	66.82939			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	12.02969	6.28760	1.42156	3.66	0.0624
H	0.05587	0.02379	2.14236	5.52	0.0235
SD	-0.01651	0.01757	0.34299	0.88	0.3526
P	-0.20133	0.19596	0.40993	1.06	0.3100
C	-0.07004	0.02054	4.51593	11.63	0.0014
M	-0.01141	0.01803	0.15556	0.40	0.5302
BD	-2.29163	2.08375	0.46970	1.21	0.2776
SS	-0.29923	0.05758	10.48778	27.01	<.0001

Bounds on condition number: 19.993, 585

Backward Elimination: Step 1

Variable M Removed: R-Square = 0.7478 and C(p) = 6.4006

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	49.97469	8.32912	21.74	<.0001
Error	44	16.85470	0.38306		
Corrected Total	50	66.82939			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	10.73467	5.90471	1.26604	3.31	0.0759
H	0.05017	0.02186	2.01686	5.27	0.0266
SD	-0.01503	0.01729	0.28933	0.76	0.3895
P	-0.17884	0.19139	0.33445	0.87	0.3552
C	-0.05784	0.00707	25.66358	67.00	<.0001
BD	-2.19084	2.06346	0.43182	1.13	0.2942
SS	-0.29692	0.05707	10.36826	27.07	<.0001

Bounds on condition number: 19.553, 287.51

Backward Elimination: Step 2

Variable SD Removed: R-Square = 0.7435 and C(p) = 5.1456

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	49.68536	9.93707	26.08	<.0001

```
Error                 45          17.14403         0.38098
Corrected Total       50          66.82939
                      Parameter             Standard
          Variable    Estimate              Error         Type II SS         F Value     Pr > F

          Intercept   10.49394              5.88215         1.21257            3.18       0.0812
          H             0.04250             0.01995         1.72901            4.54       0.0386
          P            -0.14264             0.18630         0.22334            0.59       0.4479
          C            -0.05895             0.00693        27.55890           72.34      <.0001
          BD           -2.03070             2.04962         0.37398            0.98       0.3271
          SS           -0.30093             0.05673        10.71966           28.14      <.0001

                          Bounds on condition number: 19.397, 223.48


                                Backward Elimination: Step 3

                    Variable P Removed: R-Square = 0.7401 and C(p) = 3.7207

                                   Analysis of Variance

                                       Sum of             Mean
Source                DF              Squares            Square           F Value          Pr > F

Model                  4          49.46202          12.36550            32.75            <.0001
Error                 46          17.36737           0.37755
Corrected Total       50          66.82939


                      Parameter             Standard
          Variable    Estimate              Error         Type II SS         F Value     Pr > F

          Intercept    6.48482              2.66790         2.23066            5.91       0.0190
          H            0.03521              0.01745         1.53685            4.07       0.0495
          C           -0.05627              0.00595        33.72654           89.33      <.0001
          BD          -0.59095              0.81184         0.20005            0.53       0.4704
          SS          -0.28706              0.05352        10.86120           28.77      <.0001
```

Bounds on condition number: 3.0708, 33.99

Backward Elimination: Step 4

Variable BD Removed: R-Square = 0.7371 and C(p) = 2.2358

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	49.26196	16.42065	43.93	<.0001
Error	47	17.56743	0.37378		
Corrected Total	50	66.82939			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	4.56657	0.41410	45.45541	121.61	<.0001
H	0.04295	0.01376	3.63880	9.74	0.0031
C	-0.05454	0.00543	37.68238	100.82	<.0001
SS	-0.27373	0.05004	11.18522	29.93	<.0001

Bounds on condition number: 1.5491, 12.28

All variables left in the model are significant at the 0.0500 level.

Summary of Backward Elimination

Step	Variable Removed	Number Vars In	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	M	6	0.0023	0.7478	6.4006	0.40	0.5302
2	SD	5	0.0043	0.7435	5.1456	0.76	0.3895
3	P	4	0.0033	0.7401	3.7207	0.59	0.4479
4	BD	3	0.0030	0.7371	2.2358	0.53	0.4704

--- Size=325-400 mesh ---

Backward Elimination: Step 0

All Variables Entered: R-Square = 0.8260 and C(p) = 8.0000

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	16.91373	2.41625	29.15	<.0001
Error	43	3.56388	0.08288		
Corrected Total	50	20.47760			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	11.10100	2.88155	1.23006	14.84	0.0004
H	0.04744	0.01114	1.50436	18.15	0.0001
SD	-0.01005	0.00810	0.12781	1.54	0.2210
P	-0.26681	0.09120	0.70929	8.56	0.0055
C	-0.04520	0.00947	1.88864	22.79	<.0001
M	-0.00871	0.00832	0.09068	1.09	0.3014
BD	-2.76107	0.95757	0.68908	8.31	0.0061
SS	-0.22074	0.02692	5.57384	67.25	<.0001

Bounds on condition number: 20.293, 585.41

Backward Elimination: Step 1

Variable M Removed: R-Square = 0.8215 and C(p) = 7.0942

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	16.82304	2.80384	33.76	<.0001
Error	44	3.65456	0.08306		
Corrected Total	50	20.47760			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	10.13156	2.73136	1.14282	13.76	0.0006
H	0.04306	0.01033	1.44350	17.38	0.0001
SD	-0.00889	0.00803	0.10184	1.23	0.2742
P	-0.24989	0.08985	0.64238	7.73	0.0079
C	-0.03591	0.00330	9.84853	118.57	<.0001
BD	-2.69028	0.95619	0.65748	7.92	0.0073
SS	-0.21933	0.02691	5.51679	66.42	<.0001

Bounds on condition number: 19.655, 288.74

Backward Elimination: Step 2

Variable SD Removed: R-Square = 0.8166 and C(p) = 6.3229

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	16.72120	3.34424	40.06	<.0001
Error	45	3.75640	0.08348		
Corrected Total	50	20.47760			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	9.90943	2.73081	1.09919	13.17	0.0007
H	0.03843	0.00947	1.37531	16.48	0.0002
P	-0.22667	0.08759	0.55899	6.70	0.0130
C	-0.03649	0.00327	10.42263	124.86	<.0001
BD	-2.56842	0.95222	0.60731	7.28	0.0098
SS	-0.21996	0.02697	5.55065	66.49	<.0001

Bounds on condition number: 19.108, 223.29

All variables left in the model are significant at the 0.0500 level.

