

**Elemental Concentration Changes in Soil and
Stockpiled Tall Fescue Leaves after Liming**

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Master of Science

by
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The undersigned, appointed by the dean of the Graduate School, have examined the thesis entitled

**Elemental Concentration Changes in Soil and Stockpiled Tall
Fescue Leaves after Liming**

presented by Elizabeth J. Hamilton,
a candidate for the degree of master of science,
and hereby certify that, in their opinion, it is worthy of acceptance.

Dr. Dale Blevins

Dr. Randall Miles

Dr. Keith Goyne

For my parents...
you were my first teachers.
Thanks for all of your love and support.

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Elemental Concentration Changes in Soil and Stockpiled Tall Fescue Leaves after Liming

ABSTRACT

Many soils in Missouri are inherently acidic and possess little plant available phosphorus (P). Much of the state's forage production occurs on these soils, and tall fescue (*Festuca arundinacea* Schreb.) is the dominant forage growing on them. Little is known about the effects of lime, an amendment that increases pH and adds calcium (Ca) or both Ca and magnesium (Mg), on the macro-, micro-, and beneficial nutrient composition of stockpiled tall fescue. Others have predicted that liming will increase plant available P and reduce aluminum (Al) toxicity problems in the types of soils used in this study.

Study sites were located at the University of Missouri Southwest Center (SWC) on a Gerald silt loam (fine, mixed, active, mesic Aeris Fragiaqualf) and the University of Missouri Bradford Research and Extension Center (BREC) on Leonard silt loam (fine, smectitic, mesic Vertic Epiaqualf) and Mexico silt loam (fine, smectitic, mesic Aeris Vertic Epiaqualf). Calcitic and dolomitic limestone were applied at 0x, 1/2x, 1x and 2x the recommended soil test rate. Forage was harvested and weighed twice annually and tall fescue leaves were harvested several times throughout the stockpiling season, dried, ground, digested, and analyzed for macro-, micro-, and beneficial nutrient concentrations. Soil samples were also taken and analyzed.

The two year total forage harvest yield was increased by limestone application at SWC; however, no consistent trends were observed at BREC. Following liming, leaf P concentrations were relatively unaltered, leaf potassium (K)

and nitrogen (N) concentrations decreased, and, leaf Ca concentrations increased with liming. Additionally, leaf Mg concentrations decreased in calcitic treatments but increased with the application of dolomitic lime. As a result of the changes in leaf K, Mg, and Ca concentrations, the grass tetany ratio (meq K/ meq Ca + meq Mg) of leaves from limed plots decreased. Leaf micro- and beneficial element concentrations were also altered by liming. Leaf boron (B) concentrations decreased, leaf manganese (Mn) concentrations decreased by more than 50%, and leaf molybdenum (Mo) increased within three months of limestone application. The 2x treatments of limestone increased leaf sodium (Na) concentrations at SWC. Lime had little influence on leaf Al, iron (Fe), zinc (Zn), and copper (Cu) concentrations at either site.

For the most part, changes in leaf concentrations of the elements mirrored changes in soil test concentrations following liming. Soil Mn and K decreased with increasing rates of limestone. Calcitic limestone increased soil test Ca and had little effect on Mg whereas dolomitic limestone increased soil Mg and only slightly increased soil Ca. An increasing trend was observed for soil Na, and soil sulfate increased as a result of liming. Soil Bray I P, Bray II P, Zn, Cu, and Fe showed little effect of limestone application. Soil $\text{pH}_{\text{CaCl}_2}$ values were increased and neutralizable acidity decreased with increasing rates of limestone. Soil cation exchange capacity decreased with limestone at SWC while it showed no consistent effect at BREC. Soil organic matter content was not influenced by limestone applications.

Liming two acidic Missouri soils changed many soil chemical properties. Consequently the concentrations of macro-, micro-, and beneficial nutrients in

stockpiled tall fescue leaves changed which should improve the nutritional value of tall fescue as a forage for beef cattle.

CHAPTER 1

Literature Review

Introduction

Soil reaction is considered the master variable because it affects the physical, biological, and chemical properties of soils as well as the ecosystems that the soil supports. Soil pH is the measure used to quantify soil reaction and can be expressed as $\text{pH} = -\log (\text{H}^+)$ in soil solution; those soils with a pH less than 7.0 are considered acidic while those greater than 7.0 are basic or alkaline. Soil acidity affects 40 to 70% of the world's arable land (Rengel 2003), and over half of Missouri's soils (Nathan 1995).

Acid soils are a naturally occurring phenomenon caused by weathering processes and decay of organic matter (OM). Both processes release basic cations, as well as hydrogen (H) and aluminum (Al) cations into soil solution. In climates with large amounts of rainfall, base cations may then be leached from the soil increasing the proportion of H^+ ions and decreasing the soil pH. Consequently, Al solubility increases and the concentration of the Al^{3+} species in soil solution increases, compounding the problem by releasing additional H^+ into solution through hydrolysis reactions. Furthermore, living plants contribute to soil acidity as they excrete H^+ ions and organic acids into the rhizosphere. Carbon dioxide (CO_2) from plant and microbial respiration can dissolve in soil solution to form carbonic acid, yet another source of acidity.

Many human activities also promote soil acidification. Common agricultural practices such as fertilization with ammonium-based and potassium chloride-based fertilizers are contributors; twenty million metric tons of limestone would be required annually to neutralize the acidity created by ammonium-based fertilizers (Brady and

Weil 2004). Acidity can also be attributed to the removal of base cations via crops. The soil acidity predicament is further compounded by anthropogenic acid depositions derived from transportation and industrial air pollution emissions.

Fisher (1969) suggested that soil acidity can affect plant growth in many ways. First, large amounts of soluble manganese (Mn), iron (Fe), and Al are often present, and, in large concentrations, these elements can have negative effects on plant growth. Second, formation of highly insoluble Fe and Al phosphates lessens phosphate (PO_4^{3-}) availability to plants. Third, the activity of many soil microorganisms is reduced, affecting OM turnover and microbe-plant symbiosis. Lastly, the availability of plant essential elements is impacted. As a result of these influences, the composition of natural plant communities may be defined by the degree of soil acidity. Furthermore, agricultural crops are often chosen based on their tolerance to soil acidity. Tall fescue (*Festuca arundinacea* Schreb.) is particularly tolerant to soil acidity (Belesky and West 2005) and is found on approximately 14 million hectares in the United States (Fribourg and Hannaway 2005). In Missouri, tall fescue covers approximately seven million hectares (Roberts and Andrae 2004), and it is the dominant forage for beef cattle.

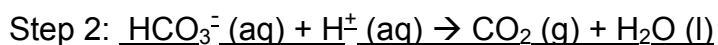
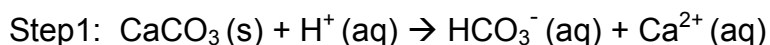
Grass tetany, or hypomagnesaemia, is a magnesium (Mg) deficiency sometimes experienced by cattle grazing pastures of tall fescue and other grasses. Grass tetany leads to a loss of muscle function and, potentially, death. The disease often occurs in lactating beef cattle grazing young, new growth during the spring green-up period; nevertheless, there have been recent reports from producers of tetany occurring during the winter on stockpiled tall fescue pastures.

Producers often supply grazing cattle with Mg supplements to prevent grass tetany, but increasing herbage Mg concentrations may also help decrease the incidence of grass tetany. Reinbott and Blevins (1994, 1997) demonstrated that P fertilization was necessary to increase the Mg content of tall fescue grown on acidic Missouri soils. With as little as 14 kg P/ha or as much as 224 kg P/ha, Mg concentrations in tall fescue leaves were 13 or 43% larger, respectively, compared to plants receiving no P (McClain and Blevins 2006).

Lime, a soil amendment used to decrease soil acidity, is often believed to increase the availability of soil P to plants (Haynes 1982, Adams 1984). If lime increases the availability of P, it follows that liming would also result in an increase in Mg concentrations in tall fescue leaves.

Lime

By definition, lime is capable of neutralizing soil acidity with its calcium (Ca) and/or Mg compounds (Barber 1984). Limestone, found as dolomite ($\text{MgCa}(\text{CO}_3)_2$) and calcite (CaCO_3), is the most commonly used liming material. The reaction of lime with acidity, as expressed by Kreutzer (1995), occurs in two steps:



Divalent cations liberated into solution via these reactions may then adsorb to the cation exchange sites in the soil.

Applying lime to an acid soil is a common agricultural practice dating back to at least 200 B.C. (Barber 1984). As a result, there exists a plethora of research on

the ability of lime to alter, directly or indirectly, the physical, biological, and chemical properties of the soil.

From a biological perspective, lime often creates a more hospitable habitat for both plant and microbial growth. Bacteria and actinomycetes are less prevalent in acidic soils, negatively impacting symbiotic dinitrogen (N_2) fixation, the rate of OM decomposition, and other microbially-mediated processes. By creating a more favorable environment for many of the microbial activities by liming, additional nutrients may become available for plant growth resulting in an increase in biomass production and, consequently, additional organic material for heterotrophic microorganisms.

Soil physical properties may also be changed by lime applications. The structure of the soil may be improved by Ca-induced flocculation and by the increased OM production.

McLean and Brown (1984) summarized the effects of lime on soil chemistry into the following points: (1) acidity is neutralized, (2) base saturation of Ca and perhaps Mg is increased, (3) ratios of base cations adsorbed and in solution change, (4) once CO_2 dissipates, soil pH increases and in so doing changes the solubility of many elements, (5) Al^{3+} and Mn^{2+} are neutralized or inactivated, (6) a decreased concentration of H^+ decreases the acid weathering of primary and secondary minerals, (7) pH-dependent cation exchange capacity (CEC) is increased and Ca^{2+} (and Mg^{2+}) are adsorbed, (8) pH-dependent anion exchange capacity (AEC) is decreased and anions are forced into solution, (9) N_2 fixation is increased, (10) N

mineralization is increased, (11) the electrolyte concentration is increased, and (12) hydroxyl (OH^-) ion concentration is increased.

The chemical changes that occur following liming may influence plant growth by supplying Ca (and Mg), changing the availability of applied and inherent plant essential and toxic elements, enhancing microbial activity, and improving plant root development (Pearson 1958). Many of the chemical changes in soil and the associated plant community as a result of liming are discussed below in detail.

Hydrogen

Soil acidity is defined by the H^+ ion activity in soil solution and is expressed as pH. With applications of both dolomitic and calcitic lime, soil pH has been observed to increase (Miller et al. 1964, Edmeades et al. 1983, Evans et al. 1983, Holford et al. 1994, Burmester et al. 1998, Mullen et al. 2006, Fageria 2006). Maximum pH may be reached within three years of the lime application (Holford et al. 1994, Wheeler 1998), but in some finer textured soils, as many as seven years may be required to observe maximum pH (Moschler et al. 1962). Wheeler (1998) estimated that lime would increase the pH of a soil above that of an unlimed soil for 11 to 12 years; the duration was essentially independent of lime rate. Kroth and Mattas (1974, 1981) found that time and incorporation of lime were effective in increasing the pH of the soil below the surface of a Gerald silt loam in southwest Missouri.

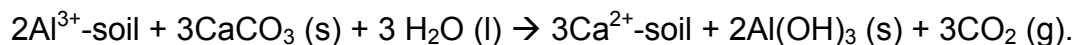
In terms of plant growth, it is difficult to separate the effects of lime on decreasing H^+ activity in the soil from the effects of lime on other aspects of soil chemistry. Moore (1974) suggested that H^+ may play a large role in limiting the

activity and survival of soil microorganisms, but the concentration of Al^{3+} and Mn^{2+} may be the primary factors limiting plant growth, especially in soils of pH 4.0 or greater (Foy 1984).

To look at the specific effects of H^+ on plants, many studies have been carried out in nutrient solution and sand culture. When H^+ activity is large enough to create a pH of 4.0 or less, plant roots may be damaged and exhibit discoloration and a reduction in the number and length of roots (Arnon et al. 1942). Acidic pH values may also alter root membrane permeability, cause the loss of previously absorbed cations and organic substances, and decrease the capacity for nutrient absorption (Foy 1984). H^+ appears to interfere with a plant's ability to obtain, retain, and utilize potassium (K), Ca, P, nitrogen (N), Mg, zinc (Zn), and copper (Cu), but additional Ca supplied by lime may help lessen the stress associated with decreased pH (Foy 1984).

Aluminum

Following oxygen (O) and silicon (Si), Al is the third most abundant element in the earth's crust (Clarke 1924) and poses a large problem for plant growth in acidic soils. Aluminum is a component of reserve or extractable acidity and has the potential to generate three H^+ ions as it is precipitated from solution as gibbsite, $\text{Al}(\text{OH})_3$, when lime is applied. Because Al is an important component in soil acidity, Thomas and Hargrove (1984) conveyed the reaction of lime with soil solution as:



Limestone applications have been shown to greatly decrease extractable and exchangeable soil Al (Foy et al. 1965, Helyar and Anderson 1971, John et al. 1972,

Edmeades et al. 1983, Sims and Ellis 1983, Kuo 1993, Holford et al. 1994, Wheeler 1998, Mullen et al. 2006). Lime also caused a small decrease in soil solution Al concentration at a 40 centimeter depth (Huber et al. 2006).

Although small concentrations of Al can be beneficial to plants (Marshner 1986), aluminum toxicity may be the most limiting factor for plant growth on soils with a pH below 5.0, or a pH below 5.5 in kaolinitic soils (Foy 1984). Al is phytotoxic as Al^{3+} and Al-polymers such as Al_{13} , $\text{Al}_7(\text{OH})_{17}^{4+}$, and soluble aluminophosphate complexes; little is known about the degree of toxicity or existence of Al polymers in soil (Marshner 1986, Menzies 2003). Al^{3+} , generally considered the culprit in plant Al toxicity is present only below pH ~5.5 and is the dominant monomeric Al species below pH 4.7 (Marion et al. 1976).

At these acid soil pH values, Al interferes with many physical and cellular processes resulting in the inhibition of root growth and function (Foy 1984). In large concentrations, Al may also impact the uptake, transport, and use of Ca, Mg, K, P, Fe, Cu, Zn, and Mn (Foy 1984). Lime has two beneficial effects with regards to Al toxicity in plants. First, lime precipitates Al^{3+} , decreasing the availability of Al to plants growing on limed soils. Second, the presence of Ca, which is supplied by lime, can decrease Al concentrations in plant foliage (Huett and Menary 1980). Research has shown that lime decreased foliar Al concentration (Helyar and Anderson 1971, John et al. 1972), but in other studies it had no effect (John et al. 1972).

Manganese

It is easy to share the sentiments of Krauskopf (1972) that “the form that Mn takes in soils can only be guessed” and Lindsay (1972) that “the chemistry of Mn and its toxic compounds in soils is very complex.” In general, Mn may be encountered as solution Mn^{2+} , exchangeable Mn^{2+} , organically-bound Mn, and Mn minerals such as oxides.

The equilibrium half reaction between vernadite ($\delta\text{-MnO}_2$), one of the most common Mn oxides in soils (Cheswort 1991), and solution Mn^{2+} was expressed by Marshner (1986) as:



The reduction of Mn is microbially mediated, but its oxidation is apparently an autocatalytic, non-biological process that occurs quickly below pH 5.5 (Moraghan and Mascagni 1991).

Solution Mn^{2+} is so responsive to pH changes that an increase of one pH unit can decrease the Mn^{2+} concentration one hundred-fold (Lindsay 1972).

Considerable concentrations of Mn^{2+} are often found in acid soils that are temporarily anaerobic because of the large concentration of H^+ and electrons. Of these two factors, pH is possibly more important. Under increasing anaerobiasis, acidic soils quickly reduce Mn IV oxides to water soluble and exchangeable Mn^{2+} . However, under more alkaline conditions, Mn IV, III, and II solids predominate, even when the soil is quite anaerobic (Gotoh and Patrick 1972). Moraghan and Mascagni (1991) suggest that at pH 5.0, redox potential has little impact on Mn solubility.

Because pH is so influential in determining Mn speciation, lime typically decreases soil Mn^{2+} solution concentrations (Willis 1928, Gupta et al. 1971, Helyar and Anderson 1971, Jackson and Reisenauer 1984, Moraghan and Mascagni 1991, Holford et al. 1994, Mullen et al. 2006). Kamprath and Foy (1972) submit that the largest decrease in exchangeable Mn occurs when a soil is limed from a pH below 5.0 to 5.3 or 5.4. A great deal of Mn is also complexed by soil OM. When lime increases soil pH, Mn^{2+} exchangeability from organic solids decreases because of a stronger attraction between the OM and Mn (Moraghan and Mascagni 1991).

The form of Mn available to plants is Mn^{2+} (Clarkson 1988). Soil pH values below 5.5 have the potential to limit yields due to the increasing availability of possibly toxic concentrations of Mn (Moraghan and Mascagni 1991). Excessive Mn levels have visible toxicity symptoms in the shoots of plants and affect plant metabolism and phytochrome balance (Marshner 1986), as well as the uptake of other mineral nutrients including Ca, Mg, Fe, Mo, P, and Si (Foy 1984, Marshner 1986).

Calcium itself helps decrease foliar Mn concentrations (Robson and Loneragan 1970, Foy 1984), and when combined with the pH induced decrease in Mn availability, lime markedly decreases plant Mn concentrations (Willis 1928, Gupta et al. 1971, Helyar and Anderson 1971, John et al. 1972, Edmeades et al. 1983, Jackson and Reisenauer 1984, Stevens and Laughlin 1996, Wheeler 1998, Hue 2004). Species less susceptible to Mn toxicity show less of an effect from the lime induced change in Ca concentrations and pH (Robson and Loneragan 1970).

Calcium

In environments where evaporation is less than precipitation, CO₂ laden water percolating through the soil profile can replace Ca²⁺, the dominant cation on exchange sites, with H⁺. The accumulation of H⁺ acidifies the soil while the loss of Ca²⁺ intensifies the toxic effects of acidity. Calcium can also be lost via erosion or biomass removal. Johnston and Whinham (1980) measured Ca losses of 650 kg Ca/ha due to removal of grass forage which may be as great as the loss from leaching.

Liming with both dolomitic and calcitic limestone has the obvious effect of increasing exchangeable soil Ca (Moschler et al. 1962, Miles and Manson 1981, Adams 1984, Kuo 1993, Fageria 2006, Mullen et al. 2006). This effect can be quite rapid (Evans et al. 1986) and is initially most pronounced in the upper five centimeters of the profile when the lime is incorporated into the soil (Edmeades et al 1983, Wheeler 1998). With time, Ca²⁺ may move down through the profile. Huber et al. (2006) found increased Ca²⁺ concentrations in soil solution at a 40 centimeter depth 10 years after a surface application of lime. In southwest Missouri, Kroth and Mattas (1981) found that within 2 ½ years, top dressed limestone increased exchangeable Ca²⁺ concentrations only in the top five centimeters of a Gerald silt loam profile. Five years after application, the top 15 centimeters of the profile were positively affected, resulting in a more even distribution of soil test Ca. They also noted that within the first 18 centimeters, doubling the lime application from 6,725 to 13,450 kg/ha did not double the increase in soil test Ca, except in the first 2.5 centimeters (Kroth and Mattas 1981).

Albrecht (1941) attributed acid soil infertility to a lack of Ca, and indeed Ca deficiency symptoms are often observed in plants growing on acid soils and are characterized by a reduction in growth in the meristematic regions (Clark 1984). Internally, Ca deficiency may not allow plants to properly control their growth and development or react to changes in local environmental conditions (Marshner 1986).

Acid soils, with the exception of very sandy, low CEC soils, are usually not deficient in Ca *per se* (Kamprath and Foy 1972). Because Ca is easily replaced by other cations from its binding site at the outside surface of the plasma membrane (Marshner 1986), large concentrations of exchangeable and soluble Al and/or Mn may be the reason behind Ca deficiencies (Kamprath and Foy 1972).

Because most soils contain adequate amounts of Ca to support plant growth, fertilization with soluble Ca salts often has little effect on yield (McCart and Kamprath 1965) and has the potential to decrease it (Fried and Peech 1946). Kamprath and Foy (1972) suggest that this is owing to Al displacement from cation exchange sites, which decreases pH, thereby increasing the toxic effects of the acid soil. Without the negative effect of increased Al toxicity, the increasing Ca concentrations at low pH values can rescue root growth (Lund 1970).

Lime adds Ca to the soil, which increases the saturation of Ca on the exchange sites and in so doing displaces Al^{3+} . Without the added ability of lime to precipitate the toxic Al^{3+} from solution and increase pH, it would have the same effect as other Ca salts. These combined effects help overcome apparent Ca deficiency in acid soils, and many researchers have found that limestone applications indeed increase plant Ca concentrations (Adams et al. 1982, Evans et

al. 1986, Stevens and Laughlin 1996, Wheeler 1998). Kroth and Mattas (1981) found that a single limestone application could increase Ca concentrations in tall fescue grown in southwest Missouri for at least five years.

Magnesium

Extractable soil Mg is found predominantly as solution and exchangeable Mg^{2+} . This magnesium may be lost via leaching, removed by plants, precipitated in secondary minerals, and trapped in the interlayer of expanding and contracting 2:1 clays (Tisdale et al. 1993). Solution and exchangeable Mg may be increased via weathering of primary and secondary minerals and addition of Mg fertilizers.

Dolomitic limestone is a common soil amendment on acid soils, and it has proven effective in increasing exchangeable soil Mg (Moschler 1962, Adams 1984, Riggs et al. 1995, Mullen et al. 2006, Fageria 2006), even in southwest Missouri (Kroth and Mattas 1974).

However, as calcitic limestone contains little or no Mg, application of calcitic limestone usually decreases soil Mg (Adams 1984, Wheeler 1998). This effect can be explained by the larger hydrated radius of Mg^{2+} compared to that of Ca^{2+} , causing Mg to be left in soil solution or adsorbed to weaker, pH-dependent cation exchange sites while Ca adsorbs to stronger, permanent cation exchange sites (McLean and Brown 1984). An onslaught of Ca caused by liming can replace the weakly bound Mg from its cation exchange sites, forcing it into solution where it is subject to leaching and loss from the system. Wheeler (1998) observed that Mg in the zero to five centimeter region indeed decreased, but that in the 15 to 20 centimeter depth increased five years after liming with calcitic limestone. Similar results were

obtained in southwest Missouri where the exchangeable Mg in the top 15 centimeters of a Gerald silt loam decreased six years after a calcitic limestone application, but exchangeable Mg in the 18 to 36 centimeter depth increased (Kroth and Mattas 1981). The Mg may also become trapped in nonexchangeable forms following an application of calcitic limestone (Adams 1984, McLean and Brown 1984).

Magnesium deficiency is not usually experienced by plants growing on acid soils. However, those growing in acid, sandy, highly leached soils with a small CEC or acid soils that have received large quantities of calcitic lime (Kamprath and Foy 1972) have an increased likelihood of displaying chlorosis on fully expanded leaves, a visible Mg deficiency symptom resulting from the structural role of Mg in the chlorophyll molecule (Marshner 1986).

Dolomitic limestone has the obvious effect of increasing plant Mg by the addition of Mg to the soil. However, decreased acidity and the associated decrease in availability of toxic elements also has a positive effect. Magnesium uptake can be depressed by other cations including Mn^{2+} , H^+ , and Al^{3+} (Kamprath and Foy 1972, Foy 1984, Marshner 1986). Because liming decreases the availability of these cations by altering pH, Mg uptake should be increased above pH ~5.0 (Clark 1984). Many researchers have found dolomitic limestone to increase plant Mg (Jones and Sparrow 1977, Adams et al. 1982, Riggs et al. 1995). Kroth and Mattas (1981) found that ~18,000 kg limestone/ha containing two percent $MgCO_3$ was enough to increase leaf Mg concentrations of tall fescue growing on a Gerald soil in southwest Missouri by 10% in March harvests or 13% in November harvests.

As with dolomitic limestone, calcitic limestone decreases the availability of Al^{3+} , Mn^{2+} , and H^+ and, subsequently, the inhibitory effect this “toxic trio” has on Mg uptake. However, it contributes an overabundance of Ca, which can also inhibit Mg uptake (Hiatt and Leggett 1974, Clark 1984). In Missouri, R.G. Hanson suggested that to prevent visual Mg deficiency symptoms, Mg needs to occupy five percent of the base saturation; less than 10% saturation may result in mineral imbalances in some forages (McLean and Brown, 1984). As would be expected, calcitic limestone increases the Ca:Mg ratio of soil (Riggs et al. 1995) and decreases the Mg content of many plants (John et al. 1972, Jones and Sparrow 1977, Evans et al. 1986, Stevens and Laughlin 1996, Wheeler 1998, Bailey and Laidlaw 1999). Edmeades et al. (1983) also found a decrease in leaf Mg concentrations, but the yield increase attributable to the lime resulted in no net change in Mg uptake per hectare, suggesting a dilution effect. Presumably because of decreased availability of Al^{3+} and Mn^{2+} with increasing pH, others have found no net change or even an increase in plant Mg (Kamprath and Foy 1972, Riggs et al. 1995).

Nitrogen

All soil nitrogen initially comprised part of the 78% of the earth’s atmosphere that is N_2 gas (Tisdale et al. 1993). At some point, N was fixed and made plant available via symbiotic bacteria, non-symbiotic bacteria, lightening, or synthetic N fertilizer production. Lime affects at least four processes in the soil N cycle, and all require microorganisms: biological N_2 fixation, nitrification, mineralization, and denitrification.

Excluding anthropogenic N₂ fixation, which accounts for 34.5 percent of the total N fixation on land, 95 percent of the remaining N₂ fixation is microbially mediated (Brady and Weil 1999). For optimum production of plants hosting N₂-fixing bacteria, liming to a pH between 6.5 and 7.0 is ideal (McLean and Brown 1984).

Mineralization is the conversion of organic N to inorganic N. This process is progressively curtailed below pH 6 or 6.5 (Adams and Martin 1984). Liming, as it increases pH, shows a positive effect on mineralization (Pearson 1958, Ministry of Agriculture, Fisheries, and Food 1981).

Nitrification is the microbially mediated conversion of ammonium (NH₄⁺) to nitrate (NO₃⁻). Soil pH is the best indicator of nitrification in the soil (Pearson 1958, Foy 1984). Below pH 5.0, there is a notable decrease in nitrification (Lucas and Davis 1961), and below pH 4.5, the rate of this biological process is negligible (Adams and Martin 1984, Foy 1984). Nitrification appears to be optimal above pH 6.0 or 6.6 and decreases in optimality above pH 8.0 (Adams and Martin 1984, Foy 1984). Morrill and Dawson (1976) found that *Nitrobacter*, which is involved in the conversion of nitrite (NO₂⁻) to NO₃⁻, is much more negatively affected by acidity than *Nitrosomonas*, which catalyzes NH₄⁺ to NO₂⁻.

Denitrification is a process involving the reduction and volatilization of NO₃⁻ to N₂; it occurs most rapidly between pH 7.0 and 7.5 and is quite limited below pH 5.0 (Adams and Martin 1984). Lime, especially when surface applied, can increase the pH in the region where surface applied N fertilizers are concentrated. As a result, denitrification of NH₄⁺ and urea based fertilizers may increase after lime applications (Adams 1984).

Pearson (1958) found that N utilization, return, and recycling by subsequent crops is increased by the use of lime, partially due to the enhanced mineralization and partially to the increased plant biomass being returned to the soil. However, in the short term, full benefit of N fertilization may not be received because of losses to denitrification. As a result, N concentration in the plant may decrease with lime use (Stevens and Laughlin 1996). In situations where N fertilizer is not being applied, such as legume-grass pastures or soybean fields, improved legume habitat created by lime-induced increases in pH may result in greater leaf N concentrations (Burmester et al. 1998, Bailey and Laidlaw 1999); in other studies, no consistent effect is observed (Edmeades et al. 1983).

Phosphorus

Liming acid soils is commonly believed to increase phosphate (PO_4^{3-}) availability to plants, but results in the literature are not as conclusive (Haynes 1982, Adams 1984). Phosphorus exists in many forms and lime affects each form differently. The variety of affects, no doubt, attributes to the variability in effects of lime on soil P availability.

First, P in soil may be encountered as organic P. This form constitutes $1/2$ to $1/3$ of the total P in most mineral soils (Cosgrove 1967), and in acid soils, Fe and Al phytates comprise a large part of the organic P compounds (Foy 1984). Organic P is predominantly made available via microbial reactions, and increasing pH promotes the mineralization of these compounds (Cosgrove 1967). For this reason, mineralization of organic P generally increases with limestone applications (Cosgrove 1967, Haynes 1982).

A second form of inorganic P in soils can be found in mineral structures . In acid soils, it is mainly secondary Fe/Al – PO₄ minerals (Tisdale 1993). Variscite (AlPO₄ · 2H₂O) is more stable than its counterpart, strengite (FePO₄ · 2H₂O). Thermodynamics indicate that the pH increase associated with liming should liberate PO₄⁻³ from variscite and strengite, but it usually does not because the kinetics of the reaction are exceedingly slow (Singh and Seatz 1961, Adams 1984). More recent work indicates that Fe/Al – phosphates are also encountered as amorphous substances that are stable between pH 2.5 and 8.5 (Haynes 1982). A few investigators found an increase in soluble P with lime and attributed it to the hydrolysis of these sparingly soluble, amorphous compounds (Holford et al. 1994); however, the rate of dissolution is very slow (Haynes et al. 1982). Liming to pH 6.0 or 6.5 decreases the concentrations of solution and exchangeable Fe and Al, which should decrease precipitation of subsequently applied P fertilizers, thereby increasing their effectiveness (Singh and Seatz 1961, Haynes 1982, Adams 1984). On the other hand, liming to slightly acid or alkaline soils can increase the precipitation of poorly crystalline Ca/Mg – PO₄ minerals; this is an especially large concern when both lime and P are surface applied (Pearson 1958, Haynes 1982).

Third, P occurs as inorganic, adsorbed PO₄ on hydrated Al and Fe oxides. At pH 2.4, maximum adsorption occurs on the surfaces of these amphoteric metal hydrous oxides (Haynes 1982). Lime applications increase pH and cause the surface charge of pH dependent metal oxides to become more negative and decrease the strength with which PO₄ is held (Bache 1964, Haynes 1982, Holford et al. 1994,). However, HPO₄²⁻, which is preferentially adsorbed to oxide surfaces over

H_2PO_4^- , increases 10-fold for each unit increase in pH between pH 2 and 7 (Haynes 1982). The increasing concentration of HPO_4^{2-} and the increasingly negative surface charge result in a slow decrease in PO_4 adsorption to pH 7.0 (Haynes 1982). This is further complicated by increased Ca from lime that increases cationic electrolyte concentration near negatively charged oxide surface, resulting in a less negative adsorption plane, to which PO_4 adsorbs more readily (Haynes 1982). Therefore, Ca in lime also counteracts the effect of increased pH from the lime. One last consideration with adsorbed P is soil wetting and drying cycles. As lime increases pH, some Al^{3+} is precipitated as amorphous hydroxy-Al polymers that can adsorb four to five times as much PO_4 as a crystalline Al hydroxide such as gibbsite (Kwong and Huang 1979). Drying a limed soil is likely to cause crystallization of the amorphous polymers that can decrease P adsorption of later applied fertilizer (Haynes 1982).

Finally, P may be encountered in a fourth manner, in the soil solution. Here, P is found as orthophosphates; H_2PO_4^- is the predominant form below pH 7.2 and HPO_4^{2-} dominates above that pH (Tisdale et al. 1993). This plant available pool of P is subject to sorption, immobilization, and plant uptake.

With a very complex set of factors controlling soil P, one is left to guess how a given soil and its P pool will respond to liming. Liming has been found to increase (Sims and Ellis 1983, Evans et al. 1986, Hue 2004), decrease (Kroth and Mattas 1974, 1981, Haynes 1982) and not change plant P availability (Moschler et al. 1962, Edmeades et al. 1983, Hue 2004).

Phosphorus availability to plants has an added factor; lime decreases the concentrations of the “toxic trio”, all of which inhibit P uptake by plants (Foy 1984). Jackson and Reisenauer (1984) suggest that P uptake following liming may be especially pronounced with Al and Mn sensitive crops. There may also be large differences between species and even genotypes in the ability to accumulate P in acid soils (Kochian et al. 2004).

Plants can show the same unpredictability as soils (Haynes 1982, Whitehead 2000) but generally tend to increase aboveground in P concentrations (Pearson 1958, Shoop et al. 1961, Sims and Ellis 1983, Wheeler 1998, Bailey and Laidlaw 1999, Hue 2004) or remain unchanged (Edmeades et al. 1983, Evans et al. 1986, Stevens and Laughlin 1996) following lime applications. In southwest Missouri, tall fescue P concentrations appear to increase or not change following liming (Kroth and Mattas 1981).

Potassium

Many primary minerals such as feldspar and mica contain K, but weathering is slow. Non-exchangeable or fixed K is found trapped between silicate layers of illitic clay minerals, especially vermiculite, and 2:1 intergrade clays; this K is slowly available (Tisdale et al. 1993). Exchangeable K is held on cation exchange sites. Solution K^+ is a very small portion of the total K and is subject to plant uptake, leaching, and K fixation by clay minerals.

Lime influences soil K. The large influx of Ca^{2+} and Mg^{2+} directly from the lime replaces Al^{3+} held on the exchange sites; K^+ competes better with Ca^{2+} than Al^{3+} . Consequently, more exchange sites become available to K^+ (Pearson 1958,

Kamprath and Foy 1972). This, coupled with the increase in pH-dependent CEC (Adams 1984, Tisdale et al. 1993), results in K^+ moving from solution to exchange positions, decreasing both leaching and plant availability of inherent and fertilizer K (Pearson 1958, Kamprath and Foy 1972, Adams et al. 1982, Adams 1984, Foy 1984). Additionally, hydroxyaluminum cations wedged between silicate layers of expanding clays may be precipitated following liming allowing the clay layers to collapse and trap K^+ , making it unavailable for plant uptake (Tisdale et al. 1993).

Soil test K is not consistent in response to lime, in that it has been reported to remain the same (Moschler et al. 1962, Edmeades et al. 1983, Mullen et al. 2006) and decrease (Sims and Ellis 1983, Hue 2004). In southwest Missouri, Kroth and Mattas (1974) reported that five years after lime was incorporated eight to 10 centimeters deep, exchangeable K decreased in each of the first 18 centimeters of a Gerald soil. When top dressed, the lime decreased exchangeable K in the top eight centimeters but did not affect the K from 10 to 15 centimeters within six years (Kroth and Mattas 1981).

Plant available K^+ is decreased by the shift of solution K to exchangeable K that is caused by lime. The Ca and Mg supplied by limestone also have negative effects and compete with K^+ for uptake (Lucas and Davis 1961, Hiatt and Leggett 1974, Clark 1984). The one positive effect of lime on K^+ uptake is the precipitation of Al^{3+} ; this cation inhibits to K^+ uptake (Foy 1984). As a result of these factors interacting, K in plants has been observed to increase (Jones and Sparrow 1977), decrease (Stevens and Laughlin 1996, Bailey and Laidlaw 1999, Hue 2004) and not change (Jones and Sparrow 1977, Adams et al. 1982, Edmeades et al. 1983, Evans

et al. 1986) following liming. Kroth and Mattas (1981) reported that tall fescue K concentrations in March decreased with ~18,000 kg/ha of plowdown lime but did not change with 6,725 or 13,450 kg/ha of topdressed lime; lime made no difference in November forage concentrations.

Sulfur

Ninety percent of the S in the top ten centimeters of acid grassland soils is organic, and its mineralization is microbially mediated (Whitehead 2000). The inorganic fraction of S in well drained acid soils includes solution sulfate (SO_4^{2-}) and adsorbed SO_4^{2-} . Solution SO_4^{2-} is plant available and subject to leaching. Often it is highest near the surface of impermeable horizons that restrict water movement (Lucas and Davis 1961). Sulfate may also be adsorbed to the positively charged surface sites on Fe and Al oxides and the edges of aluminosilicate clays (Rendig and Taylor 1989); in this respect, S is very similar to P. Large concentrations of adsorbed SO_4^{2-} are often found in subsoils because of eluviation from the upper horizons and the abundant concentration of oxides at deeper depths (Tisdale et al. 1993).

Lime has many effects on S. First, mineralization of organic S can be increased as pH increases (Adams 1984, Foy 1984). Second, S adsorption decreases sharply above pH 6.0 because the capacity of Fe/Al oxides to adsorb is decreased (Kamprath et al. 1956, Elkins and Ensminger 1971, Adams 1984, Rendig and Taylor 1989). As a result of these two factors, soil solution SO_4^{2-} increases (Elkins and Ensminger 1971, Adams et al. 1982).

Since solution SO_4^{2-} increases with lime, plant S would be expected to increase as well. The possibility of improved rooting depth with lime may also allow plants to capture SO_4^{2-} that accumulates in the subsoil or above physical rooting restrictions (Lucas and Davis 1961). However, two other aspects of lime may have a negative impact on plant S concentrations. First, lime increases soil molybdenum (Mo) availability, and Mo has an antagonistic effect on S uptake by plants (Bush et al. 1981, Marshner 1986). Second, calcitic lime often decreases Mg availability that may, in turn, decrease S uptake (Clark 1984). Elkins and Ensminger (1971) found that in acid soils, calcitic lime increases plant S; however, many others found that calcitic limestone has no effect on S concentrations in plants (Edmeades et al. 1983, Stevens and Laughlin 1996, Bailey and Laidlaw 1999).

Molybdenum

Five fractions of soil Mo are recognized. Primary crystalline materials undergo weathering processes to supply molybdate, MoO_4^{2-} , that may subsequently be found in one of the other four forms. Water soluble Mo in soil solution is dominated by the anion MoO_4^{2-} above pH 4.0, whereas H_2MoO_4 and HMoO_4^- become less important species (Lindsay 1991). MoO_4^{2-} is subject to plant uptake and leaching. It may be taken out of solution as it is organically complexed, adsorbed, or precipitated. Organically complexed Mo is apparently plant available and may help protect Mo from leaching and sorption (Mitchell 1964). The positively charged surface sites on hydrous oxides of Fe and Al are the principal sites of Mo adsorption, with Fe oxides being the more effective of the two (Jones 1957). Maximum adsorption occurs at pH 4.0 because of a large amount of positive

charges on the oxide surfaces and the large concentration of HMoO_4^- , which is preferentially adsorbed (Harter 1991). Lastly, Mo may be found as secondary compounds. The differentiation between these compounds and those adsorbing Mo is not very clear, and adsorbed Mo may slowly transition into discrete secondary compounds (Gupta and Lipsett 1981). Wulfenite (PbMoO_4) is considered the principal Mo precipitate, but $\text{Fe}_2(\text{MoO}_4)_3$ may also be important (Gupta and Lipsett 1981).

Concentrations of MoO_4^{2-} increase one hundred fold for every one unit increase in pH (Lindsay 1972). Because Mo is so responsive to pH changes, lime can have a large effect on soil Mo species (Adams 1984, Clark 1984, Lathwell and Reid 1984). The solubility of precipitated molybdates, even wulfenite, the least soluble, increases with pH (Lindsay 1991). The mono-acid form of Mo is preferentially adsorbed and is found in greatest concentrations at pH 3.0 to 5.0 (Harter 1991). This, coupled with the decreasing charges on the oxides as pH increases, results in solution Mo increasing (Gupta and Lipsett 1981).

Because liming increases solution MoO_4^{2-} , plant Mo concentrations also increase with lime (Reith and Mitchell 1964, Reith 1970, Gupta et al. 1971, John et al. 1972, Edmeades et al. 1983, Wheeler 1998); however, this response is not always obtained (John et al. 1972). Inherently small concentrations of soil Mo (Moraghan and Mascagni 1991) and competition with SO_4^{2-} (Bush et al. 1981, Clark 1984, Moraghan and Mascagni 1991) during absorption and translocation within the plant (Gupta and Lipsett 1981) result in these inconsistent effects of lime on foliage Mo.

Molybdenosis, Mo toxicity, is experienced by cattle and sheep when Mo concentrations are greater than 5 to 10 mg/kg in forage (Welch et al. 1991). A Cu:Mo ratio greater than 4:1 may also result in molybdenosis causing metabolic problems in animals (Gupta and Lipsett 1981, Pasricha et al. 1997). On the other hand, Cu:Mo ratios less than 2:1 may result in Cu deficiencies (Pasricha et al. 1997).

Boron

Tourmaline is the most prevalent B containing mineral in soils (Tisdale et al. 1993, Whitehead 2000); it slowly weathers, possibly controlling B solubility (Lindsay 1991). Boron can also be found substituting for Al^{3+} and/or Si^{4+} in silicate clay minerals; B adsorbed onto the broken Si-O and Al-O bonds at the edges of the clay minerals, especially illites, may slowly diffuse into the interlayer position of the clays (Tisdale et al. 1993, Whitehead 2000). Boron may also be adsorbed onto amorphous hydroxide surfaces and Fe and Al oxy and hydroxyl compounds (Harter 1991, Tisdale et al. 1993). Organic B is complexed to diol functional groups and may also be associated with the microbial biomass (Harter 1991). Organically complexed B is a good source of plant available B upon mineralization (Moraghan and Mascagni, 1991). Lastly, B may be found in soil solution; in acid soils it is predominately $\text{B}(\text{OH})_3$.

Increasing pH, as a result of liming, can affect soil B. Sorption of B is proportional to pH, with maximum sorption being near 8.0 (Harter 1991); when sorption is high, solution B is low (Gupta et al. 1971, Moraghan and Mascagni 1991).

The combined effects of lime increasing the pH and soil Ca result in decreased concentrations of plant B (Gupta et al. 1971, Peterson and Newman

1976, Adams 1984, Lathwell and Reid 1984, Hue 2004), but at times no change is observed (Naftel 1937, Edmeades et al. 1983). Large amounts of Ca or high pH alone have no or very little effect on B uptake (Cook and Millar 1939, Fox 1968). Peterson and Newman (1976) showed that tall fescue B concentrations decreased when the soil was limed to a pH above 6.5.

Copper

Most Cu in soils is insoluble, but organically complexed Cu is in equilibrium with soil solution. The Cu^{2+} cation dominates soil solution below pH 7.0, but solution Cu^{2+} may also be found complexed by organic compounds in soil solution (Lindsay 1991). Copper is very strongly adsorbed to Fe and Al oxides via chemisorption and also to clay minerals and OM by electrostatic attraction (Tisdale et al. 1993). Copper is found buried in the octahedral layer of clay minerals and is an impurity in Fe and Al oxides (Tisdale et al. 1993). Lastly, Cu is strongly bound to OM, especially groups containing N (Stevenson 1991).

Soil Cu is influenced by liming via the change in pH. Copper solubility decreases 100-fold for every one unit increase in pH (Rengel et al. 1999). Adsorption increases as pH is raised from 4.0 to 7.0, and the ability of the soil solution to complex Cu also increases (Moraghan and Mascagni, 1991). However, Cu availability is closely related to OM transformation, and OM mineralization generally increases with increasing pH (Foy 1984). Gupta et al. (1971) observed that soil Cu did not change as a result of liming.

Although liming is generally associated with decreasing or not changing soil Cu, additional factors complicate plant uptake. Hydrogen ions are inhibitory to Cu

uptake (Foy 1984), as are Ca^{2+} ions (Kamprath and Foy 1972). The positive effect that lime has on root growth may consequently increase the zone from which Cu is extracted (Younts and Patterson 1964). With all of these factors interacting, plant Cu concentrations have been observed to decrease (Reith and Mitchell 1964, Stevens and Laughlin 1996, Hue 2004) or not change (Gupta et al. 1971, Edmeades et al. 1983) due to liming.

Zinc

Zn chemistry in the soil is similar to that of Cu. In acid soils, Zn^{2+} occurs in soil solution (Harter 1991). Organic matter plays a less dominant role in Zn availability than it does with Cu because Zn—OM complexes are weaker (Whitehead 2000). Additionally, only about half of soil solution Zn is complexed by organic and inorganic compounds whereas almost all Cu in solution is complexed (Whitehead 2000). Lastly, Zn is typically not found as an impurity in Fe and Al oxides.

More so than Cu, Zn is responsive to pH changes caused by lime. Zinc solubility decreases 100-fold for every unit increase in pH (Rengel et al. 1999), and solution Zn decreases 30-fold for the same increase in pH from 5.0 to 7.0 (Tisdale et al. 1993). The observed decrease in solution Zn after liming (Gupta et al. 1971, Adams et al. 1982) can be attributed to increased adsorption above pH 5.5 of Zn by Al, Fe, and Mn oxides and other soil compounds and precipitation of Zn compounds at higher pH values (Moraghan and Mascagni 1991).

The resulting concentration of Zn in plants is also decreased following limestone applications (Miller et al. 1964, Reith and Mitchell 1964, Gupta et al. 1971, John et al. 1972, Rashid et al. 1976, Adams et al. 1982, Edmeades et al. 1983,

Stevens and Laughlin 1996, Wheeler 1998, Hue 2004). Wear (1956) attributed the decrease in Zn in foliage as a result of liming to the increase in pH, rather than Ca. Rashid et al. (1976) noted that increased Ca and Mg concentrations could decrease Zn absorption. The effects of lime on Zn are further exacerbated by any possible increases in P availability (Lathwell and Reid 1984, Moraghan and Mascagni 1991).

Iron

Iron exists as Fe minerals, organic and solution Fe. In well drained soils, Fe^{3+} dominates soil solution and Fe^{2+} is present in smaller quantities. In reality, neither exists in very large quantities (Tisdale et al. 1993). Their presence is pH dependent and is controlled by dissolution and precipitation of hydrous ferric oxides such as hematite ($\alpha\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$) and amorphous $\text{Fe}(\text{OH})_3$. Iron is also complexed, or chelated, by OM.

Plant roots are able to obtain chelated Fe as well as Fe^{3+} and Fe^{2+} . The presence of the latter two is affected by lime because they are pH dependent. For every unit increase in pH, the concentration of Fe^{3+} decreases 1000-fold and Fe^{2+} decreases 100-fold (Tisdale et al. 1993). However, the effectiveness of Fe chelates increases with pH because the surface ligands exhibit better dispersion and ionization (Stevenson and Ardakani 1972).

Liming tends to decrease the availability of Fe to plants (Adams 1984, Whitehead 2000). Counteracting this effect may be the decreased concentrations of Al and Mn resulting from lime applications, both of which antagonize Fe (Foy 1984).

Sodium

Sodium weathers from Na-bearing minerals and is found in the soil as solution and exchangeable Na. Very little work has been done to determine the affect of liming acid soils on Na. Edmeades et al. (1983) found that soil test Na was increased from zero to five centimeters and slightly increased from five to ten centimeters after lime application.

The fact that Ca^{2+} decreases the absorption of Na^+ (Hiatt and Leggett 1974, Clark 1984) suggests that lime could decrease plant Na, but the available data suggests that lime does not have an effect on leaf Na (McNaught et al. 1973, Edmeades et al. 1983, Stevens and Laughlin 1996).

Yield

The changes in soil properties brought about by lime generally create an improved habitat for plants that often results in a yield increase in a variety of agricultural plants including legumes (Adams et al. 1982, Burmester et al. 1998, Bailey and Laidlaw 1999, Mullen et al. 2006) and grasses (Edmeades et al. 1983, Riggs et al. 1995, Stevens and Laughlin 1996). In a mixed grass/legume pasture, Wheeler (1998) found that liming increased the grass yield but decreased the legume yield in the first two years following limestone application; in years three and four, the grass yield was unchanged by limestone treatment while the legumes increased in biomass production. In southwest Missouri, Kroth and Mattas (1981) described an increase in tall fescue yield on a Gerald silt loam with ~18,000 kg/ha of plowdown limestone but not with 6,725 or 13,450 kg/ha of topdressed limestone. However, on the same soil, they found that yields in a tall fescue-lespedeza pasture

increased with both 6,725 and 13,450 kg/ha of topdressed limestone treatments (Kroth and Mattas 1974). Fisher (1969) reported a yield increase in alfalfa, soybeans, and corn on a limed Mexico silt loam in central Missouri, with legumes showing the largest increase.