Summary of Backward Elimination

Step	Variable Removed	Number Vars In	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	M	6	0.0044	0.8215	7.0942	1.09	0.3014
2	SD	5	0.0050	0.8166	6.3229	1.23	0.2742

3. Results of the r^2 procedure which gives the contribution of each limestone physical or chemical property, as well as all combinations thereof, on limestone reactivity.

    a. Particle size is included in the model.

The RSQUARE Procedure
Model: MODEL1

Dependent Variable: RT

```
          R-Square Selection Method
Number in                    Variables
Model          R-Square      in Model
1              0.3513        PS
1              0.2104        C
1              0.1880        M
1              0.0732        BD
1              0.0588        SS
1              0.0499        H
1              0.0372        P
1              0.0341        SD
----------------------------------------------------------------
2              0.5618        PS C
2              0.5393        PS M
2              0.4246        PS BD
2              0.4012        PS H
2              0.3894        PS SS
2              0.3886        PS P
2              0.3855        PS SD
2              0.2779        C SS
2              0.2561        M SS
2              0.2116        C M
2              0.2113        P C
2              0.2108        H C
2              0.2105        SD C
2              0.2104        C BD
2              0.1891        M BD
2              0.1890         H M
2              0.1887        SD M
2              0.1880        P M
2              0.1233        P BD
2              0.0984        BD SS
2              0.0888        SD BD
2              0.0860        H SS
2              0.0836        SD SS
2              0.0745        P SS
2              0.0739        H BD
2              0.0606        SD P
2              0.0602        H SD
2              0.0504        H P
----------------------------------------------------------------
3              0.6069        PS C SS
3              0.5850        PS M SS
3              0.5630        PS C M
3              0.5626        PS P C
3              0.5622        PS H C
```

3	0.5618	PS SD C
3	0.5618	PS C BD
3	0.5404	PS M BD
3	0.5403	PS H M
3	0.5401	PS SD M
3	0.5394	PS P M
3	0.4747	PS P BD
3	0.4402	PS SD BD
3	0.4362	PS BD SS
3	0.4252	PS H BD
3	0.4210	PS H SS
3	0.4160	PS SD SS
3	0.4119	PS SD P
3	0.4115	PS H SD
3	0.4091	PS P SS
3	0.4018	PS H P
3	0.2956	P C SS
3	0.2945	C BD SS
3	0.2908	H C SS
3	0.2788	SD C SS
3	0.2787	C M SS
3	0.2675	P M SS
3	0.2649	M BD SS
3	0.2590	H M SS
3	0.2562	SD M SS
3	0.2207	P C BD
3	0.2125	H C M
3	0.2125	P C M
3	0.2117	SD C M
3	0.2116	C M BD
3	0.2113	SD P C
3	0.2113	H C BD
3	0.2113	H P C
3	0.2110	H SD C
3	0.2105	SD C BD
3	0.2024	P M BD
3	0.1909	H P M
3	0.1898	SD M BD
3	0.1894	H SD M
3	0.1892	H M BD
3	0.1888	SD P M
3	0.1422	P BD SS
3	0.1366	H P BD
3	0.1315	SD P BD
3	0.1125	SD BD SS
3	0.0990	H BD SS
3	0.0960	H SD SS
3	0.0941	SD P SS
3	0.0894	H SD BD
3	0.0860	H P SS
3	0.0631	H SD P

4	0.6201	PS P C SS
4	0.6180	PS C BD SS
4	0.6163	PS H C SS
4	0.6078	PS C M SS
4	0.6075	PS SD C SS
4	0.5929	PS P M SS
4	0.5900	PS M BD SS
4	0.5865	PS H M SS
4	0.5850	PS SD M SS
4	0.5721	PS P C BD
4	0.5639	PS H C M
4	0.5638	PS P C M
4	0.5630	PS SD C M
4	0.5630	PS C M BD
4	0.5627	PS SD P C
4	0.5627	PS H C BD
4	0.5626	PS H P C
4	0.5623	PS H SD C
4	0.5618	PS SD C BD
4	0.5538	PS P M BD
4	0.5422	PS H P M
4	0.5411	PS SD M BD

4	0.5407	PS H SD M
4	0.5406	PS H M BD
4	0.5401	PS SD P M
4	0.4880	PS H P BD
4	0.4829	PS SD P BD
4	0.4822	PS P BD SS
4	0.4508	PS SD BD SS
4	0.4407	PS H SD BD
4	0.4369	PS H BD SS
4	0.4311	PS H SD SS
4	0.4297	PS SD P SS
4	0.4210	PS H P SS
4	0.4145	PS H SD P
4	0.2971	SD P C SS
4	0.2965	P C M SS
4	0.2965	H P C SS
4	0.2964	H C BD SS
4	0.2959	SD C BD SS
4	0.2957	P C BD SS
4	0.2953	C M BD SS
4	0.2944	H C M SS
4	0.2908	H SD C SS
4	0.2797	SD C M SS
4	0.2685	H P M SS
4	0.2680	P M BD SS
4	0.2677	SD P M SS
4	0.2651	SD M BD SS
4	0.2650	H M BD SS
4	0.2591	H SD M SS
4	0.2222	P C M BD
4	0.2211	H P C BD
4	0.2207	SD P C BD
4	0.2135	H C M BD
4	0.2128	H SD C M
4	0.2126	H P C M
4	0.2125	SD P C M
4	0.2117	SD C M BD
4	0.2117	H SD C BD
4	0.2113	H SD P C
4	0.2066	H P M BD
4	0.2028	SD P M BD
4	0.1909	H SD P M
4	0.1898	H SD M BD
4	0.1543	H P BD SS
4	0.1498	SD P BD SS
4	0.1383	H SD P BD
4	0.1129	H SD BD SS
4	0.0965	H SD P SS

5	0.6211	PS P C M SS
5	0.6211	PS SD P C SS
5	0.6207	PS H P C SS
5	0.6202	PS P C BD SS
5	0.6197	PS H C BD SS
5	0.6196	PS H C M SS
5	0.6189	PS SD C BD SS
5	0.6189	PS C M BD SS
5	0.6163	PS H SD C SS
5	0.6084	PS SD C M SS
5	0.5945	PS P M BD SS
5	0.5942	PS H P M SS
5	0.5929	PS SD P M SS
5	0.5901	PS H M BD SS
5	0.5900	PS SD M BD SS
5	0.5865	PS H SD M SS
5	0.5735	PS P C M BD
5	0.5724	PS H P C BD
5	0.5721	PS SD P C BD
5	0.5649	PS H C M BD
5	0.5641	PS H SD C M
5	0.5640	PS H P C M
5	0.5639	PS SD P C M
5	0.5630	PS SD C M BD
5	0.5630	PS H SD C BD

5	0.5627	PS H SD P C
5	0.5579	PS H P M BD
5	0.5541	PS SD P M BD
5	0.5422	PS H SD P M
5	0.5411	PS H SD M BD
5	0.4947	PS H P BD SS
5	0.4900	PS SD P BD SS
5	0.4896	PS H SD P BD
5	0.4513	PS H SD BD SS
5	0.4321	PS H SD P SS
5	0.2985	H C M BD SS
5	0.2983	H P C M SS
5	0.2981	SD P C M SS
5	0.2974	H SD P C SS
5	0.2972	SD P C BD SS
5	0.2970	H SD C BD SS
5	0.2968	SD C M BD SS
5	0.2967	H P C BD SS
5	0.2966	P C M BD SS
5	0.2944	H SD C M SS
5	0.2695	H SD P M SS
5	0.2692	H P M BD SS
5	0.2682	SD P M BD SS
5	0.2653	H SD M BD SS
5	0.2222	H P C M BD
5	0.2222	SD P C M BD
5	0.2211	H SD P C BD
5	0.2141	H SD C M BD
5	0.2128	H SD P C M
5	0.2067	H SD P M BD
5	0.1559	H SD P BD SS

6	0.6224	PS H P C M SS
6	0.6221	PS SD P C M SS
6	0.6218	PS H C M BD SS
6	0.6212	PS H SD P C SS
6	0.6212	PS P C M BD SS
6	0.6212	PS SD P C BD SS
6	0.6207	PS H P C BD SS
6	0.6200	PS H SD C BD SS
6	0.6198	PS SD C M BD SS
6	0.6196	PS H SD C M SS
6	0.5962	PS H P M BD SS
6	0.5948	PS H SD P M SS
6	0.5946	PS SD P M BD SS
6	0.5902	PS H SD M BD SS
6	0.5735	PS H P C M BD
6	0.5735	PS SD P C M BD
6	0.5724	PS H SD P C BD
6	0.5654	PS H SD C M BD
6	0.5641	PS H SD P C M
6	0.5581	PS H SD P M BD
6	0.4963	PS H SD P BD SS
6	0.2989	H SD C M BD SS
6	0.2989	H SD P C M SS
6	0.2986	H P C M BD SS
6	0.2982	SD P C M BD SS
6	0.2975	H SD P C BD SS
6	0.2704	H SD P M BD SS
6	0.2222	H SD P C M BD

7	0.6228	PS H SD P C M SS
7	0.6224	PS H P C M BD SS
7	0.6222	PS SD P C M BD SS
7	0.6220	PS H SD C M BD SS
7	0.6213	PS H SD P C BD SS
7	0.5971	PS H SD P M BD SS
7	0.5735	PS H SD P C M BD
7	0.2991	H SD P C M BD SS

8	0.6228	PS H SD P C M BD SS

b. Particle size was held constant at three size fractions: Coarse (600-300 µm or 30-50 mesh U.S. Standard screen), Medium (90-75 µm or 170-200 mesh screen), and fine (45-38 µm or 325-400 mesh screen).

-- Size=30-50 mesh --

R-Square Selection Method

Number in Model	R-Square	Variables in Model
1	0.5845	C
1	0.5070	M
1	0.2084	BD
1	0.1652	H
1	0.1037	SS
1	0.1023	P
1	0.0856	SD
2	0.7620	C SS
2	0.6846	M SS
2	0.5942	C M
2	0.5871	P C
2	0.5847	C BD
2	0.5846	H C
2	0.5846	SD C
2	0.5164	H M
2	0.5117	M BD
2	0.5081	SD M
2	0.5070	P M
2	0.3661	P BD
2	0.2449	SD BD
2	0.2414	BD SS
2	0.2228	H SS
2	0.2163	H BD
2	0.1839	H SD
2	0.1707	SD SS
2	0.1653	H P
2	0.1596	SD P
2	0.1569	P SS
3	0.8269	P C SS
3	0.8148	C BD SS
3	0.7821	H C SS
3	0.7682	SD C SS
3	0.7679	C M SS
3	0.7254	P M SS
3	0.7103	M BD SS
3	0.6862	SD M SS
3	0.6859	H M SS
3	0.6232	P C BD
3	0.5969	P C M
3	0.5945	H C M
3	0.5943	C M BD
3	0.5942	SD C M
3	0.5912	H P C
3	0.5871	SD P C
3	0.5847	SD C BD
3	0.5847	H C BD
3	0.5846	H SD C
3	0.5619	P M BD
3	0.5299	H P M
3	0.5164	H SD M
3	0.5164	H M BD

3	0.5126	SD M BD
3	0.5081	SD P M
3	0.4295	H P BD
3	0.3983	P BD SS
3	0.3829	SD P BD
3	0.2755	SD BD SS
3	0.2515	H BD SS
3	0.2452	H SD BD
3	0.2400	H SD SS
3	0.2275	H P SS
3	0.2081	SD P SS
3	0.1848	H SD P

4	0.8374	SD P C SS
4	0.8327	P C M SS
4	0.8292	H P C SS
4	0.8276	P C BD SS
4	0.8248	SD C BD SS
4	0.8202	C M BD SS
4	0.8148	H C BD SS
4	0.7956	H C M SS
4	0.7844	H SD C SS
4	0.7743	SD C M SS
4	0.7496	H P M SS
4	0.7332	P M BD SS
4	0.7283	SD P M SS
4	0.7185	H M BD SS
4	0.7128	SD M BD SS
4	0.6869	H SD M SS
4	0.6340	P C M BD
4	0.6326	H P C BD
4	0.6234	SD P C BD
4	0.5979	H P C M
4	0.5970	SD P C M
4	0.5956	H C M BD
4	0.5946	H SD C M
4	0.5944	SD C M BD
4	0.5924	H SD P C
4	0.5919	H P M BD
4	0.5847	H SD C BD
4	0.5621	SD P M BD
4	0.5312	H SD P M
4	0.5164	H SD M BD
4	0.4675	H P BD SS
4	0.4296	H SD P BD
4	0.4134	SD P BD SS
4	0.2766	H SD BD SS
4	0.2410	H SD P SS