Study Objectives

Tall fescue is the most important forage for beef production in Missouri with over half of the pastures grown on soils that are acidic with low plant available P (Nathan 1995). McClain and Blevins (2006) found that tall fescue grown on an acid soil, low in plant available P, may not have adequate concentrations of P and Mg for grazing cattle throughout the stockpiling season. Of special concern are low concentrations of leaf Mg during late winter and early spring that may lead to grass tetany in lactating beef cattle. Reinbott and Blevins (1994, 1997) demonstrated that P fertilization increased leaf Mg of tall fescue grown on these southwest Missouri soils.

Limestone is commonly used to decrease soil acidity, and is often believed to increase the availability of soil P to plant roots (Haynes 1982, Adams 1984). If liming increases the availability of P in many acidic soils, it follows that liming would also result in an increase in Mg concentrations in tall fescue leaves. Therefore, the objective of this study was to determine if applications of either calcitic or dolomitic limestone to tall fescue pastures growing on low plant available P, acidic soils in southwest and central Missouri would increase leaf Mg and result in lower grass tetany ratios in early spring forage.

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CHAPTER 2

**Liming Stockpiled Tall Fescue Growing on Acidic
Soils Low in Plant Available Phosphorus Improved
Macronutrient Concentrations of Forage and
Decreased the Likelihood of Grass Tetany**

Synopsis

Many soils in Missouri are inherently acidic and possess little plant available phosphorus (P). Much of the state's forage production occurs on these soils, and tall fescue (*Festuca arundinacea* Schreb.) is the dominant forage. Many people have predicted that liming will increase P availability to plants in the types of soils used in this study. This study was initiated to examine the effects of two types of limestone on soil properties and the subsequent elemental concentrations of stockpiled tall fescue leaves.

Sites were chosen at the University of Missouri Southwest Center (SWC) and the University of Missouri Bradford Research and Extension Center (BREC). Calcitic and dolomitic limestone were applied at 0x, 1/2x, 1x and 2x the recommended soil test rate. Forage was harvested and weighed twice annually, and tall fescue leaves were harvested several times throughout the stockpiling season, dried, ground, digested, and analyzed. Soil samples to a 15 cm depth were also taken and analyzed.

The two year total forage harvest was increased by limestone at SWC but not consistently impacted at BREC. Following liming, leaf P concentrations were relatively unaltered, but leaf potassium (K) and nitrogen (N) concentrations decreased while leaf calcium (Ca) increased. Additionally, leaf magnesium (Mg) concentrations decreased with calcitic treatments but increased with the application of dolomitic limestone. As a result of the changes in leaf K, Mg, and Ca concentrations, the grass tetany ratio (meq K/ meq Ca + meq Mg) of leaves from limed plots decreased.

For the most part, leaf concentrations of the elements mirrored the soil test concentrations after liming. Extractable soil K exhibited a decreasing trend with increasing rates of limestone, but soil sulfate increased. Calcitic limestone increased soil test Ca and had little effect on soil test Mg while dolomitic limestone increased soil test Mg and only slightly increased soil test Ca. Soil Bray I P and Bray II P showed little effect of limestone application. Soil $\text{pH}_{\text{CaCl}_2}$ values were increased and neutralizable acidity decreased with increasing rates of limestone. The cation exchange capacity was decreased with limestone. Soil organic matter content decreased following limestone applications.

Liming two acidic Missouri soils changed many soil chemical properties; consequently the concentrations of macronutrients in stockpiled tall fescue leaves changed, which improved the grass tetany ratio and should positively impact the health of grazing beef cattle.

Introduction

Tall fescue is the most important forage for beef production in Missouri; over half of the tall fescue pastures grow on soils that are acidic with low plant available P (Nathan 1995). McClain and Blevins (2006) found that tall fescue grown on an acid soil low in plant available P may not have adequate concentrations of P and Mg for grazing cattle throughout the stockpiling season. Of special concern for lactating beef cattle are inadequate concentrations of leaf Mg during late winter and early spring that may lead to grass tetany. Reinbott and Blevins (1994, 1997) demonstrated that P fertilization increased leaf Mg of tall fescue grown on acid southwest Missouri soils.

Limestone is commonly used to decrease soil acidity, and is often believed to increase the availability of soil P to plant roots (Haynes 1982, Adams 1984). If liming increases the availability of P, it follows that liming would also result in an increase in Mg concentrations in tall fescue leaves. Therefore, the objective of this study was to determine if applications of either calcitic or dolomitic limestone to tall fescue pastures growing on acid soils with little plant available P in southwest and central Missouri would increase leaf Mg and result in more favorable grass tetany ratios in early spring forage.

Materials and Methods

This study was initiated at two sites in October 2004 on established Kentucky 31 tall fescue pastures. The first site was at the University of Missouri Southwest Research Center (SWC) near Mt. Vernon, Missouri (37° 04' N 93° 53' W; elevation 350 m) on a Gerald silt loam (fine, mixed, active, mesic Aeric Fragiaqualf). The second site was at the University of Missouri Bradford Research and Extension Center (BREC) near Columbia, Missouri (38° 30' N 92° 06' W; elevation 270 m) where the soils are the Leonard silt loam (fine, smectitic, mesic Vertic Epiaqualf) and the Mexico silt loam (fine, smectitic, mesic Aeric Vertic Epiaqualf). Sites were selected for acid soil pH values and small Bray I P values. Soil samples were taken to a 15 centimeter depth for complete analysis (Tables 2-1 and 2-2); procedures are described below. Forage was removed from the areas and 3 x 7.6 m plots with 3 m alleys were flagged. At each location, each treatment was randomly applied to one plot in all six blocks. Treatments of topdressed dolomitic and calcitic limestone were applied at 0, ½, 1, and 2 times the recommended rate as determined by Woodruff

Buffer. At SWC, dolomitic limestone was applied at 4,320 kg/ha and calcitic limestone at 4,838 kg/ha for the 1x treatment; at BREC, rates were 4,888 kg dolomitic limestone/ha and 4,354 kg calcitic limestone/ha. At SWC, all plots received 112 kg N/ha, 73 kg P₂O₅/ha and 258 kg K₂O/ha in fall 2004, and in April 2005, all plots at BREC received 118 kg P₂O₅/ha and 280 kg K₂O/ha, all according to initial soil test analyses and recommendations from the University of Missouri Soil Testing Laboratory. In the fall of 2005, plots at both sites received 112kg N/ha.

In May and August of 2005 and 2006, forage was removed from plots at both sites and weighed to determine forage yield; subsamples were taken for dry weight measurements. Monthly, starting in January 2005 and continuing through April 2005, then beginning again in October 2005 and ending in April 2006, twenty of the most recently collared leaves were removed from each plot at both BREC and SWC for elemental analyses. Leaves were dried, ground, and digested in nitric acid with a microwave accelerated digestion system. Samples were then filtered and brought to 25 ml. All element concentrations in leaf samples were measured via ICP-OES (Varian Inc., USA) except N. Thermal conductivity of nitrogenous gases was measured with a Leco Model FP-428 nitrogen analyzer (Leco Corp., USA) to determine total N of leaf samples.

Soil was sampled to a 15 cm depth from each plot in May 2006 and analyzed by the University of Missouri Soil Testing Laboratory. Soil pH_{CaCl2} was measured in 0.01 M CaCl₂, and neutralizable acidity was determined using the Woodruff buffer solution. Percent loss by ignition was used to determine organic matter content and CEC was estimated from exchangeable K, Ca, Mg, and neutralizable acidity.

Extractable P was measured with both Bray I and Bray II reagents and exchangeable K, Ca, and Mg were determined by extraction with ammonium acetate. Extractable sulfate was determined with calcium phosphate in acetic acid. All of these soil test procedures are described in depth by Nathan et al. (2006).

The experiment was randomized complete block design analyzed as a split plot in time model with six replicate blocks. The main plot consisted of treatment (lime), and harvest date (month) was considered the split plot; both were considered fixed effect factors, and block was a random factor. This model was used to test for statistical significance of treatment effects as well as interactions with harvest date using PROC MIXED in SAS version 9.1 (SAS Institute). All effects and interactions were considered significant when $P < 0.05$. When F test showed significance ($P < 0.05$), means were separated using Fisher's protected LSD ($\alpha = 0.05$).

Results and Discussion

Yield

At SWC, limestone applications impacted forage yields (Figures 2-1 through 2-5). Dolomitic and calcitic limestone increased the two year total forage harvest by as much as 15% over the control (Figure 2-5). All calcitic treatments showed a larger increase in yield than the dolomitic treatments, but even the smallest yield for the dolomitic treatments was 7% above that of the control. The May 2005 harvest had very similar trends to the two year total, with calcitic limestone exhibiting yield increases as great as 20% and the smallest dolomitic treatment increasing yield by 9% (Figure 2-1). May 2006 forage yields showed incremental increases with increasing rates of limestone (Figure 2-3). The 2x calcitic limestone treatment

increased dry weight removal by 20% and the dolomitic 2x treatment yield was increased by 17%. The forage harvest in August 2005 was not increased by limestone treatments (Figure 2-2), and the August 2006 yield decreased as a result of liming (Figure 2-4).

At BREC, neither dolomitic nor calcitic limestone had consistent effects on tall fescue yield (Figures 2-6 through 2-10). This was likely a result of the large topographical and soil variability within the plot area.

Acidity is a major factor limiting the growth of many agricultural crops, and liming has been used successfully to increase pasture yields (Edmeades et al. 1983, Stevens and Laughlin 1996, Wheeler 1998). On a Gerald silt loam at the SWC, Kroth and Mattas (1974, 1981) reported a forage yield increase in a tall fescue-lespedeza pasture following 6,725 or 13,450 kg/ha of topdressed limestone, but they saw no yield response to limestone applications in a tall fescue pasture with the same treatments on the same soil. In a Mexico silt loam at BREC, Fisher (1969) observed no increase in corn yield following liming.

Soil pH_{CaCl_2} and Neutralizable Acidity

The salt pH increased 19 months after limestone applications (Figures 2-11 and 2-12). The 2x calcitic limestone treatment showed the largest increase over the control, 0.8 pH units, at both BREC and SWC. The response to dolomitic limestone was less pronounced with the 2x treatment increasing the pH 0.6 pH units at both locations. In the same time period, the neutralizable acidity (N.A.) generally decreased with increasing limestone (Figures 2-13 and 2-14). Compared to the N.A.

of the control, the 2x treatments of calcitic and dolomitic limestone decreased 53% and 38%, respectively, at SWC and 49% and 36%, respectively, at BREC.

Increasing soil pH is a commonly described consequence of applying dolomitic and calcitic limestone (Miller et al. 1964, Evans et al. 1983, Fageria 2006, Mullen et al. 2006). Each increment of limestone did not decrease the N.A. proportionally, suggesting that some limestone had not yet reacted with the acidity. Holford et al. (1994) and Wheeler (1998) found that three years are required to reach maximum pH. Kroth and Mattas (1981) noted that the $\text{pH}_{\text{CaCl}_2}$ of the top 15 centimeters of a Gerald silt loam in southwest Missouri responded similarly, increasing by 0.52 and 0.64 pH units in response to 6,725 and 13,450 kg/ha of topdressed limestone, respectively. They also reported that only the pH in the top 5 cm was altered within 2.5 years.

Soil Cation Exchange Capacity

Limestone applications decreased the cation exchange capacity (CEC) of the soils at both locations (Figures 2-15 and 2-16). At SWC, limestone applications negatively impacted the CEC by as much as 2.0 meq/100 g. Kroth and Mattas (1974) found that 6,725 kg limestone/ha decreased the CEC to a greater extent than did 13,450 kg limestone/ha. Fageria (2006) measured a decrease in CEC in the zero to 10 and 10 to 20 centimeter depths after incorporating limestone into an acid soil. The observed decrease in CEC could be partially attributable to the decreased organic matter content of limed plots. Additionally, Al-OH polymers that are formed following liming may occupy cation exchange sites and may not be easily removed during extraction procedures.

Soil Organic Matter

Soil organic matter (OM) generally decreased with increasing limestone application at SWC (Figure 2-17) but showed no consistent response at BREC (Figure 2-18). At SWC, forage yield increased, thus it follows that organic matter breakdown must have also increased in lime plots in order to decrease the soil OM content. Kroth and Mattas (1981) observed little impact of limestone on OM content of a Gerald silt loam at SWC. Pearson (1958) reported that liming, as it increases pH, increases OM mineralization.

Plant Nitrogen

Leaf N concentrations decreased from October 2005 to February 2006 and then increased in March and April 2006 at SWC (Figures 2-19 and 2-20). McClain and Blevins (2006) observed a similar seasonal pattern of leaf N, and they attribute it to remobilization of phloem-mobile nutrients. The seasonal trend at BREC was similar except January 2005 and October 2005 exhibited very small concentrations of N (Figures 2-21 and 2-22).

At SWC, limestone treatments decreased leaf N beginning in October 2006 (Figures 2-19 and 2-20). A decreasing trend in leaf N concentrations was observed during the second stockpiling season at BREC. At both locations, lime and ammonium nitrate were surface applied. Because surface applied lime increases the surface pH appreciably, subsequent surface applied N may be subject to greater rates of denitrification, which occurs most rapidly above pH 5.0 (Adams and Martin 1984). The expected increase in N availability from mineralization and symbiotic fixation in limed plots provides only a small portion of the plant available N compared

to fertilizer N, and the full benefit of the fertilizer N is not seen on limed plots. The increased yield as a result of liming may also have a dilution effect on N concentrations in the plant. The decrease in leaf N content observed in this experiment agrees with the results of Stevens and Laughlin (1996).

Plant and Soil Phosphorus

The P concentrations of tall fescue leaves in all treatments at SWC and BREC decreased from fall to mid-winter then increased into spring (Figures 2-23, 2-24, 2-25, and 2-26). Similar trends have been observed by others (Fleming and Murphy 1968, McClain and Blevins 2006).

At SWC, leaf P concentrations showed a decreasing trend following the application of both types of limestone; however, the P concentrations of tall fescue leaves were not significantly altered by limestone at BREC or SWC (Figures 2-23, 2-24, 2-25, and 2-26). Limestone is often believed to increase the availability of soil P to plants (Haynes 1982, Adams 1984), but others have described a lack of plant P response as well (Edmeades et al. 1983, Evans et al. 1986, and Stevens and Laughlin 1996). In an earlier study, tall fescue leaves in southwest Missouri on a Gerald silt loam also showed no effect of liming on P concentrations (Kroth and Mattas 1981).

The Bray I and II P values for the soils at SWC and BREC showed no consistent change resulting from liming treatments (Figures 2-27, 2-28, 2-29, and 2-30) owing to the interaction of a complex set of factors controlling soil P and its availability. Increased mineralization of organic P (Cosgrove 1967), slow hydrolysis of amorphous Al/Fe—PO₄ compounds (Holford et al. 1982), slow decrease in PO₄

adsorption by Fe and Al oxides (Haynes 1982), and precipitation of poorly crystalline Ca/Mg—PO₄ minerals (Pearson 1958, Haynes 1982) can all result from limestone applications, and all of these processes can affect soil P and consequently available plant P.

Plant and Soil Potassium

At both SWC and BREC, K concentrations in tall fescue leaves exhibited a decline through February and a sharp increase in spring (Figures 2-31, 2-32, 2-33, and 2-34); this pattern is very similar to the seasonal change in leaf P concentrations. Fleming and Murphy (1968), Wheeler (1998), Opitz von Boberfeld and Banzhaf (2006), and McClain and Blevins (2006) have, at least in part, reported similar trends.

Leaf K concentration decreased with calcitic limestone (Figure 2-31) and, to a slightly lesser extent, with dolomitic limestone at SWC (Figure 2-32). Reflecting the effects of limestone on K concentrations in the plant, exchangeable soil K also exhibited a decreasing trend in the Gerald silt loam (Figure 2-35). The decreased availability of K following liming can be attributed to the large influx of divalent cations from the limestone that replace Al³⁺ from the cation exchange sites; this allows K⁺ to compete for exchange sites in the soil where it adsorbs and becomes less available to plants (Kamprath and Foy 1972, Pearson 1958). Additionally, hydroxyaluminum cations wedged between silicate layers of expanding clays may be precipitated following liming allowing the clay layers to collapse and trap K⁺ (Tisdale et al. 1993). Furthermore, Ca²⁺ and Mg²⁺ cations compete with K⁺ for uptake (Lucas and Davis 1961, Clark 1984). Following liming, others have observed

similar responses in plant (Stevens and Laughlin 1996, Bailey and Laidlaw 1999) and exchangeable soil K (Kroth and Mattas 1974, Sims and Ellis 1983). Kroth and Mattas (1981) described a decrease in soil K in only the top eight centimeters of a Gerald silt loam following a surface application of limestone.

At BREC, leaf K concentrations, in general, showed no treatment effect (Figures 2-33 and 2-34). The difference in leaf K concentrations between BREC and SWC could be partially attributable to the exchangeable soil K concentrations being nearly twice as great at BREC as at SWC. Since the soils at BREC are younger, they have a greater concentration of weatherable minerals than those of SWC. Like the leaf K concentrations at BREC, the soil test K showed very little treatment effect except that dolomitic limestone applications resulting in an increasing trend in exchangeable soil K (Figure 2-45).

Plant and Soil Calcium

Calcium is much less mobile than the other macronutrient elements in plants, as evidenced by the absence of a large decline in leaf Ca concentrations during winter at both SWC and BREC (Figures 2-37, 2-38, 2-39, and 2-40). McClain and Blevins (2006) reported similar results for stockpiled tall fescue leaves.

As expected, limestone generally increased leaf Ca concentrations with calcitic limestone having a much larger and quicker effect at both SWC and BREC (Figures 2-37 and 2-39) than dolomitic limestone (Figures 2-38 and 2-40). The increase in leaf Ca concentrations in plots treated with calcitic limestone was seen within three months of application at BREC and four months at SWC. Exchangeable soil Ca at both sites mirrored the foliar Ca concentrations. At SWC, there was a

significant increase in soil test Ca with increasing rates of limestone, and calcitic limestone increased soil test Ca to a greater extent than did dolomitic limestone (Figure 2-41). Soil samples from BREC indicated only an increasing trend in soil test Ca with increasing limestone (Figure 2-42).

Applying limestone has the obvious effect of adding Ca to the soil exchange sites and consequently increased amounts of Ca become available to plants. Additionally, Ca^{2+} replaces Al^{3+} on the exchange sites in the soil, and as pH is increased, Al^{3+} is precipitated (Kamprath and Foy 1972), which decreases the competition of Al for Ca binding sites at the outside surface of the root's plasma membrane (Marshner 1986). Many researchers have found that lime increased the Ca content of the soil (Moschler et al. 1962, Miles and Manson 1981, Fageria 2006, Mullen et al. 2006) and plant (Adams et al. 1982, Evans et al. 1986, Stevens and Laughlin 1996, Wheeler 1998). Kroth and Mattas (1981) noted increased Ca concentrations in tall fescue for five years following liming.

Plant and Soil Magnesium

Leaf Mg concentrations decreased into spring at both locations (Figure 2-43, 2-44 2-45, and 2-46), and at SWC it was slowest of the mobile macronutrients to begin increasing in the spring. This seasonal pattern for Mg concentrations in tall fescue leaves was also described by McClain and Blevins (2006). In addition, Fleming and Murphy (1968) observed decreasing Mg concentrations going into winter.

At SWC, dolomitic limestone increased Mg concentrations of tall fescue leaves; the largest effect was in October 2005 and it became progressively less

pronounced until there was no difference in April 2006 (Figure 2-44). At BREC, dolomitic limestone was much less effective in increasing leaf Mg concentrations (Figure 2-46); this may have been a result of the soil Mg concentrations being three times greater at BREC than at SWC. Soil test data from SWC and BREC reflect the addition of Mg to soil via dolomitic limestone (Figures 2-47 and 2-48). The increase in exchangeable soil (Moschler et al. 1962, Kroth and Mattas 1974, Fageria 2006, Mullen et al. 2006) and plant (Jones and Sparrow 1977, Adams et al. 1982, Riggs et al. 1995) Mg concentrations has been measured by others, and is due, in large part, to the Mg added to the soil. However, liming also decreases the availability of Al^{3+} , Mn^{2+} , and H^{+} , potential antagonists of Mg^{2+} uptake (Kamprath and Foy 1972, Marshner 1986).

Calcitic limestone decreased leaf Mg concentrations within three months of limestone application at SWC, and this trend continued through April 2005; it was again visible in March and April 2006 (Figure 2-43). The remaining months at SWC showed little effect of lime on leaf Mg concentrations. At BREC, calcitic limestone had no consistent effect on leaf Mg concentrations (Figure 2-45). Exchangeable soil Mg was relatively unresponsive to calcitic limestone at both sites (Figures 2-47 and 2-48). The large amount of added Ca^{2+} displaces Mg^{2+} from exchange sites because Mg^{2+} has a larger hydrated radius; as a result, Mg^{2+} moves into solution (McLean and Brown 1984). Wheeler (1998) observed that soil Mg was decreased, only a small decrease in year one and progressively larger decreases through the following four years. The abundance of Ca, itself, also inhibits Mg uptake, resulting

in decreased Mg concentrations in plants (Jones and Sparrow 1977, Evans et al. 1986, Stevens and Laughlin 1996, Wheeler 1998, Bailey and Laidlaw 1999).

Soil Sulfur

At SWC, there was not a consistent effect of lime (Figure 2-49); at BREC, soil SO_4 concentrations increased with increasing rates of dolomitic and calcitic limestone (Figure 2-50). Limestone usually results in an increase in SO_4 (Elkins and Ensminger 1971, Adams et al. 1982). Liming increases mineralization of organic S (Adams 1984, Foy 1984) and S adsorption on Fe/Al oxides decreases (Elkins and Ensminger 1971, Adams 1984, Rendig and Taylor 1989) to increase extractable soil SO_4 .

Grass Tetany Cation Ratio

A grass tetany cation ratio is the ratio of K to the sum of Ca and Mg, all expressed in milliequivalents. Forage with ratios above 2.2 predicts an increased likelihood of grass tetany (Kemp and t'Hart, 1957). Both dolomitic and calcitic limestone decreased the cation ratio (Figures 2-51, 2-52, 2-53, and 2-54). In the winter of 2005-2006, the cation ratio of the forage remained well below 2.2, but yearly variations in the ratio account for the sporadic occurrence of grass tetany in beef cattle. Kroth and Mattas (1981) also observed a decrease in the March grass tetany cation ratio of tall fescue after liming in southwest Missouri.

Summary

The hypothesis being tested was that lime would increase the availability of P and consequently increase leaf Mg concentrations to help combat grass tetany. Liming did not increase the availability of soil P, and as a result, the calcitic lime did

not have a large effect on leaf Mg concentrations; because dolomitic lime is essentially a Mg fertilizer, it increased the Mg in tall fescue leaves. Albeit not via the proposed mechanism, lime positively affected the grass tetany cation ratio; both types of limestone substantially decreased K concentrations of the forage while dolomitic limestone increased leaf Mg concentrations and calcitic limestone increased leaf Ca concentrations.

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May 2005 Forage Harvest

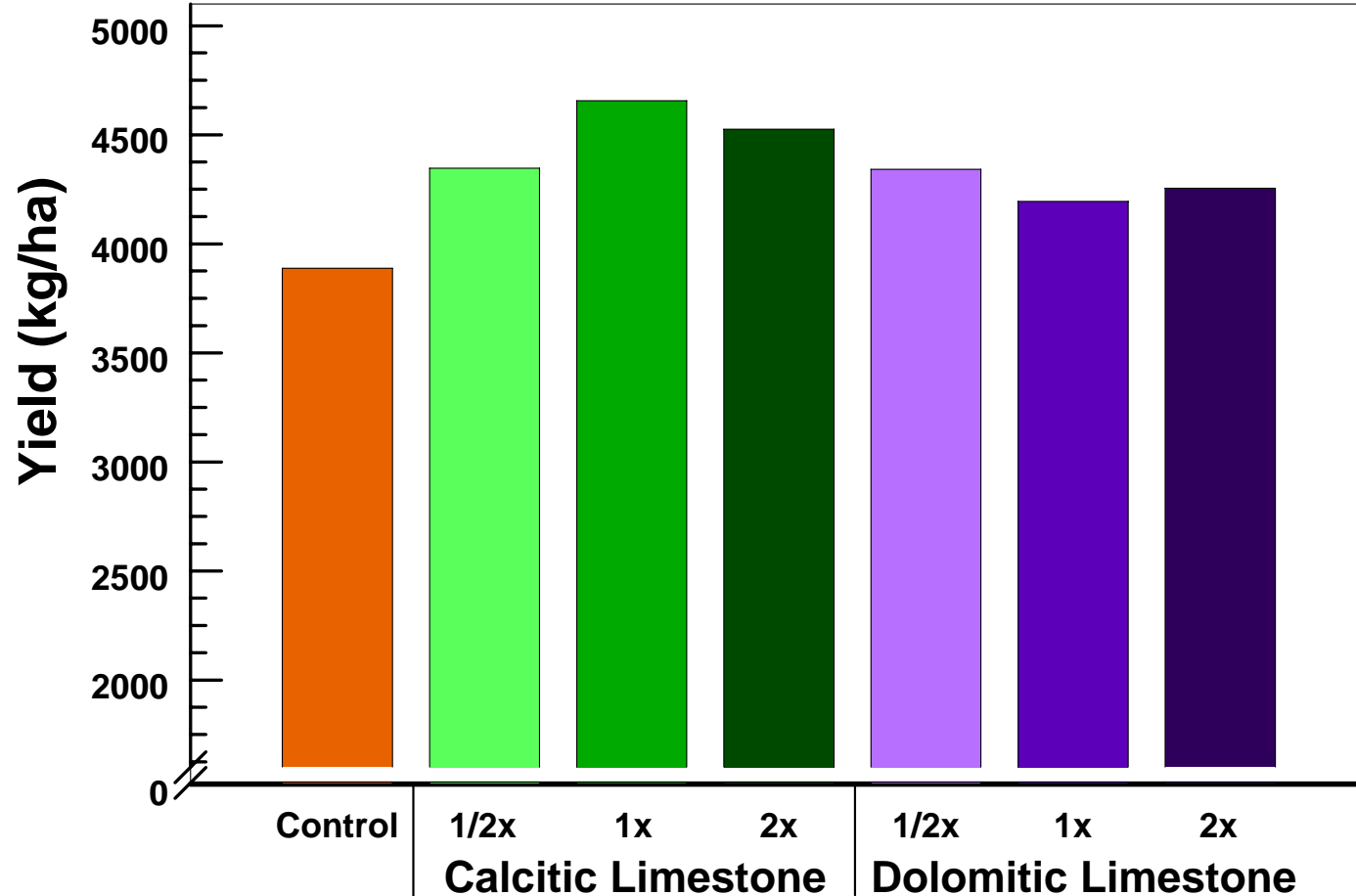


Figure 2-1. May 2005 forage harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 477.37 for comparing treatments.

August 2005 Forage Harvest

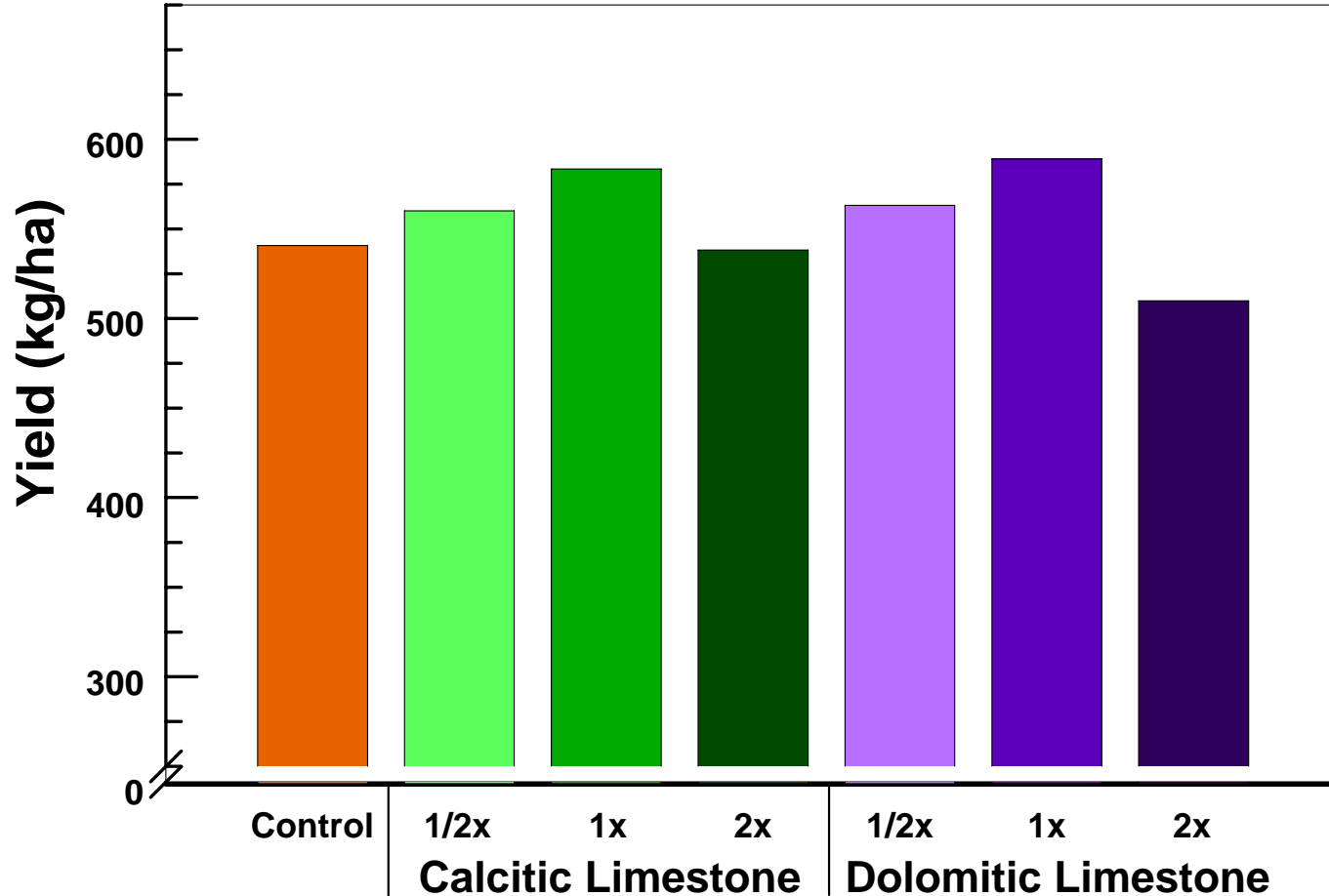


Figure 2-2. August 2005 forage harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 69.44 for comparing treatments.

May 2006 Forage Harvest

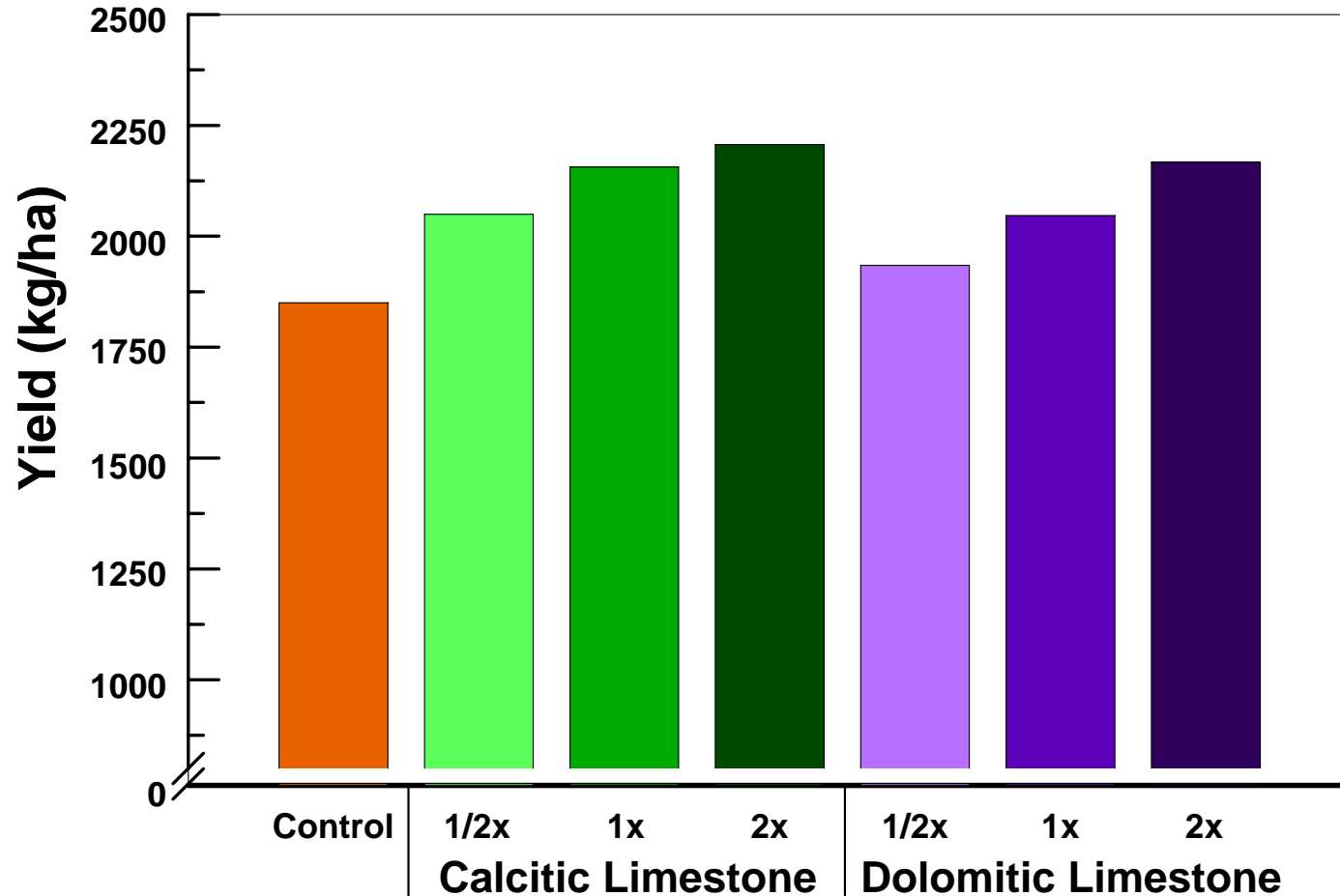


Figure 2-3. May 2006 forage harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 290.30 for comparing treatments.

August 2006 Forage Harvest

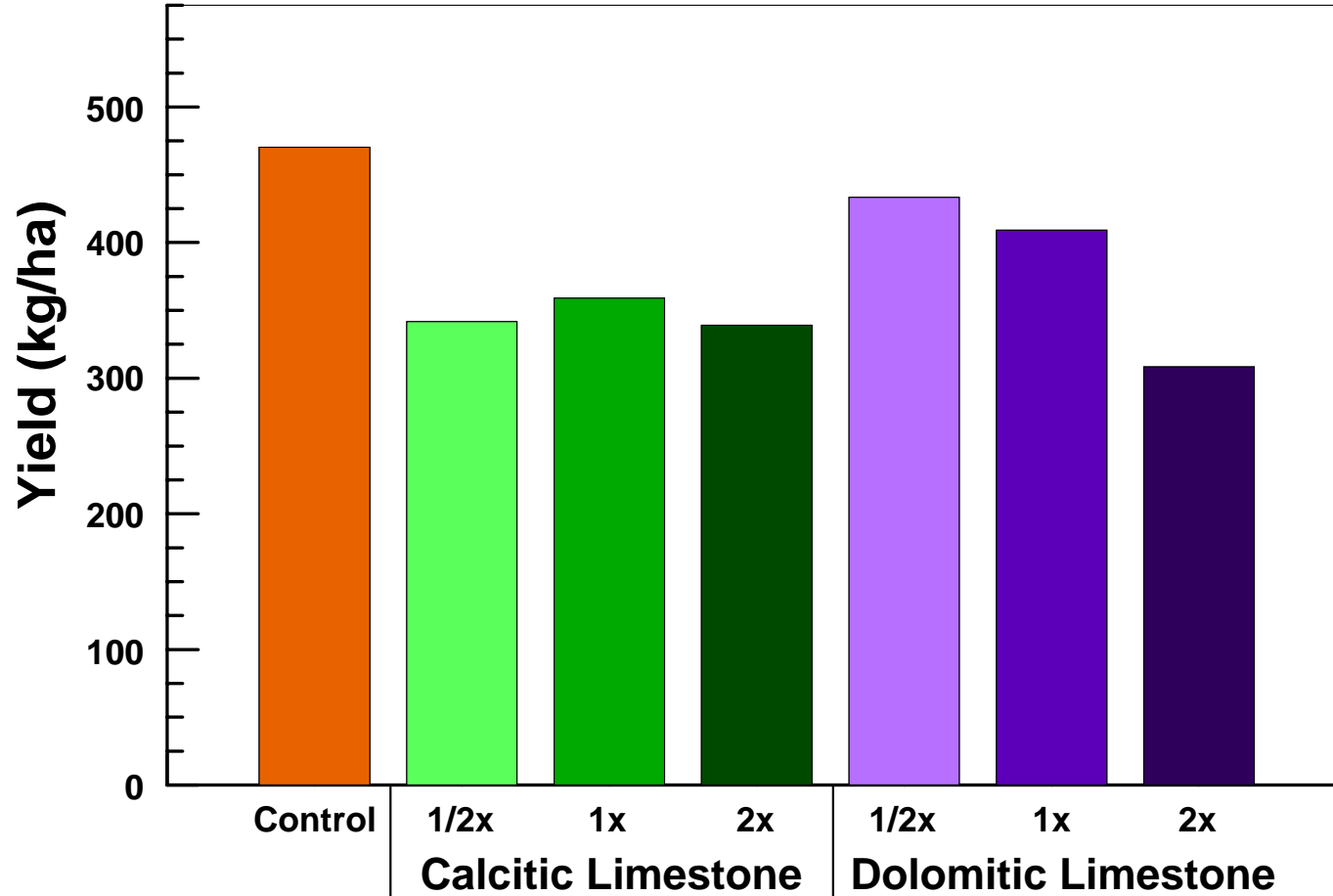


Figure 2-4. August 2006 harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 91.18 for comparing treatments.

Two Year Total Forage Harvest

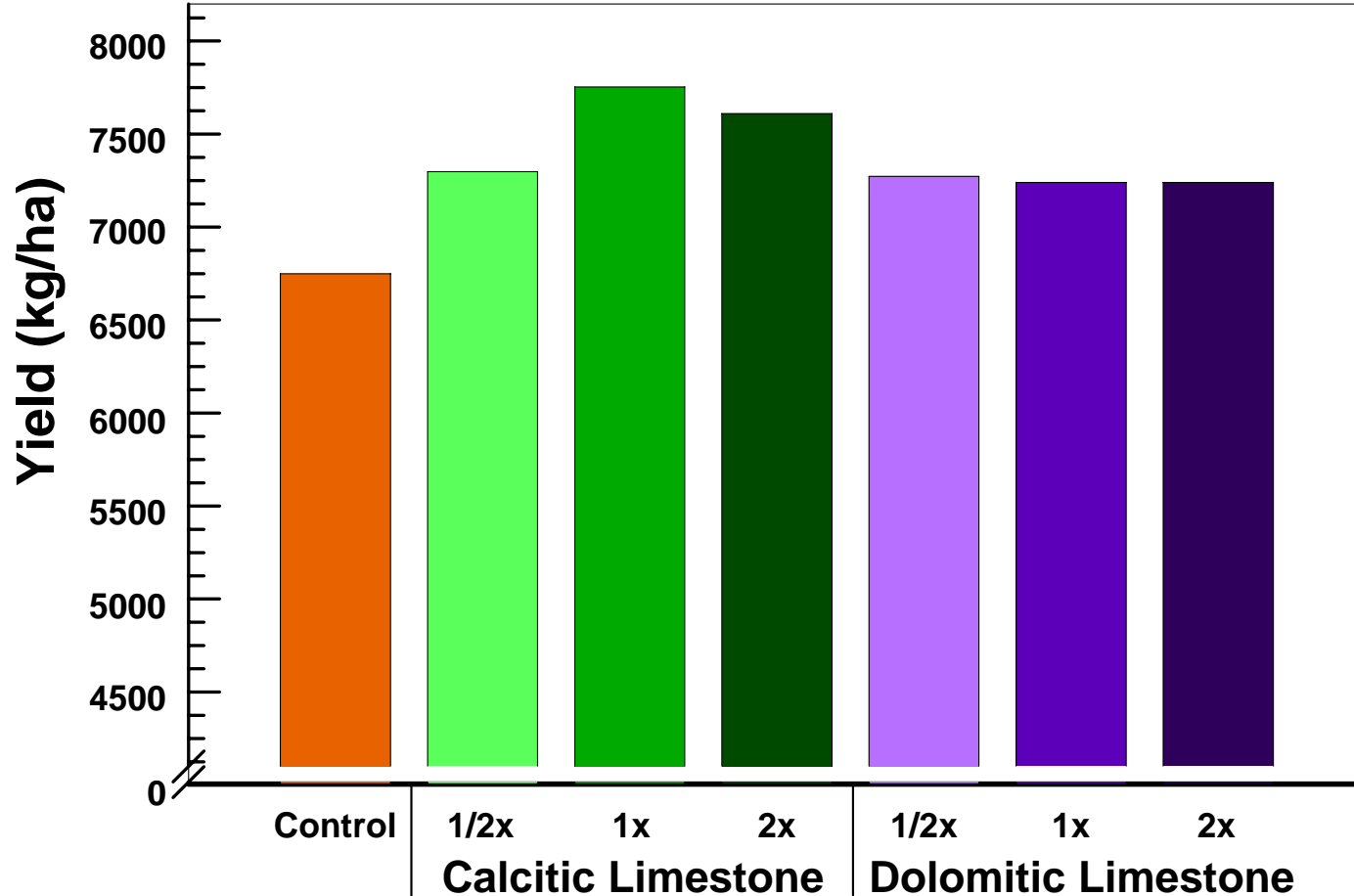


Figure 2-5. Two year total forage harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 602.58 for comparing treatments.

May 2005 Forage Harvest

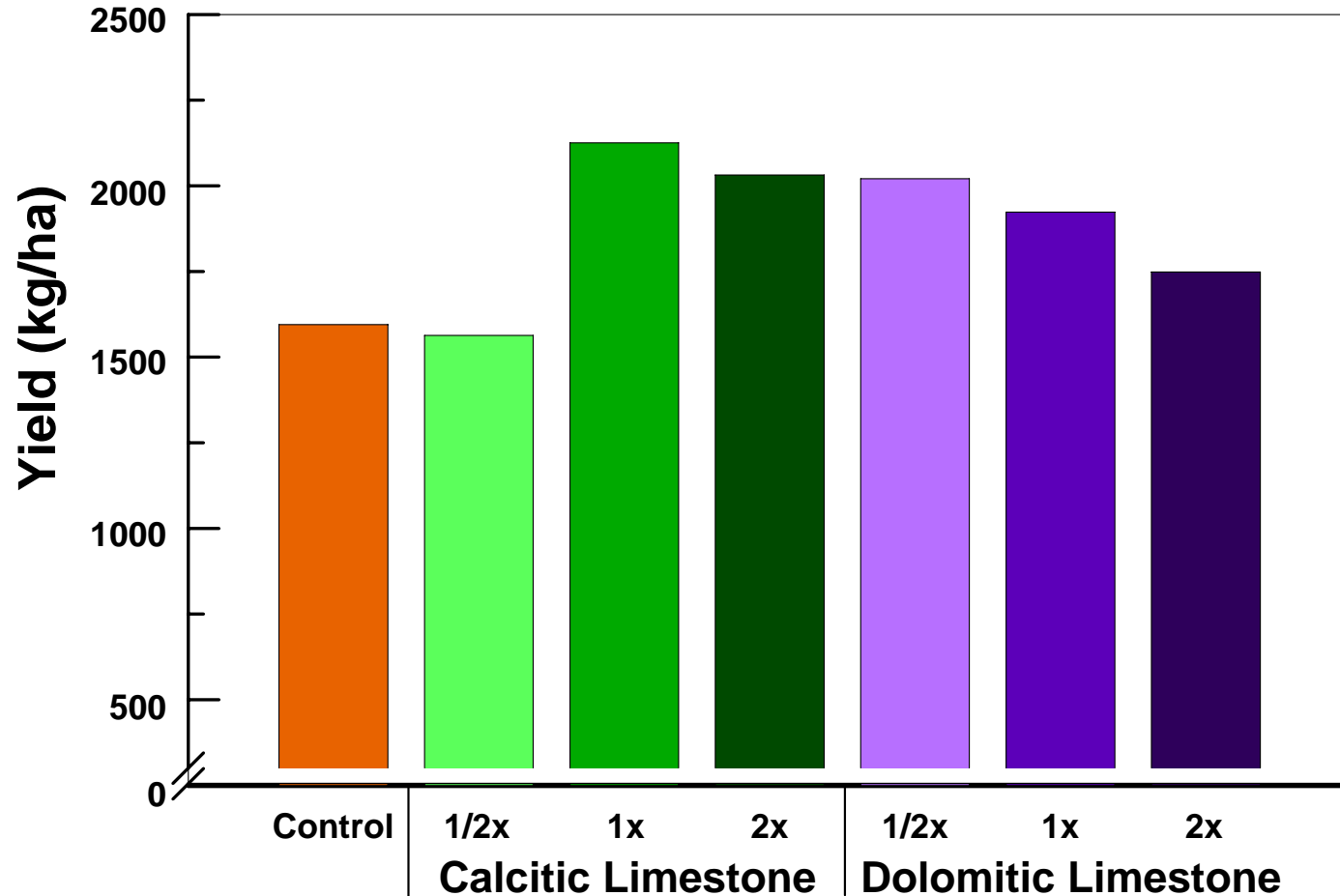


Figure 2-6. May 2005 forage harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 495.10 for comparing treatments.