5	0.8472	H SD P C SS
5	0.8436	SD P C M SS
5	0.8381	SD P C BD SS
5	0.8337	P C M BD SS
5	0.8333	H P C M SS
5	0.8307	H P C BD SS
5	0.8305	SD C M BD SS
5	0.8260	H SD C BD SS
5	0.8210	H C M BD SS
5	0.7975	H SD C M SS
5	0.7685	H SD P M SS
5	0.7602	H P M BD SS
5	0.7362	SD P M BD SS
5	0.7271	H SD M BD SS
5	0.6382	H P C M BD
5	0.6365	H SD P C BD
5	0.6344	SD P C M BD
5	0.5985	H SD P C M
5	0.5967	H SD P M BD
5	0.5956	H SD C M BD
5	0.4675	H SD P BD SS

6	0.8495	H SD P C BD SS
6	0.8492	H SD P C M SS
6	0.8445	SD P C M BD SS

```
6                 0.8346            H P C M BD SS
6                 0.8306            H SD C M BD SS
6                 0.7811            H SD P M BD SS
```

```
6                 0.6409            H SD P C M BD
----------------------------------------------------------
7                 0.8514            H SD P C M BD SS
```

-- Size =170-200 mesh --

```
        R-Square Selection Method
Number in                           Variables
Model             R-Square          in Model
1                 0.5590            C
1                 0.5305            M
1                 0.1894            BD
1                 0.1296            SS
1                 0.1185            SD
1                 0.1017            P
1                 0.0922            H
----------------------------------------------------------
2                 0.6827            C SS
2                 0.6540            M SS
2                 0.5698            H C
2                 0.5624            SD C
2                 0.5608            P C
2                 0.5597            C M
2                 0.5590            C BD
2                 0.5373            SD M
2                 0.5315            M BD
2                 0.5312            H M
2                 0.5307            P M
2                 0.2986            P BD
2                 0.2515            SD BD
2                 0.2335            BD SS
2                 0.2181            SD SS
2                 0.1914            H BD
2                 0.1870            SD P
2                 0.1752            P SS
2                 0.1733            H SS
```

```
2                 0.1499            H SD
2                 0.1083            H P
----------------------------------------------------------
3                 0.7371            H C SS
3                 0.7171            C BD SS
3                 0.7160            P C SS
3                 0.6833            C M SS
3                 0.6827            SD C SS
3                 0.6765            P M SS
3                 0.6750            H M SS
3                 0.6744            M BD SS
3                 0.6550            SD M SS
3                 0.5778            H SD C
3                 0.5776            H C BD
3                 0.5752            P C BD
3                 0.5723            H P C
3                 0.5698            H C M
3                 0.5642            SD P C
3                 0.5632            SD C M
3                 0.5625            SD C BD
3                 0.5614            P C M
3                 0.5597            C M BD
3                 0.5514            P M BD
3                 0.5401            H SD M
3                 0.5381            SD M BD
3                 0.5375            SD P M
3                 0.5360            H M BD
3                 0.5313            H P M
3                 0.3383            SD P BD
3                 0.3257            P BD SS
```

3	0.3053	H P BD
3	0.2903	SD BD SS
3	0.2738	H SD BD
3	0.2480	SD P SS
3	0.2355	H BD SS
3	0.2280	H SD SS
3	0.1906	H SD P
3	0.1798	H P SS

4	0.7413	H SD C SS
4	0.7401	H C BD SS
4	0.7387	H C M SS
4	0.7379	H P C SS
4	0.7176	C M BD SS
4	0.7176	P C BD SS
4	0.7171	SD C BD SS
4	0.7164	P C M SS
4	0.7160	SD P C SS
4	0.6834	SD C M SS
4	0.6805	H SD M SS
4	0.6794	H P M SS
4	0.6791	H M BD SS
4	0.6772	SD P M SS
4	0.6765	P M BD SS
4	0.6752	SD M BD SS
4	0.5905	H SD C BD
4	0.5846	H SD P C
4	0.5831	H P C BD
4	0.5780	H C M BD
4	0.5779	SD P C BD
4	0.5778	H SD C M
4	0.5757	P C M BD
4	0.5725	H P C M
4	0.5649	SD P C M
4	0.5632	SD C M BD
4	0.5566	SD P M BD
4	0.5515	H P M BD
4	0.5493	H SD M BD
4	0.5420	H SD P M
4	0.3634	SD P BD SS
4	0.3385	H SD P BD
4	0.3311	H P BD SS
4	0.3110	H SD BD SS
4	0.2519	H SD P SS

5	0.7435	H P C BD SS
5	0.7431	H SD C M SS
5	0.7428	H SD C BD SS
5	0.7413	H SD P C SS
5	0.7410	H C M BD SS
5	0.7390	H P C M SS
5	0.7180	P C M BD SS
5	0.7176	SD C M BD SS
5	0.7176	SD P C BD SS
5	0.7165	SD P C M SS
5	0.6825	H SD M BD SS
5	0.6823	H SD P M SS
5	0.6795	H P M BD SS
5	0.6772	SD P M BD SS
5	0.5926	H SD P C BD
5	0.5914	H SD C M BD
5	0.5854	H SD P C M
5	0.5832	H P C M BD
5	0.5785	SD P C M BD
5	0.5589	H SD P M BD
5	0.3638	H SD P BD SS

6	0.7478	H SD P C BD SS
6	0.7450	H P C M BD SS
6	0.7440	H SD C M BD SS
6	0.7431	H SD P C M SS
6	0.7181	SD P C M BD SS
6	0.6825	H SD P M BD SS
6	0.5932	H SD P C M BD

```
------------------------------------------------------------
7               0.7501          H SD P C M BD SS
```

-- Size=325-400 mesh --

```
        R-Square Selection Method
Number in                       Variables
Model           R-Square        in Model
1               0.5208          C
1               0.4935          M
1               0.1653          SS
1               0.1643          BD
1               0.0933          P
1               0.0897          SD
1               0.0716          H
------------------------------------------------------------
2               0.6988          C SS
2               0.6759          M SS
2               0.5377          H C
2               0.5227          P C
2               0.5213          C M
2               0.5212          SD C
2               0.5212          C BD
2               0.4964          H M
2               0.4955          SD M
2               0.4938          P M
2               0.4937          M BD
2               0.2474          BD SS
2               0.2425          P BD
2               0.2320          SD SS
2               0.2086          SD BD
2               0.2047          P SS
2               0.1901          H SS
2               0.1687          H BD
2               0.1553          SD P
2               0.1146          H SD
2               0.0948          H P
------------------------------------------------------------
3               0.7866          H C SS
3               0.7475          C BD SS
3               0.7369          P C SS
3               0.7197          H M SS
3               0.7098          M BD SS
3               0.7039          P M SS
3               0.7002          C M SS
3               0.6998          SD C SS
3               0.6760          SD M SS
3               0.5454          H C BD
3               0.5436          H P C
3               0.5411          H SD C
3               0.5378          H C M
3               0.5271          P C BD
3               0.5232          P C M
3               0.5231          SD P C
3               0.5218          SD C M
3               0.5217          C M BD
3               0.5217          SD C BD
3               0.5019          P M BD
3               0.5013          H M BD
3               0.5004          H SD M
3               0.4978          H P M
3               0.4957          SD P M
3               0.4956          SD M BD
```

3	0.3074	P BD SS
3	0.2882	SD BD SS
3	0.2708	SD P BD
3	0.2577	SD P SS
3	0.2539	H BD SS
3	0.2441	H P BD
3	0.2354	H SD SS
3	0.2330	H SD BD
3	0.2047	H P SS
3	0.1626	H SD P

4	0.7893	H C BD SS
4	0.7884	H SD C SS
4	0.7883	H C M SS
4	0.7869	H P C SS
4	0.7494	P C BD SS
4	0.7493	SD C BD SS
4	0.7489	C M BD SS
4	0.7386	SD P C SS
4	0.7381	P C M SS
4	0.7238	H M BD SS
4	0.7222	H SD M SS
4	0.7203	H P M SS
4	0.7104	P M BD SS
4	0.7100	SD M BD SS
4	0.7041	SD P M SS
4	0.7011	SD C M SS
4	0.5520	H SD C BD
4	0.5511	H SD P C
4	0.5463	H C M BD
4	0.5455	H P C BD
4	0.5445	H P C M
4	0.5412	H SD C M
4	0.5275	P C M BD
4	0.5274	SD P C BD
4	0.5236	SD P C M
4	0.5222	SD C M BD
4	0.5082	H SD M BD
4	0.5050	H P M BD
4	0.5042	H SD P M
4	0.5034	SD P M BD
4	0.3349	SD P BD SS
4	0.3168	H SD BD SS
4	0.3076	H P BD SS
4	0.2728	H SD P BD
4	0.2707	H SD P SS

5	0.8166	H P C BD SS
5	0.7902	H C M BD SS
5	0.7902	H SD C M SS
5	0.7902	H SD C BD SS
5	0.7894	H SD P C SS
5	0.7891	H P C M SS
5	0.7510	SD P C BD SS
5	0.7509	P C M BD SS
5	0.7506	SD C M BD SS
5	0.7397	SD P C M SS
5	0.7305	H P M BD SS
5	0.7250	H SD M BD SS
5	0.7223	H SD P M SS
5	0.7105	SD P M BD SS
5	0.5534	H SD C M BD
5	0.5529	H SD P C M
5	0.5521	H SD P C BD
5	0.5463	H P C M BD
5	0.5279	SD P C M BD
5	0.5099	H SD P M BD
5	0.3406	H SD P BD SS

6	0.8215	H SD P C BD SS
6	0.8197	H P C M BD SS
6	0.7923	H SD P C M SS
6	0.7913	H SD C M BD SS
6	0.7525	SD P C M BD SS

```
6              0.7337         H SD P M BD SS
6              0.5538         H SD P C M BD
-----------------------------------------------------------
7              0.8260         H SD P C M BD SS
```

Appendix II

B. Properties Affecting Peat Moss Neutralization Requirement

B. Results of the multiple regression procedures conducted on peat moss physical/chemical properties.

1. Results of the correlation procedure to evaluate interrelationships among several peat moss physical/chemical properties as well as their impact on peat moss neutralization requirement.

The CORR Procedure

12 Variables: NR = neutralization requirement, CEC = cation exchange capacity, BS = base saturation, pH_{inh} or pH = inherent pH, BC = buffering capacity, $[Fe^{3+}]$ or Fe = iron concentrations, decomp = degree of decomposition, dtrts = detritus, *fuscum* = *Sphagnum fuscum*, *angust* = *S. angustifolium*, *magell* = *S. magellanicum*, and sedge

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
NR	192	70.72813	13.08981	13580	14.22000	105.03000
CEC	192	138.56521	13.95179	26605	103.25000	188.74000
BS	192	26.15031	9.72142	5021	9.98000	68.57000
pH	192	3.69156	0.32195	708.78000	3.19000	5.20000
BC	192	42.47620	18.00702	8155	7.86000	127.21000
Fe	192	0.55672	0.33309	106.89000	0	2.69000
Decomp	192	2.50781	0.71168	481.50000	1.50000	4.00000
Dtrts	192	11.42188	10.37537	2193	1.00000	60.00000
fuscum	192	37.79844	30.85097	7257	0	99.00000
angust	192	25.98750	27.75659	4990	0	92.00000
magell	192	8.83750	15.79842	1697	0	76.00000
sedge	192	14.99844	23.58212	2880	0	86.00000