May 2005 Forage Harvest

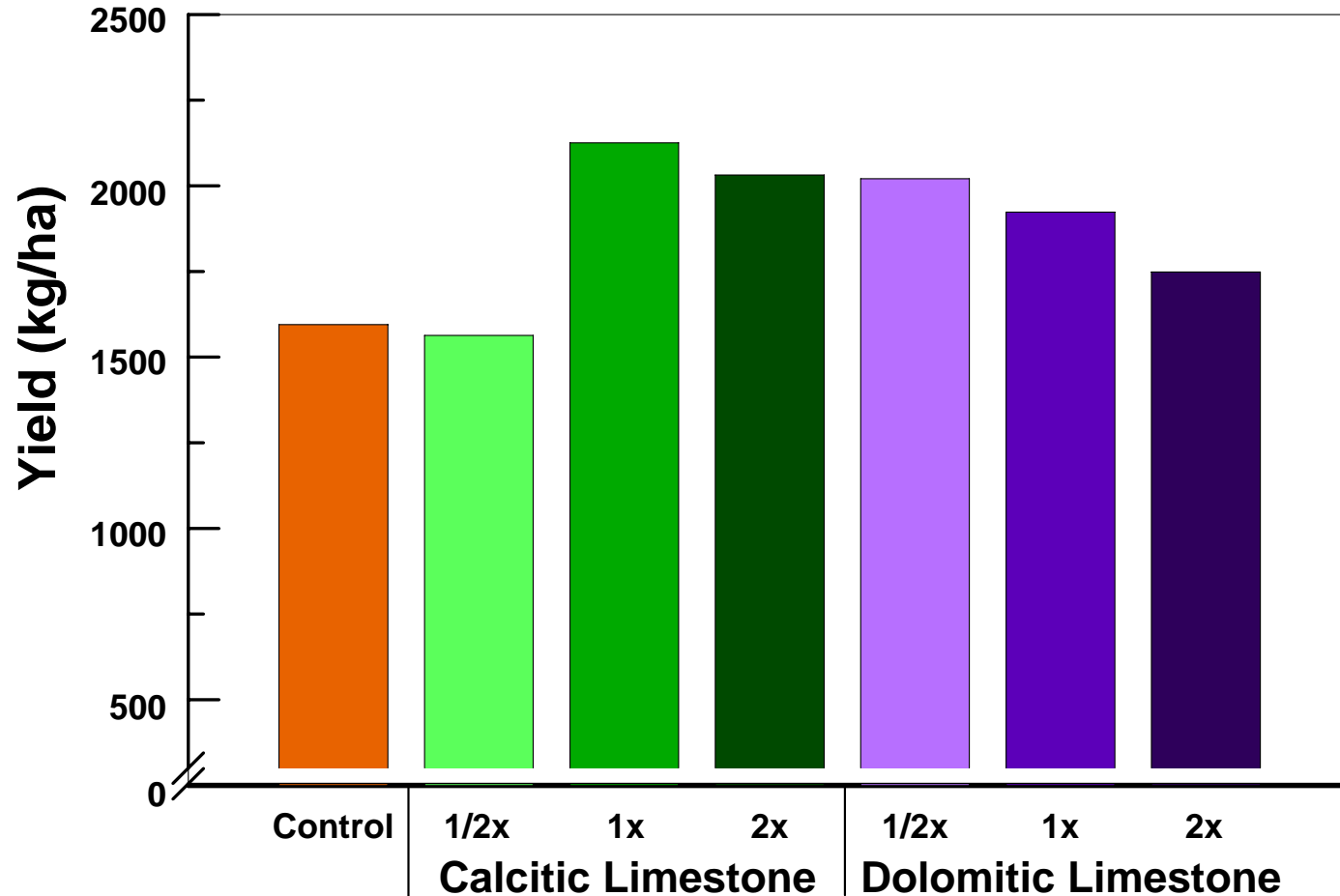


Figure 2-7. September 2005 forage harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 400.30 for comparing treatments.

May 2006 Forage Harvest

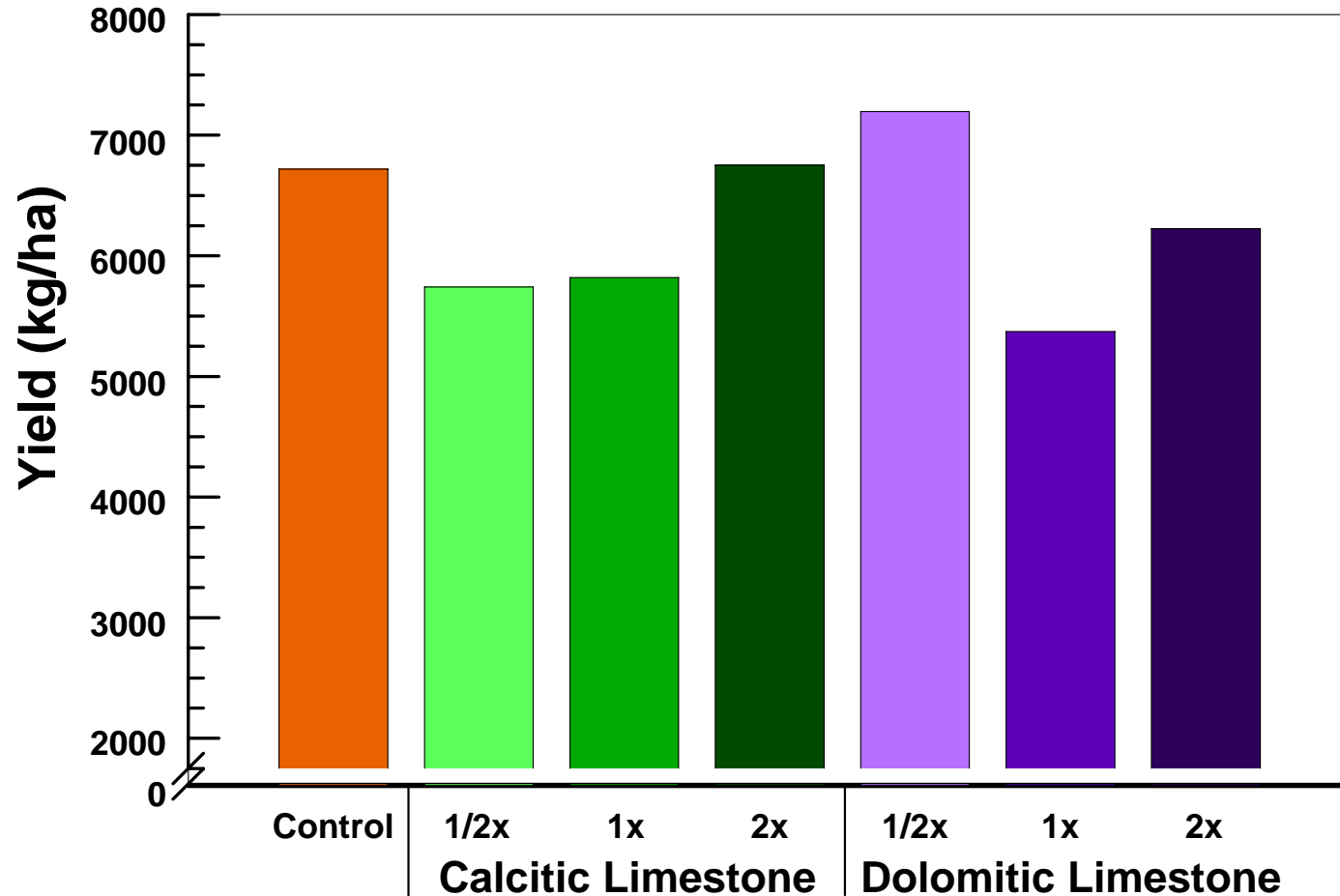


Figure 2-8. May 2006 forage harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 1209.23 for comparing treatments.

August 2006 Forage Harvest

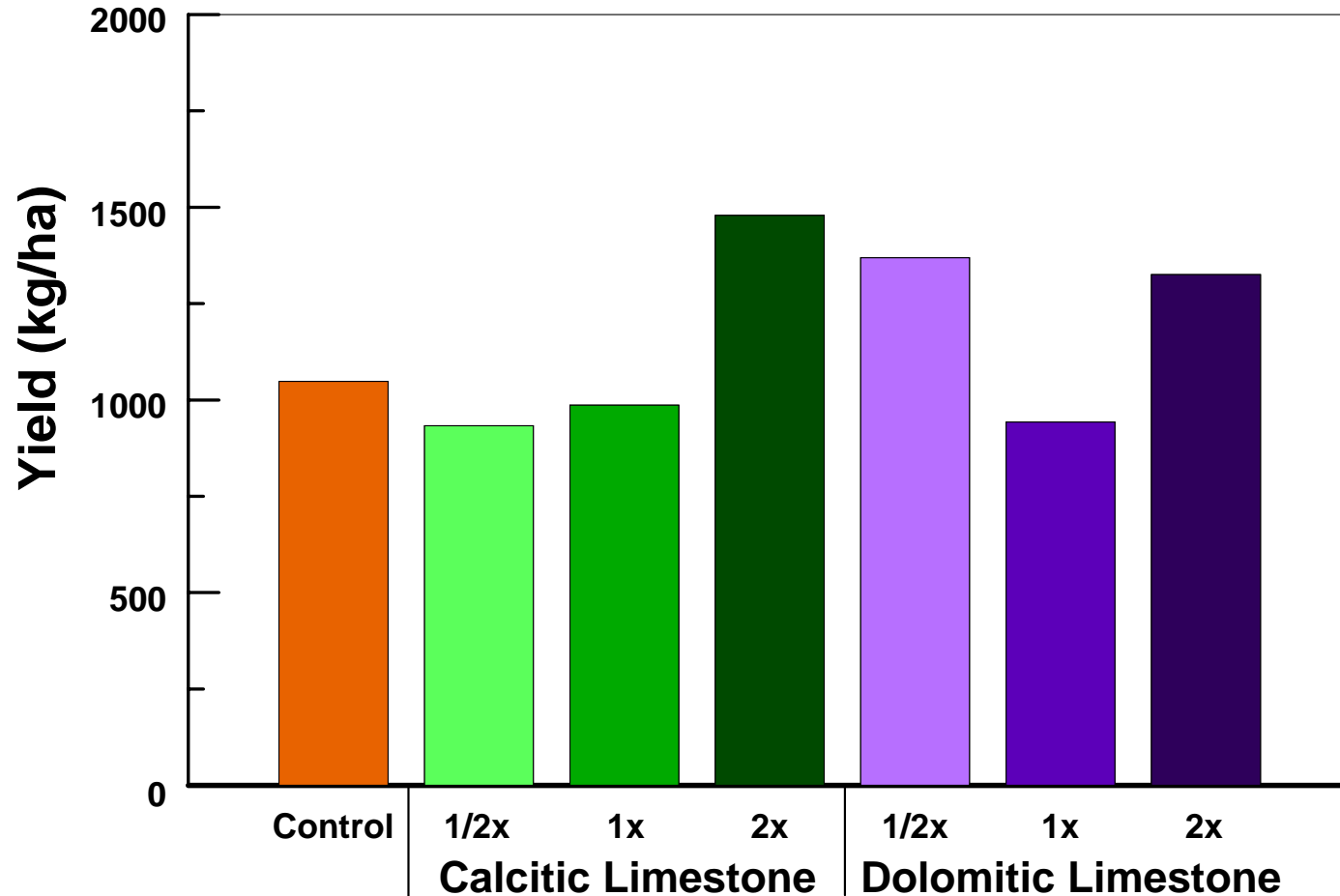


Figure 2-9. August 2006 forage harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 419.87 for comparing treatments.

Two Year Total Forage Harvest

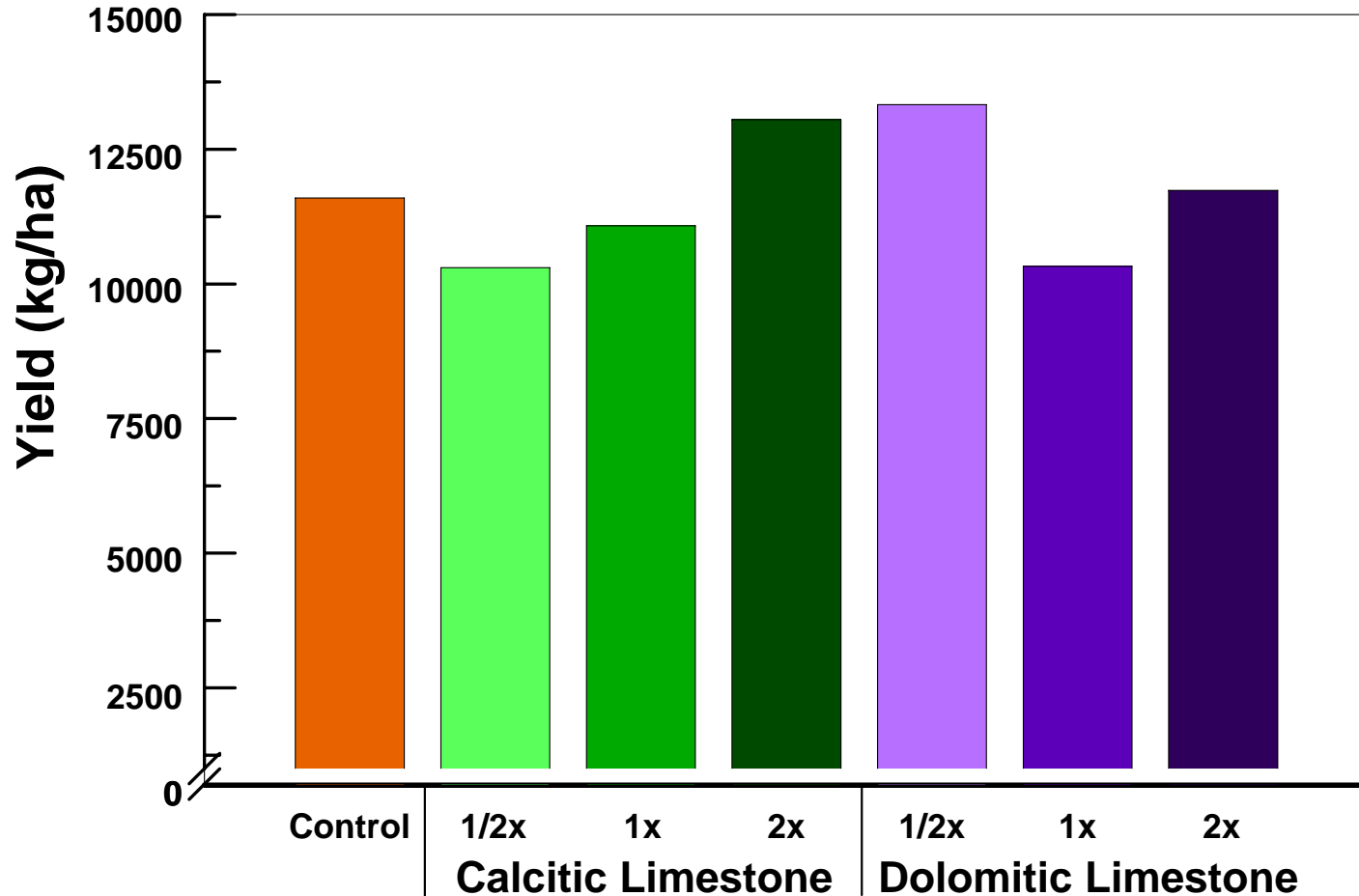


Figure 2-10. Two year total forage harvest of tall fescue treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic and calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 1867.90 for comparing treatments.

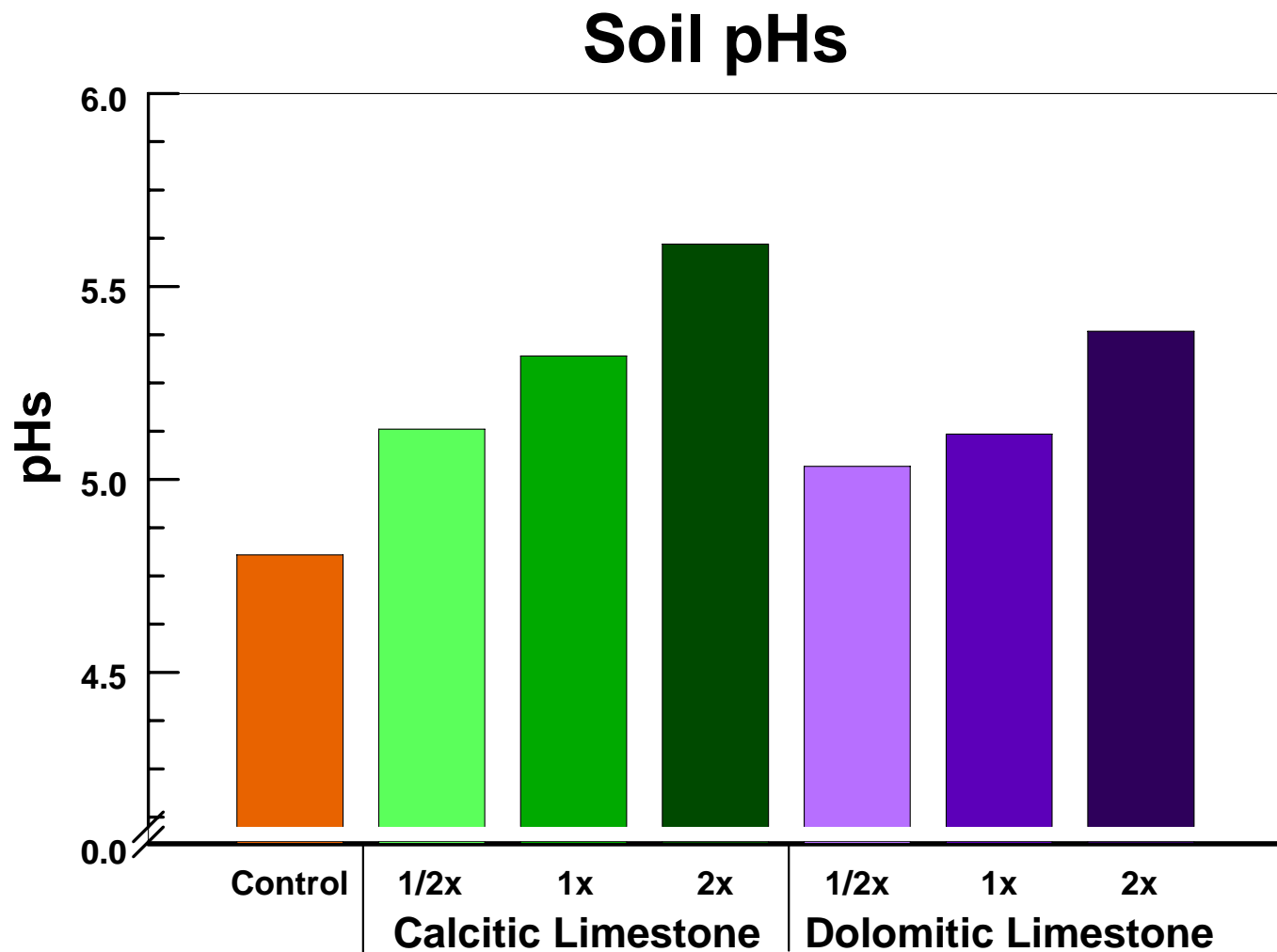


Figure 2-11. Soil pHs 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.202 for comparing treatments.

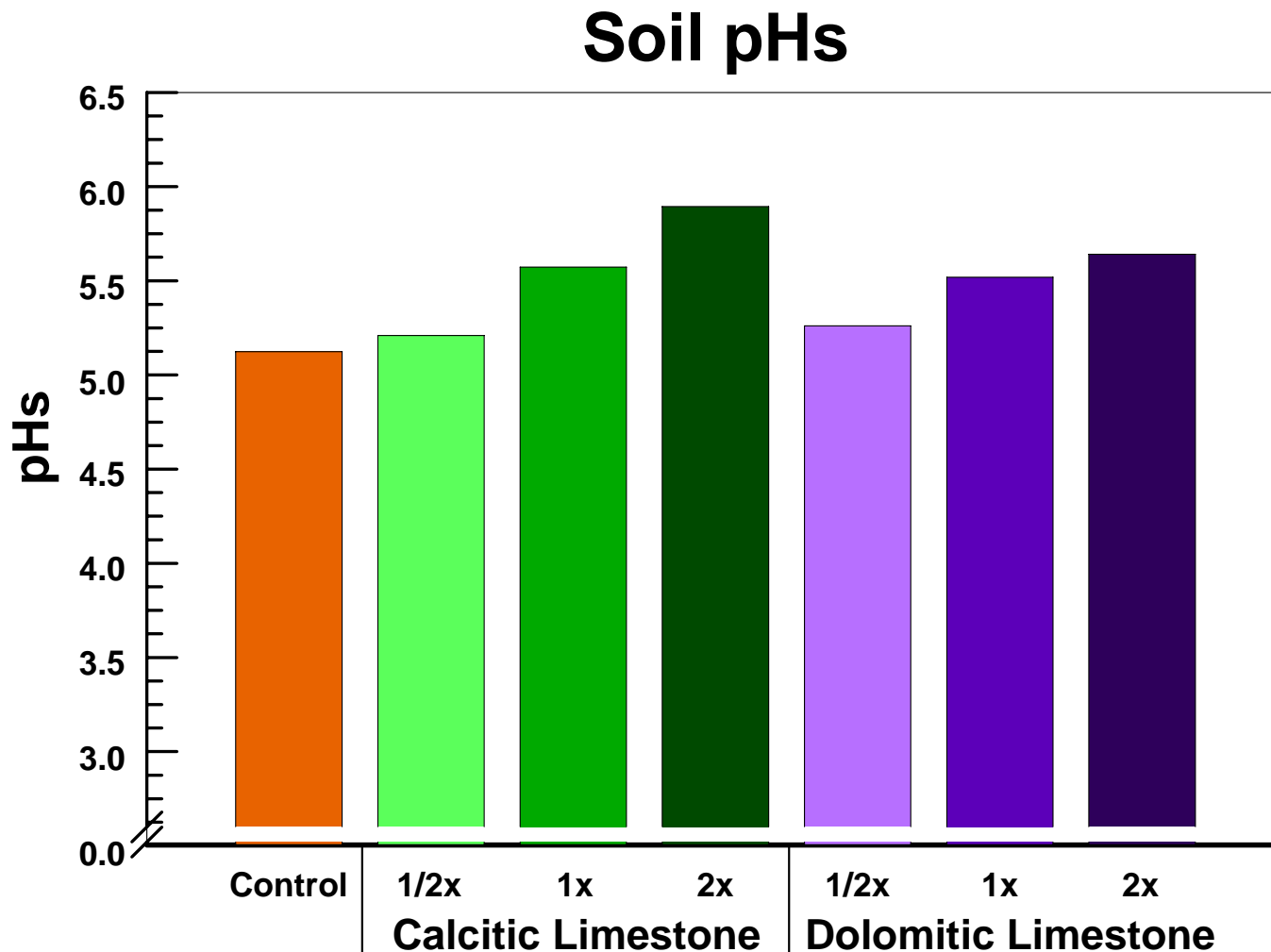


Figure 2-12. Soil pHs 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.131 for comparing treatments.

Soil Neutralizable Acidity

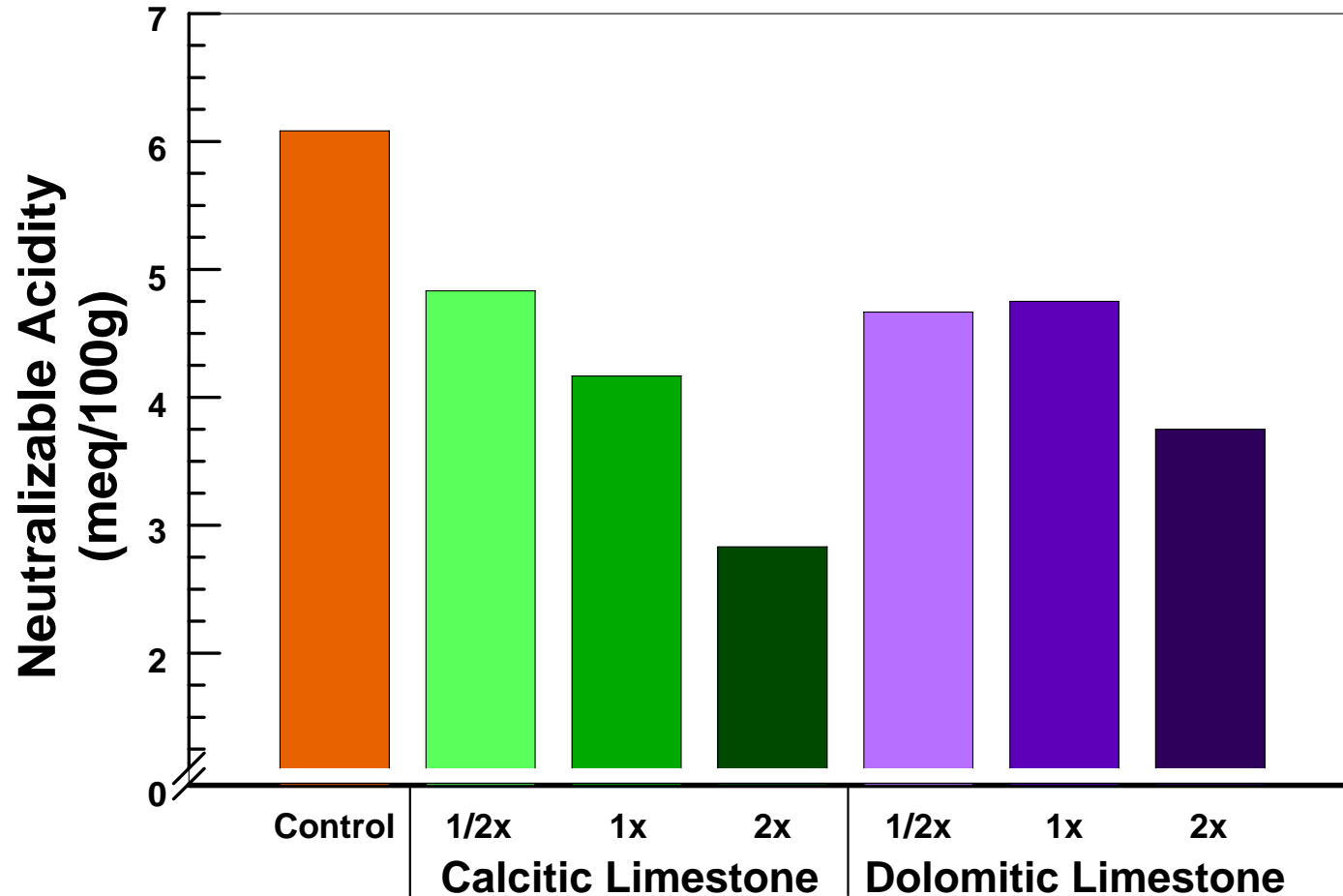


Figure 2-13. Soil neutralizable acidity 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD (P<0.05) = 0.848 for comparing treatments.

Soil Neutralizable Acidity

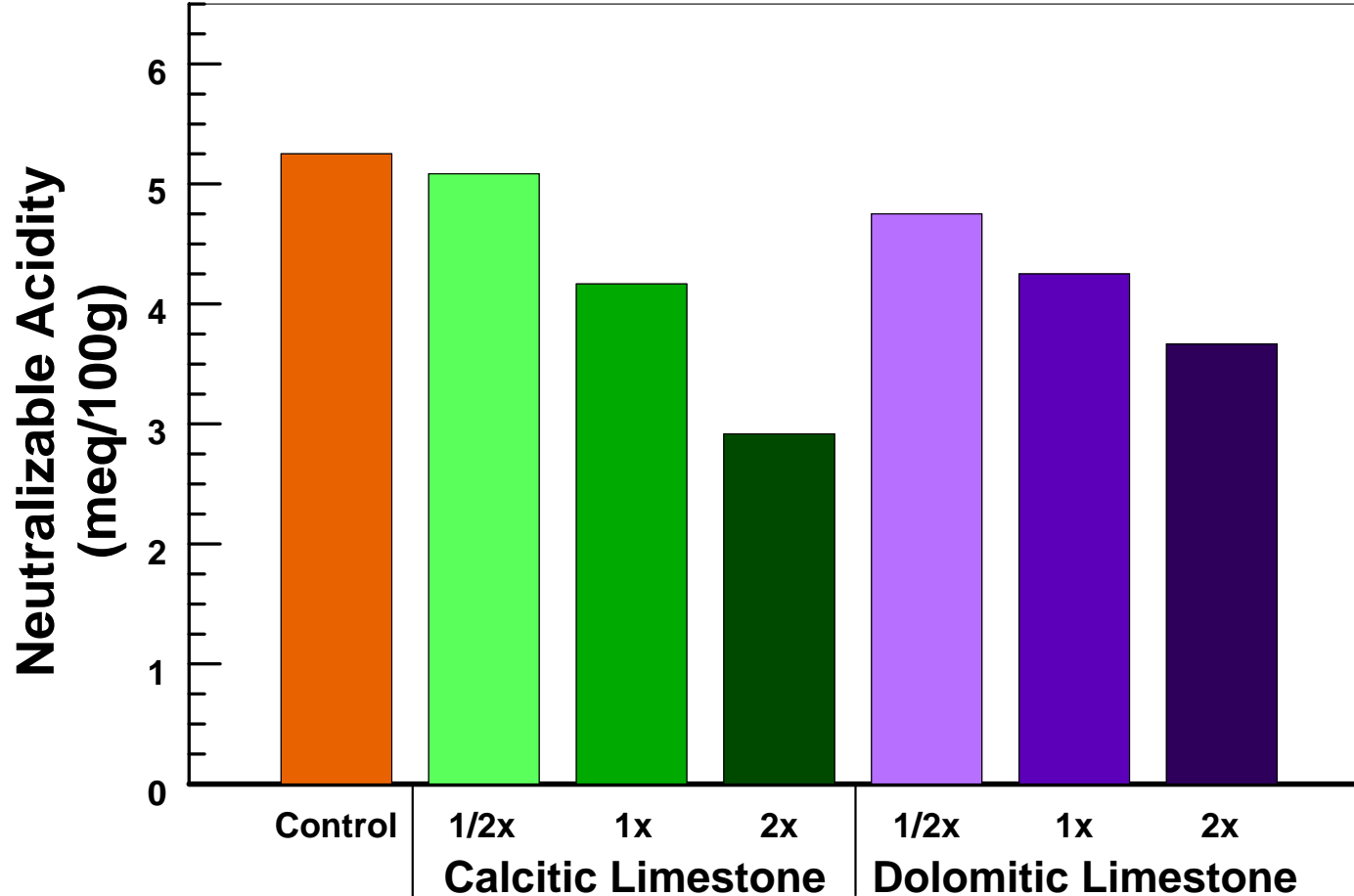


Figure 2-14. Soil neutralizable acidity 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.587 for comparing treatments.

Soil Cation Exchange Capacity

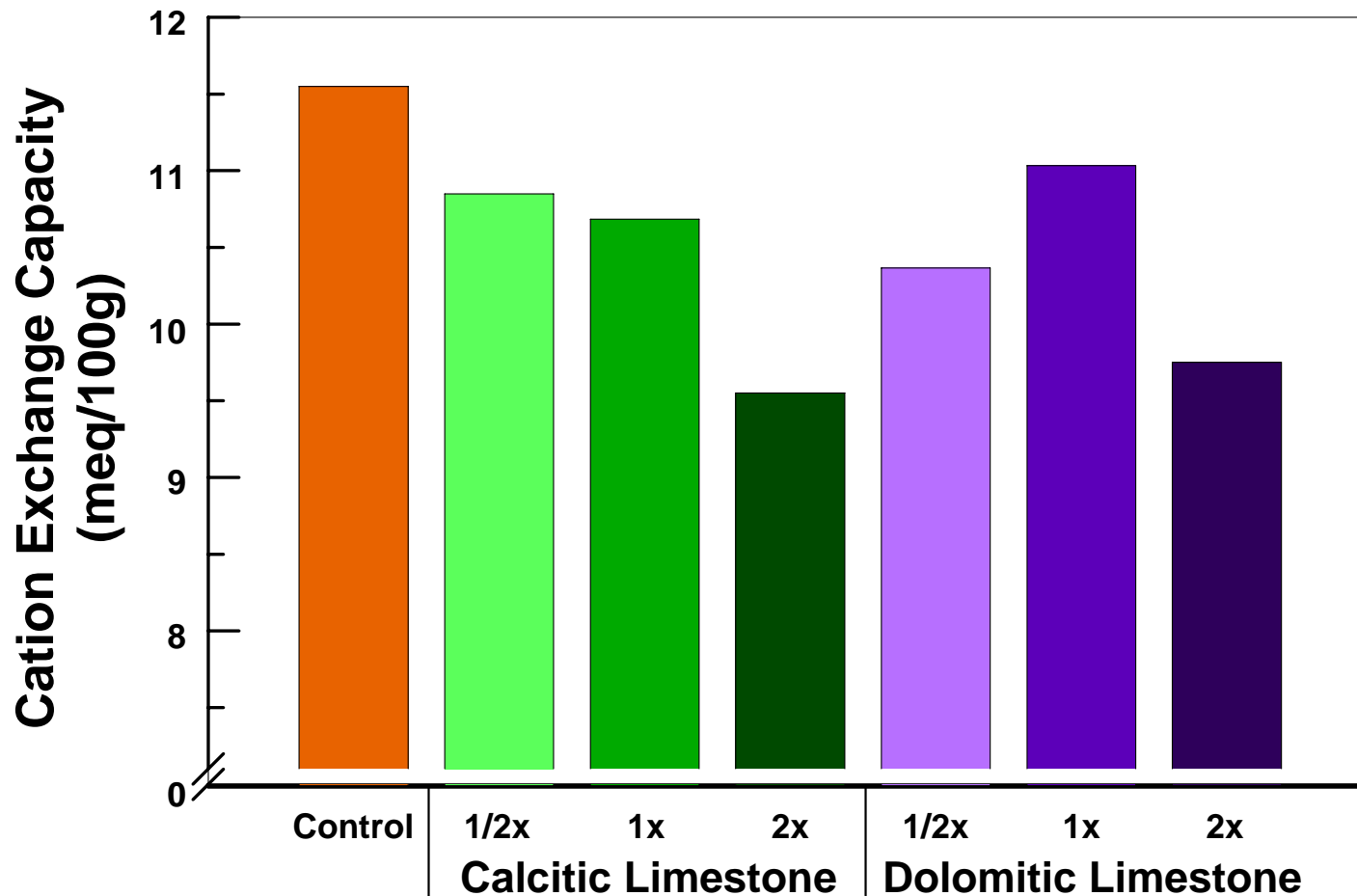


Figure 2-15. Soil cation exchange capacity 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.707 for comparing treatments.

Soil Cation Exchange Capacity

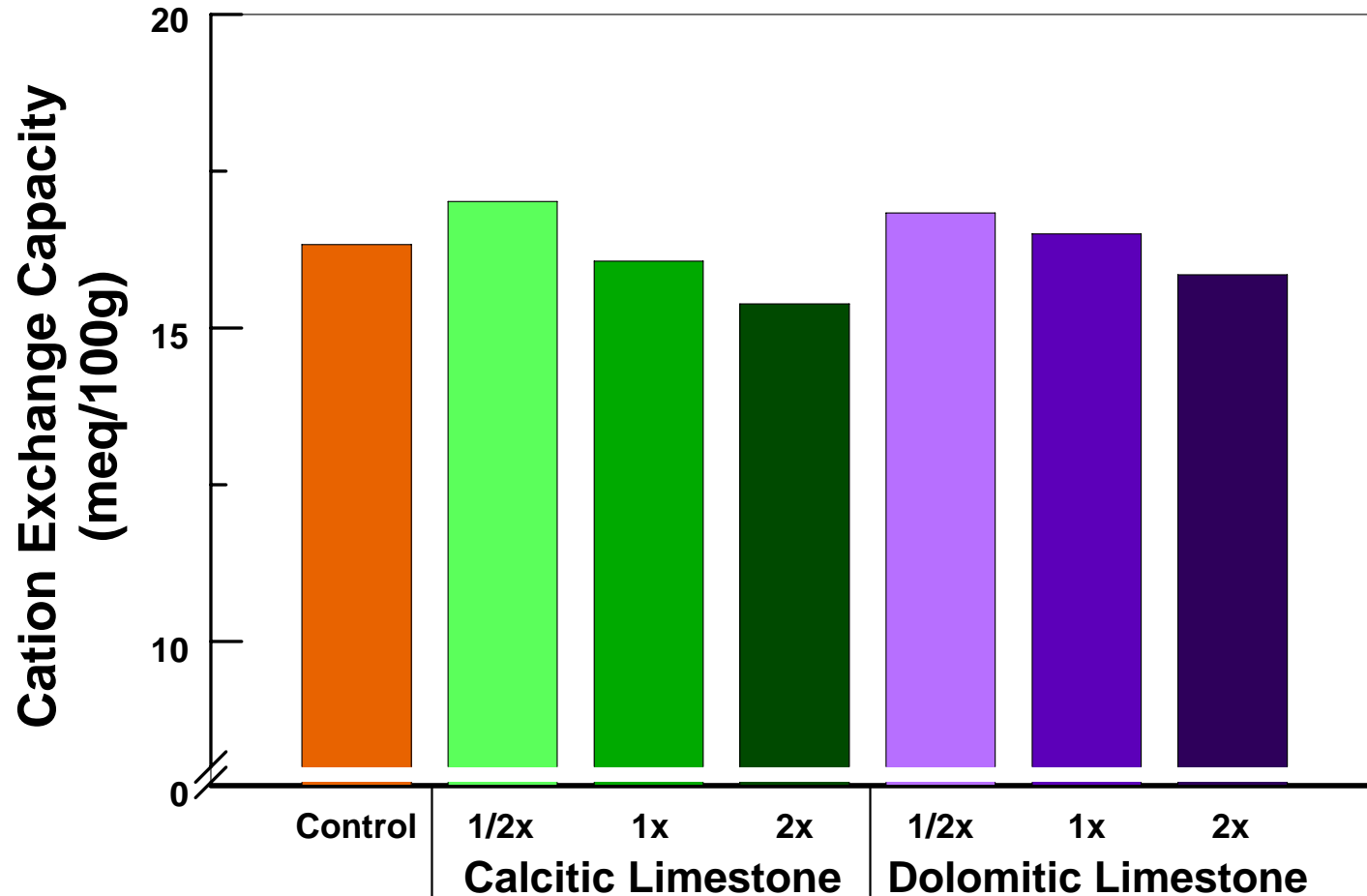


Figure 2-16. Soil cation exchange capacity 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 1.15 for comparing treatments.

Soil Organic Matter

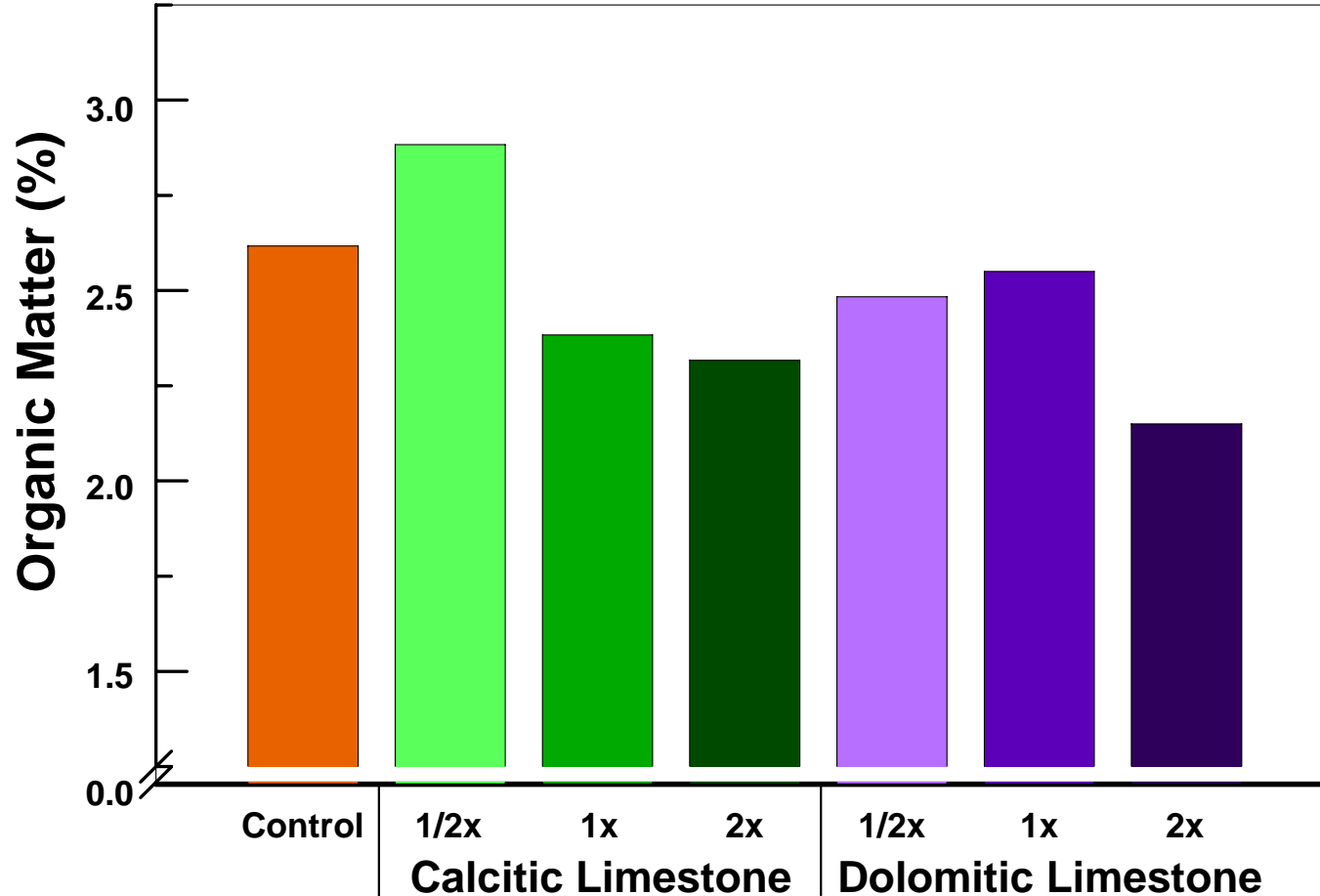


Figure 2-17. Soil organic matter content 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Organic matter is 58% carbon. Means (n=6). LSD (P<0.05) = 0.410 for comparing treatments.

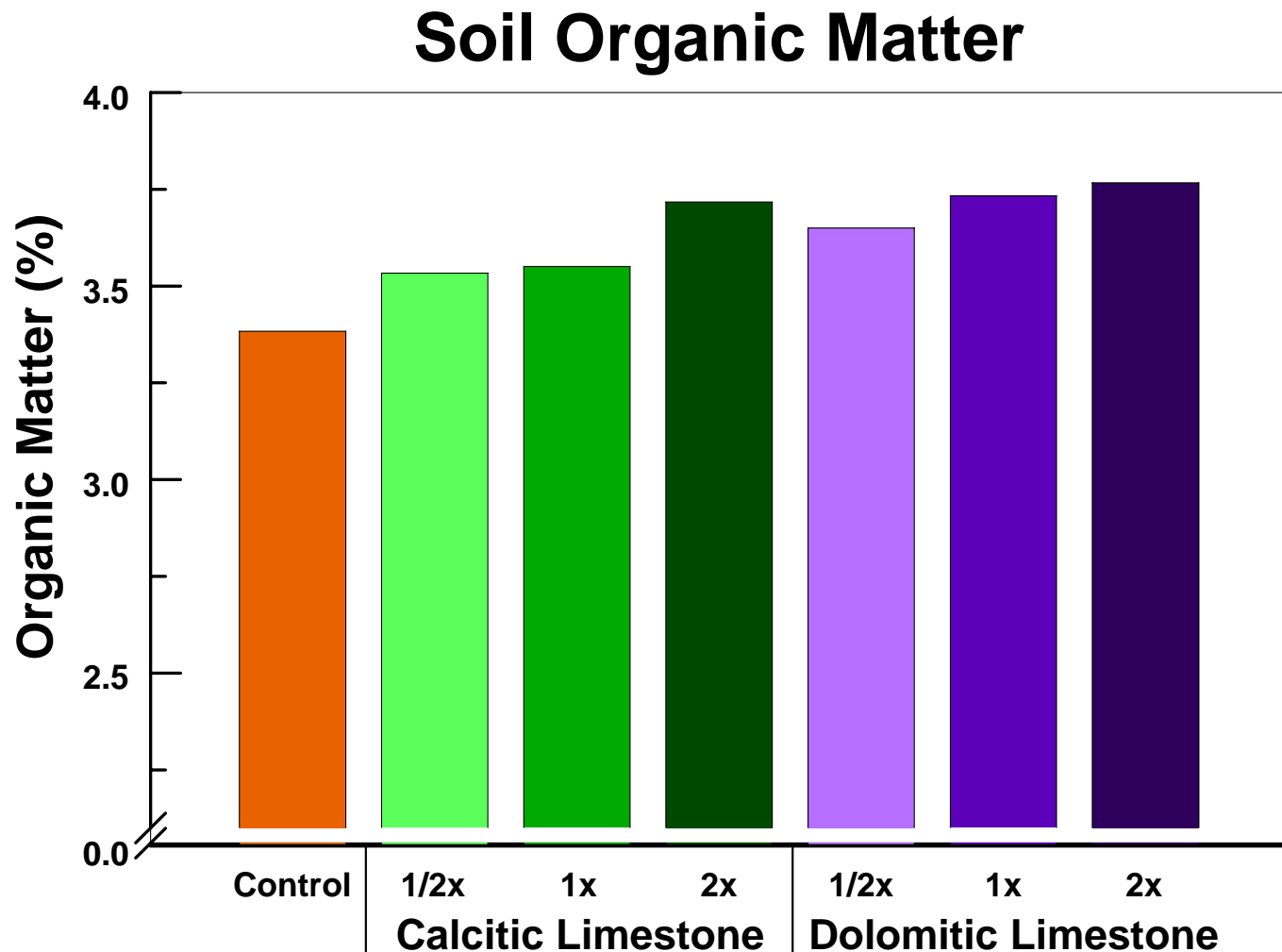


Figure 2-18. Soil organic matter content 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Organic matter is 58% carbon. Means (n=6). LSD (P<0.05) = 0.347 for comparing treatments.

Leaf Nitrogen

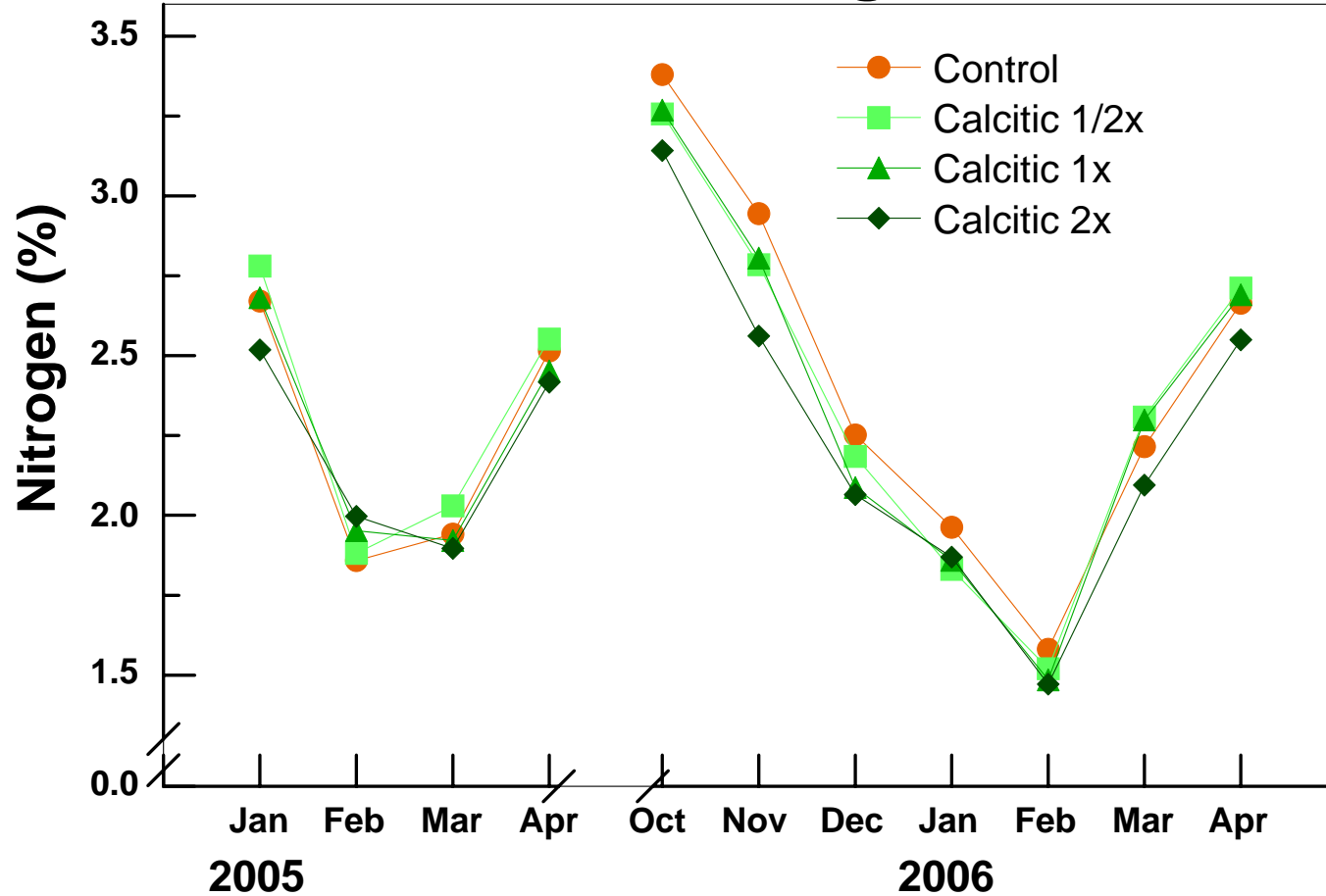


Figure 2-19. Nitrogen concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.299 for comparing treatments within a month and LSD ($P < 0.05$) = 0.099 for comparing months within the same treatment.

Leaf Nitrogen

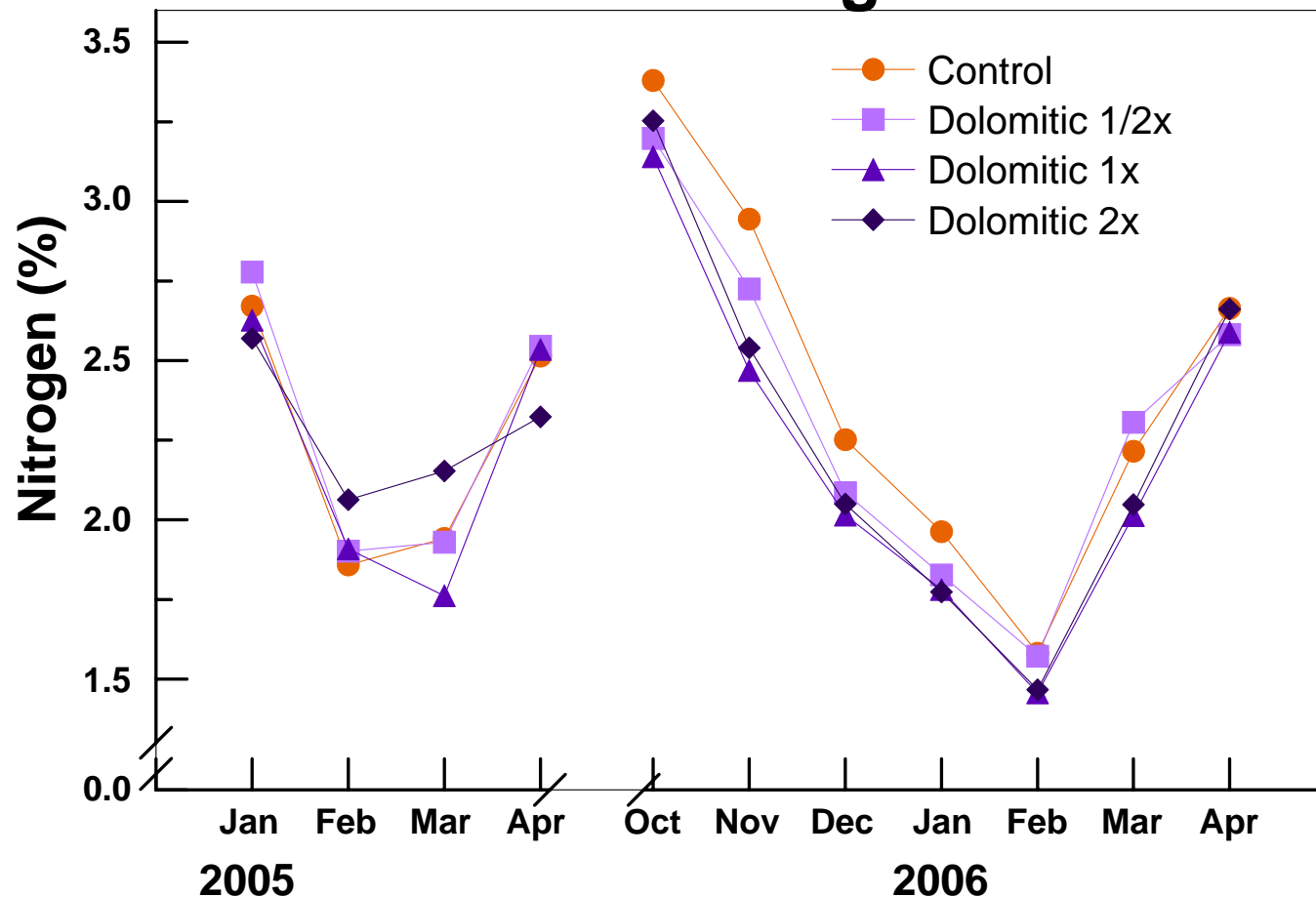


Figure 2-20. Nitrogen concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.299 for comparing treatments within a month and LSD ($P < 0.05$) = 0.099 for comparing months within the same treatment.

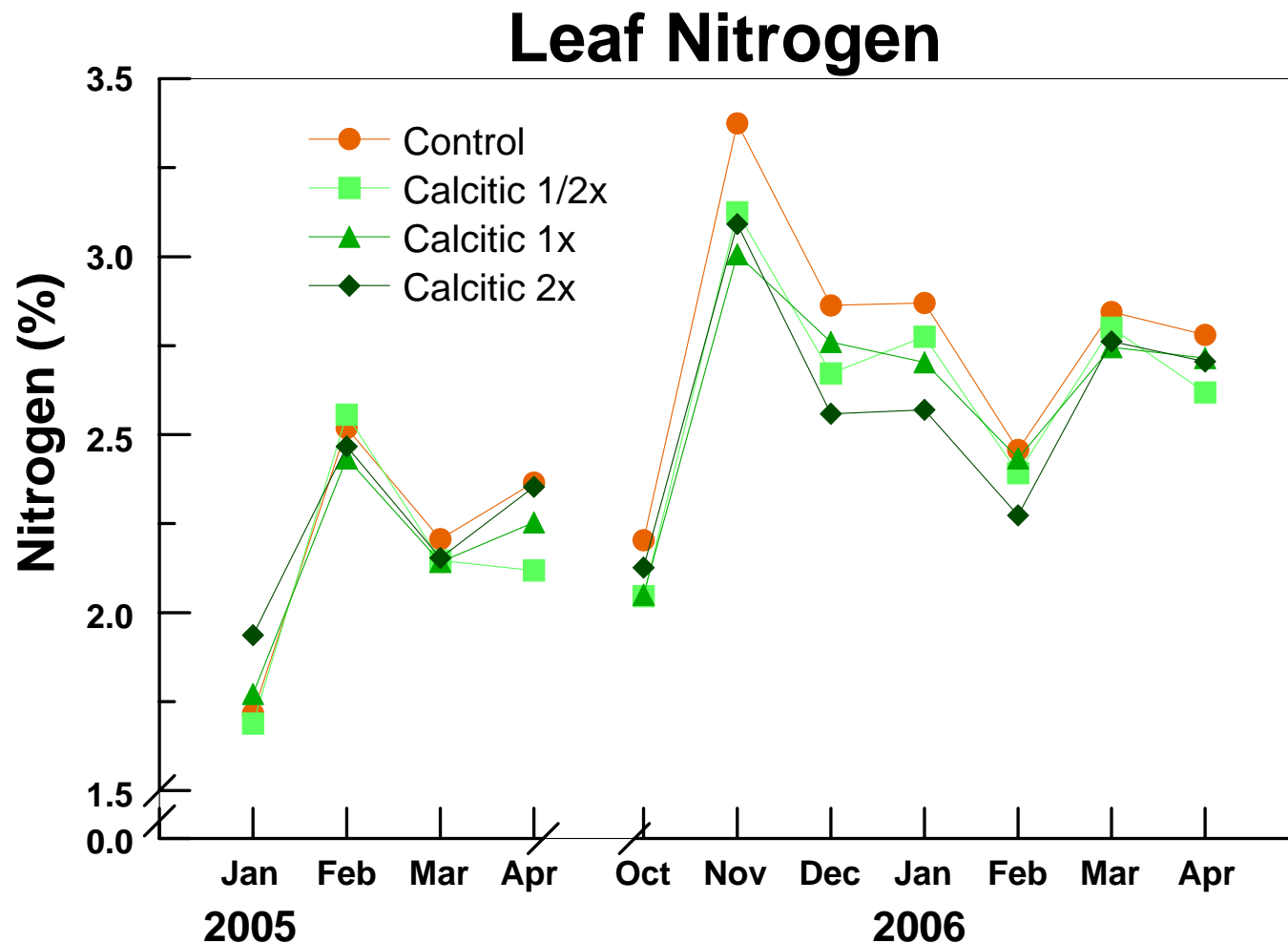


Figure 2-21. Nitrogen concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.232 for comparing treatments within a month and LSD ($P < 0.05$) = 0.077 for comparing months within the same treatment.

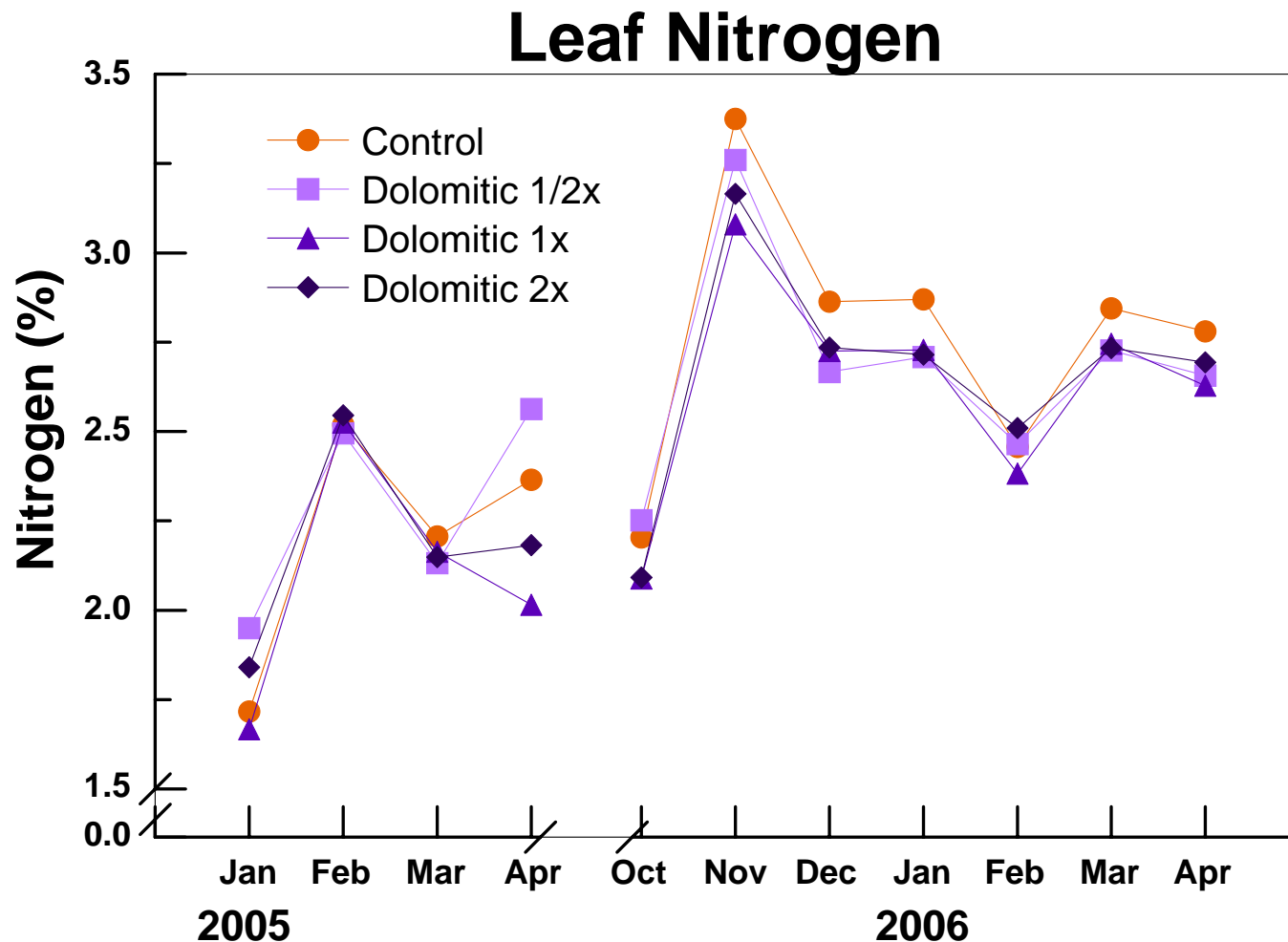


Figure 2-22. Nitrogen concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.232 for comparing treatments within a month and LSD ($P < 0.05$) = 0.077 for comparing months within the same treatment.

Leaf Phosphorus

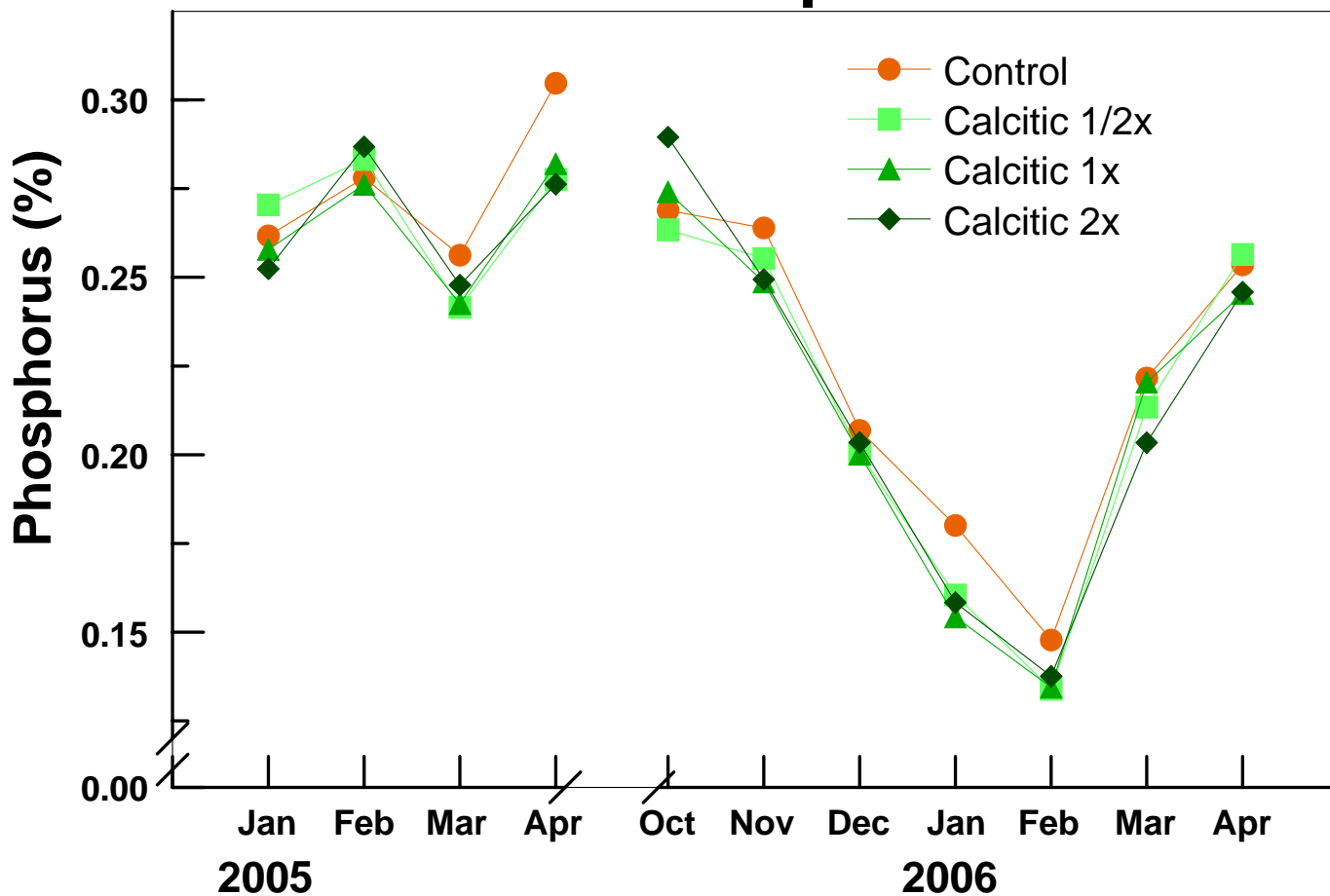


Figure 2-23. Phosphorus concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.022 for comparing treatments within a month and LSD ($P < 0.05$) = 0.008 for comparing months within the same treatment.

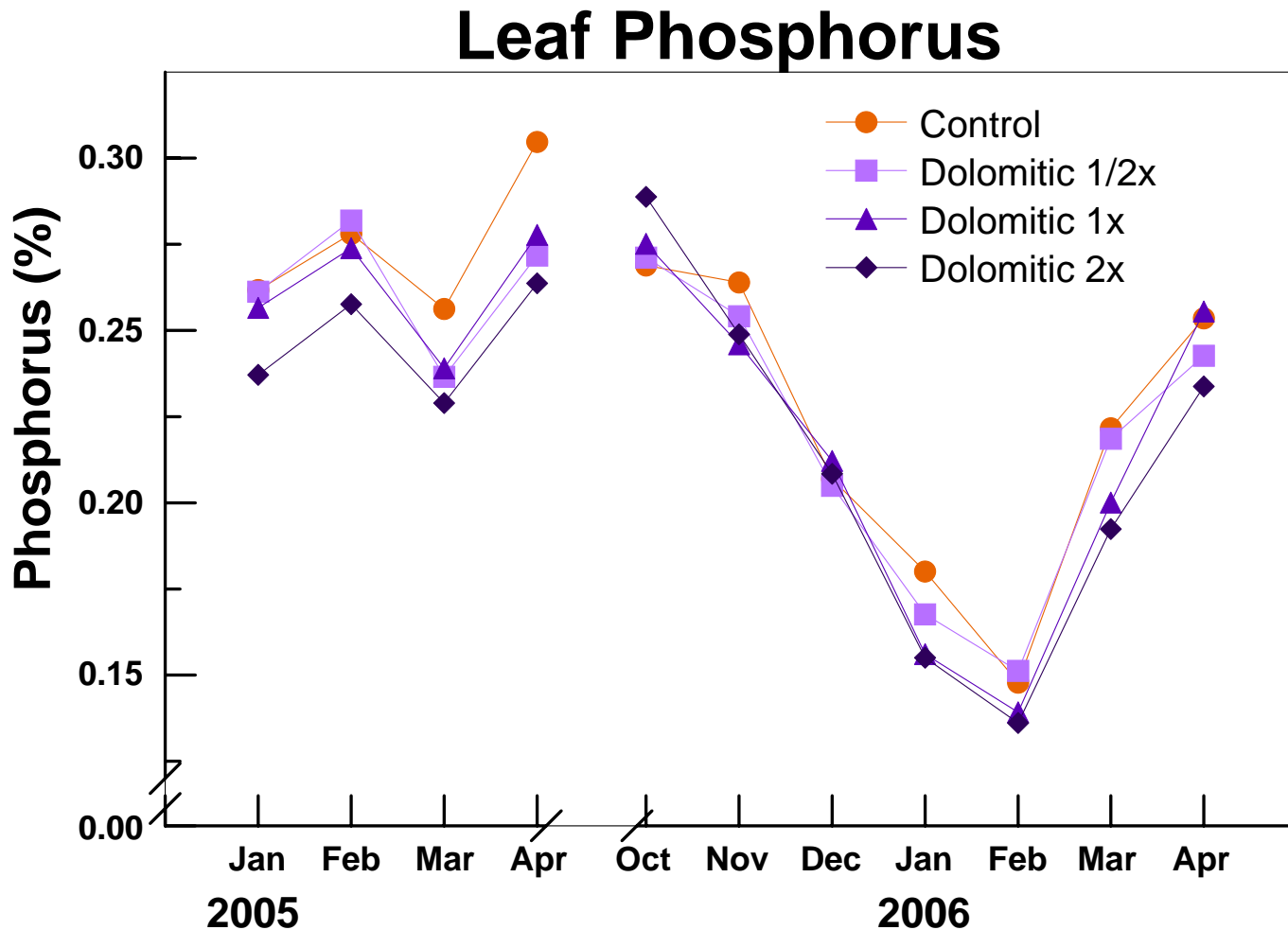


Figure 2-24. Phosphorus concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.022 for comparing treatments within a month and LSD ($P < 0.05$) = 0.008 for comparing months within the same treatment.

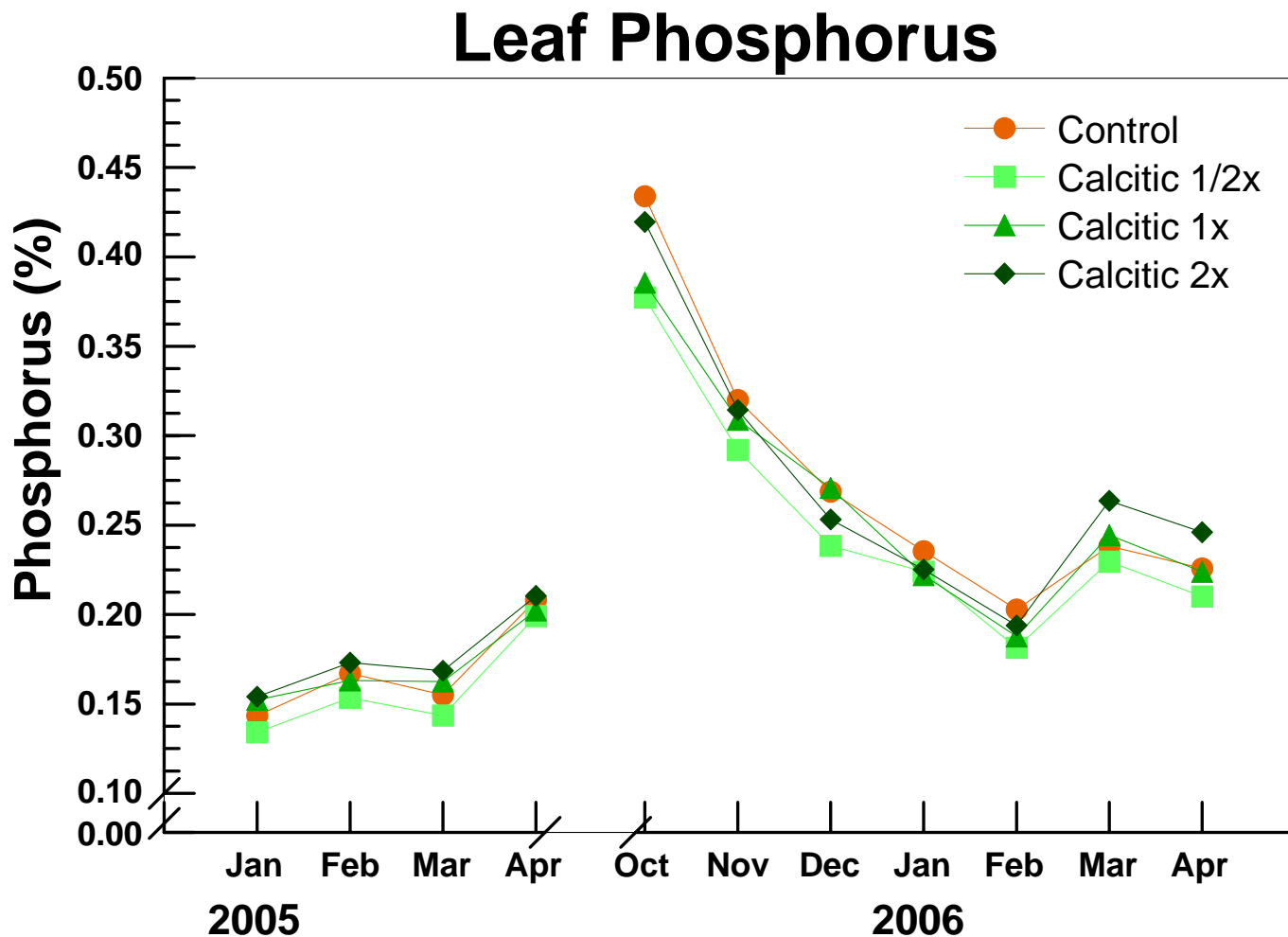


Figure 2-25. Phosphorus concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.034 for comparing treatments within a month and LSD ($P < 0.05$) = 0.010 for comparing months within the same treatment.

Leaf Phosphorus

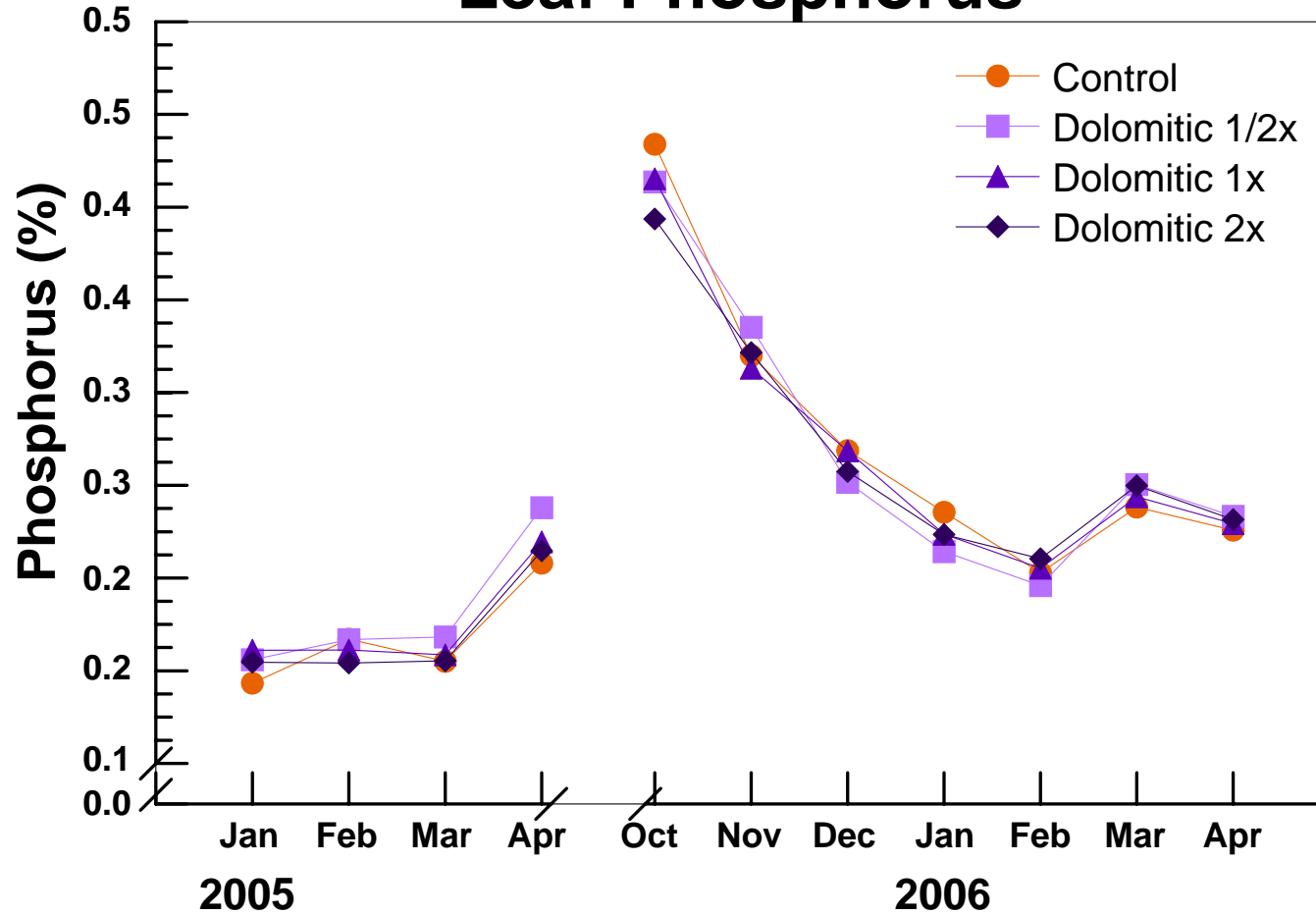


Figure 2-26. Phosphorus concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.034 for comparing treatments within a month and LSD ($P < 0.05$) = 0.010 for comparing months within the same treatment.

Soil Bray I Phosphorus

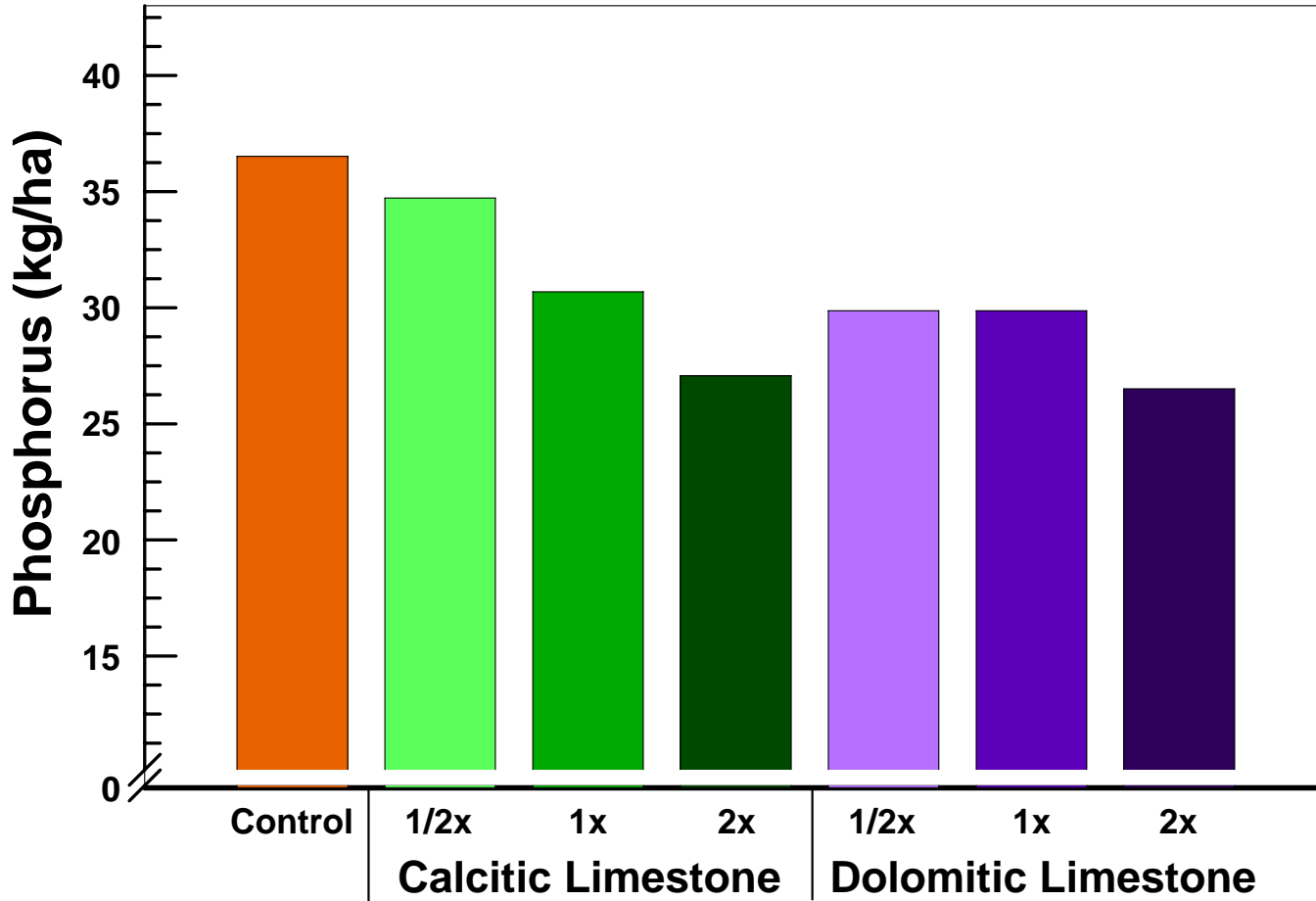


Figure 2-27. Soil Bray I phosphorus concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 9.70 for comparing treatments.

Soil Bray II Phosphorus

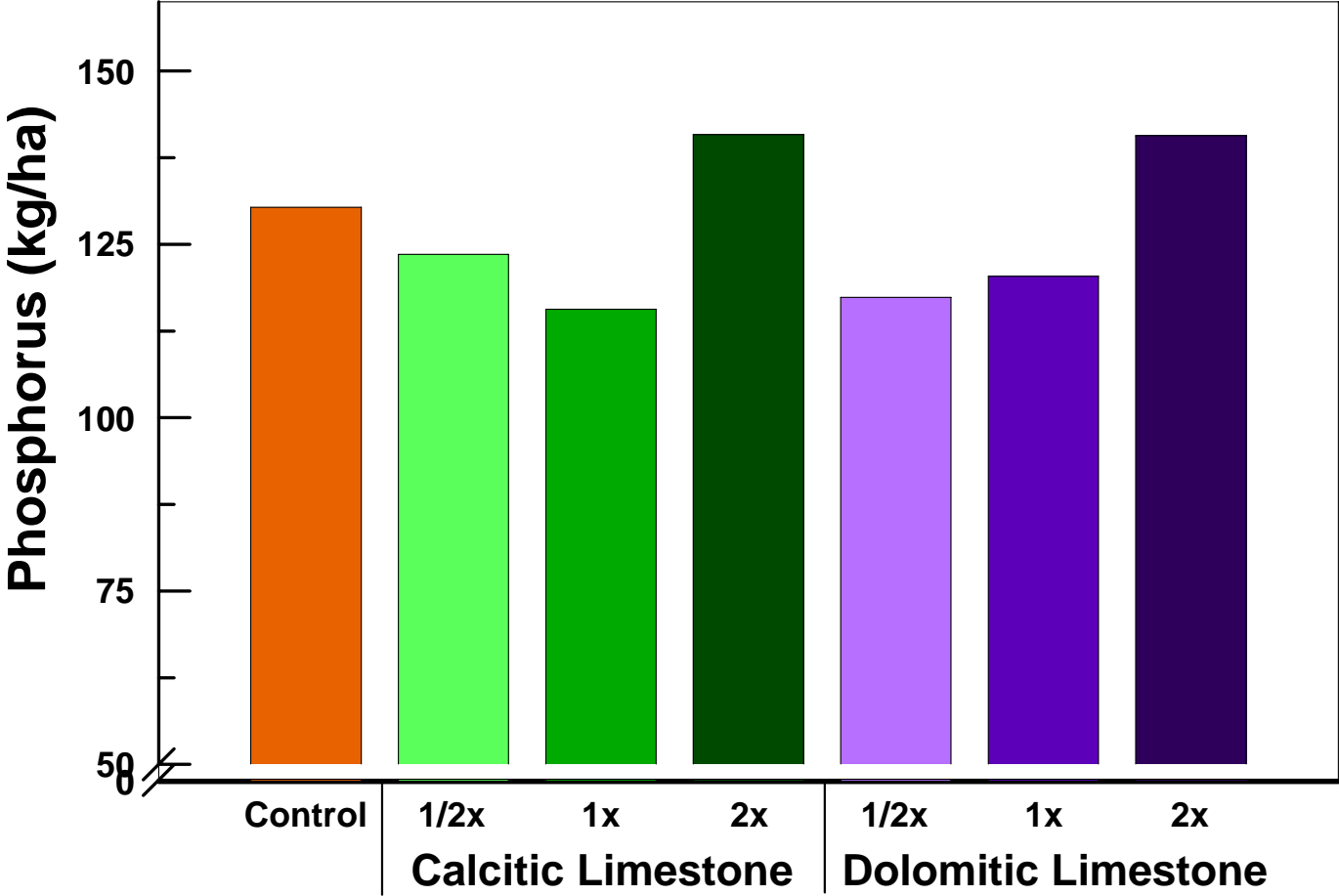


Figure 2-28. Soil Bray II phosphorus concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P<0.05$) = 21.27 for comparing treatments.

Soil Bray I Phosphorus

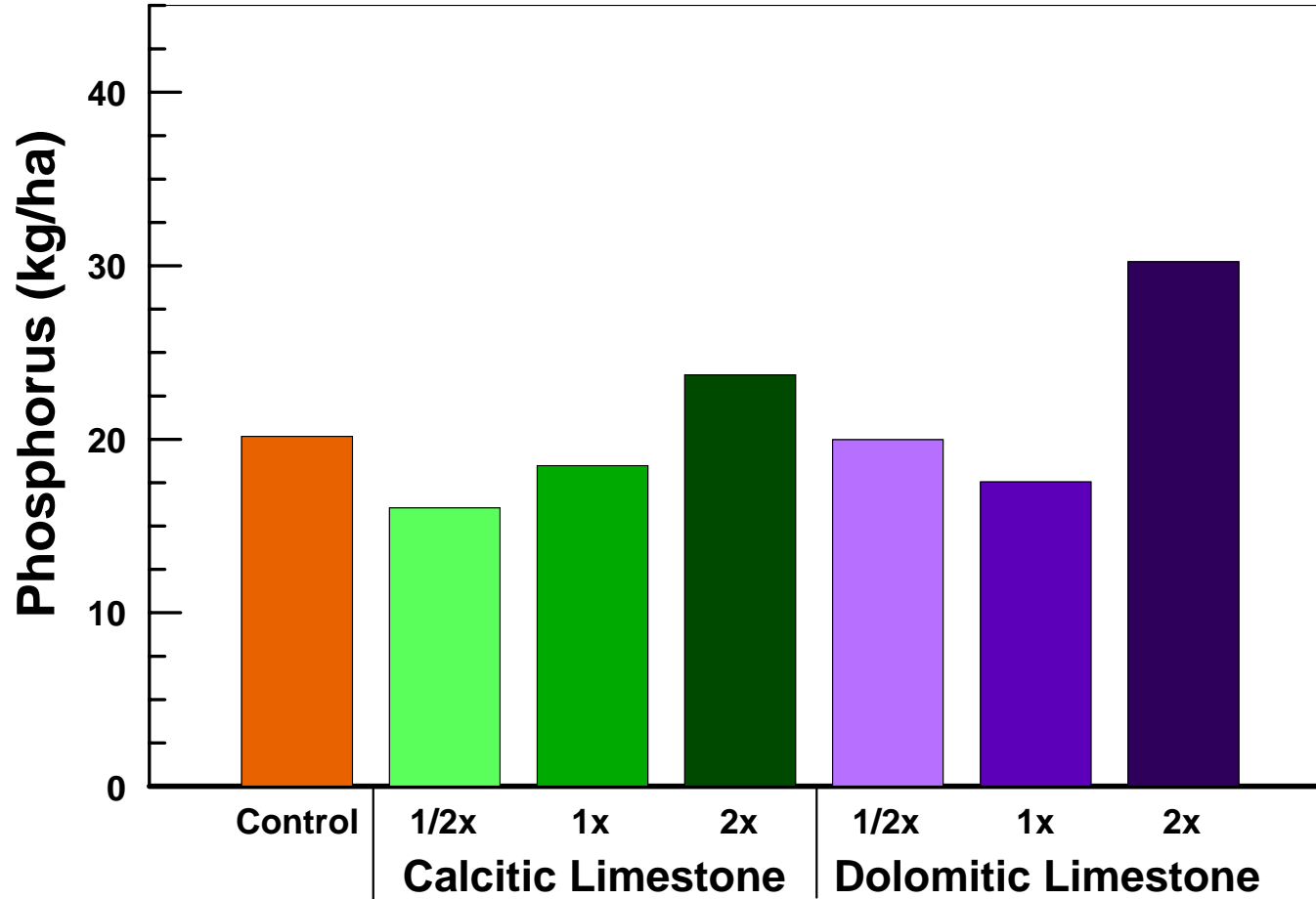


Figure 2-29. Soil Bray I phosphorus concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD (P<0.05) = 9.46 for comparing treatments.

Soil Bray II Phosphorus

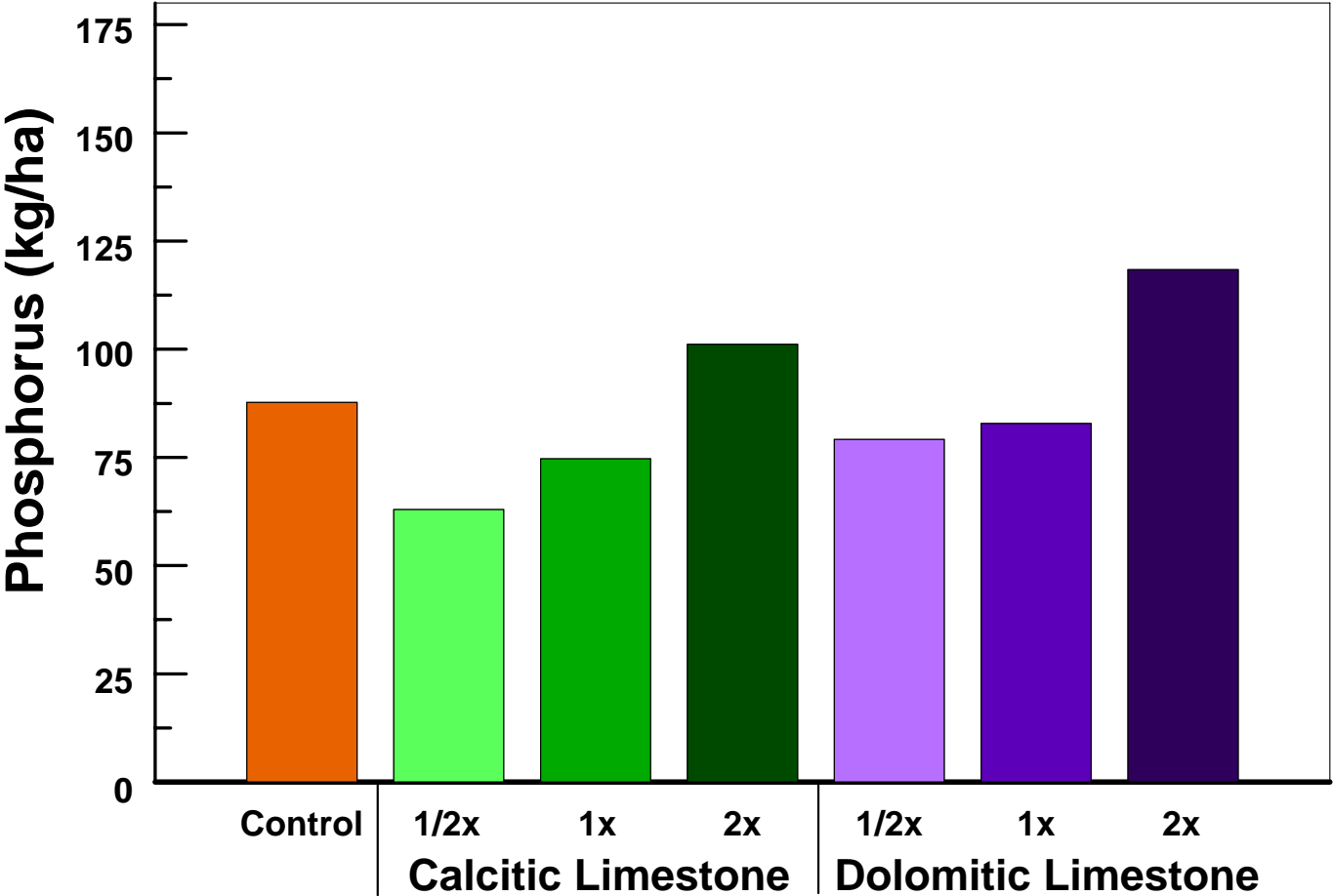


Figure 2-30. Soil Bray II phosphorus concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD (P<0.05) = 40.64 for comparing treatments.

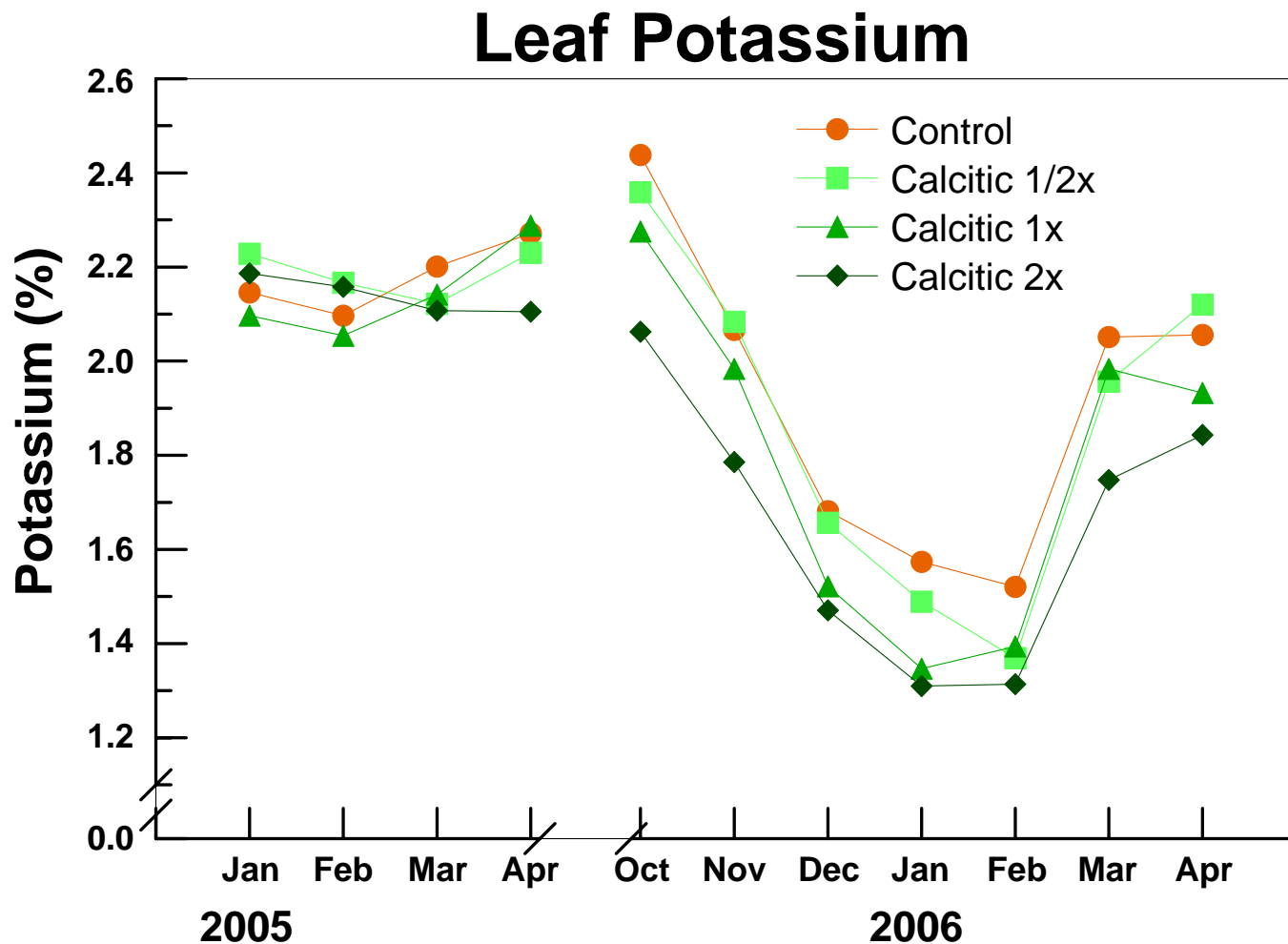


Figure 2-31. Potassium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.154 for comparing treatments within a month and LSD ($P < 0.05$) = 0.051 for comparing months within the same treatment.