Pearson Correlation Coefficients, N = 192

Prob > |r| under H0: Rho=0

									Sphagnum species			
	NR	**CEC**	**BS**	**pH$_{inh}$**	**BC**	**[Fe^{3+}]**	**decomposition**	**detritus**	***fuscum***	***angust***	***magell***	**sedge**
NR	1.00000	0.04243	-0.40173	-0.21121	0.10568	-0.14953	-0.27167	-0.13503	0.00978	0.15032	0.13855	-0.23136
		0.5590	<.0001	0.0033	0.1446	0.0384	0.0001	0.0618	0.8929	0.0374	0.0553	0.0012
CEC	0.04243	1.00000	0.02367	0.06647	-0.04390	-0.03098	0.00198	0.01140	0.22272	-0.04927	-0.23581	-0.08462
	0.5590		0.7445	0.3597	0.5455	0.6697	0.9782	0.8753	0.0019	0.4973	0.0010	0.2432
BS	-0.40173	0.02367	1.00000	0.49244	-0.09001	0.35383	0.07827	0.06786	0.14124	-0.33498	-0.15886	0.27744
	<.0001	0.7445		<.0001	0.2144	<.0001	0.2806	0.3497	0.0507	<.0001	0.0277	<.0001
pH$_{inh}$	-0.21121	0.06647	0.49244	1.00000	0.07457	0.07805	0.14219	0.23744	-0.02677	-0.24203	-0.12876	0.29441
	0.0033	0.3597	<.0001		0.3040	0.2819	0.0491	0.0009	0.7125	0.0007	0.0751	<.0001
BC	0.10568	-0.04390	-0.09001	0.07457	1.00000	-0.00467	-0.12572	-0.06826	0.08199	-0.03311	0.05021	-0.07524
	0.1446	0.5455	0.2144	0.3040		0.9487	0.0823	0.3468	0.2583	0.6484	0.4892	0.2997
[Fe^{3+}]	-0.14953	-0.03098	0.35383	0.07805	-0.00467	1.00000	0.11473	0.06685	0.03441	-0.25632	-0.17343	0.33666
	0.0384	0.6697	<.0001	0.2819	0.9487		0.1130	0.3569	0.6356	0.0003	0.0161	<.0001
decomposition	-0.27167	0.00198	0.07827	0.14219	-0.12572	0.11473	1.00000	0.79192	-0.23922	-0.11767	-0.10291	0.18928
	0.0001	0.9782	0.2806	0.0491	0.0823	0.1130		<.0001	0.0008	0.1040	0.1555	0.0086
detritus	-0.13503	0.01140	0.06786	0.23744	-0.06826	0.06685	0.79192	1.00000	-0.30341	-0.12761	-0.15337	0.21929
	0.0618	0.8753	0.3497	0.0009	0.3468	0.3569	<.0001		<.0001	0.0777	0.0337	0.0022
S. fuscum	0.00978	0.22272	0.14124	-0.02677	0.08199	0.03441	-0.23922	-0.30341	1.00000	-0.52097	-0.31724	-0.36107
	0.8929	0.0019	0.0507	0.7125	0.2583	0.6356	0.0008	<.0001		<.0001	<.0001	<.0001
S. angustifolium	0.15032	-0.04927	-0.33498	-0.24203	-0.03311	-0.25632	-0.11767	-0.12761	-0.52097	1.00000	-0.00193	-0.42477
	0.0374	0.4973	<.0001	0.0007	0.6484	0.0003	0.1040	0.0777	<.0001		0.9788	<.0001
S. magellanicum	0.13855	-0.23581	-0.15886	-0.12876	0.05021	-0.17343	-0.10291	-0.15337	-0.31724	-0.00193	1.00000	-0.17929
	0.0553	0.0010	0.0277	0.0751	0.4892	0.0161	0.1555	0.0337	<.0001	0.9788		0.0128
sedge	-0.23136	-0.08462	0.27744	0.29441	-0.07524	0.33666	0.18928	0.21929	-0.36107	-0.42477	-0.17929	1.00000
	0.0012	0.2432	<.0001	<.0001	0.2997	<.0001	0.0086	0.0022	<.0001	<.0001	0.0128	

2. Results of the step-by-step backwards elimination ANOVAs which eliminate peat moss physical or chemical properties one at a time from the least to most highly correlated to neutralization requirement. Properties are eliminated until all left in the model are significantly correlated at α=0.05.

The STEPWISE Procedure

Model: MODEL1
Dependent Variable: NR

Backward Elimination: Step 0

All Variables Entered: R-Square = 0.2615 and C(p) = 12.0000

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	8558.30442	778.02767	5.79	<.0001
Error	180	24168.00000	134.26803		
Corrected Total	191	32727.00000			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	117.65254	36.26896	1412.87922	10.52	0.0014
CEC	0.05689	0.06323	108.69586	0.81	0.3695
BS	-0.49553	0.11086	2682.81213	19.98	<.0001
pH_{inh}	-0.27376	3.24060	0.95818	0.01	0.9328
BC	0.02022	0.04823	23.59367	0.18	0.6756
$[Fe^{3+}]$	2.23547	2.88681	80.51469	0.60	0.4397
Decomp	-7.51148	1.98526	1922.16465	14.32	0.0002
Dtrts	0.04100	0.37052	1.64432	0.01	0.9120
fuscum	-0.27610	0.33682	90.22197	0.67	0.4135
angust	-0.28063	0.33365	94.99059	0.71	0.4014
magell	-0.20756	0.33801	50.63171	0.38	0.5399
sedge	-0.33397	0.33464	133.73081	1.00	0.3196

Bounds on condition number: 153.6, 4788.5

```
                         Backward Elimination: Step 1

          Variable pH Removed: R-Square = 0.2615 and C(p) = 10.0071


                             Analysis of Variance

                                  Sum of          Mean
Source                 DF       Squares         Square     F Value      Pr > F

Model                  10    8557.34624      855.73462        6.41      <.0001
Error                 181   24169.00000      133.53152
Corrected Total       191   32727.00000


            Parameter     Standard
Variable     Estimate        Error     Type II SS     F Value      Pr > F

Intercept   116.67556     34.28124     1546.78666       11.58      0.0008
CEC           0.05647      0.06286      107.76459        0.81      0.3702
BS           -0.50002      0.09703     3545.94652       26.56      <.0001
BC            0.01953      0.04742       22.66245        0.17      0.6809
[Fe3+]        2.28028      2.82987       86.70167        0.65      0.4214
Decomp       -7.49954      1.97478     1925.81514       14.42      0.0002
Dtrts         0.04031      0.36941        1.59018        0.01      0.9132
fuscum       -0.27457      0.33541       89.48392        0.67      0.4141
angust       -0.27909      0.33223       94.23243        0.71      0.4020
magell       -0.20601      0.33658       50.02508        0.37      0.5413
sedge        -0.33316      0.33358      133.18895        1.00      0.3193

                 Bounds on condition number: 153.16, 4322.8

--------------------------------------------------------------------------------
```

Backward Elimination: Step 2

Variable dtrts Removed: R-Square = 0.2614 and C(p) = 8.0190

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	9	8555.75606	950.63956	7.16	<.0001
Error	182	24171.00000	132.80656		
Corrected Total	191	32727.00000			