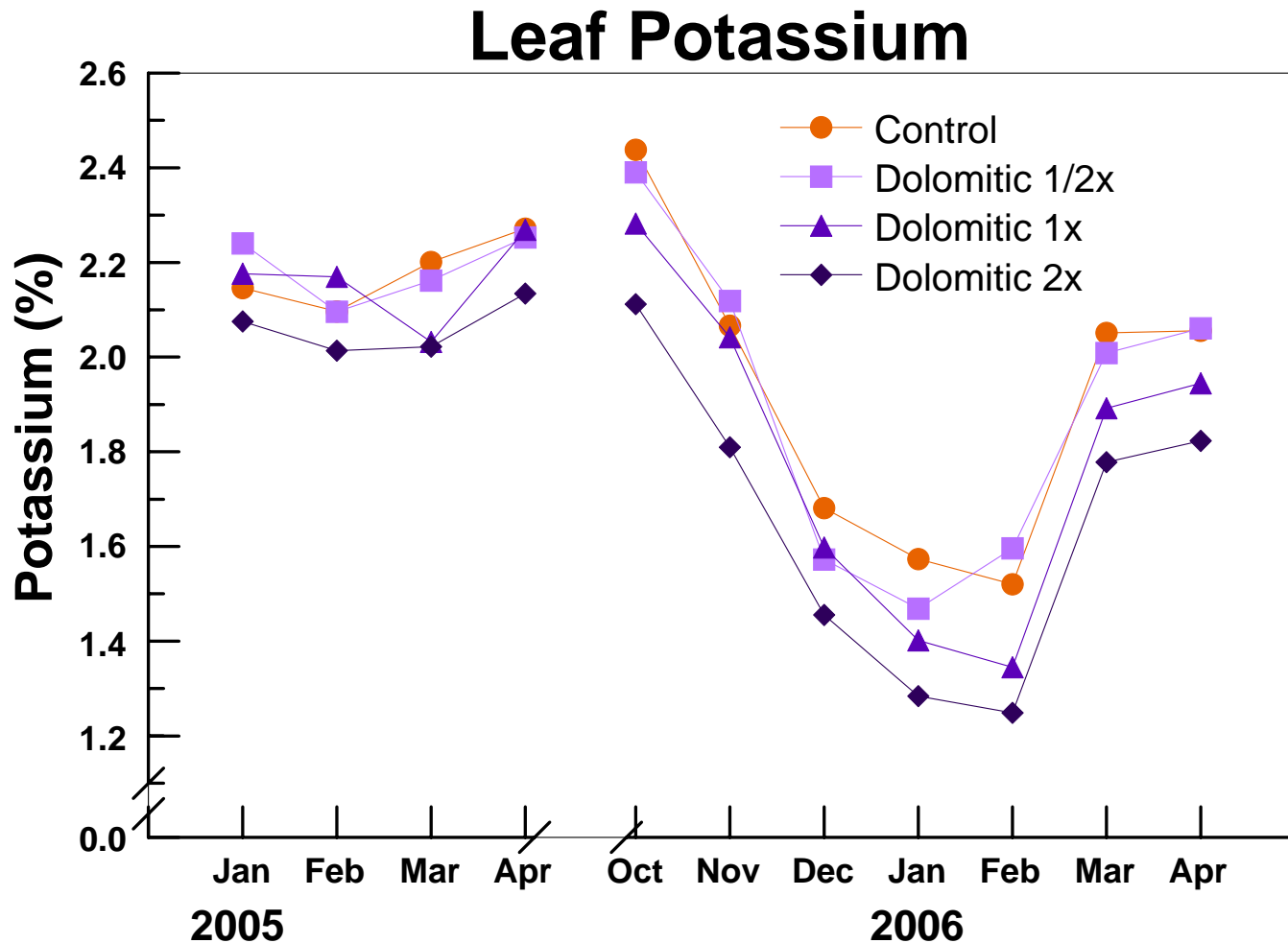


Figure 2-32. Potassium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.154 for comparing treatments within a month and LSD ($P < 0.05$) = 0.051 for comparing months within the same treatment.

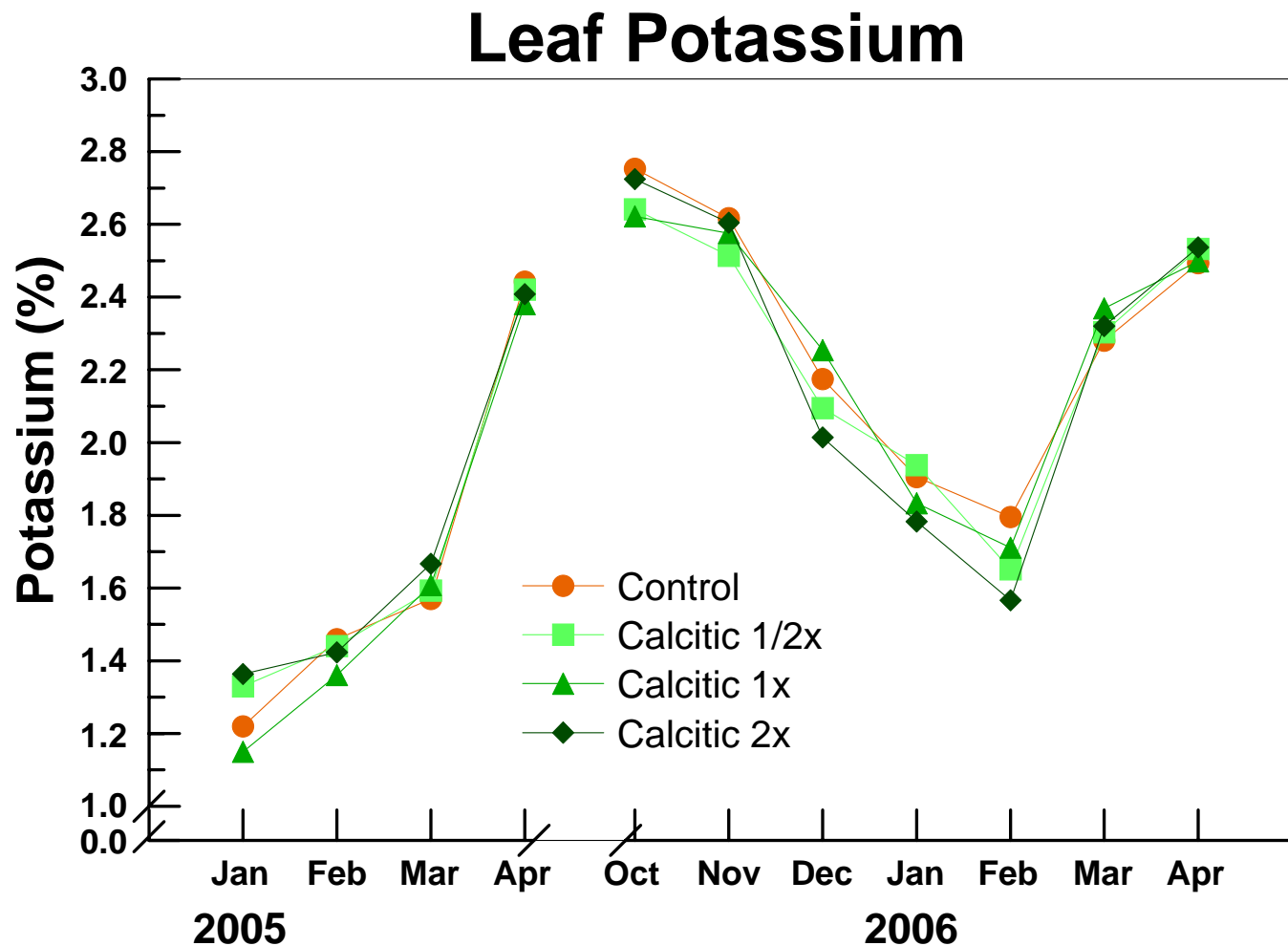


Figure 2-33. Potassium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.172 for comparing treatments within a month and LSD ($P < 0.05$) = 0.060 for comparing months within the same treatment.

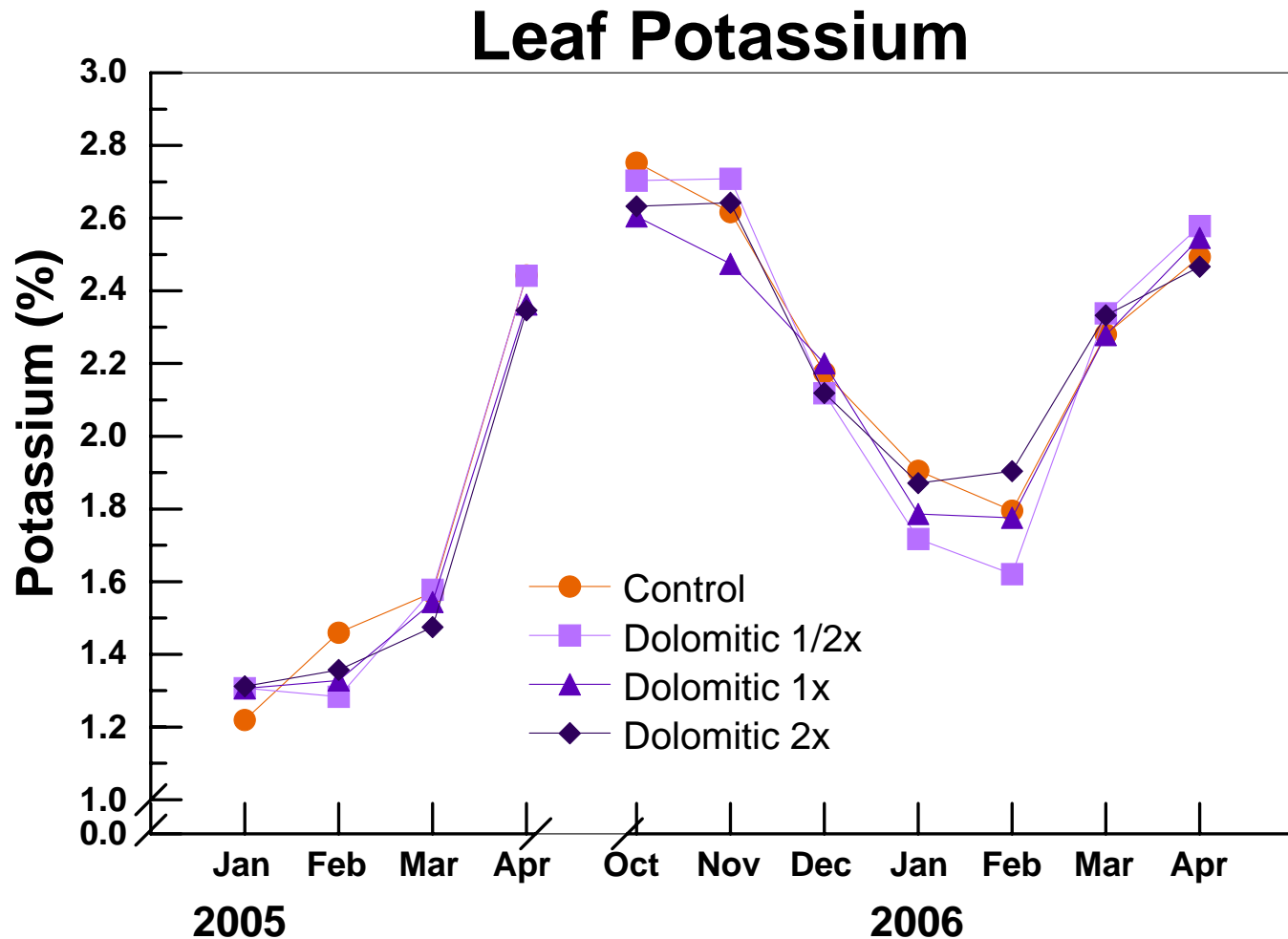


Figure 2-34. Potassium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means ($n=6$). LSD ($P<0.05$) = 0.172 for comparing treatments within a month and LSD ($P<0.05$) = 0.060 for comparing months within the same treatment.

Soil Potassium

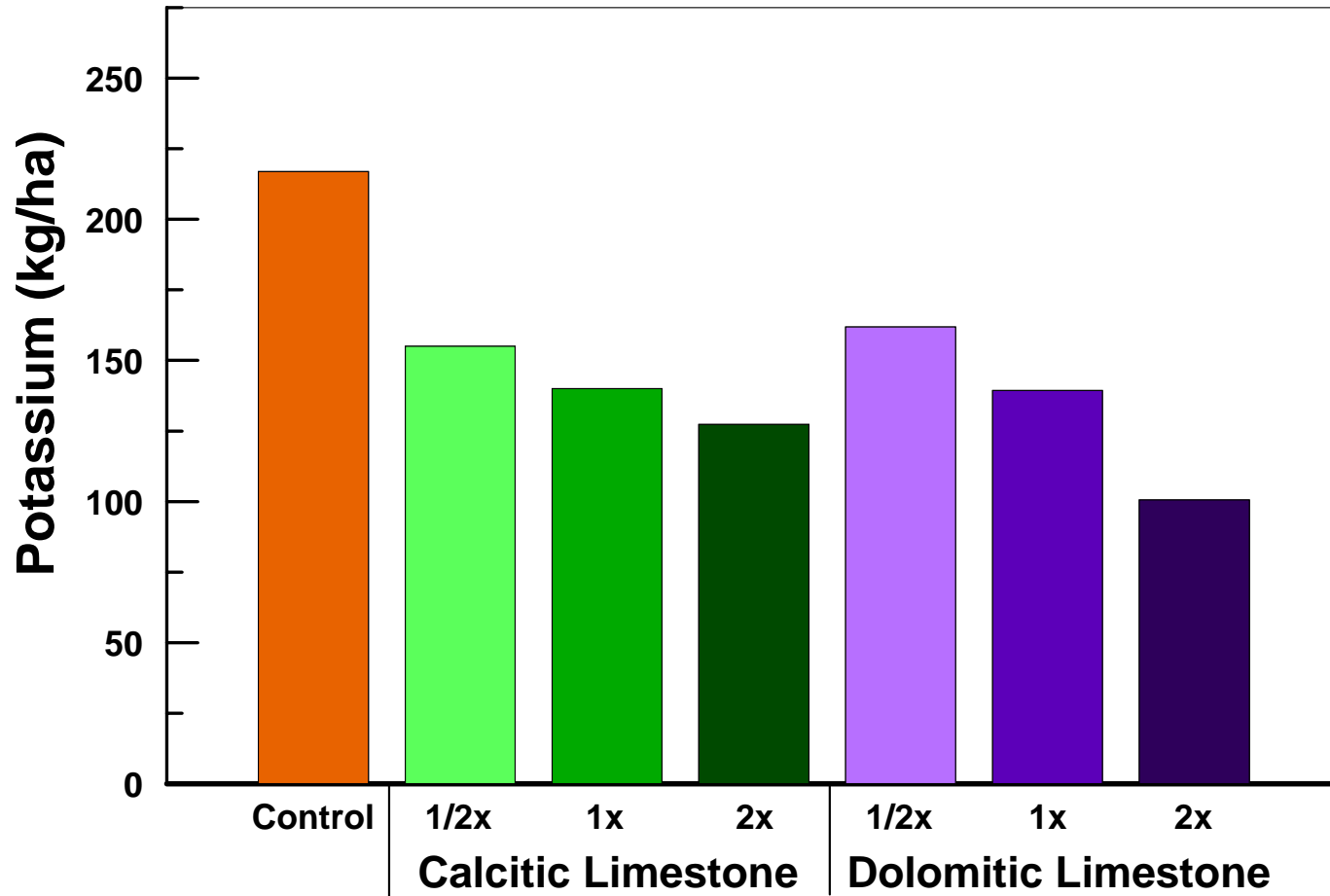


Figure 2-35. Soil potassium concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 55.06 for comparing treatments.

Soil Potassium

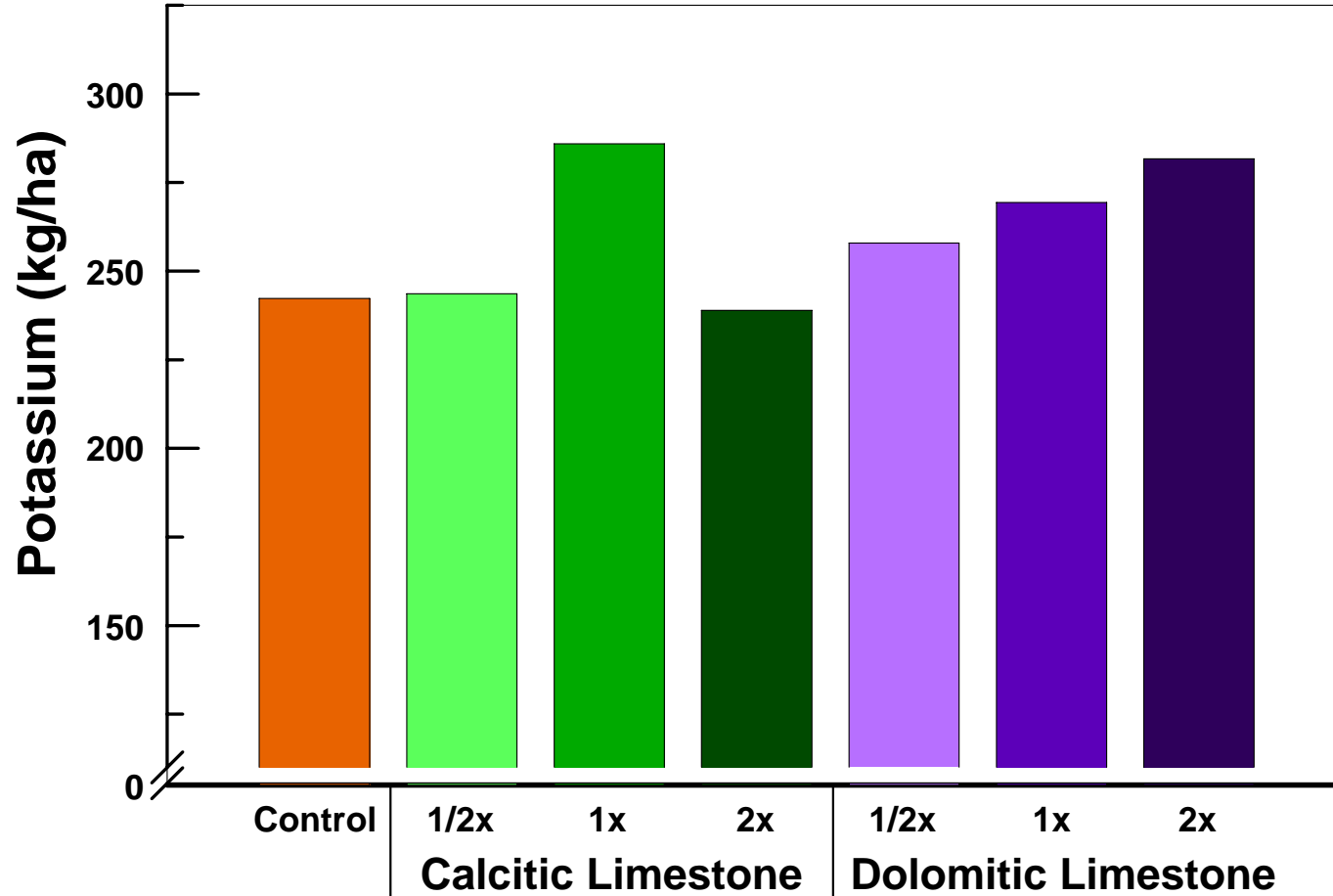


Figure 2-36. Soil potassium concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 42.56 for comparing treatments.

Leaf Calcium

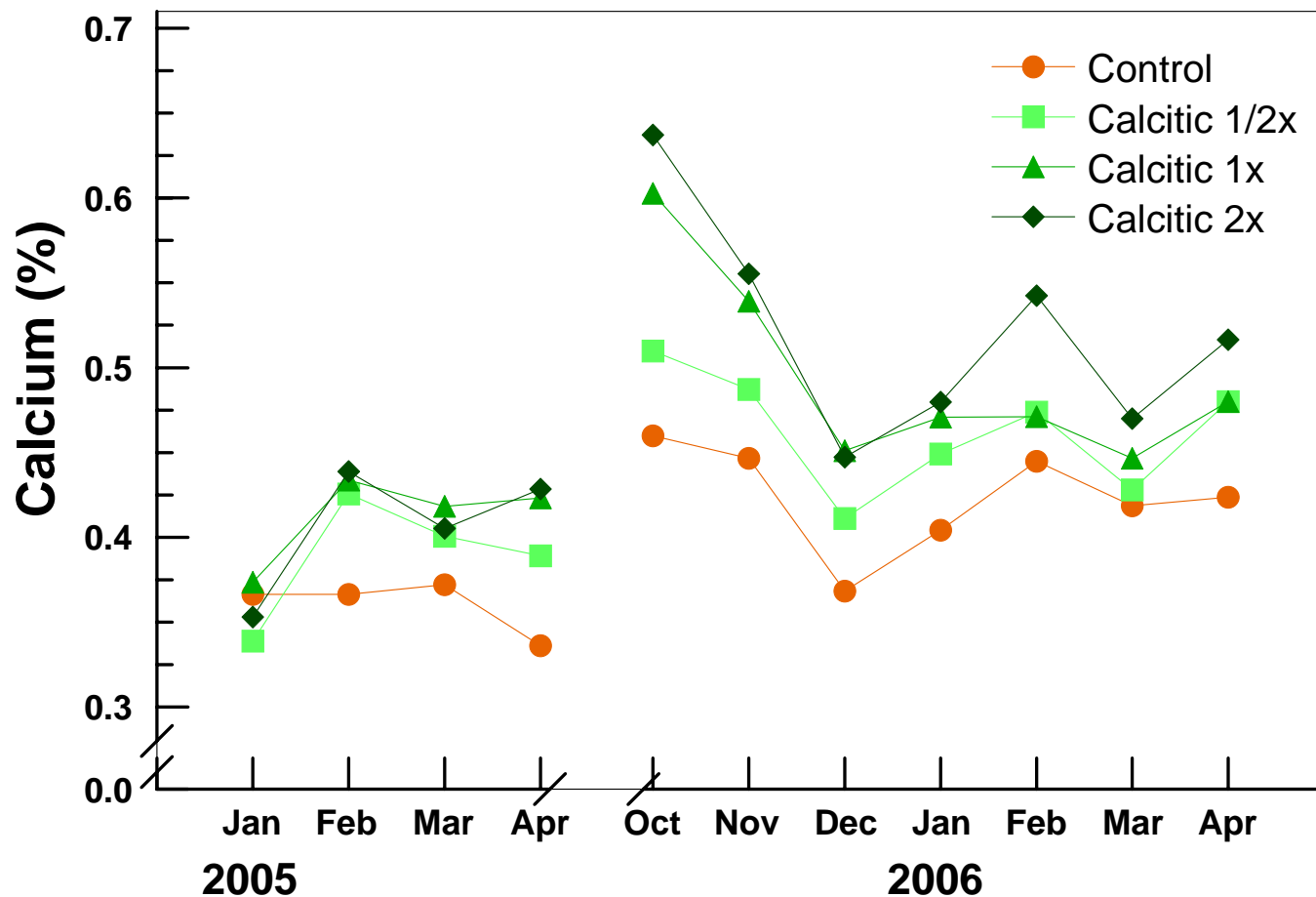


Figure 2-37. Calcium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.043 for comparing treatments within a month and LSD ($P < 0.05$) = 0.016 for comparing months within the same treatment.

Leaf Calcium

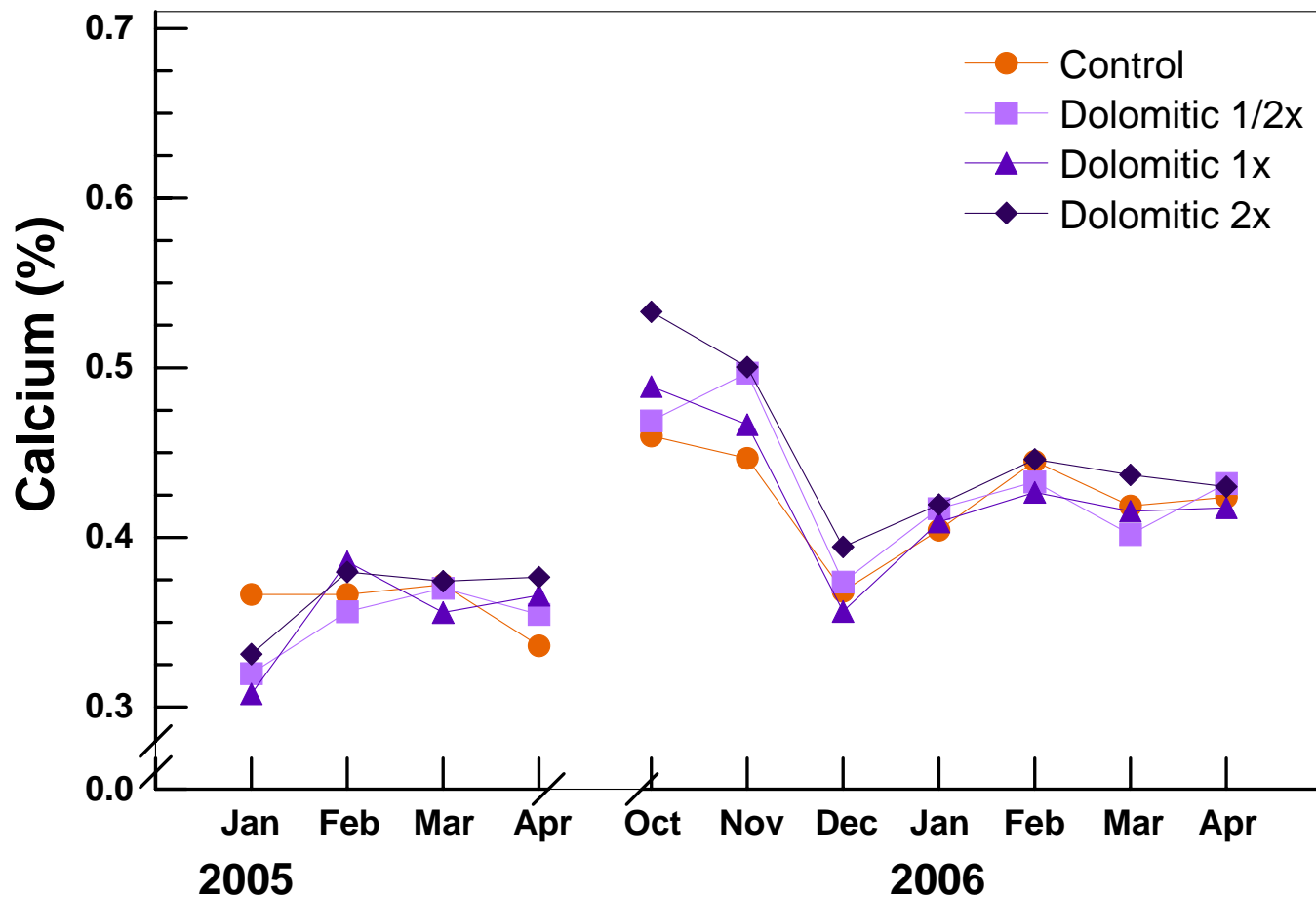


Figure 2-38. Calcium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.043 for comparing treatments within a month and LSD ($P < 0.05$) = 0.016 for comparing months within the same treatment.

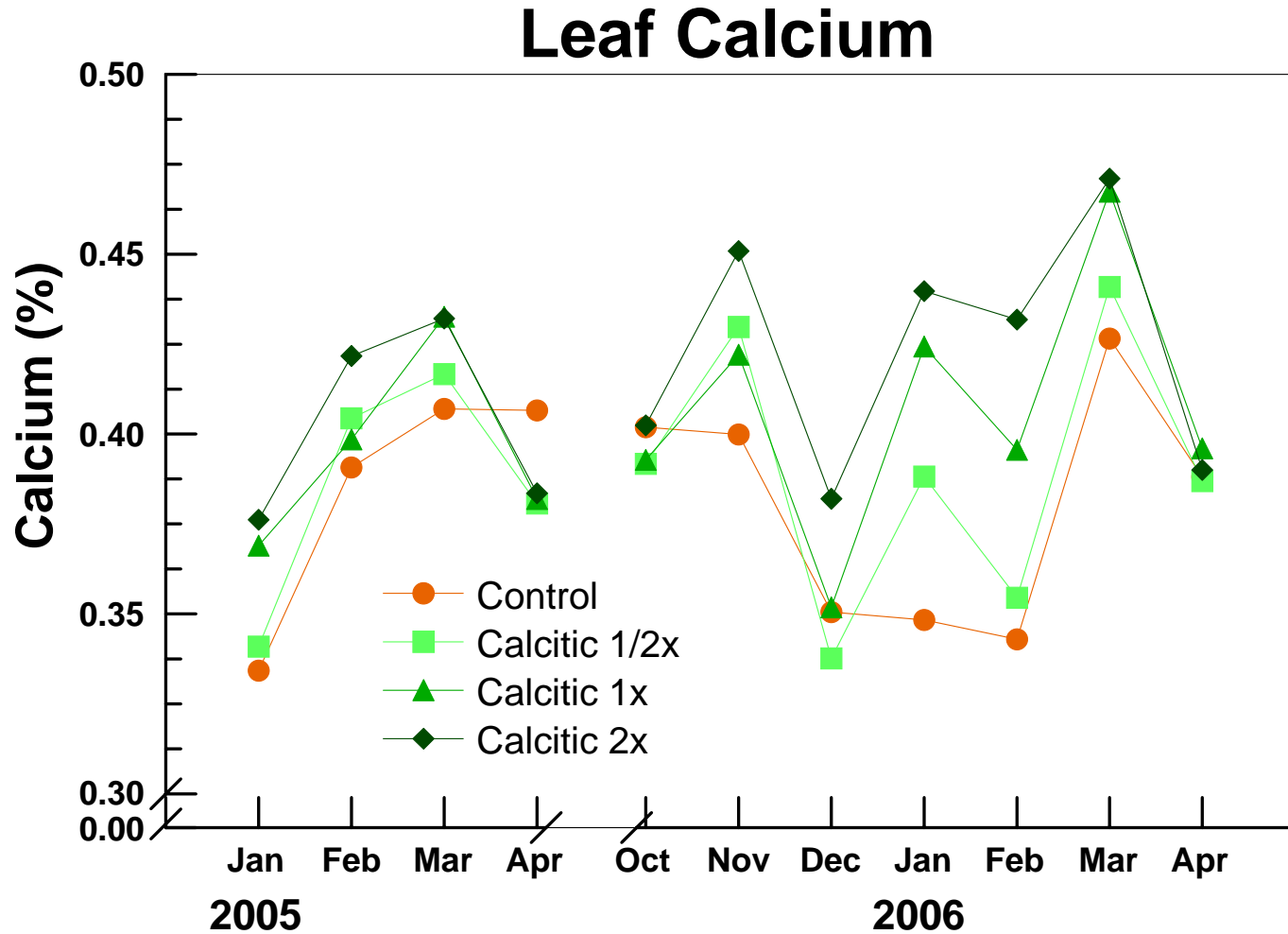


Figure 2-39. Calcium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.040 for comparing treatments within a month and LSD ($P < 0.05$) = 0.015 for comparing months within the same treatment.

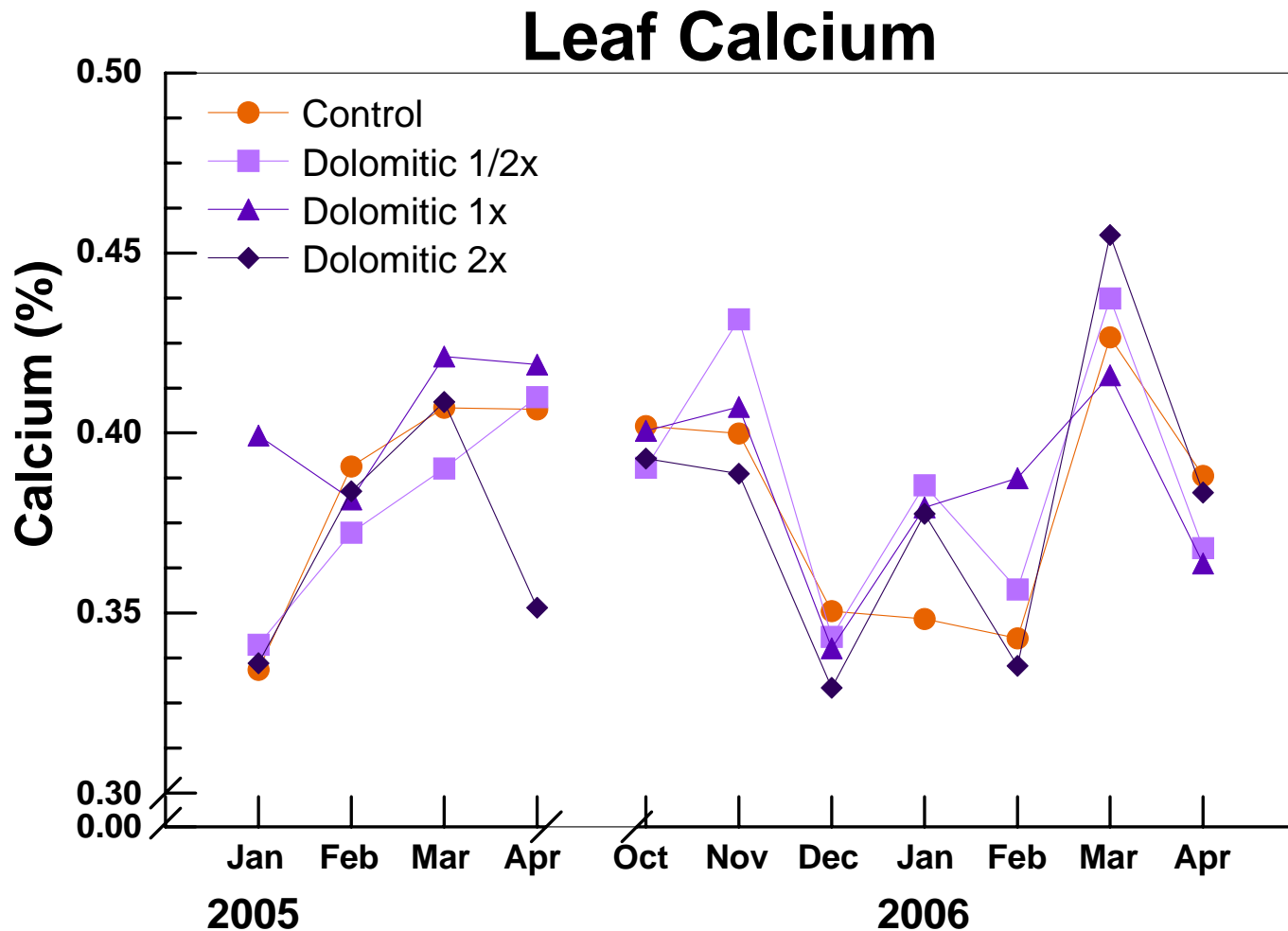


Figure 2-40. Calcium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.040 for comparing treatments within a month and LSD ($P < 0.05$) = .015 for comparing months within the same treatment.

Soil Calcium

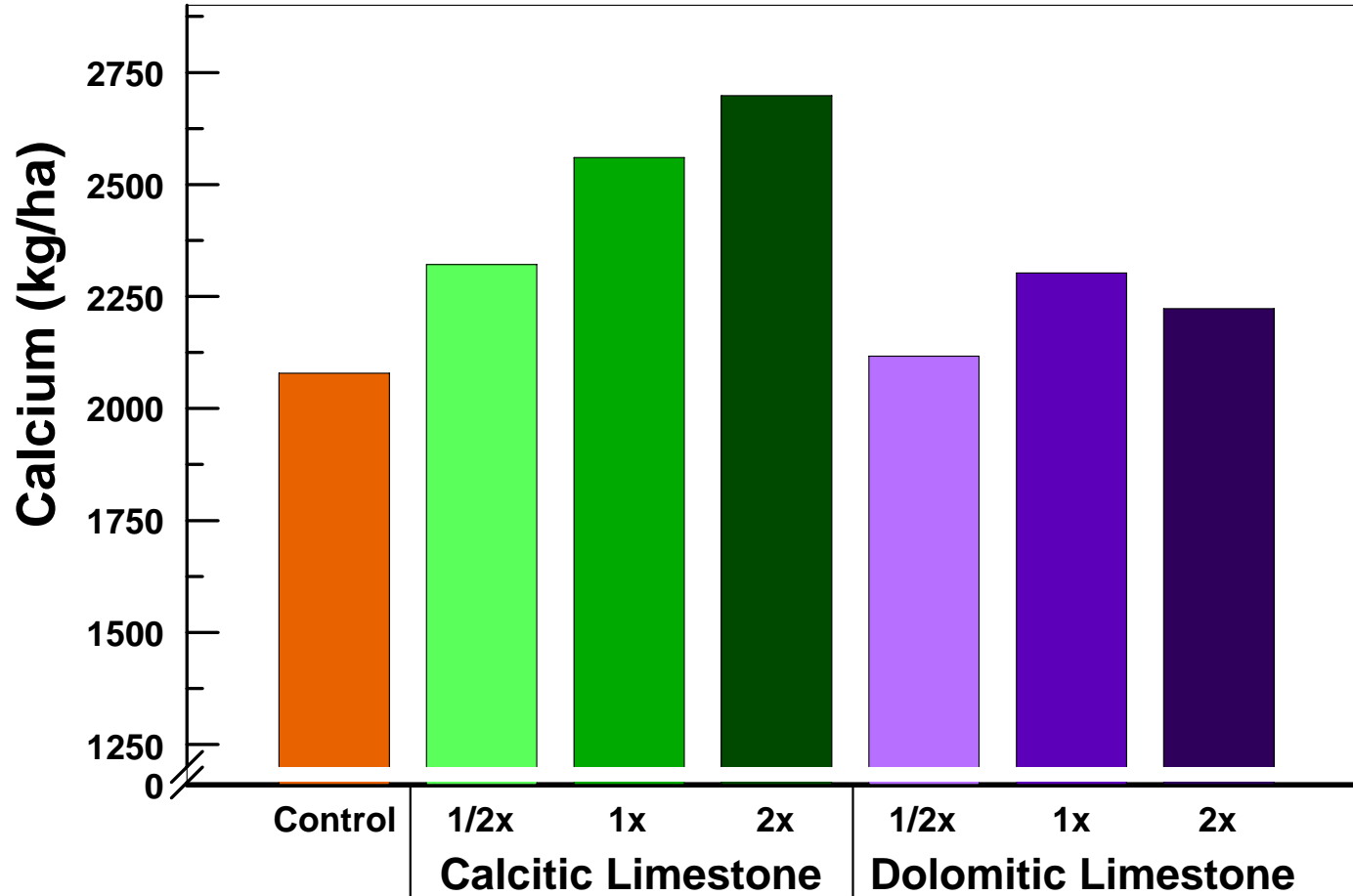


Figure 2-41. Soil calcium concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 264.42 for comparing treatments.

Soil Calcium

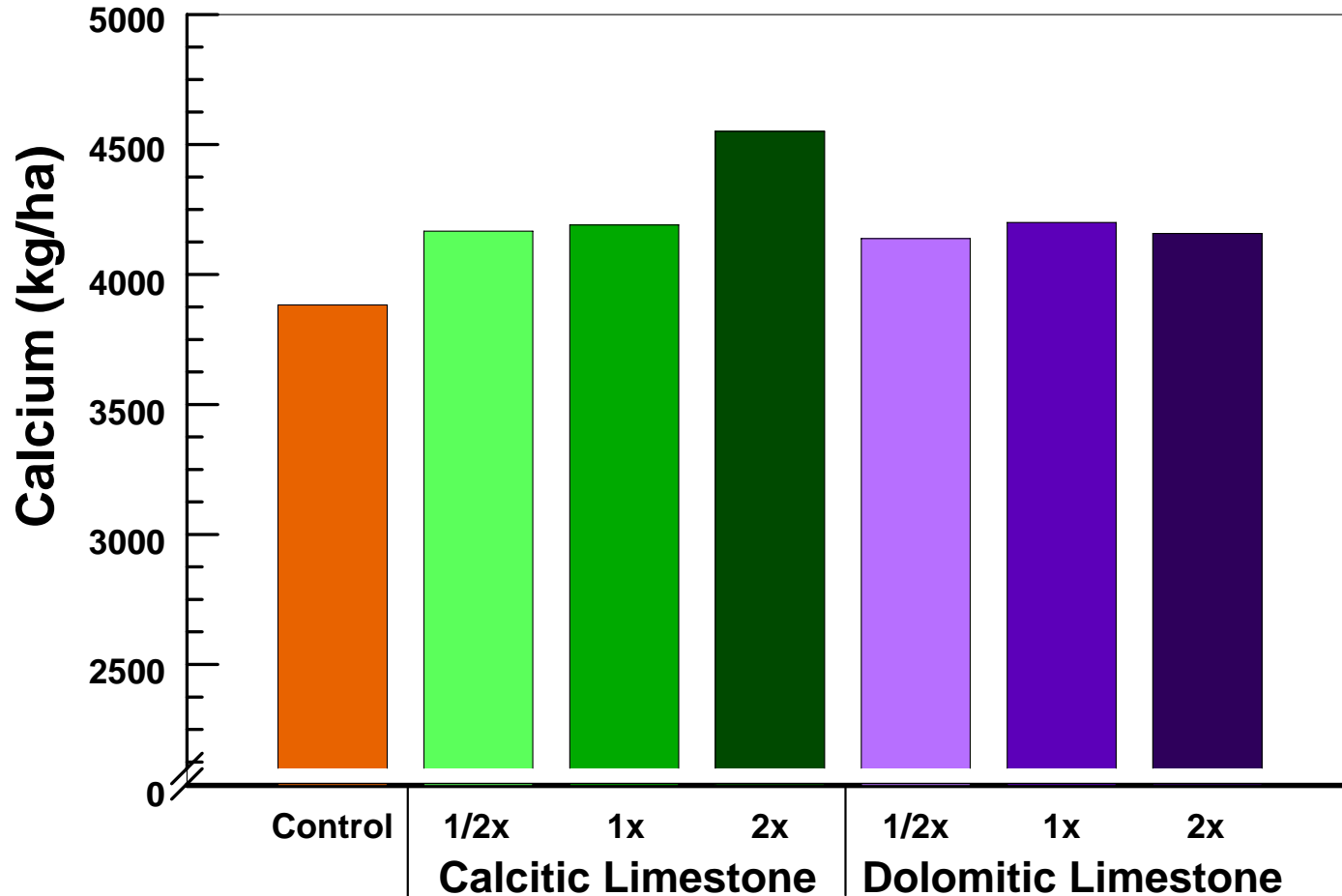


Figure 2-42. Soil calcium concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 314.09 for comparing treatments.

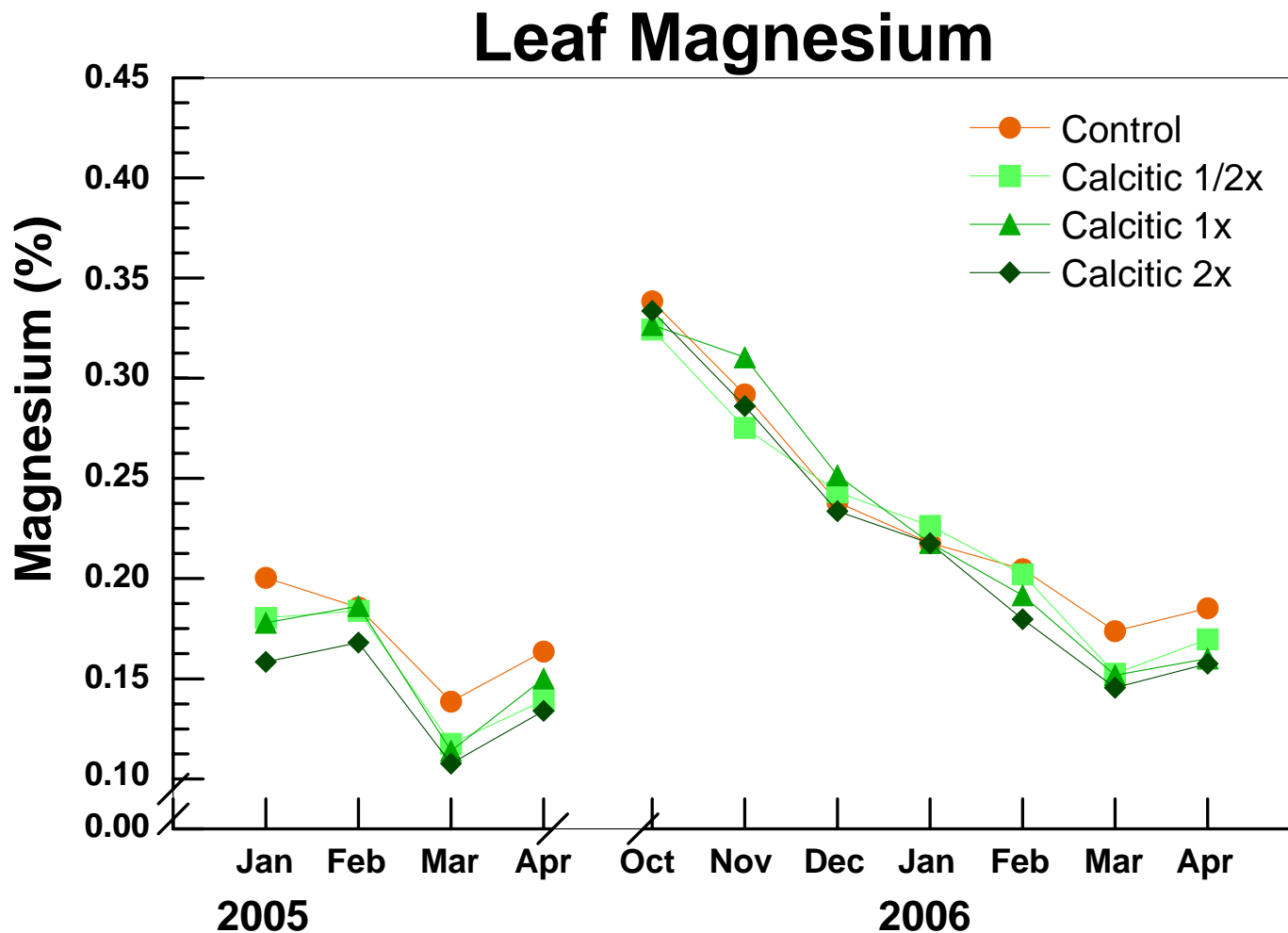


Figure 2-43. Magnesium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.021 for comparing treatments within a month and LSD ($P < 0.05$) = 0.007 for comparing months within the same treatment.

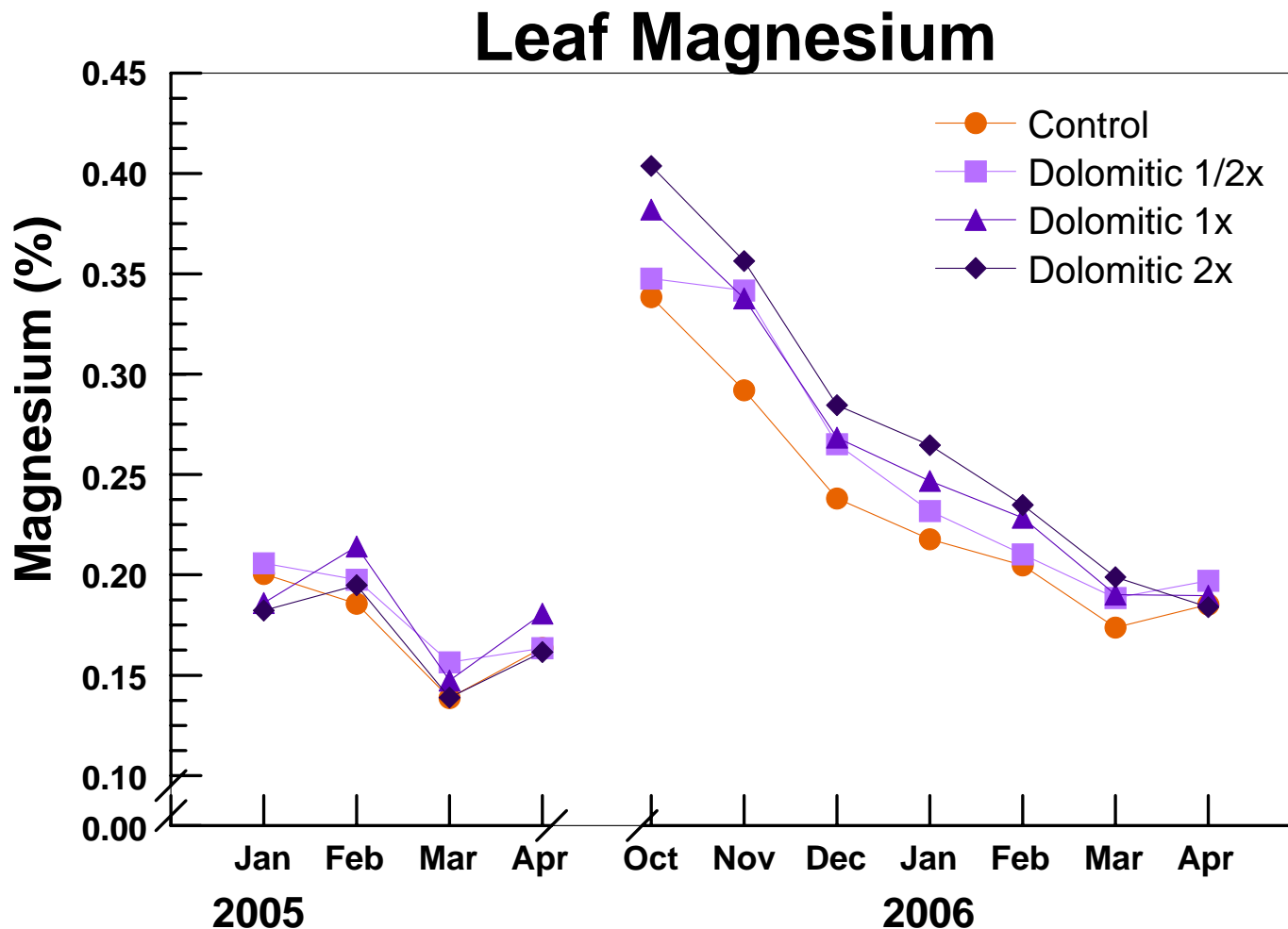


Figure 2-44. Magnesium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.021 for comparing treatments within a month and LSD ($P < 0.05$) = 0.007 for comparing months within the same treatment.

Leaf Magnesium

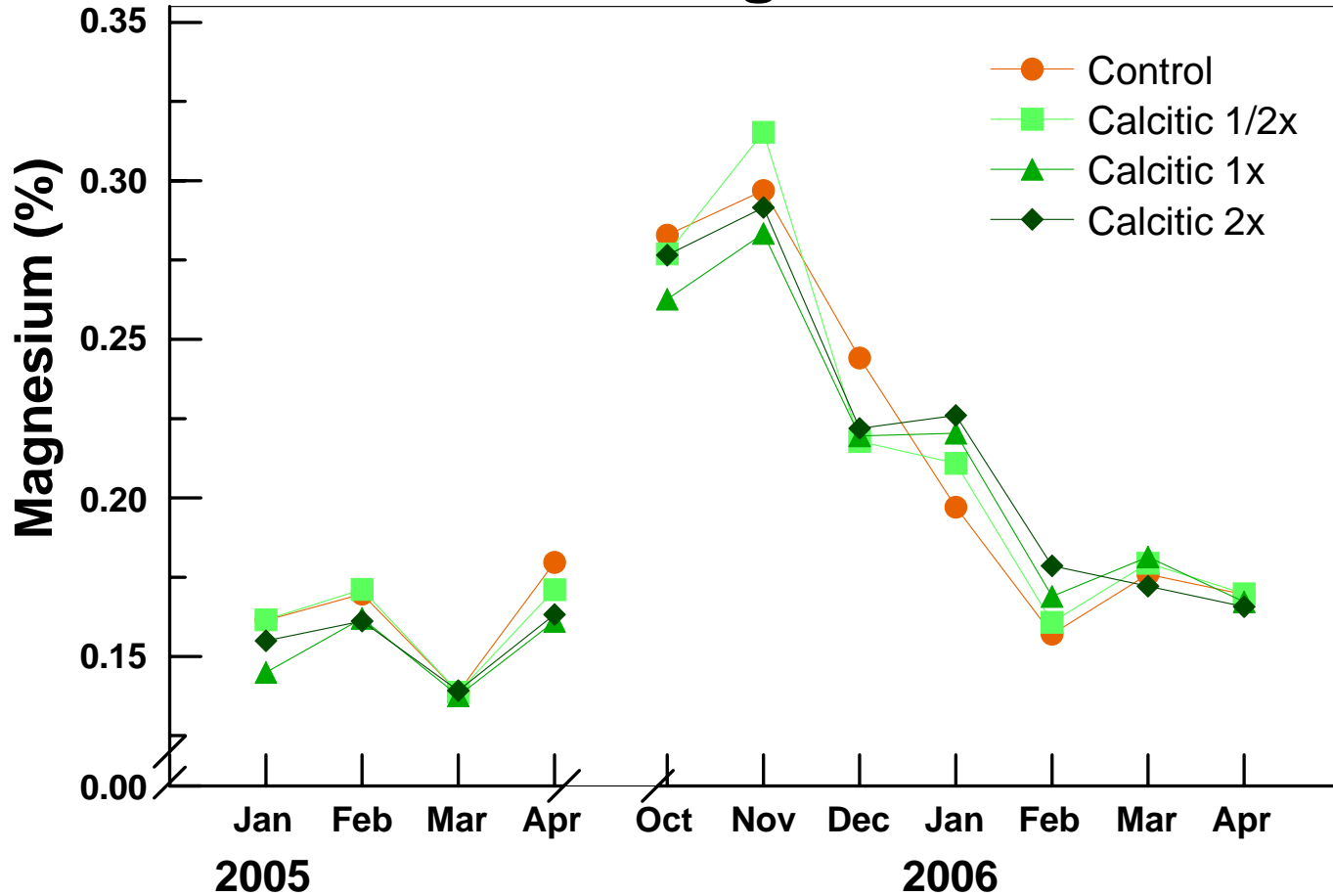


Figure 2-45. Magnesium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.023 for comparing treatments within a month and LSD ($P < 0.05$) = 0.008 for comparing months within the same treatment.

Leaf Magnesium

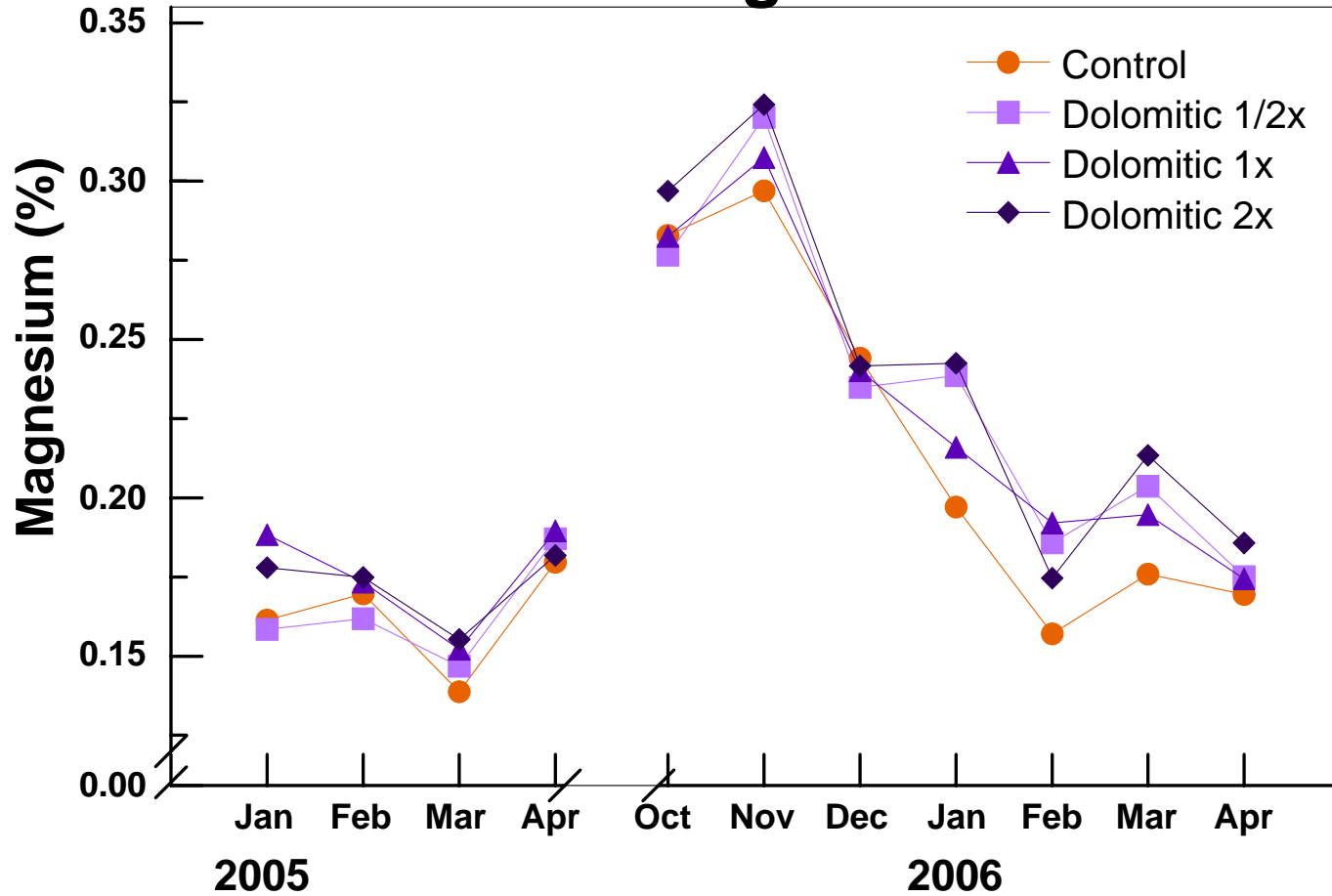


Figure 2-46. Magnesium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.023 for comparing treatments within a month and LSD ($P < 0.05$) = 0.008 for comparing months within the same treatment.

Soil Magnesium

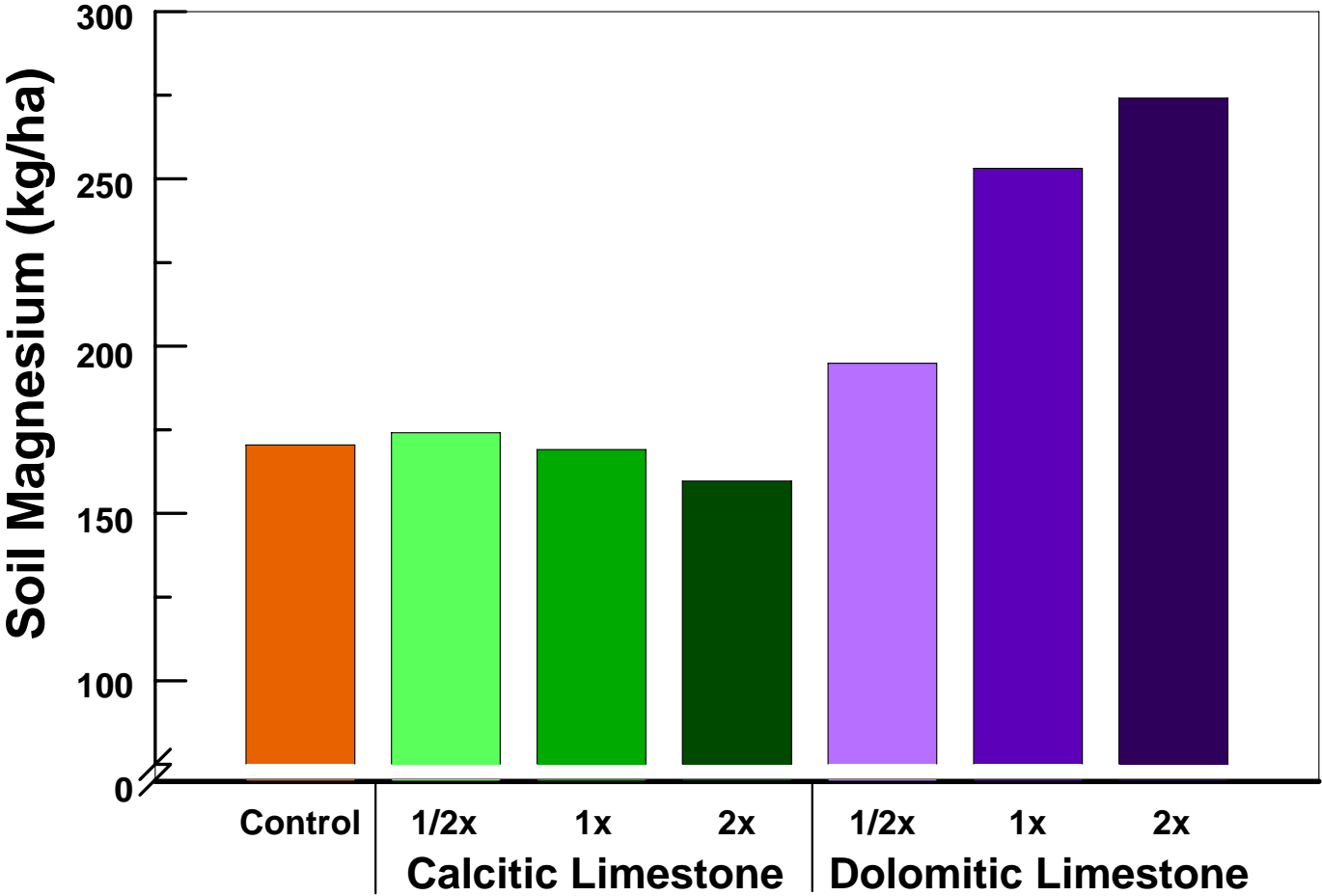


Figure 2-47. Soil magnesium concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P<0.05$) = 31.21 for comparing treatments.

Soil Magnesium

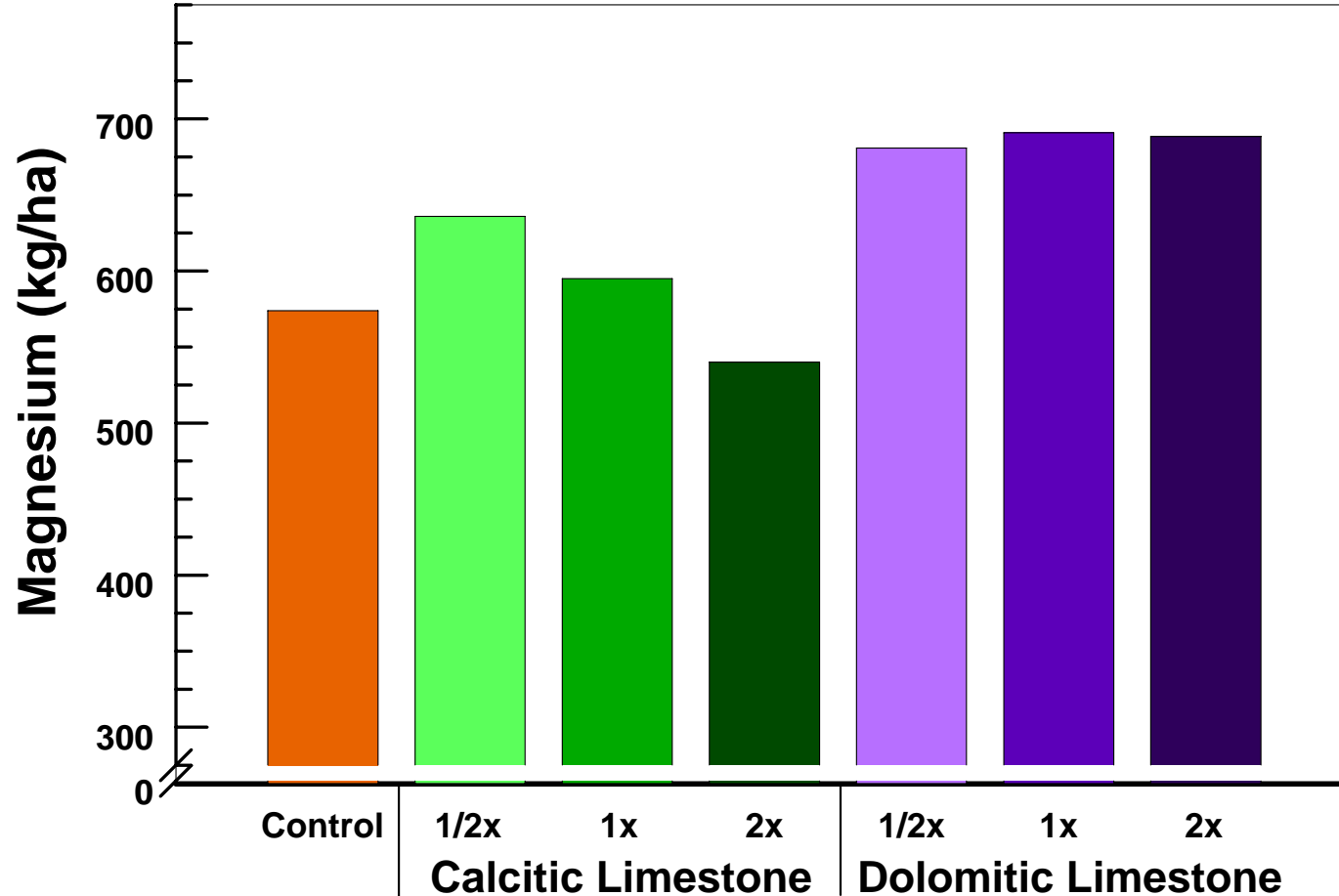


Figure 2-48. Soil magnesium concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 68.89 for comparing treatments.

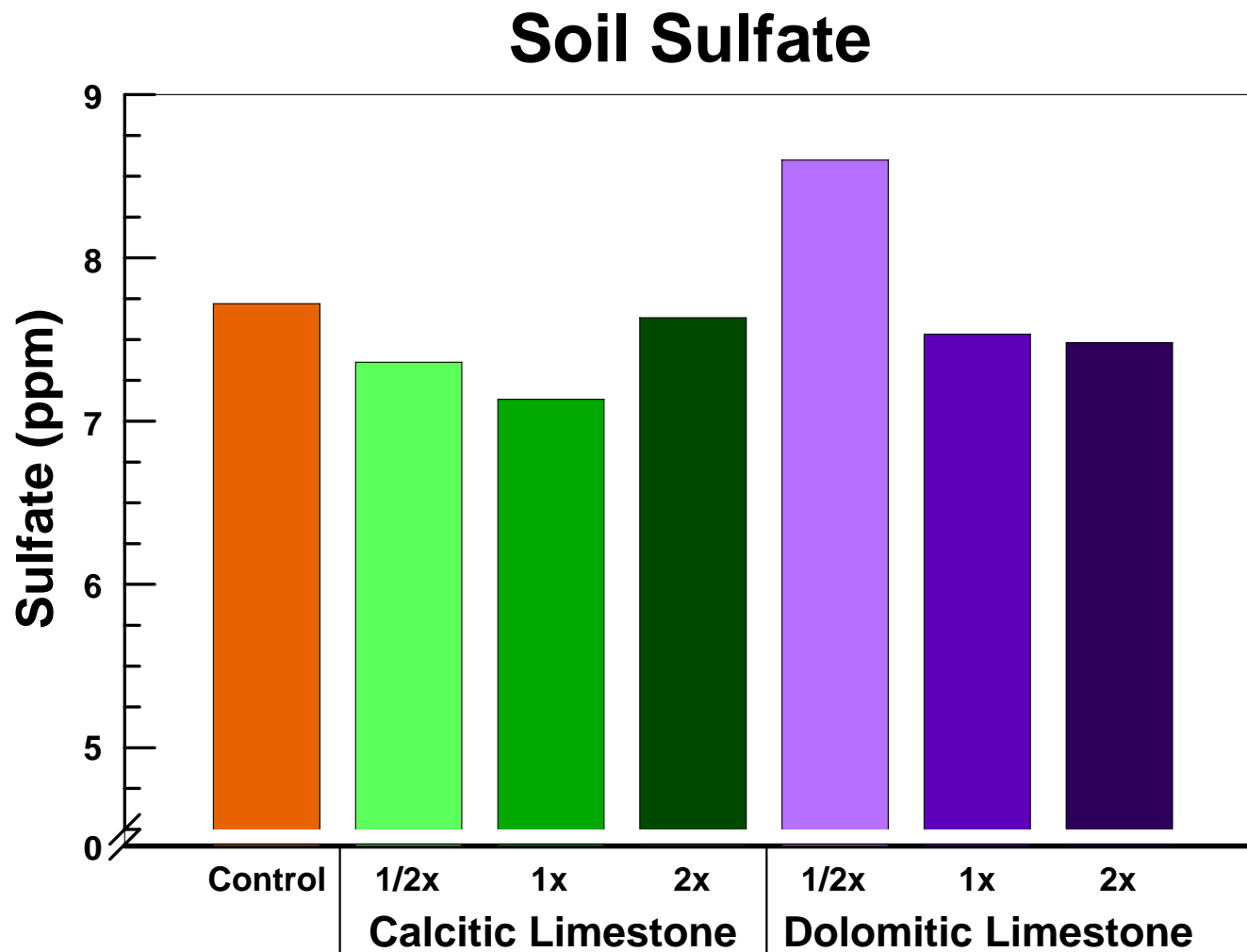


Figure 2-49. Soil sulfate concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 1.10 for comparing treatments.

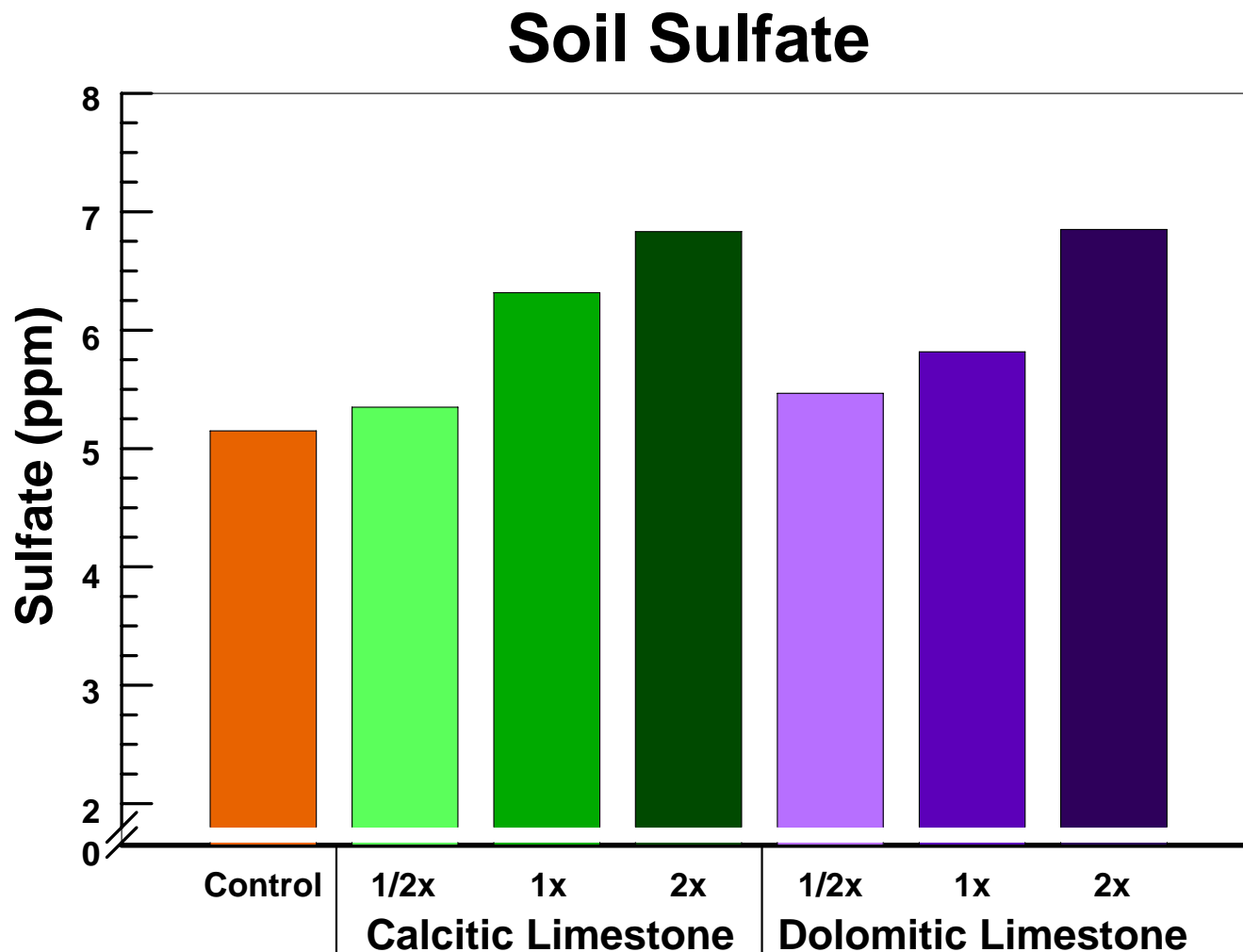


Figure 2-50. Soil sulfate concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 1.08 for comparing treatments.

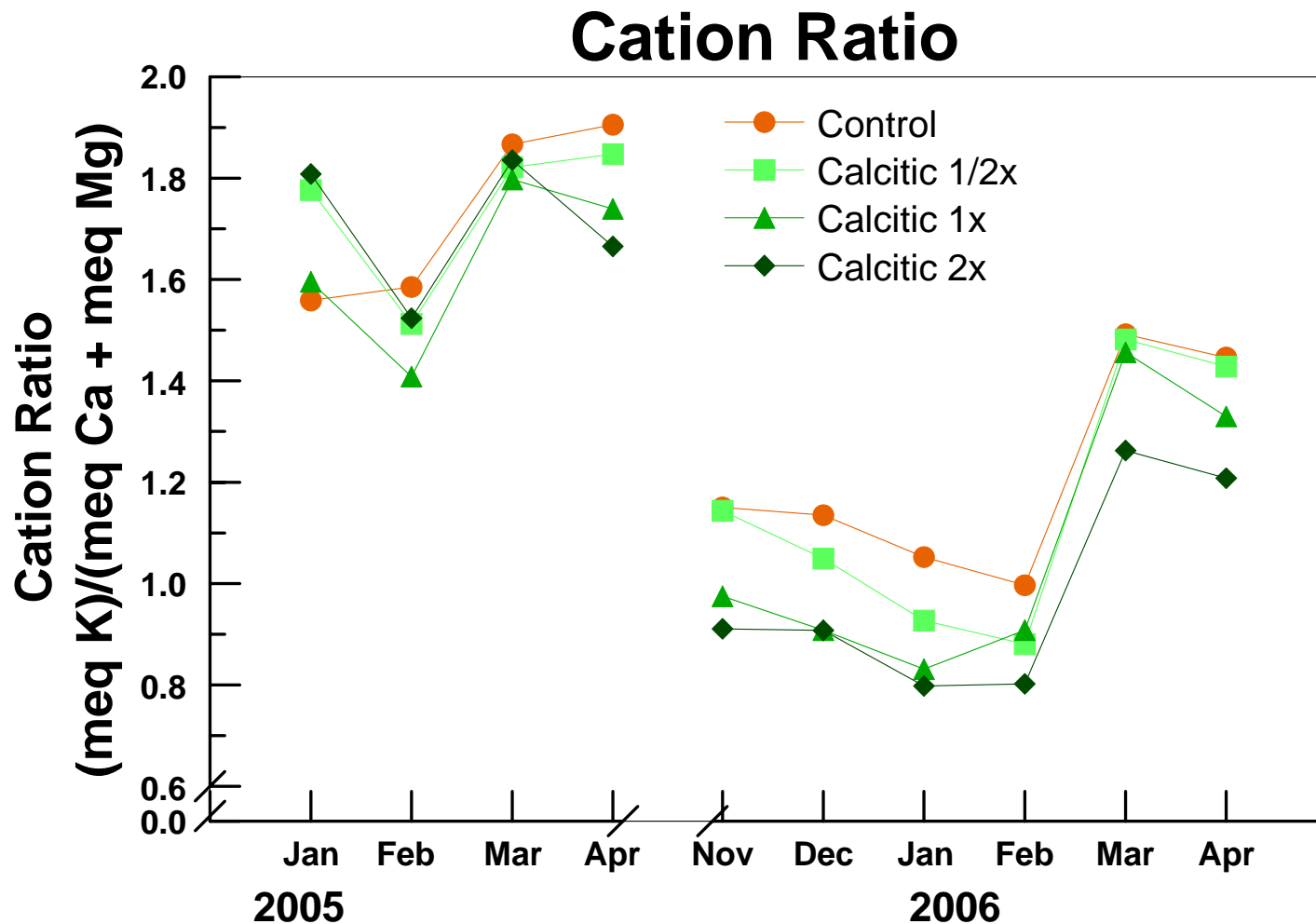


Figure 2-51. Cation ratio of stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means.

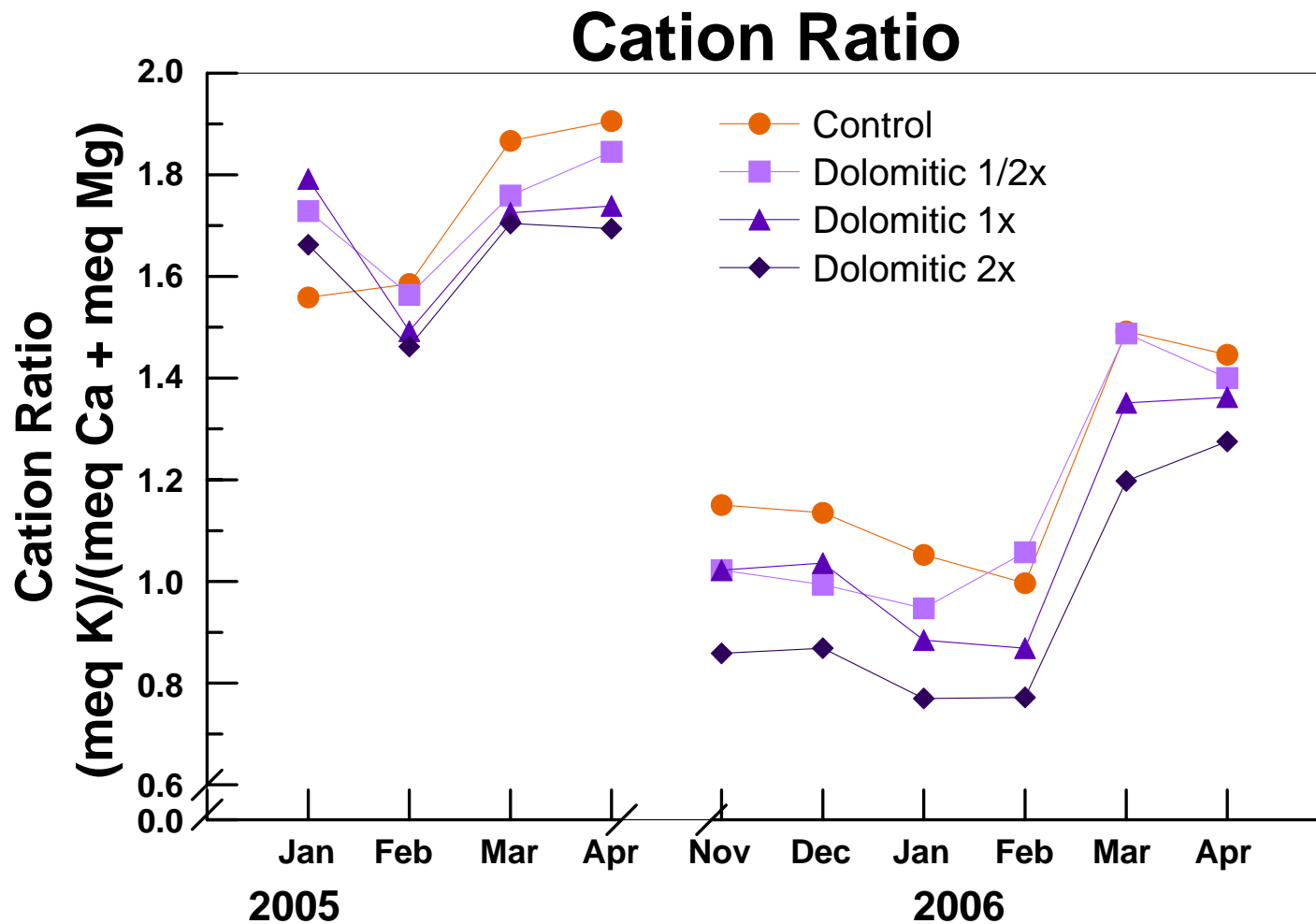


Figure 2-52. Cation ratio of stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means.

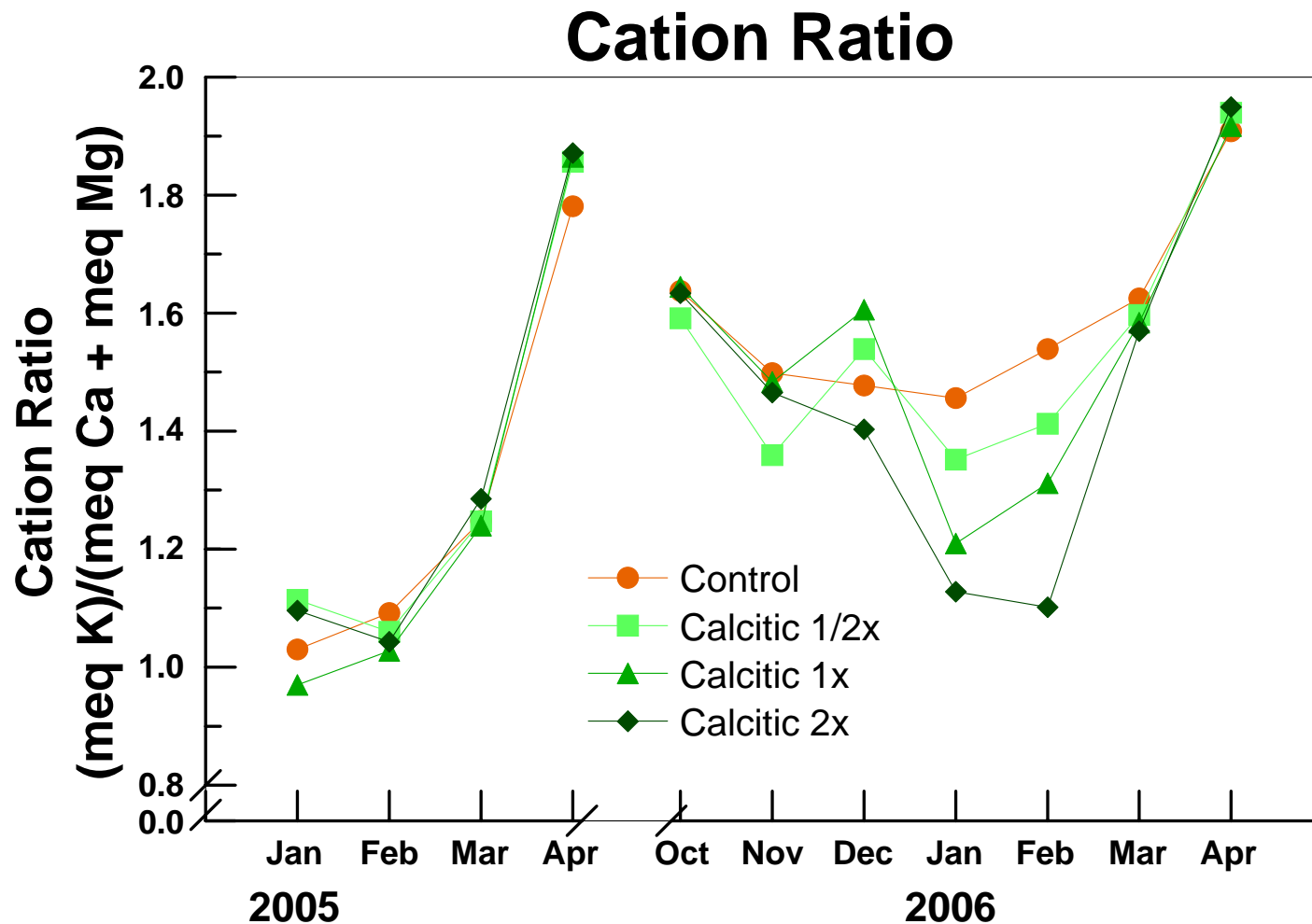


Figure 2-53. Cation ratio of stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means.

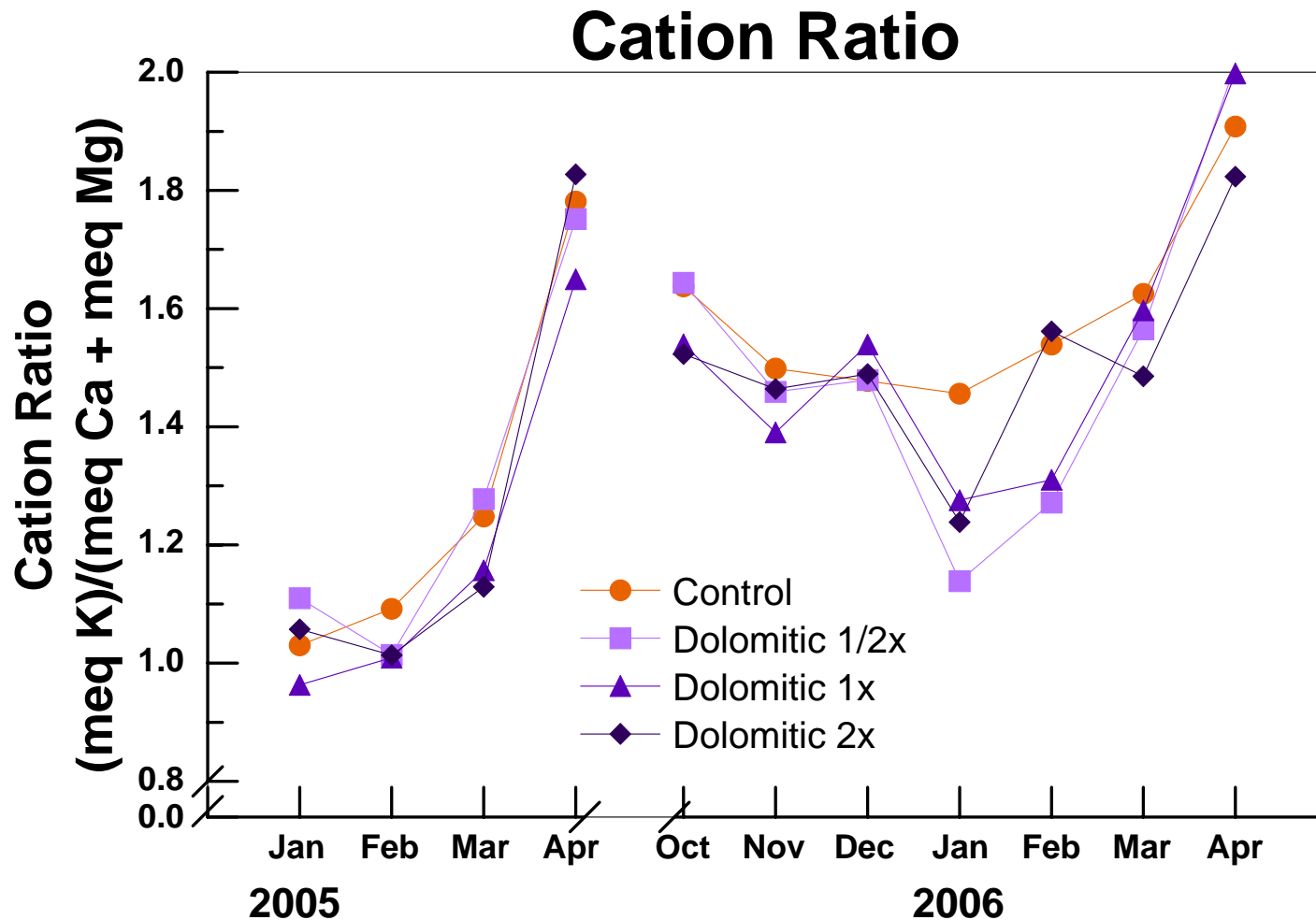


Figure 2-54. Cation ratio of stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means.

pH_{CaCl2}		5.00
Neutralizable Acidity	meq/100g	5.00
Organic Matter	%	2.30
Cation Exchange Capacity	meq/100 g	11.13
Bray I P	kg/ha	31.00
Bray 2 P	kg/ha	128.0
Ca	kg/ha	2121
Mg	kg/ha	162.7
K	kg/ha	120.7
Na	kg/ha	81.10
SO4-S	ppm	7.97
Zn	ppm	0.63
Fe	ppm	57.10
Mn	ppm	43.77
Cu	ppm	1.28

Table 2-1: Initial soil test from SWC

pH_{CaCl2}		5.09
Neutralizable Acidity	meq/100g	5.75
Organic Matter	%	3.08
Cation Exchange Capacity	meq/100 g	18.20
Bray I P	kg/ha	19.23
Bray 2 P	kg/ha	77.28
Ca	kg/ha	4301
Mg	kg/ha	689.7
K	kg/ha	247.1
Na	kg/ha	100.1
SO4-S	ppm	7.32
Zn	ppm	0.85
Fe	ppm	56.85
Mn	ppm	39.03
Cu	ppm	1.66

Table 2-2: Initial soil test from BREC

CHAPTER 3

Liming Stockpiled Tall Fescue Growing on Acidic Soils Altered the Micro- and Beneficial Nutrient Concentrations of Leaves

Synopsis

Many soils in Missouri are inherently acidic and possess little plant available phosphorus (P). Much of the state's forage production occurs on these soils, and tall fescue (*Festuca arundinacea* Schreb.) is the dominant forage growing on them. Little is known about the effects of lime, an amendment that increases pH and adds Ca/Mg, on the micro- and beneficial nutrient composition of stockpiled tall fescue. Many people have predicted that liming will reduce aluminum (Al) toxicity problems in the types of soils used in this study.

Sites were chosen at the University of Missouri Southwest Center (SWC) and the University of Missouri Bradford Research and Extension Center (BREC). Calcitic and dolomitic limestone were applied at 0x, 1/2x, 1x and 2x the recommended soil test rate. Tall fescue leaves were harvested several times throughout the stockpiling season, dried, ground, digested, and analyzed. Soil samples were also collected and analyzed.

Leaf manganese (Mn) concentrations decreased by more than 50% and leaf molybdenum (Mo) increased within three months of lime applications at both sites. At SWC, leaf boron (B) concentrations were decreased following liming, but the 2x treatments of limestone increased leaf sodium (Na) concentrations. Lime had little influence on leaf Al, iron (Fe), zinc (Zn), and copper (Cu) concentrations.

For the most part, leaf concentrations of the elements mirrored the soil test concentrations. Extractable soil Mn decreased with increasing rates of limestone, and an increasing trend was observed for exchangeable soil Na. Extractable soil Zn, Cu, and Fe showed little effect of limestone application.

Liming two acidic Missouri soils changed many soil chemical properties and consequently the concentrations of macro-, micro-, and beneficial nutrients in stockpiled tall fescue leaves.

Introduction

Soil pH is considered the master variable in soils because of its effects on physical, biological, and chemical properties. Soil acidity, affects 40% to 70% of the world's arable land (Rengel 2003) and over half of Missouri's soils (Nathan 1995). Soil acidity is a naturally occurring phenomenon that is augmented by human activities. The plant availability of many elements is affected by soil pH. Some elements decrease in availability while others, such as Al, Mn, and Fe, may become available in such large concentrations under increasing acidity that toxicity may become a problem (Adams 1984). Liming is a common agricultural practice used to decrease soil acidity, decrease the plant availability of toxic elements, and ameliorate the negative effects of soil acidity on plant growth.

Tall fescue is a forage grass tolerant of soil acidity and large concentrations of associated toxic elements (Belesky and West 2005). The objective of this study was to determine the effects of calcitic and dolomitic limestone on elemental concentrations in leaves of stockpiled tall fescue growing on acids soil in southwest and central Missouri.

Materials and Methods

This study was initiated at two sites in October 2004 on established Kentucky 31 tall fescue pastures. The first site was at the University of Missouri Southwest Research Center (SWC) near Mt. Vernon, Missouri (37° 04' N 93° 53' W; elevation

350 m) on a Gerald silt loam (fine, mixed, active, mesic Aeric Fragiaqualf). The second site was at the University of Missouri Bradford Research and Extension Center (BREC) near Columbia, Missouri (38° 30' N 92° 06' W; elevation 270 m) where the underlying soils are the Leonard silt loam (fine, smectitic, mesic Vertic Epiaqualf) and the Mexico silt loam (fine, smectitic, mesic Aeric Vertic Epiaqualf). Sites were selected for acid soil pH values and small Bray I P values. Soil samples were taken for complete analysis (Tables 2-1 and 2-2). Forage was removed from the areas, and 3 x 7.6 m plots with 3 m alleys were flagged. At each location, a treatment was randomly applied to one plot in all six blocks, totaling six plots per treatment per site. Treatments of dolomitic and calcitic limestone were applied at 0, ½, 1, and 2 times the recommended rate as determined by Woodruff Buffer. At SWC, dolomitic limestone was applied at 4,320 kg/ha and calcitic limestone at 4,838 kg/ha for the 1x treatment; at BREC, rates were 4,888 kg dolomitic limestone/ha and 4,354 kg calcitic limestone/ha. At SWC, plots received 112 kg N/ha, 73 kg P₂O₅/ha and 258 kg K₂O/ha in fall 2004, and in April 2005, plots at BREC received 118 kg P₂O₅/ha and 280 kg K₂O/ha, all according to University of Missouri Soil Testing Laboratory recommendations. In the fall of 2005, plots at both sites received 112 kg N/ha.

In May and August of 2005 and 2006, forage was removed from the plots at both sites and weighed to determine forage yield; subsamples were taken for dry weight measurements. Monthly, starting in January 2005 and continuing through April 2005 then beginning again in October 2005 and ending in April 2006, twenty of the most recently collared leaves were removed from each plot at both BREC and

SWC for elemental analyses. Leaves were dried, ground, and digested in nitric acid with a microwave accelerated digestion system. Samples were then filtered and brought to volume. Elemental concentrations in the leaf samples were measured via ICP-OES (Varian Inc., USA).

Soil was sampled again in May 2006 and analyzed by the University of Missouri Soil Testing Laboratory. Exchangeable Na was determined by extraction with ammonium acetate, and extractable Zn, Fe, Mn, and Cu were extracted with DPTA. All of these soil test procedures are described in depth by Nathan et al. (2006).