Variable	Parameter Estimate	Standard Error	Type II SS	F Value	Pr > F
Intercept	119.89397	17.42826	6285.01165	47.32	<.0001
CEC	0.05643	0.06269	107.63387	0.81	0.3692
BS	-0.50042	0.09670	3556.77966	26.78	<.0001
BC	0.01966	0.04727	22.95811	0.17	0.6781
$[Fe^{3+}]$	2.25430	2.81217	85.34127	0.64	0.4238
Decomp	-7.40750	1.78075	2298.04712	17.30	<.0001
Fuscum	-0.30866	0.12180	852.86903	6.42	0.0121
angust	-0.31271	0.12403	844.27329	6.36	0.0125
magell	-0.23998	0.12772	468.84136	3.53	0.0619
sedge	-0.36661	0.13120	1036.90001	7.81	0.0058

Bounds on condition number: 20.307, 575.64

Backward Elimination: Step 3

Variable BC Removed: R-Square = 0.2607 and C(p) = 6.1900

```
                          Analysis of Variance

                              Sum of          Mean
Source              DF       Squares         Square          F Value      Pr > F

Model                8     8532.79795     1066.59974           8.07      <.0001
Error              183    24194.00000      132.20630
Corrected Total    191    32727.000000

               Parameter   Standard
Variable        Estimate      Error        Type II SS      F Value      Pr > F

Intercept      121.51703   16.94702       6797.35376        51.41      <.0001
CEC              0.05510    0.06246        102.87860         0.78       0.3789
BS              -0.50438    0.09601       3648.54882        27.60      <.0001
[Fe3+]           2.30920    2.80272         89.74635         0.68       0.4111
Decomp          -7.49707    1.76367       2388.91426        18.07      <.0001
fuscum          -0.31152    0.12133        871.54898         6.59       0.0110
angust          -0.31694    0.12333        873.11305         6.60       0.0110
magell          -0.24267    0.12727        480.63237         3.64       0.0581
sedge           -0.37089    0.13050       1067.83469         8.08       0.0050

               Bounds on condition number: 20.242, 500.69
-----------------------------------------------------------------------------------------------------------------------------

                      Backward Elimination: Step 4

          Variable Fe Removed: R-Square = 0.2580 and C(p) = 4.8584

                          Analysis of Variance

                              Sum of               Mean
Source              DF       Squares              Square          F Value      Pr > F

Model                7     8443.05160          1206.15023           9.14      <.0001
Error              184    24283.00000           131.97554
Corrected Total    191    32727.00000
```

Variable	**Parameter Estimate**	**Standard Error**	**Type II SS**	**F Value**	**Pr > F**
Intercept	121.82002	16.92823	6834.51111	51.79	<.0001
CEC	0.05239	0.06232	93.25854	0.71	0.4017
BS	-0.48460	0.09288	3592.53232	27.22	<.0001
Decomp	-7.38726	1.75709	2332.76758	17.68	<.0001
fuscum	-0.30490	0.12096	838.55452	6.35	0.0126
angust	-0.31283	0.12312	852.01652	6.46	0.0119
magell	-0.24156	0.12715	476.32286	3.61	0.0590
sedge	-0.35762	0.12939	1008.13538	7.64	0.0063

Bounds on condition number: 20.153, 426.35

Backward Elimination: Step 5

Variable CEC Removed: R-Square = 0.2551 and C(p) = 3.5529

Analysis of Variance

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	6	8349.79306	1391.63218	10.56	<.0001
Error	185	24377.00000	131.76626		
Corrected Total	191	32727.00000			

Variable	**Parameter Estimate**	**Standard Error**	**Type II SS**	**F Value**	**Pr > F**
Intercept	129.38619	14.32570	10749.00000	81.57	<.0001
BS	-0.48553	0.09280	3606.77862	27.37	<.0001
Decomp	-7.39109	1.75569	2335.20312	17.72	<.0001
fuscum	-0.30472	0.12086	837.56201	6.36	0.0125
angust	-0.31617	0.12296	871.18820	6.61	0.0109
magell	-0.25397	0.12619	533.70085	4.05	0.0456
sedge	-0.36318	0.12912	1042.50137	7.91	0.0054

Bounds on condition number: 20.153, 358.09

All variables left in the model are significant at the 0.0500 level.

Summary of Backward Elimination

Step	Variable Removed	Number Vars In	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	pH	10	0.0000	0.2615	10.0071	0.01	0.9328
2	dtrts	9	0.0000	0.2614	8.0190	0.01	0.9132
3	BC	8	0.0007	0.2607	6.1900	0.17	0.6781
4	$[Fe^{3+}]$	7	0.0027	0.2580	4.8584	0.68	0.4111
5	CEC	6	0.0028	0.2551	3.5529	0.71	0.4017

3. Results of the r^2 procedure which gives the contribution of each peat moss physical or chemical property, as well as all combinations thereof, on peat moss neutralization requirement.

The RSQUARE Procedure
Model: MODEL1

Dependent Variable: NR

Number in Model	R-Square	Variables in Model
1	0.1614	BS
1	0.0738	decomp
1	0.0535	sedge
1	0.0446	pH
1	0.0226	angust
1	0.0224	Fe
1	0.0192	magell
1	0.0182	dtrts
1	0.0112	BC
1	0.0018	CEC
1	0.0001	fuscum
2	0.2195	BS, decomp
2	0.1770	BS, sedge
2	0.1731	BS, dtrts
2	0.1671	BS, magell
2	0.1663	BS, BC
2	0.1659	BS, fuscum
2	0.1641	CEC, BS
2	0.1617	BS, angust

2	0.1616	BS, pH
2	0.1614	BS, Fe
2	0.1074	decomp, sedge
3	0.2376	BS, decomp, dtrts
3	0.2265	BS, decomp, sedge
3	0.2223	BS, decomp, magell
3	0.2222	CEC, BS, decomp
3	0.2212	BS, BC, decomp
3	0.2197	BS, Fe, decomp
3	0.2196	BS, pH, decomp
3	0.2195	BS, decomp, angust
3	0.2195	BS, decomp, fuscum
3	0.1840	BS, dtrts, sedge
3	0.1810	BS, BC, sedge
4	0.2477	BS, decomp, dtrts, sedge
4	0.2426	BS, decomp, dtrts, magell
4	0.2401	CEC, BS, decomp, dtrts
4	0.2388	BS, BC, decomp, dtrts
4	0.2388	BS, decomp, dtrts, fuscum
4	0.2381	BS, Fe, decomp, dtrts
4	0.2380	BS, pH, decomp, dtrts
4	0.2376	BS, decomp, dtrts, angust
4	0.2284	CEC, BS, decomp, sedge
4	0.2284	BS, decomp, magell, sedge
4	0.2280	BS, decomp, angust, sedge
5	0.2512	BS, decomp, dtrts, magell, sedge
5	0.2501	BS, Fe, decomp, dtrts, sedge
5	0.2494	CEC, BS, decomp, dtrts, sedge
5	0.2491	BS, decomp, dtrts, angust, sedge
5	0.2487	BS, BC, decomp, dtrts, sedge
5	0.2478	BS, decomp, dtrts, fuscum, sedge
5	0.2478	BS, pH, decomp, dtrts, sedge
5	0.2472	CEC, BS, decomp, dtrts, magell
5	0.2467	BS, decomp, dtrts, fuscum, magell
5	0.2436	BS, BC, decomp, dtrts, magell
5	0.2435	BS, Fe, decomp, dtrts, magell
6	0.2551	BS, decomp, fuscum, angust, magell, sedge
6	0.2544	CEC, BS, decomp, dtrts, magell, sedge
6	0.2542	BS, Fe, decomp, dtrts, magell, sedge
6	0.2531	BS, decomp, dtrts, fuscum, angust, sedge
6	0.2521	BS, decomp, dtrts, angust, magell, sedge
6	0.2520	BS, BC, decomp, dtrts, magell, sedge
6	0.2518	CEC, BS, Fe, decomp, dtrts, sedge
6	0.2518	BS, decomp, dtrts, fuscum, magell, sedge
6	0.2513	BS, Fe, decomp, dtrts, angust, sedge
6	0.2512	BS, pH, decomp, dtrts, magell, sedge
6	0.2509	BS, BC, Fe, decomp, dtrts, sedge
7	0.2580	CEC, BS, decomp, fuscum, angust, magell, sedge
7	0.2577	CEC, BS, Fe, decomp, dtrts, magell, sedge
7	0.2576	BS, Fe, decomp, fuscum, angust, magell, sedge
7	0.2561	CEC, BS, decomp, dtrts, fuscum, angust, sedge
7	0.2559	BS, Fe, decomp, dtrts, fuscum, angust, sedge
7	0.2558	BS, BC, decomp, fuscum, angust, magell, sedge
7	0.2554	CEC, BS, BC, decomp, dtrts, magell, sedge
7	0.2552	BS, pH, decomp, fuscum, angust, magell, sedge
7	0.2551	BS, decomp, dtrts, fuscum, angust, magell, sedge
7	0.2550	CEC, BS, decomp, dtrts, angust, magell, sedge
7	0.2549	BS, BC, Fe, decomp, dtrts, magell, sedge
8	0.2607	CEC, BS, Fe, decomp, fuscum, angust, magell, sedge
8	0.2593	CEC, BS, Fe, decomp, dtrts, fuscum, angust, sedge
8	0.2588	CEC, BS, BC, decomp, fuscum, angust, magell, sedge
8	0.2585	CEC, BS, BC, Fe, decomp, dtrts, magell, sedge
8	0.2581	BS, BC, Fe, decomp, fuscum, angust, magell, sedge
8	0.2581	CEC, BS, pH, decomp, fuscum, angust, magell, sedge
8	0.2581	CEC, BS, Fe, decomp, dtrts, angust, magell, sedge
8	0.2580	CEC, BS, dcomp, dtrts, fuscum, angust, magell, sedge
8	0.2579	CEC, BS, Fe, decomp, dtrts, fuscum, magell, sedge
8	0.2577	CEC, BS, pH, Fe, decomp, dtrts, magell, sedge
8	0.2576	BS, Fe, decomp, dtrts, fuscum, angust, magell, sedge
9	0.2614	CEC, BS, BC, Fe, decomp, fuscum, angust, magell, sedge
9	0.2608	CEC, BS, Fe, dcmp, dtrts, fuscum, angust, magell, sedge
9	0.2607	CEC, BS, pH, Fe, dcomp, fuscum, angust, magell, sedge
9	0.2600	CEC, BS, BC, Fe dcomp, dtrts, fuscum, angust, sedge
9	0.2593	CEC, BS, pH, Fe, decomp, dtrts, fuscum, angust, sedge
9	0.2590	CEC, BS, pH, BC, dcomp, fuscum, angust, magell, sedge

9	0.2588	CEC, BS, BC, decomp, dtrts, fuscum, angust, magell, sedge
9	0.2587	CEC, BS, BC, Fe, decomp, dtrts, angust, magell, sedge
9	0.2586	CEC, BS, BC, Fe, decomp, dtrts, fuscum, magell, sedge
9	0.2585	CEC, BS, pH, BC, Fe, decomp, dtrts, magell, sedge
9	0.2582	BS, BC, Fe, decmp, dtrts, fuscum, angust, magell, sedge

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10	0.2615	CEC, BS, BC, Fe, decomp, dtrts, fuscum, angust, magell, sedge
10	0.2615	CEC, BS, pH, BC, Fe, decomp, fuscum, angust, magell, sedge
10	0.2608	CEC, BS, pH, Fe, decomp, dtrts, fuscum, angust, magell, sedge
10	0.2600	CEC, BS, pH, BC, Fe, decomp, dtrts, fuscum, angust, sedge
10	0.2590	CEC, BS, pH, BC, decomp, dtrts, fuscum, angust, magell, sedge
10	0.2588	CEC, BS, pH, BC, Fe, decomp, dtrts, angust, magell, sedge
10	0.2586	CEC, BS, pH, BC, Fe, decomp, dtrts, fuscum, magell, sedge
10	0.2582	BS, pH, BC, Fe, decomp, dtrts, fuscum, angust, magell, sedge
10	0.2574	CEC, BS, pH, BC, Fe, decomp, dtrts, fuscum, angust, magell
10	0.2028	CEC, BS, pH, BC, Fe, dtrts, fuscum, angust, magell, sedge
10	0.1795	CEC, pH, BC, Fe, decomp, dtrts, fuscum, angust, magell, sedge

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11	0.2615	CEC, BS, pH, BC, Fe, decomp, dtrts, fuscum, angust, magell, sedge