The experiment was randomized complete block design analyzed as a split plot in time model with six replicate blocks. The main plot consisted of treatment (lime) while harvest date (month) was considered the split plot; both were considered fixed effect factors, and block was a random factor. This model was used to test for statistical significance of treatment effects as well as interactions with harvest date using PROC MIXED in SAS version 9.1 (SAS Institute). All effects and interactions were considered significant when $P < 0.05$. When F test showed significance ($P < 0.05$), means were separated using Fisher's protected LSD ($\alpha = 0.05$).

Results and Discussion

Aluminum

In the 2005-2006 harvest season, Al concentrations in tall fescue leaves generally increased through the winter at both SWC and BREC (Figures 3-1, 3-2, 3-

3, and 3-4). Neither dolomitic nor calcitic limestone appeared to have an effect on tissue Al concentrations at either site.

Following liming, soil pH increased (Chapter 2) indicating that the solubility of Al^{3+} , the dominant phytotoxic species of Al, lessened. However, Foy (1984) suggests that Al toxicity may not be a large factor limiting plant growth above pH 5.0; this may explain the lack of response of leaf Al concentrations to lime treatments. Additionally, large concentrations of Al in subsurface horizons, which are not affected by surface applied limestone, may ensure a continued supply of phytoavailable Al following liming. Others have also observed no effect of lime on tissue Al concentrations of alfalfa (John et al. 1972).

Manganese

Leaf Mn concentrations increased through late fall and early winter, then decreased into spring (Figures 3-5, 3-6, 3-7, and 3-8). This seasonal leaf Mn pattern was especially pronounced in control plots. Within three months of application, both dolomitic and calcitic limestone decreased leaf Mn concentrations substantially at both locations. The first 1/2x increment of limestone showed the largest decrease in leaf Mn concentrations per unit of limestone, but the 1x and 2x treatments continued to decrease the Mn concentrations in tall fescue leaves. At both locations, soil Mn levels appeared to decrease with both limestone sources, but only the decrease at SWC was significant (Figures 3-9 and 3-10).

Others have also observed that liming decreased soil Mn^{2+} concentrations (Willis 1928, Jackson and Reisenauer 1984, Holford et al. 1994, Mullen et al. 2006) because soil solution Mn is very responsive to pH changes. One unit increase in pH

can decrease Mn^{2+} concentrations 100-fold (Lindsay 1972). Others have shown that the lime-induced pH increase coupled with the addition of Ca, which, by itself, decreases leaf Mn concentrations, result in smaller plant Mn concentrations following liming (Willis 1928, John et al. 1972, Edmeades et al. 1983, Stevens and Laughlin 1996, Wheeler 1998).

In addition to low pH, low redox potentials promote the Mn^{2+} species, but below pH 5.0, redox potential has little influence on Mn species (Moraghan and Mascagni 1991). Gotoh and Patrick (1972) observed that under increasing anaerobiasis, soils with a low pH quickly changed Mn oxides to water soluble and exchangeable Mn^{2+} , whereas much smaller changes were seen in soils with higher pH values. At both study sites, water movement is restricted. The Gerald silt loam at SWC has a fragipan while at BREC water movement in the Mexico and Leonard silt loams is restricted by a claypan. In both cases, temporary anaerobic conditions may exist, catalyzing the formation of Mn^{2+} under the more acidic conditions of unlimed plots.

Boron

At SWC, increasing rates of limestone decreased leaf B concentrations, especially in spring 2005 and winter 2006 (Figures 3-11 and 3-12). Others have described decreased concentrations of B in plants following liming (Peterson and Newman 1976, Adams 1984, Lathwell and Reid 1984) owing to the increasing pH and Ca concentrations, which together appear to decrease B uptake (Cook and Millar 1939, Fox 1968). Liming also results in less plant available B because larger

amounts of soil B become sorbed, therefore less B is in solution (Harter 1991, Moraghan and Mascagni 1991).

Molybdenum

Lime had a large impact on Mo concentrations in tall fescue leaves; concentrations were increased with increasing lime application rates at both locations (Figures 3-13, 3-14, 3-15, and 3-16). Calcitic limestone had larger effects on leaf Mo concentrations than dolomitic limestone. The impact of liming on leaf Mo concentration was visible within three months of limestone application at SWC, and the difference between the control and lime treatments was most pronounced in January through April 2005. At BREC, the increase in leaf Mo concentration as a result of liming was most obvious from October 2005 to April 2006.

As with Mn, Mo species in soils are greatly affected by pH, and every one unit increase in pH results in MoO_4^{2-} concentrations increasing 100-fold (Lindsay 1972). This is a result of the decreasing number of negative charges in the Fe/Al oxides (Gupta and Lipsett 1981) and the decrease in HMoO_4^- , the preferentially adsorbed Mo species (Harter 1991). Additionally, the solubility of precipitated molybdates increases with pH (Lindsay 1991). Together, these factors increase solution Mo following liming, thus increasing plant Mo concentrations (Reith and Mitchell 1964, Reith 1970, John et al. 1972, Edmeades et al. 1983, Wheeler 1998).

Sodium

At SWC, lime increased Na concentrations in leaves of tall fescue that received the 2x treatments of both dolomitic and calcitic limestone; no other treatment caused a consistent change in leaf Na concentrations (Figures 3-17 and

3-18). Lime had no effect on Na concentrations at BREC (Figures 3-19 and 3-20). The soil Na at SWC showed an increasing trend with limestone application (Figure 3-21), while at BREC there was no consistent effect of lime on soil Na (Figure 3-22).

Edmeades et al. (1983) found an increase in soil Na following liming; however, Na concentrations in plants have not been shown to change with limestone applications (McNaught et al. 1973, Edmeades et al. 1983, Stevens and Laughlin 1996).

Iron, Copper, and Zinc

Leaf Fe exhibited no effect of limestone treatment at either location (Figures 3-23, 3-24, 3-25, and 3-26). At SWC, there was a trend for extractable soil Fe to decrease following limestone applications (Figure 3-27), and at BREC, the trend for soil test Fe was to increase following liming (Figure 3-28). Leaf Cu concentrations showed no impact of liming treatments (Figures 3-29, 3-30, 3-31, and 3-32), and this reflected the paucity of change in extractable soil Cu following liming (Figures 3-33 and 3-34). At both locations, leaf Zn concentrations showed no effect of limestone treatment (Figures 3-35, 3-36, 3-37, and 3-38). Soil Zn decreased following liming at SWC and exhibited a decreasing trend at BREC (Figures 3-39 and 3-40).

Following liming, the concentrations of Fe and Zn usually decrease in soils (Gupta et al. 1971, Adams et al. 1982, Adams 1984) and plants (Miller et al. 1964, Reith and Mitchell 1964, Gupta et al. 1971, John et al. 1972, Adams et al. 1982, Edmeades et al. 1983, Stevens and Laughlin 1996, Wheeler 1998, Rashid et al. 1976, Adams 1984, Hue 2004). Soil Zn and Fe are both very responsive to changes in pH. With increasing pH, solution Zn decreases due to increasing adsorption by

Fe, Al, and Mn oxides and precipitation of Zn compounds (Moraghan and Mascagni 1991). Solution Fe^{3+} and Fe^{2+} also decrease with increasing pH, but the effectiveness of Fe chelates increases (Stevenson and Ardakani 1972).

Complicating the decreased availability of Zn and Fe in the soil following liming, the added Ca and Mg may compete with Zn for uptake by plant roots (Rashid et al. 1976, Moraghan and Mascagni 1991). Furthermore, decreased concentrations of Al and Mn as a result of liming may increase Fe uptake by roots (Foy 1984).

Soil and plant Cu concentrations may decrease (Stevens and Laughlin 1996, Reith and Mitchell 1964, Adams 1984, Hue 2004) or not change (Gupta et al. 1971, Edmeades et al. 1983) as a result of liming. Increasing pH values, as a result of liming, increase adsorption and complexation of Cu (Moraghan and Mascagni 1991). However, Cu availability is closely related to OM transformation, and OM mineralization generally increases with increasing pH (Foy 1984). Lime additionally impacts Cu uptake because hydrogen ions are inhibitory to Cu uptake (Foy 1984), as are Ca^{2+} ions (Kamprath and Foy 1972).

Summary

As lime changes pH and adds Ca and Mg, the dynamics of many elements in the soil change and, consequently, the availability of the elements to plant roots growing in the soil are altered. Plant growth is often increased, as observed in this study (Chapter 2). The lack of change in leaf Al concentrations following liming indicates that Al may not be a large factor limiting growth of tall fescue growing on acid soils in southwest and central Missouri. On the same note, Foy (1984) noted that Al toxicity was only a large factor in soil acidity limiting plant growth below pH

5.0. Soil pH in the present study was initially 5.1 and 5.0 at BREC and SWC, respectively (Chapter 2). Limestone also had very little effect on Fe, Cu, and Zn concentrations in tall fescue leaves and the underlying soils, although liming is often associated with decreases in availability of all of these elements. However, leaf concentrations B decreased at SWC; leaf Mn concentrations decreased by as much as 61% at SWC and 45% at BREC with 2x treatment of calcitic limestone. Leaf Mo concentrations increased with increasing limestone rates.

Limestone is applied with the intent of decreasing soil acidity, but there are also important changes in leaf micronutrient concentrations. Liming has the potential to positively and negatively affect plant health, and consequently, the health of grazing animals may be impacted as well.

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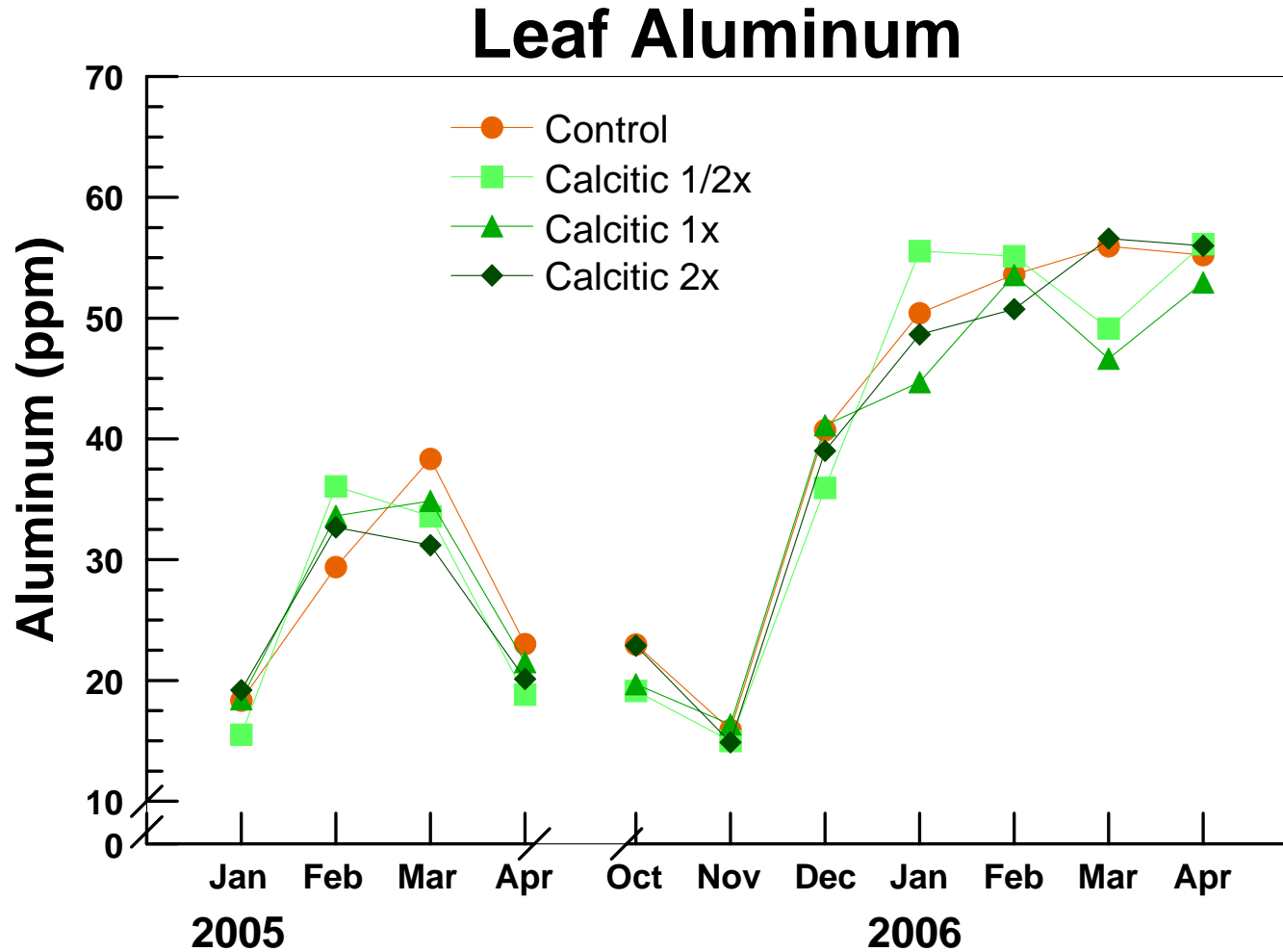


Figure 3-1. Aluminum concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 7.28 for comparing treatments within a month and LSD ($P < 0.05$) = 2.75 for comparing months within the same treatment.

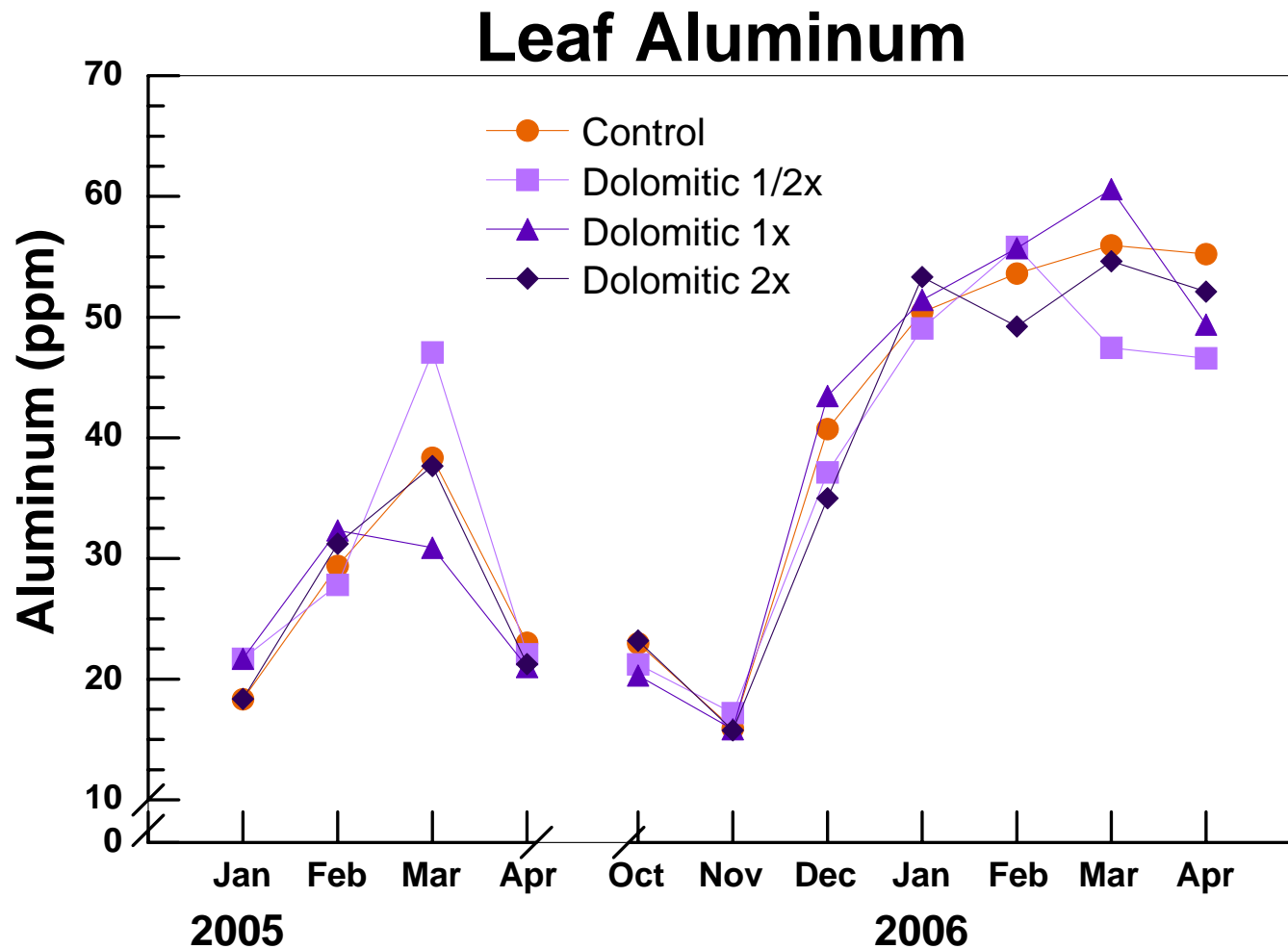


Figure 3-2. Aluminum concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 7.28 for comparing treatments within a month and LSD ($P < 0.05$) = 2.75 for comparing months within the same treatment.

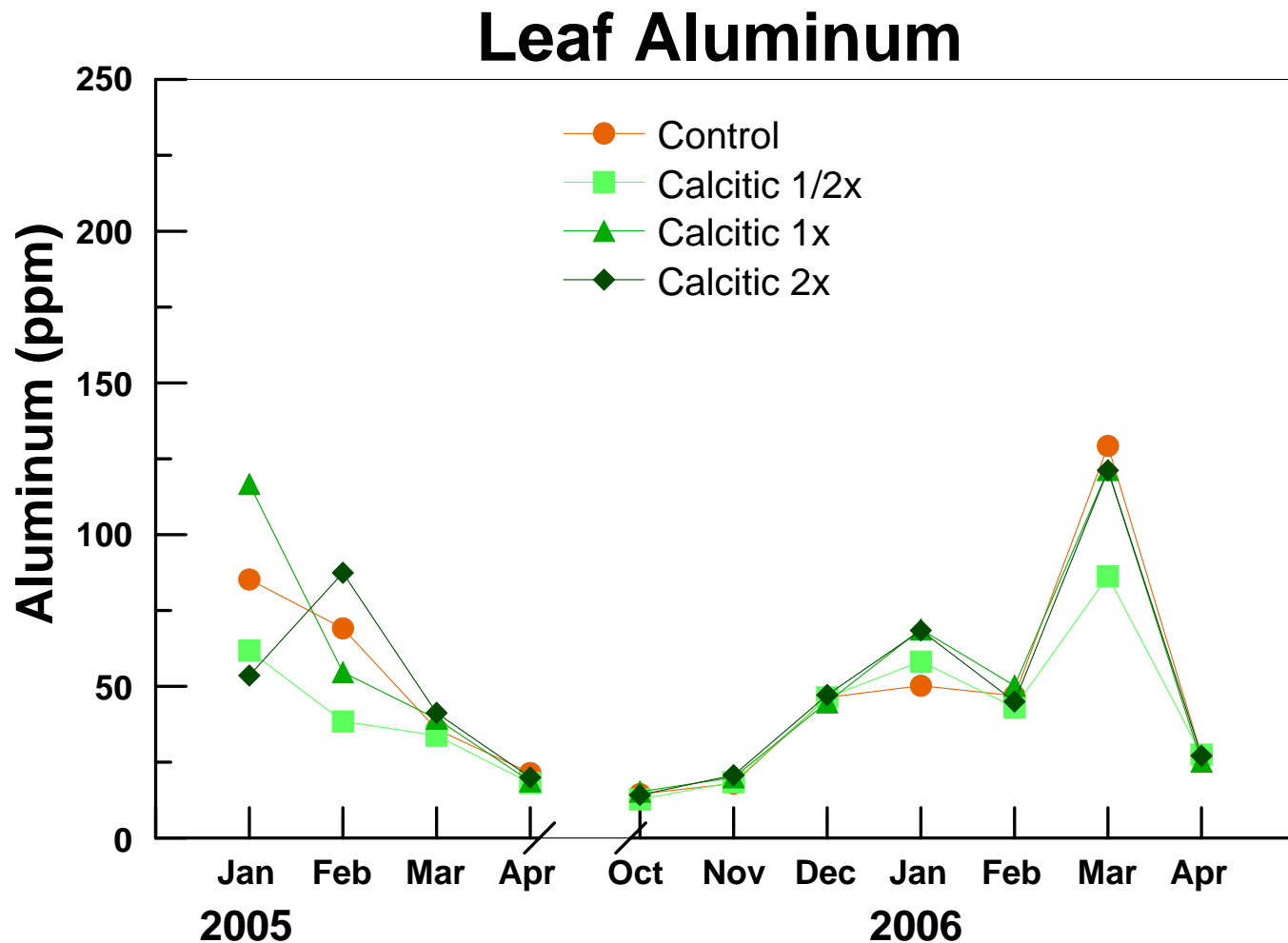


Figure 3-3. Aluminum concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 46.13 for comparing treatments within a month and LSD ($P < 0.05$) = 16.17 for comparing months within the same treatment.

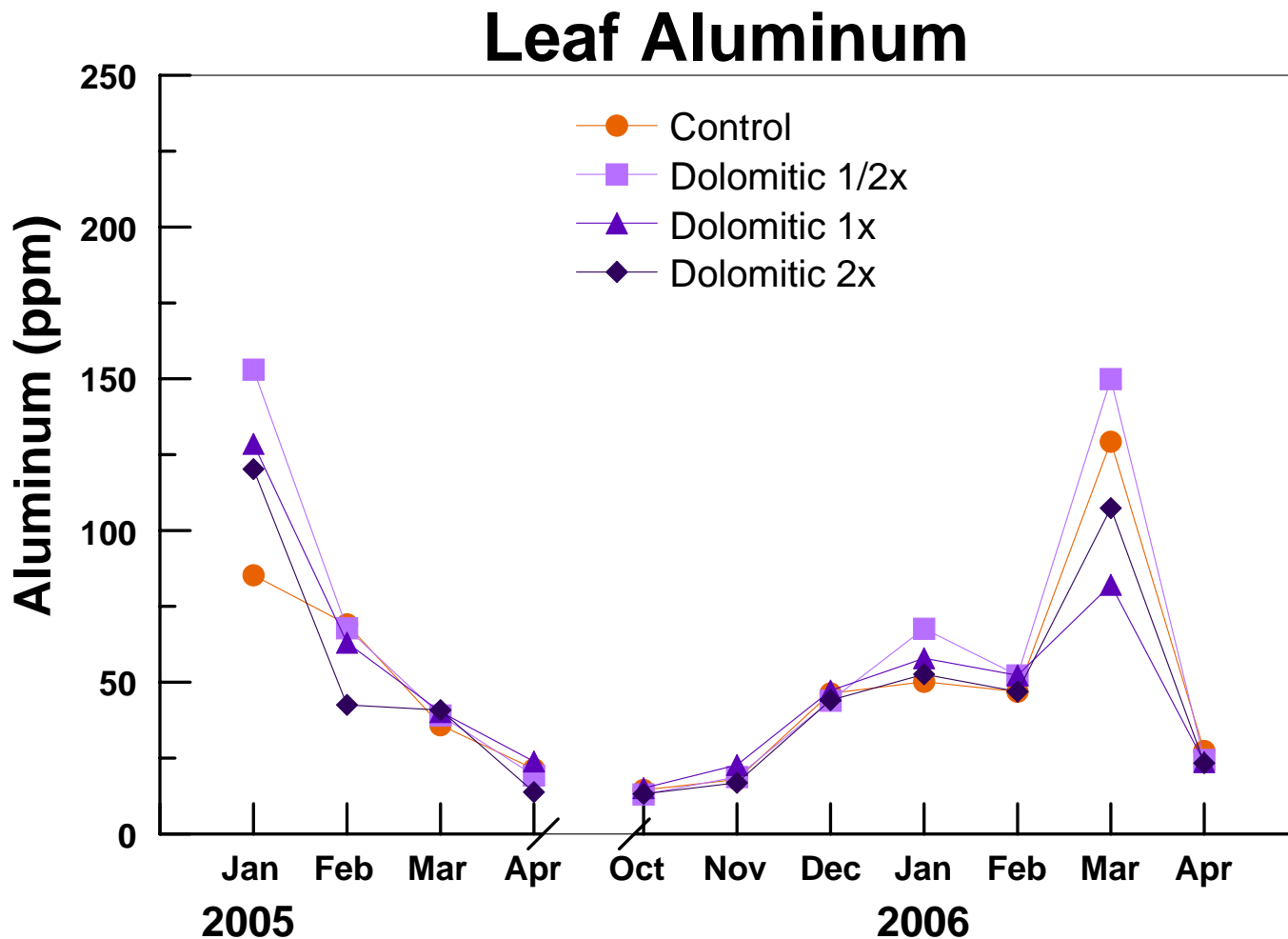


Figure 3-4. Aluminum concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means ($n=6$). LSD ($P<0.05$) = 46.13 for comparing treatments within a month and LSD ($P<0.05$) = 16.17 for comparing months within the same treatment.

Leaf Manganese

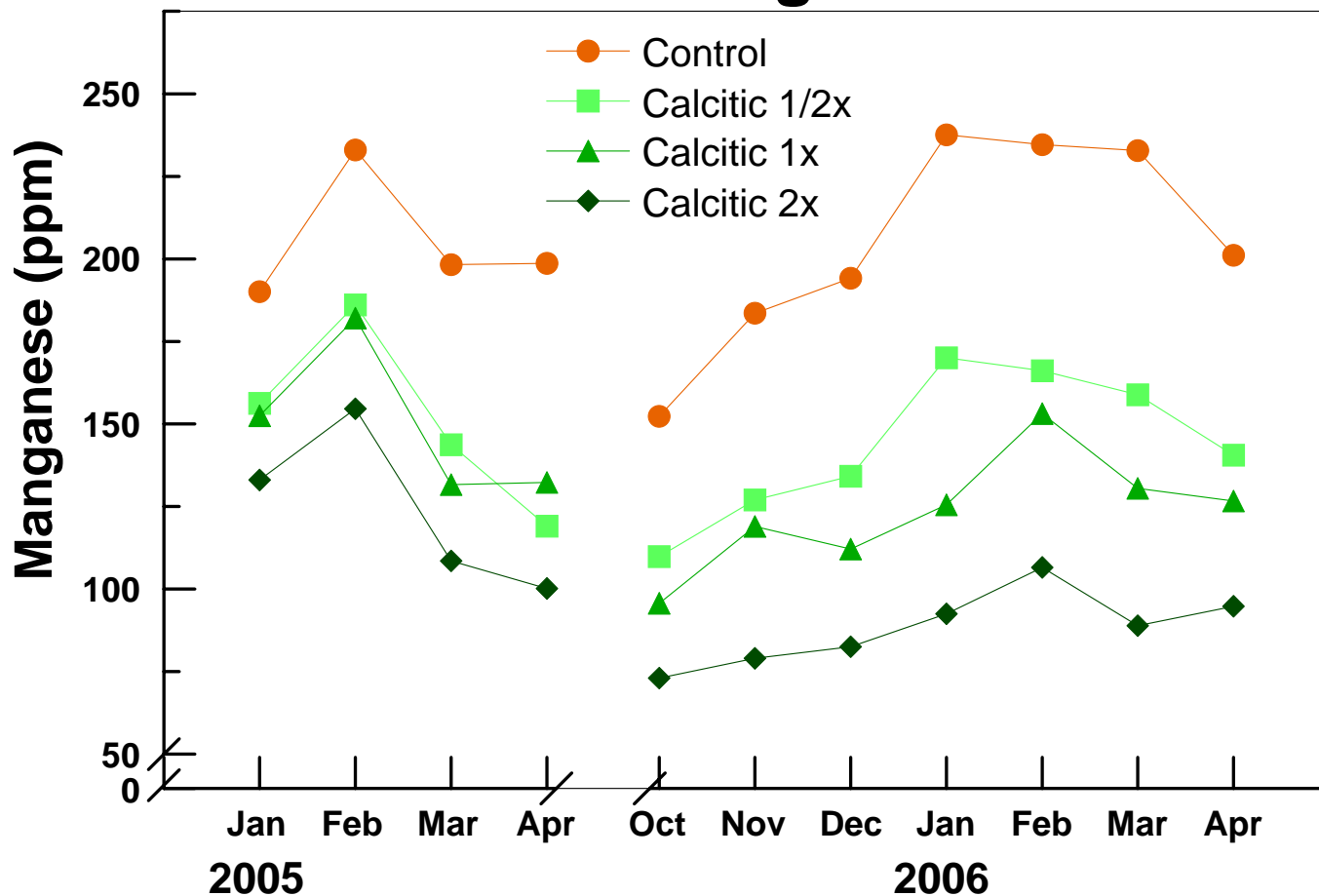


Figure 3-5. Manganese concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 23.62 for comparing treatments within a month and LSD ($P < 0.05$) = 7.45 for comparing months within the same treatment.

Leaf Manganese

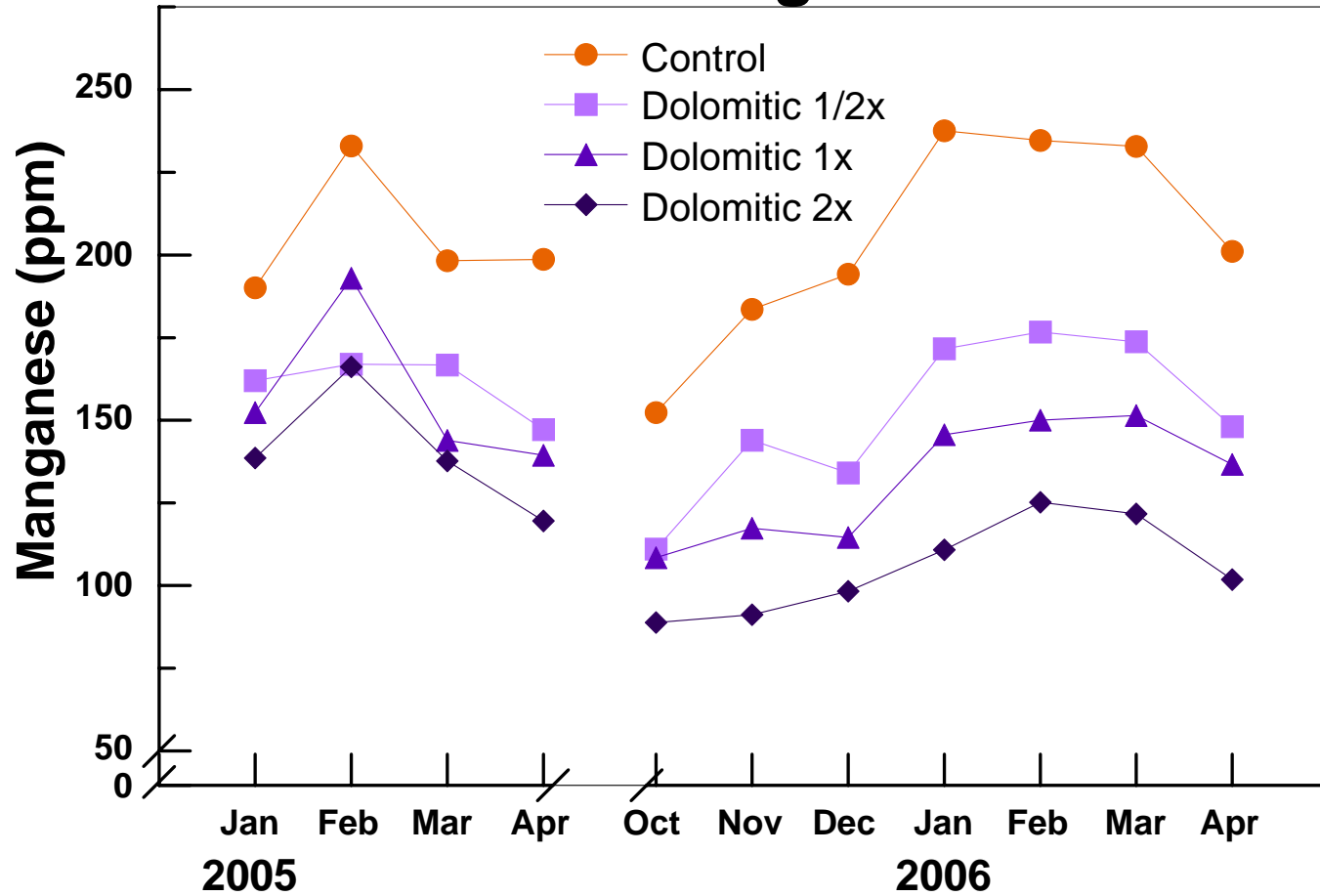


Figure 3-6. Manganese concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 23.62 for comparing treatments within a month and LSD ($P < 0.05$) = 7.45 for comparing months within the same treatment.

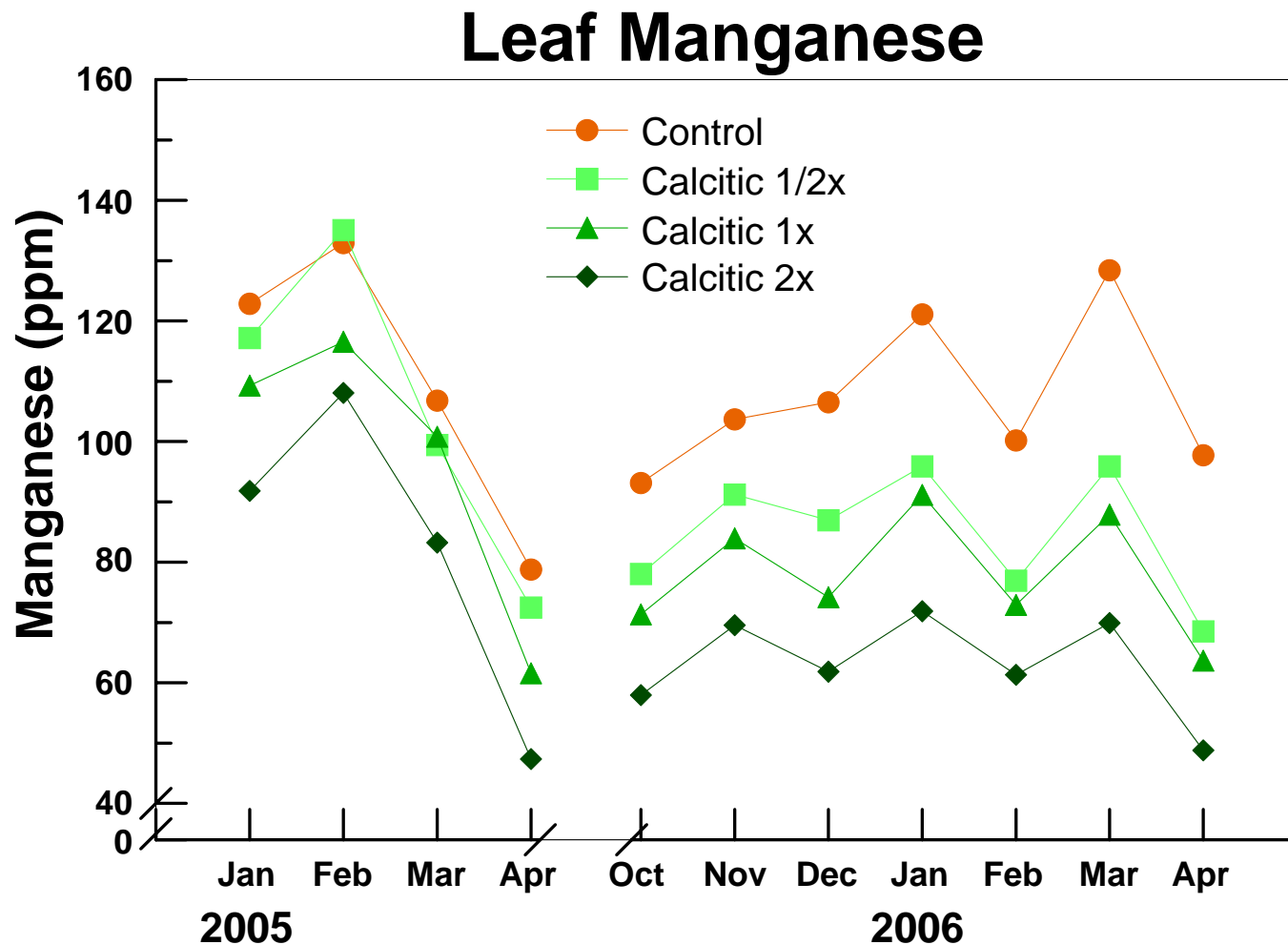


Figure 3-7. Manganese concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 17.76 for comparing treatments within a month and LSD ($P < 0.05$) = 5.08 for comparing months within the same treatment.

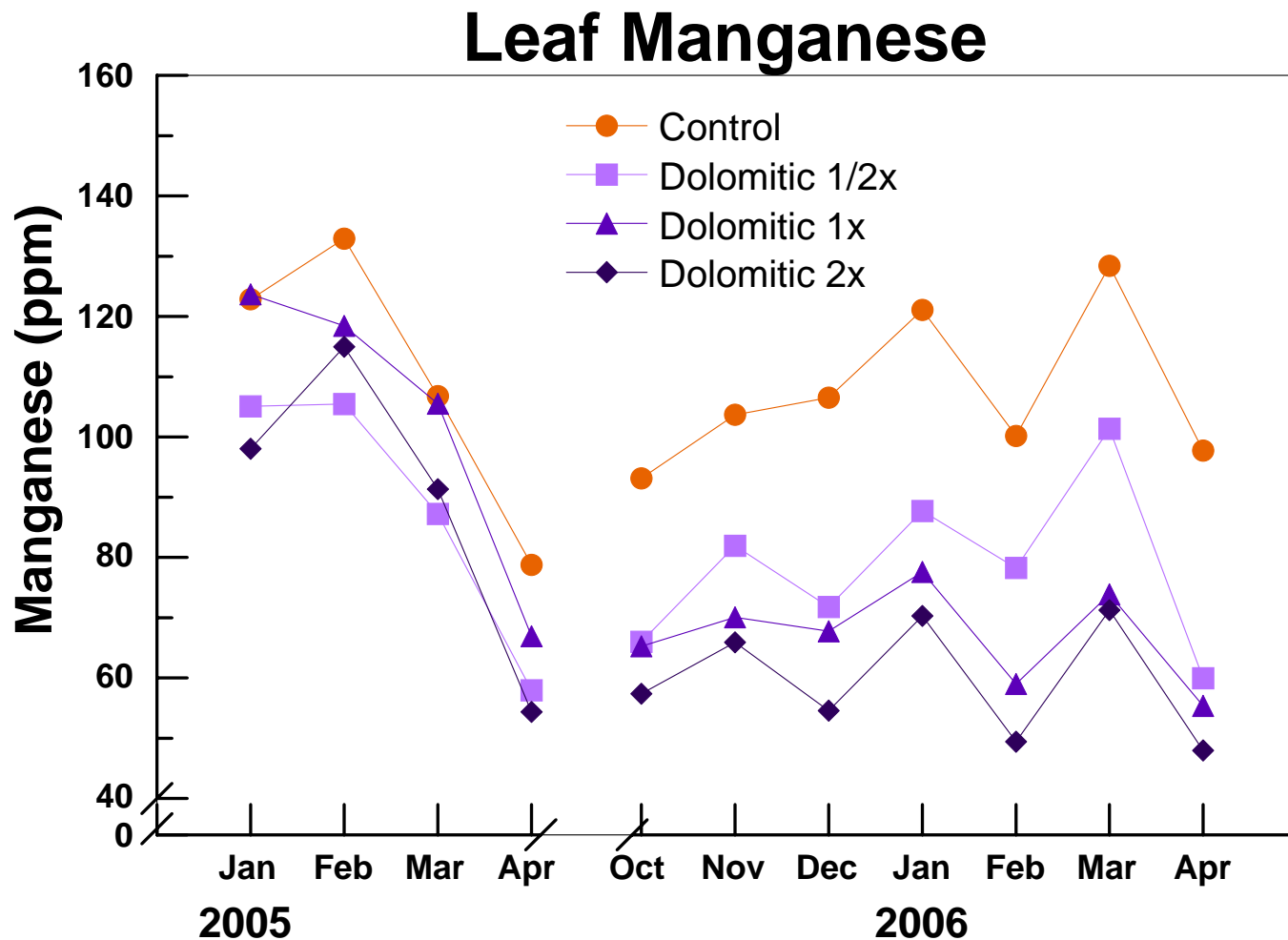


Figure 3-8. Manganese concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means ($n=6$). LSD ($P<0.05$) = 17.76 for comparing treatments within a month and LSD ($P<0.05$) = 5.08 for comparing months within the same treatment.

Soil Manganese

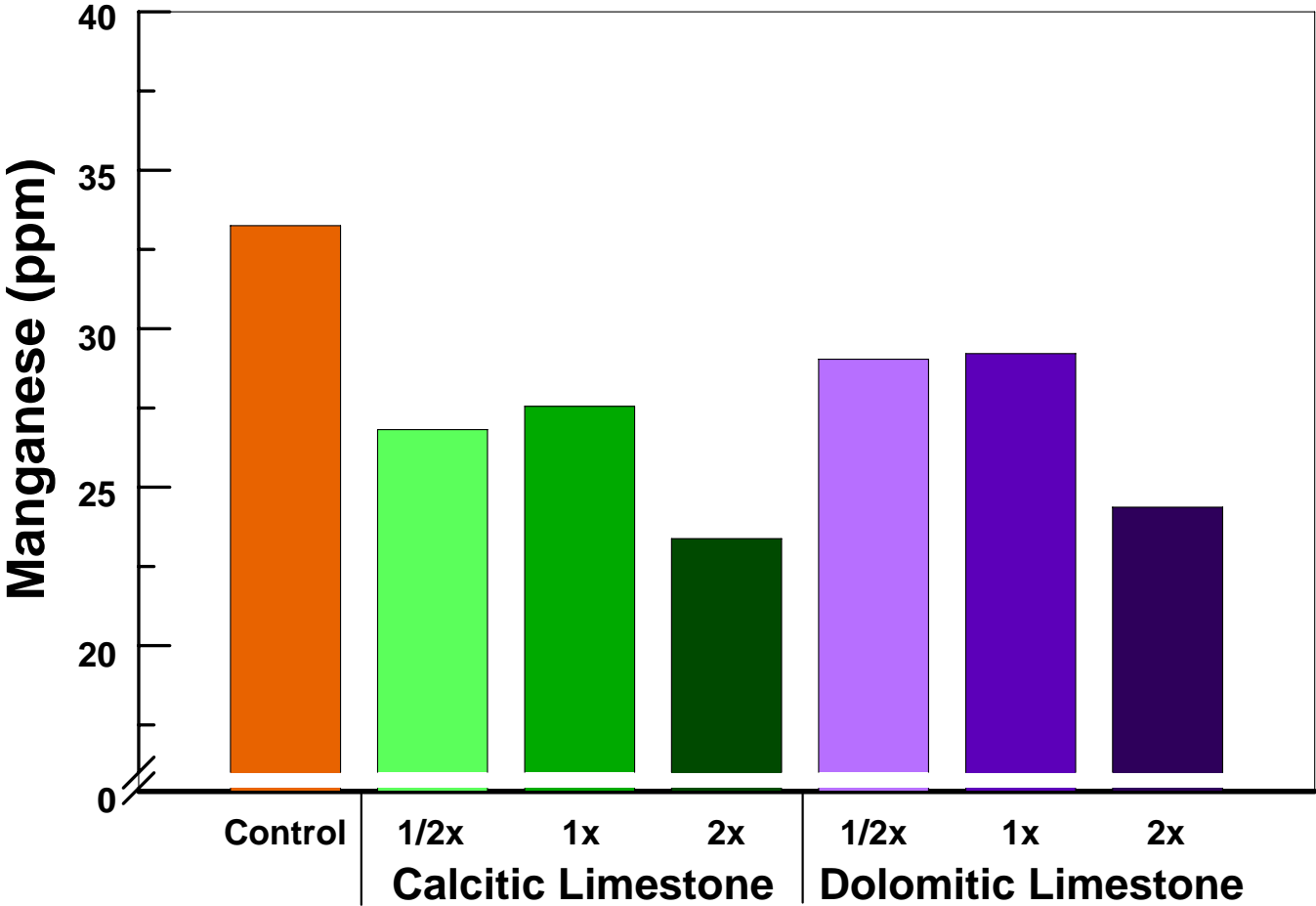


Figure 3-9. Soil manganese concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P<0.05$) = 3.39 for comparing treatments.

Soil Manganese

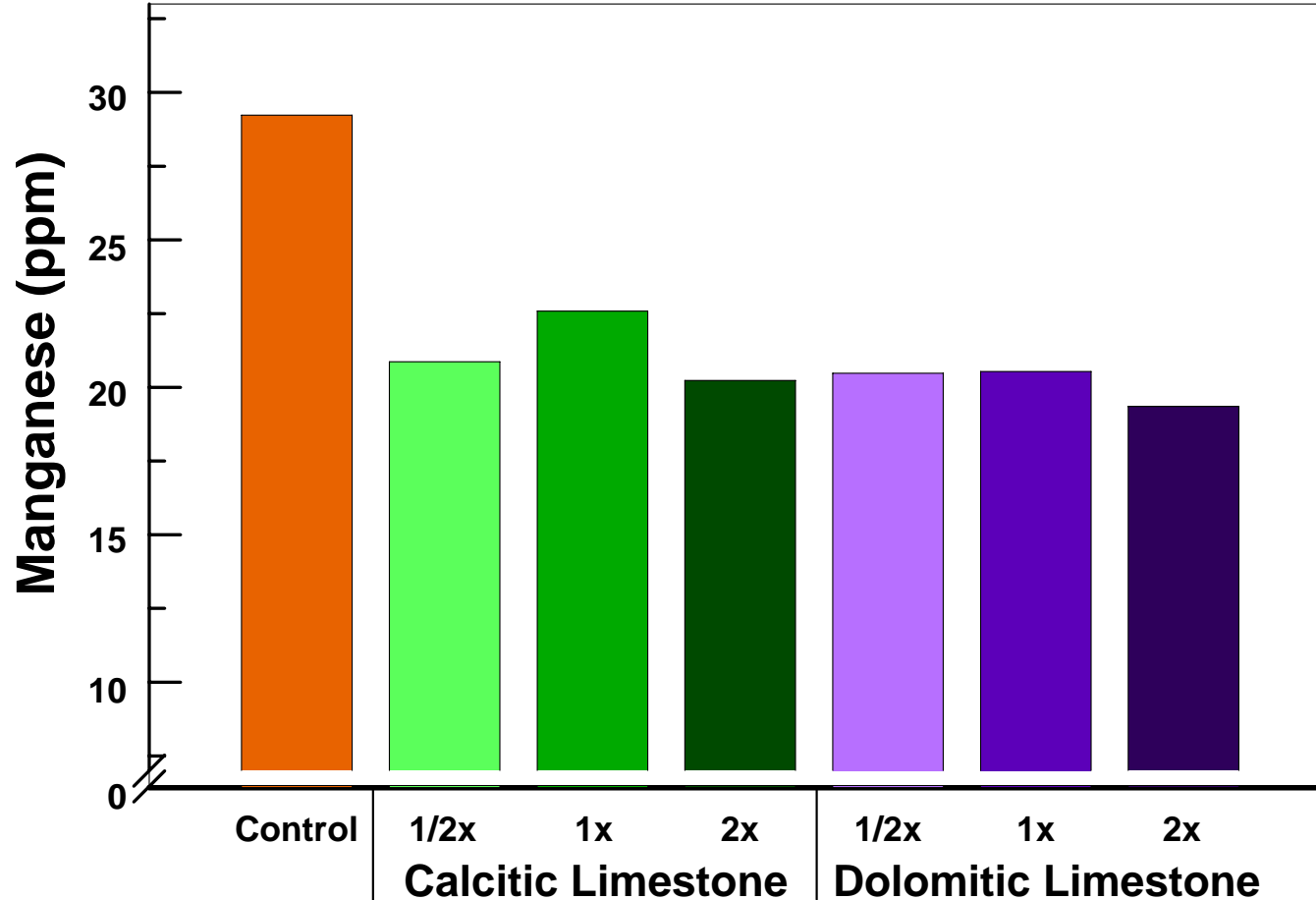


Figure 3-10. Soil manganese concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 5.55 for comparing treatments.

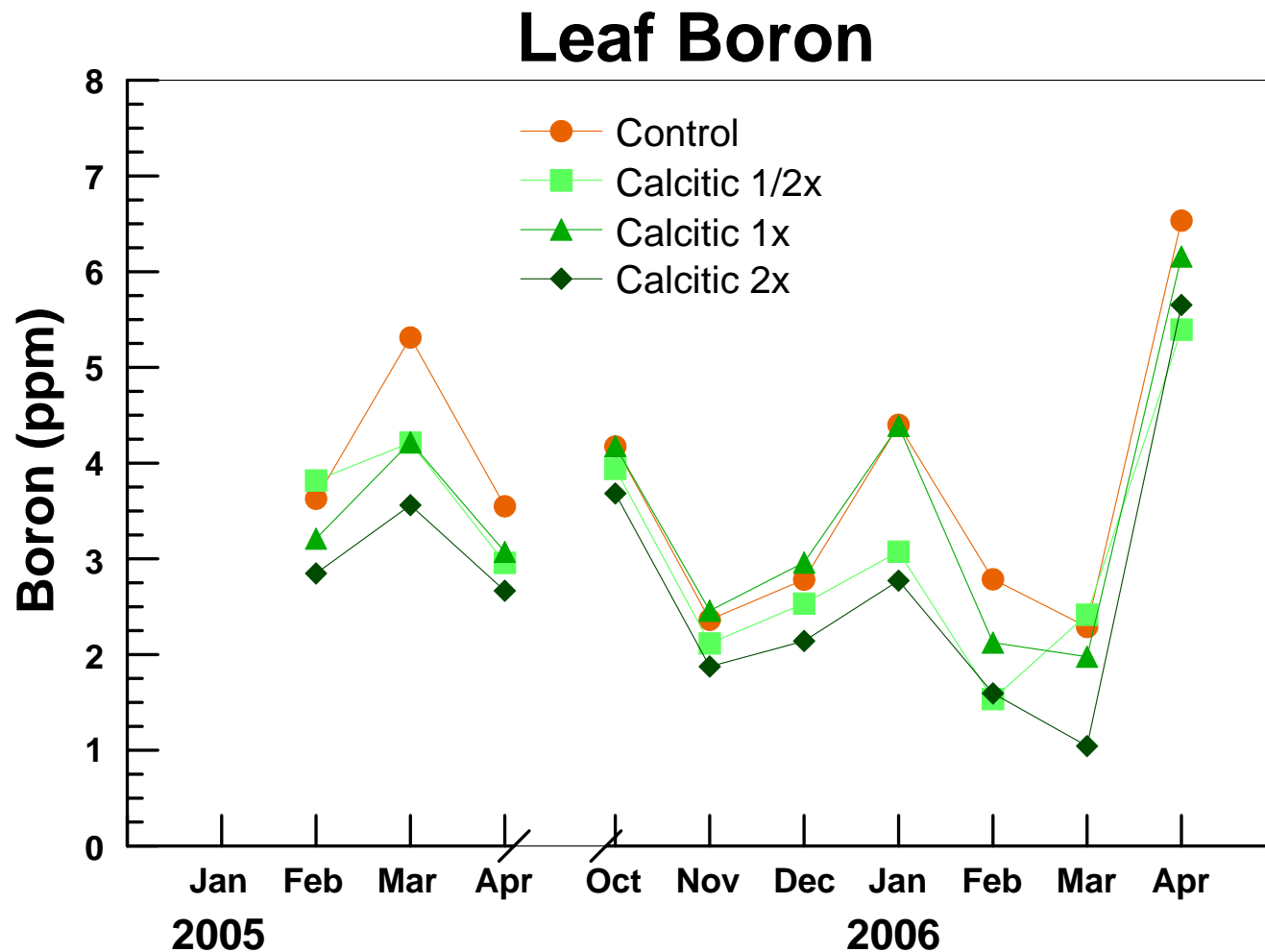


Figure 3-11. Boron concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means ($n=6$). LSD ($P<0.05$) = 1.10 for comparing treatments within a month and LSD ($P<0.05$) = 0.381 for comparing months within the same treatment.

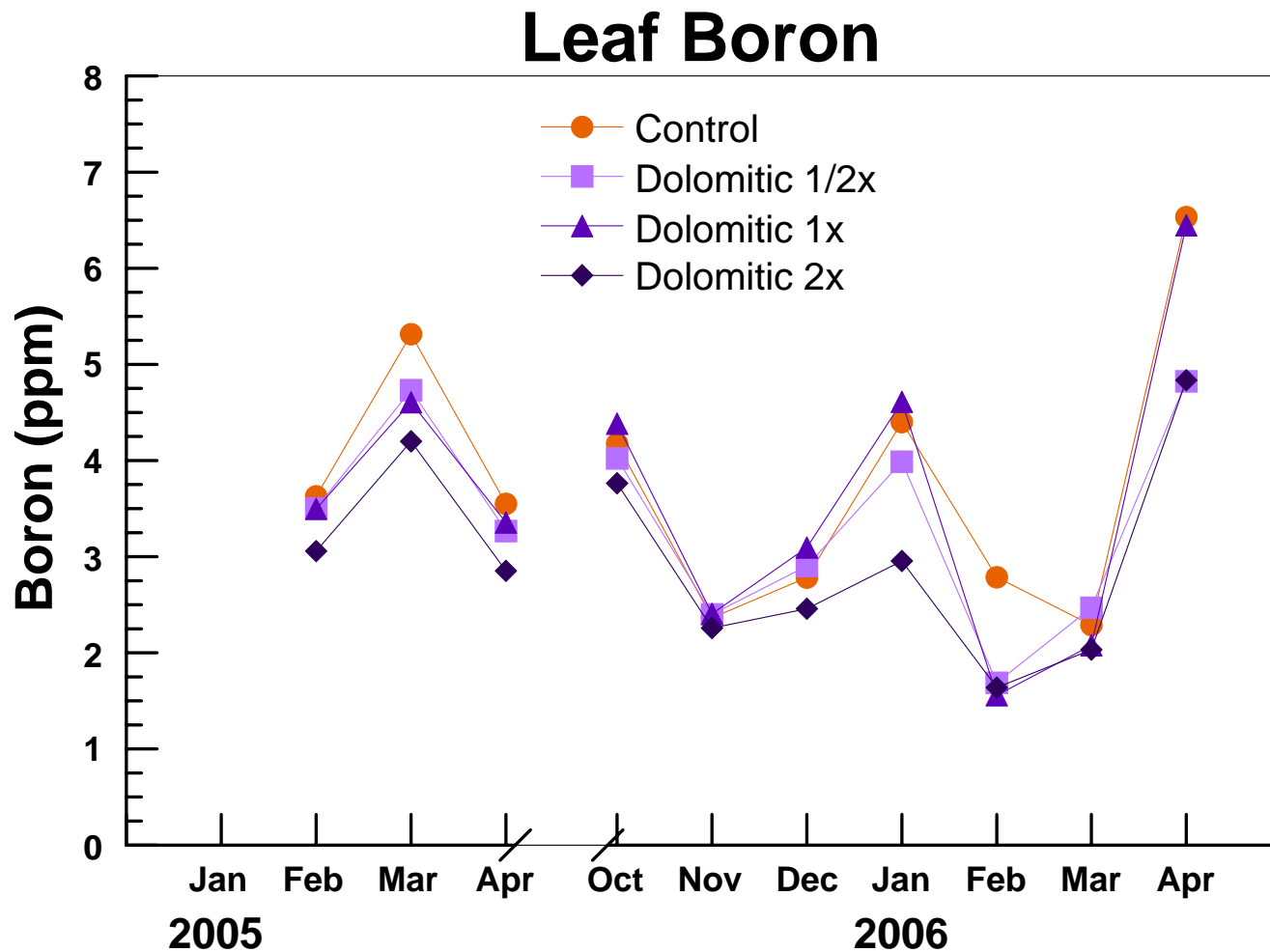


Figure 3-12. Boron concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 1.10 for comparing treatments within a month and LSD ($P < 0.05$) = .381 for comparing months within the same treatment.

Leaf Molybdenum

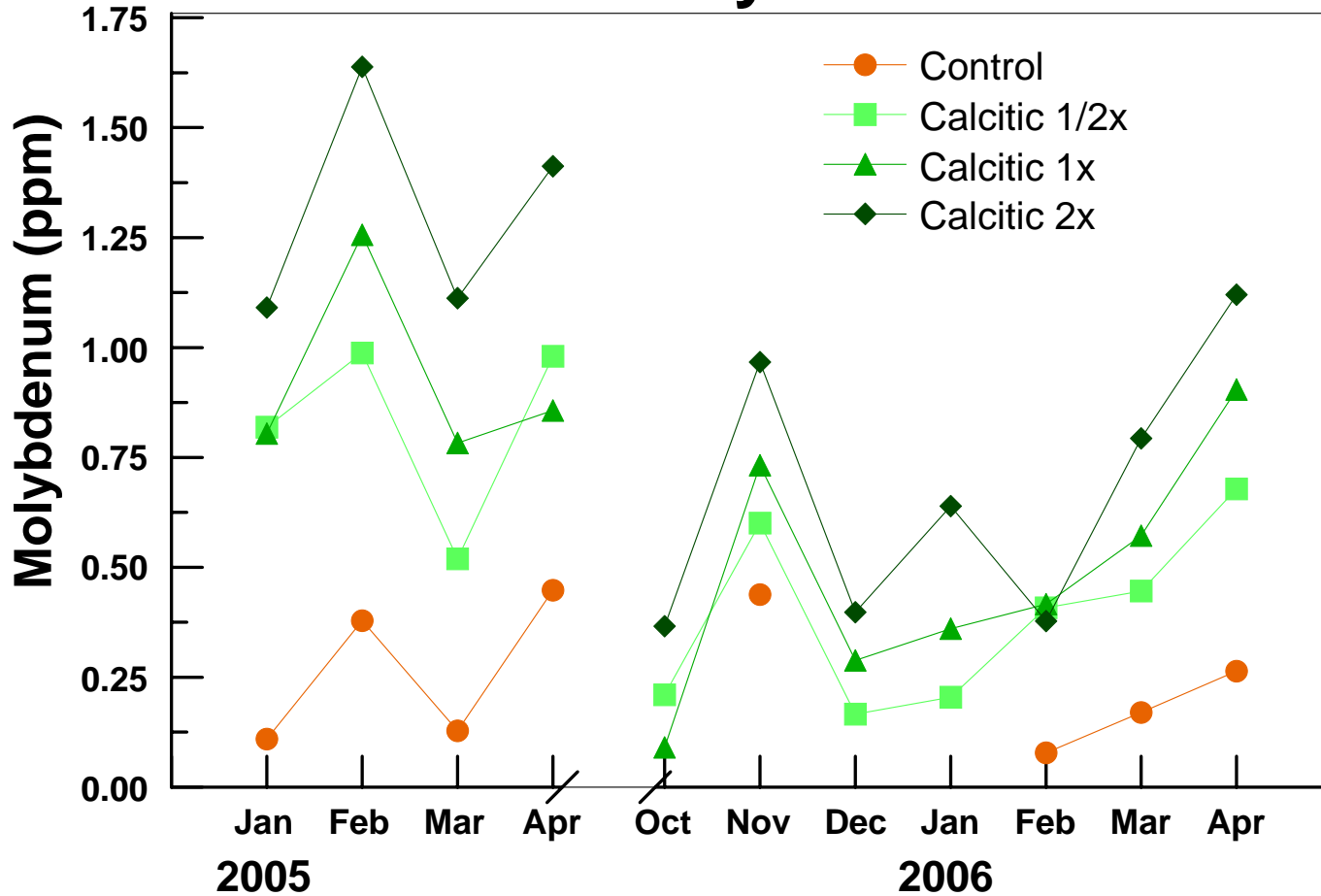


Figure 3-13. Molybdenum concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.231 for comparing treatments within a month and LSD ($P < 0.05$) = 0.079 for comparing months within the same treatment. Molybdenum concentrations in Oct 2005, Dec 2005, and Jan 2006 control plots were below the lower limit of detection.

Leaf Molybdenum

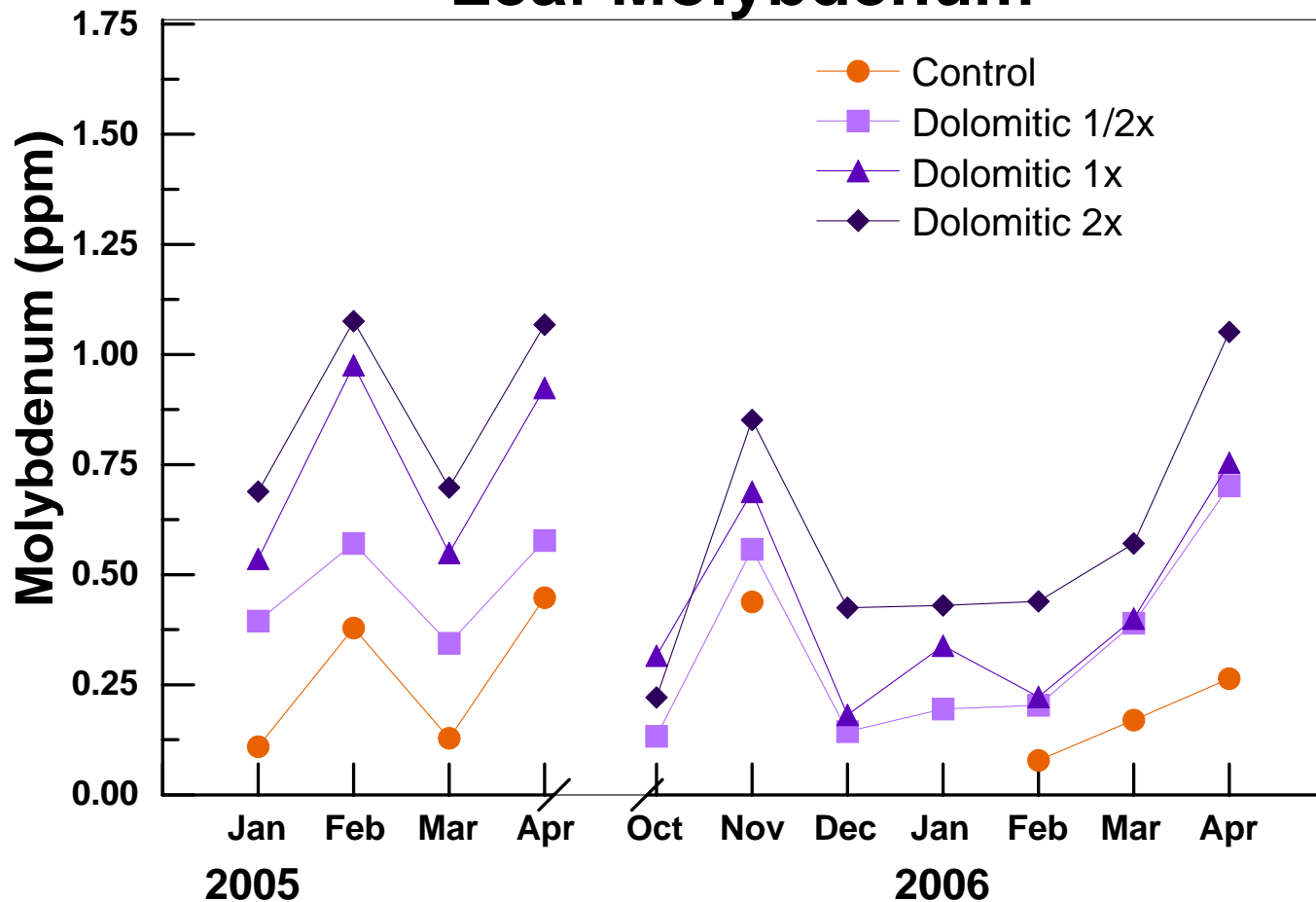


Figure 3-14. Molybdenum concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.231 for comparing treatments within a month and LSD ($P < 0.05$) = 0.079 for comparing months within the same treatment. Molybdenum concentrations in Oct 2005, Dec 2005, and Jan 2006 control plots were below the lower limit of detection.

Leaf Molybdenum

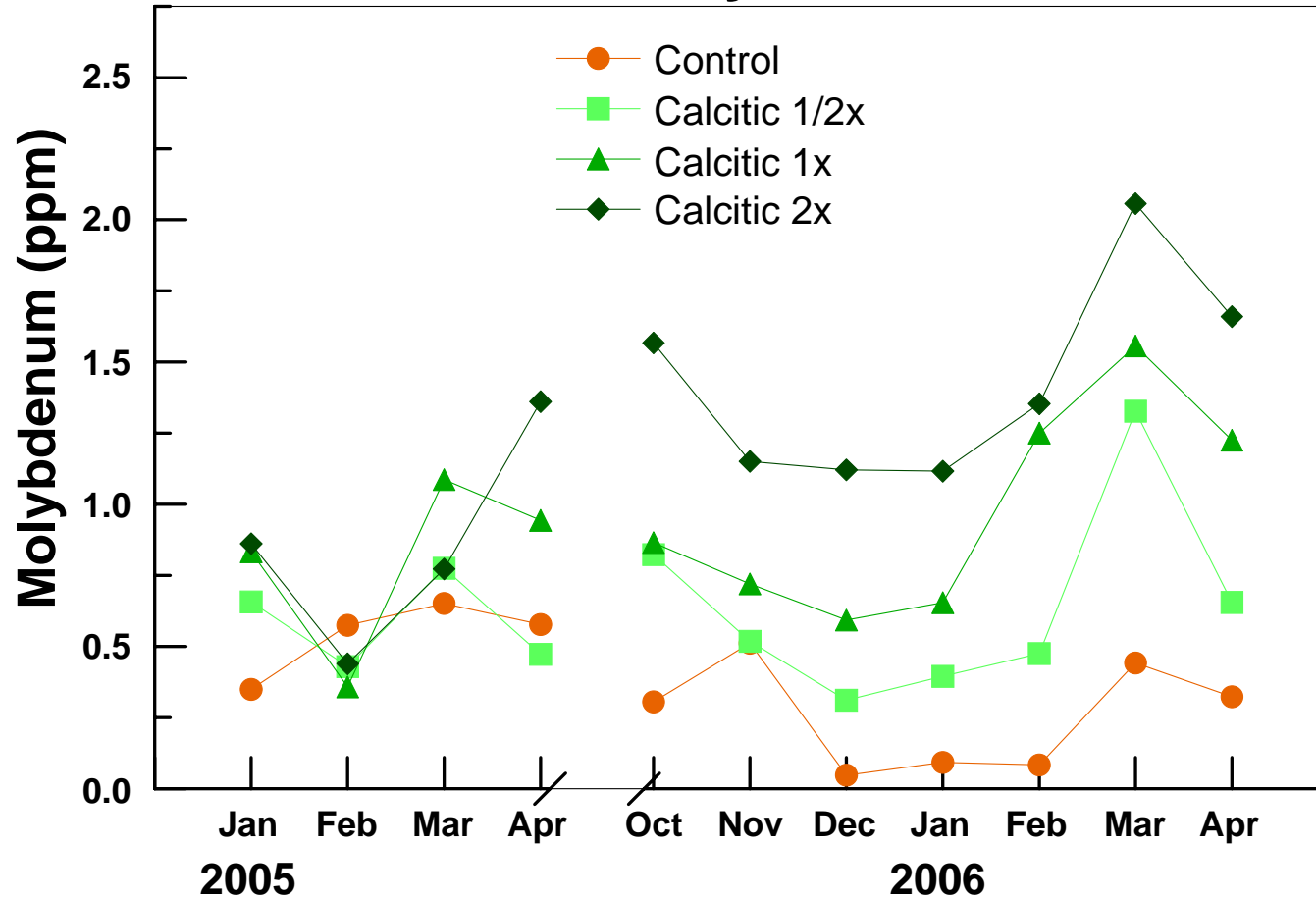


Figure 3-15. Molybdenum concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.952 for comparing treatments within a month and LSD ($P < 0.05$) = 0.322 for comparing months within the same treatment.

Leaf Molybdenum

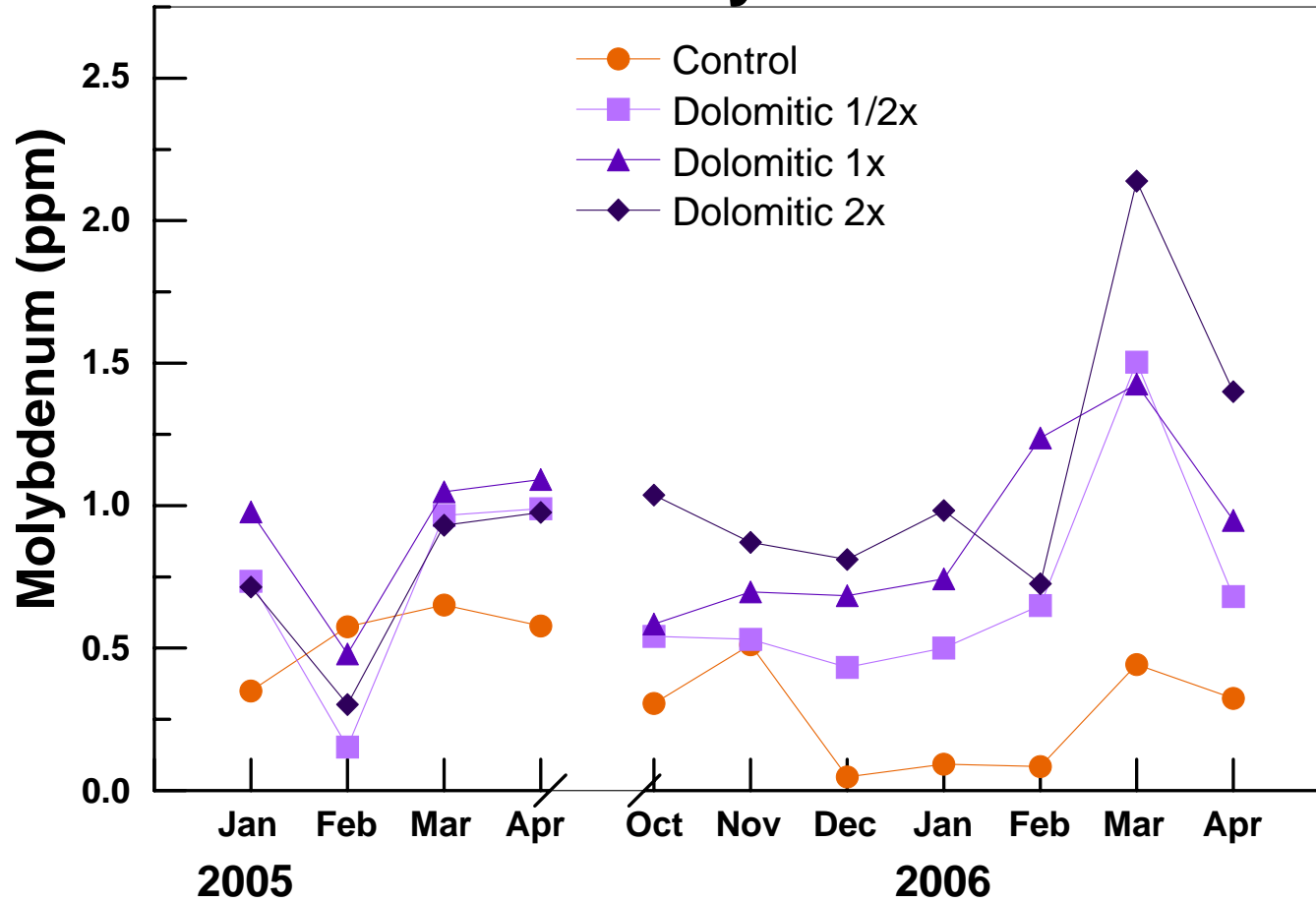


Figure 3-16. Molybdenum concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means (n=6). LSD (P<0.05) = 0.952 for comparing treatments within a month and LSD (P<0.05) = 0.322 for comparing months within the same treatment.

Leaf Sodium

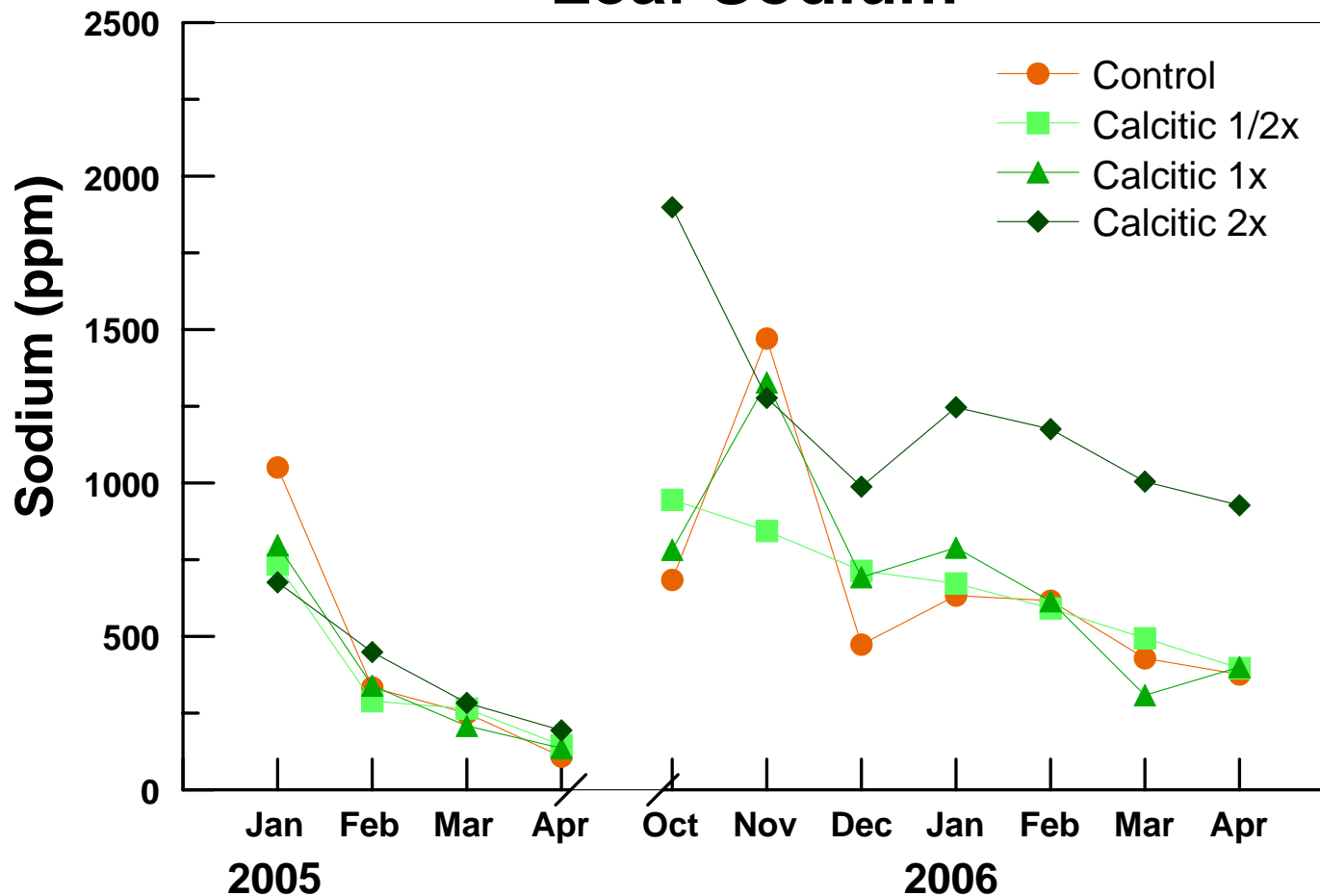


Figure 3-17. Sodium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD (P<0.05) = 445.10 for comparing treatments within a month and LSD (P<0.05) = 133.78 for comparing months within the same treatment.

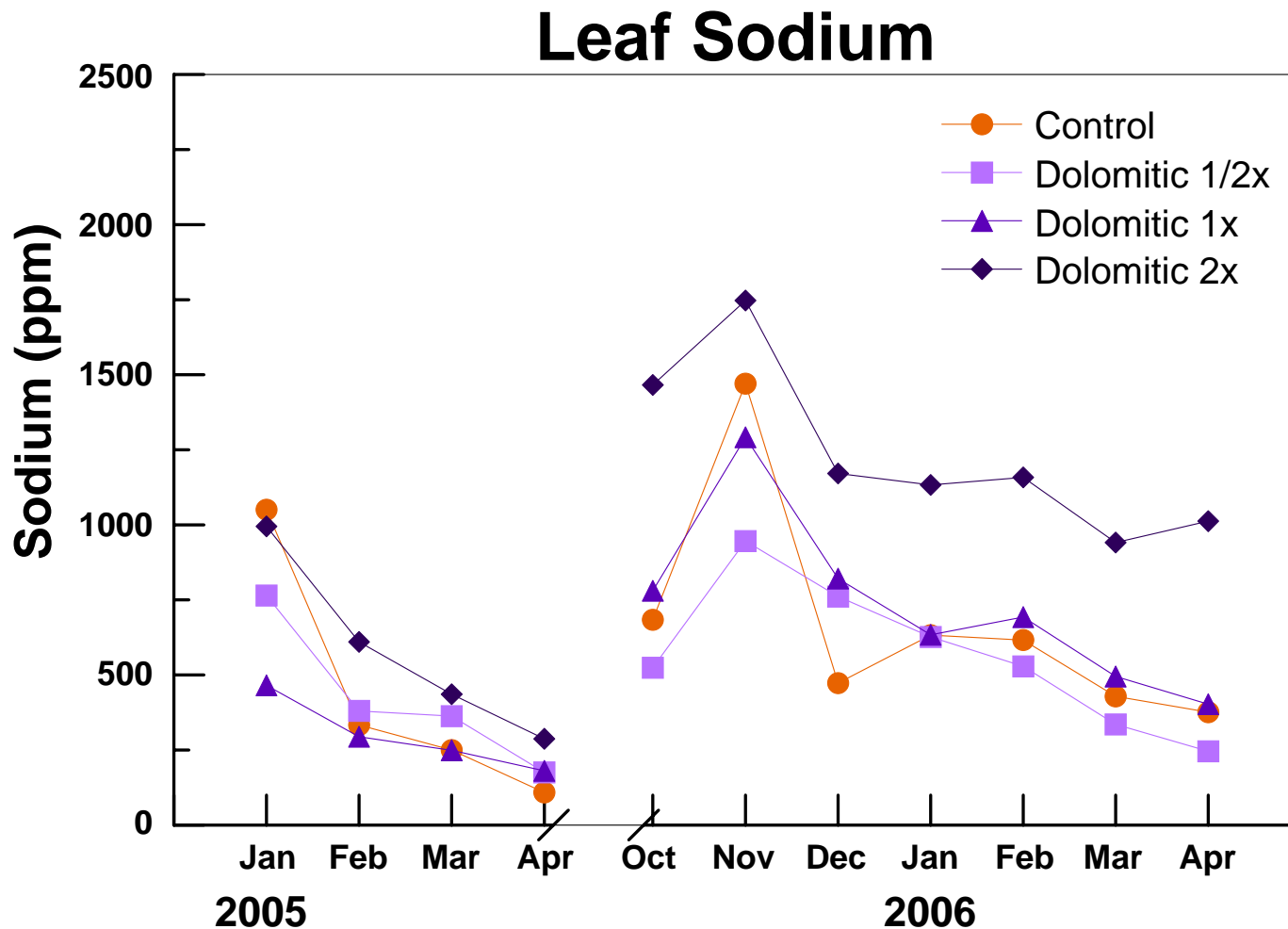


Figure 3-18. Sodium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 445.10 for comparing treatments within a month and LSD ($P < 0.05$) = 133.78 for comparing months within the same treatment.

Leaf Sodium

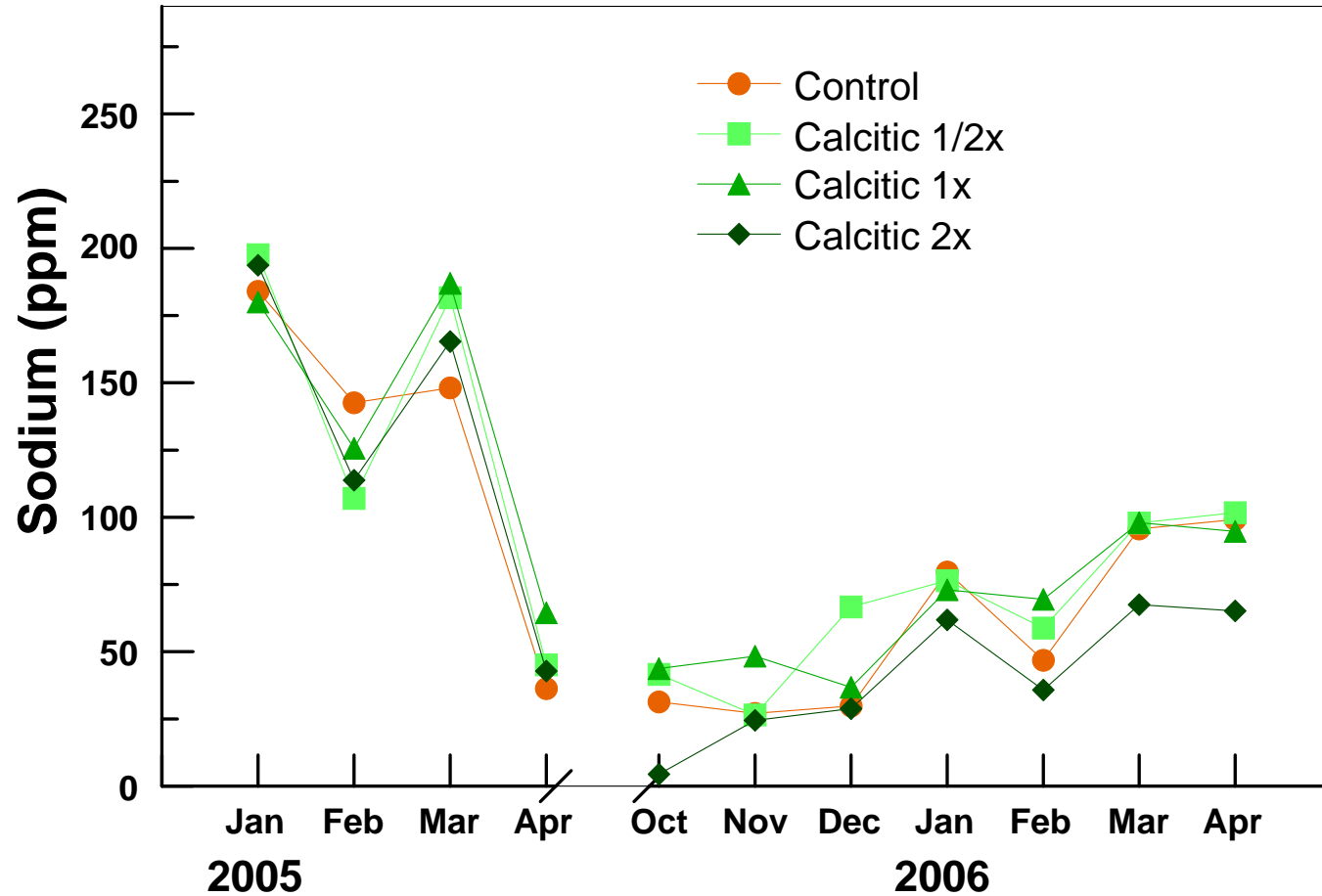


Figure 3-19. Sodium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD (P<0.05) = 67.99 for comparing treatments within a month and LSD (P<0.05) = 23.70 for comparing months within the same treatment.

Leaf Sodium

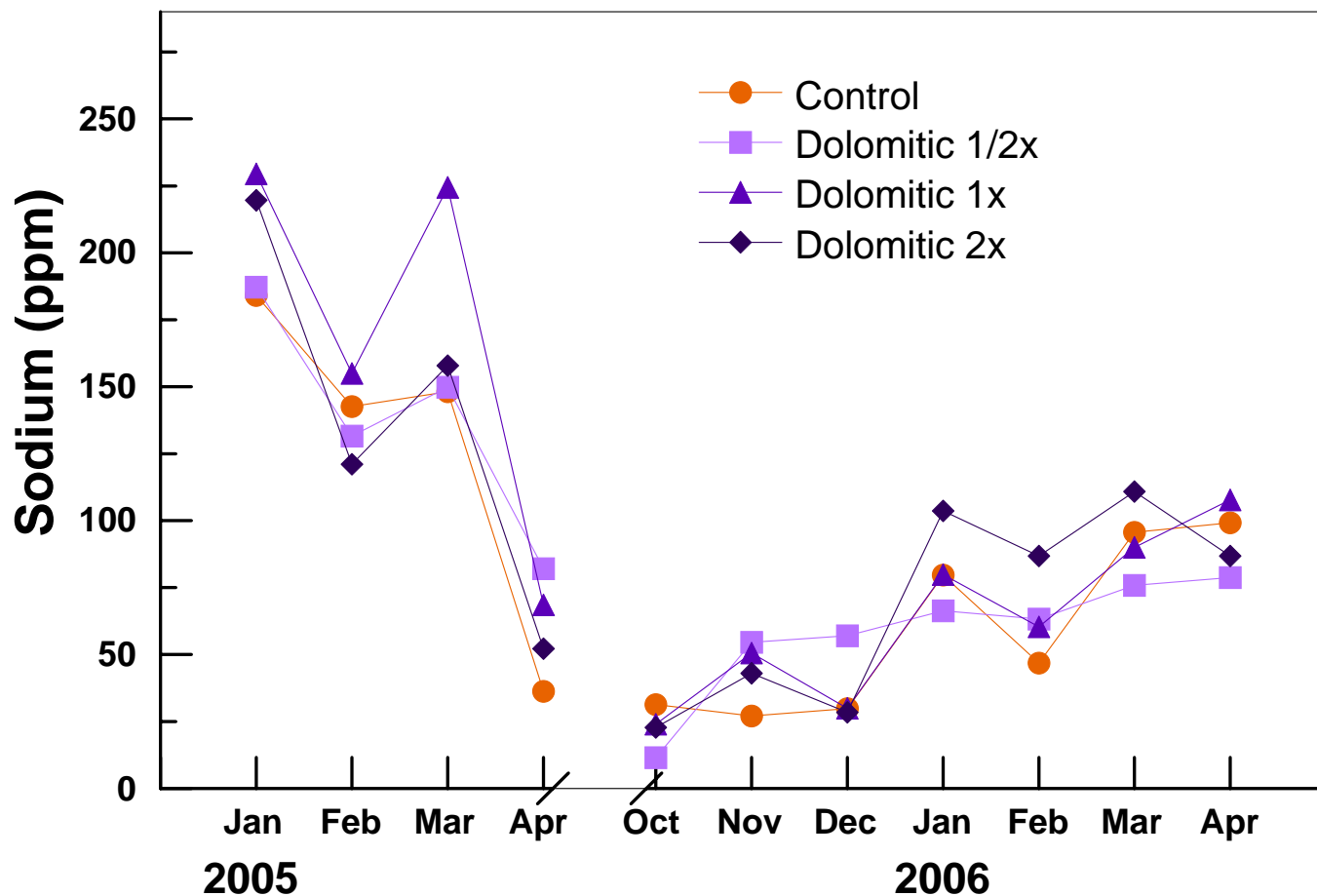


Figure 3-20. Sodium concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means (n=6). LSD (P<0.05) = 67.99 for comparing treatments within a month and LSD (P<0.05) = 23.70 for comparing months within the same treatment.

Soil Sodium

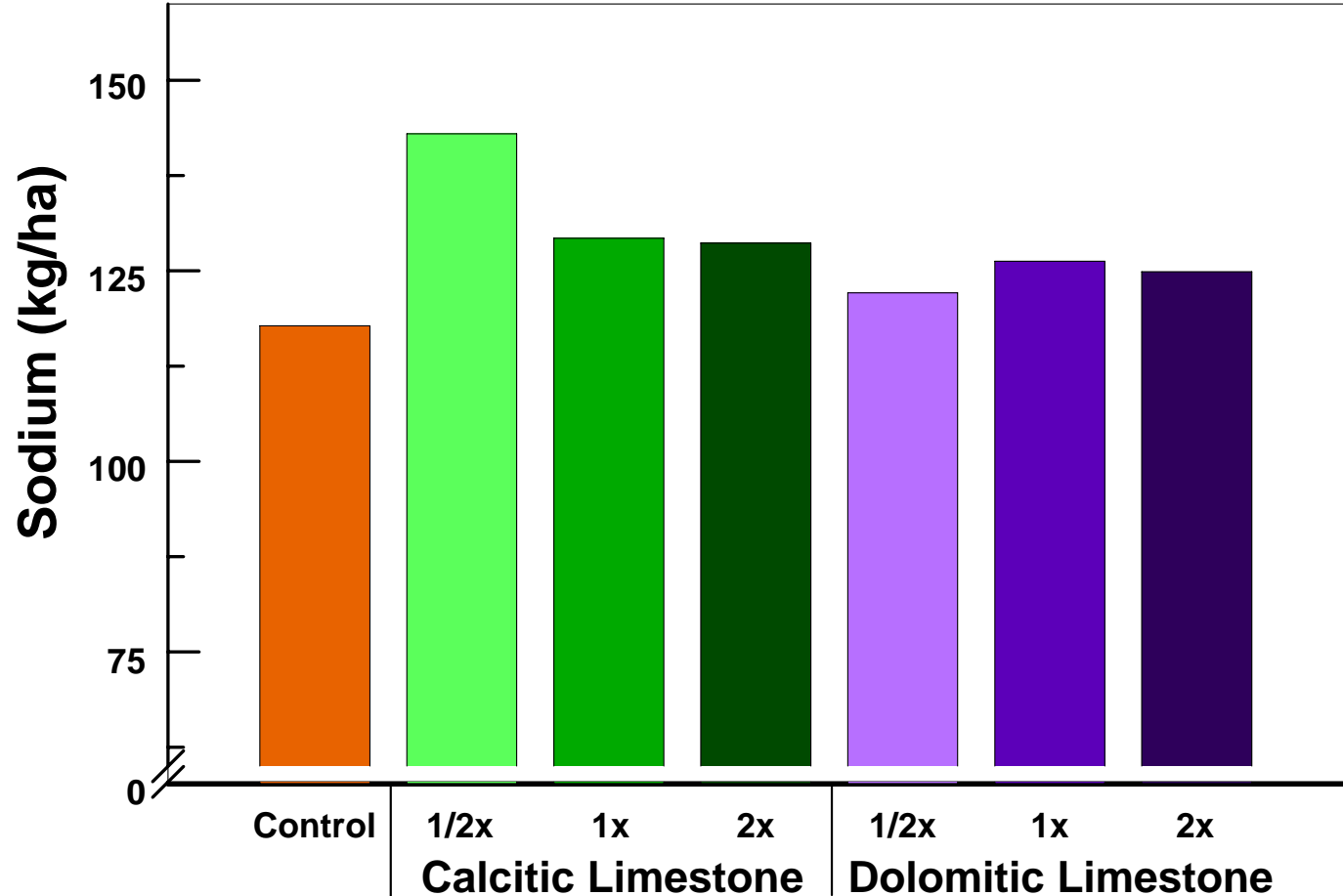


Figure 3-21. Soil sodium concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P<0.05$) = 15.75 for comparing treatments.

Soil Sodium

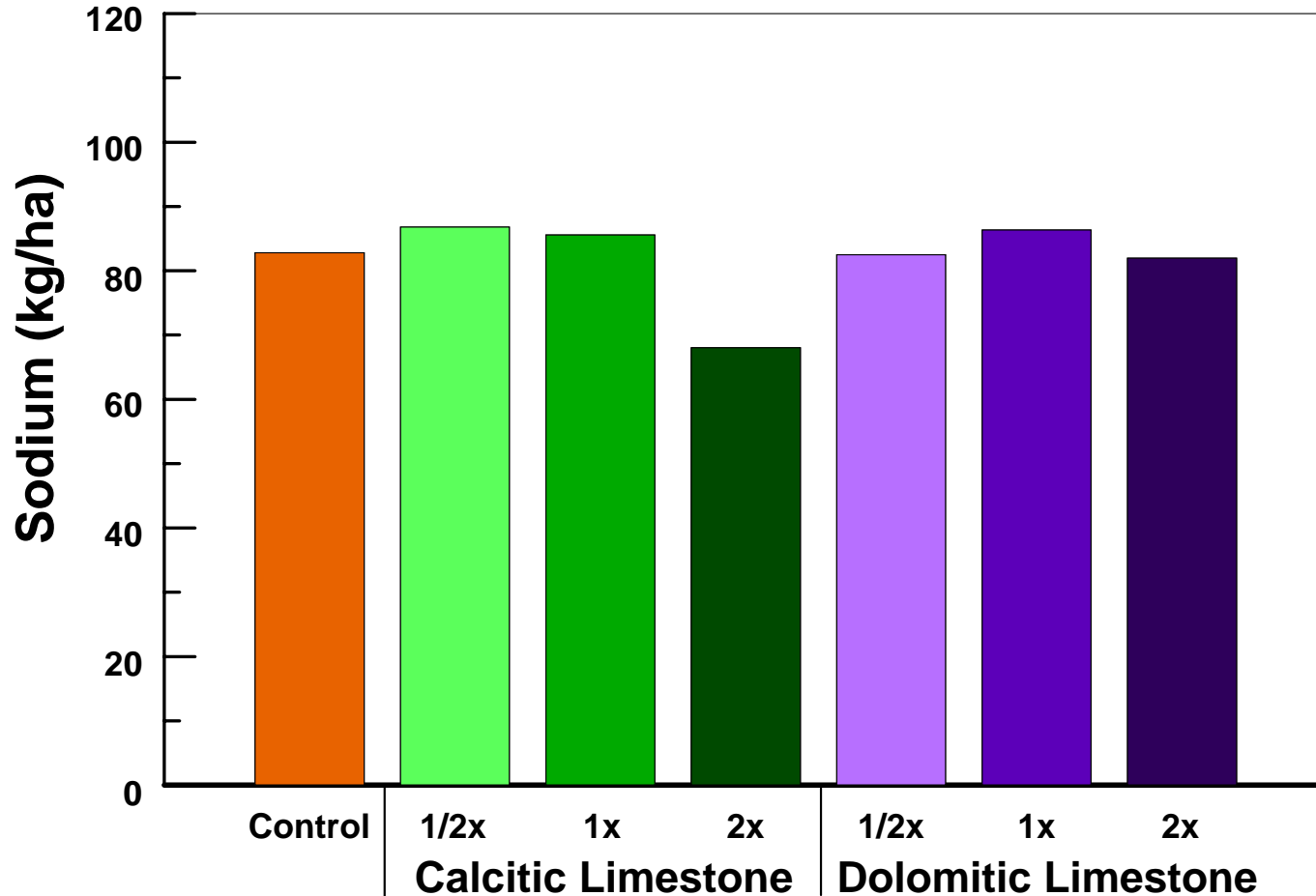


Figure 3-22. Soil sodium concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 26.97 for comparing treatments.

Leaf Iron

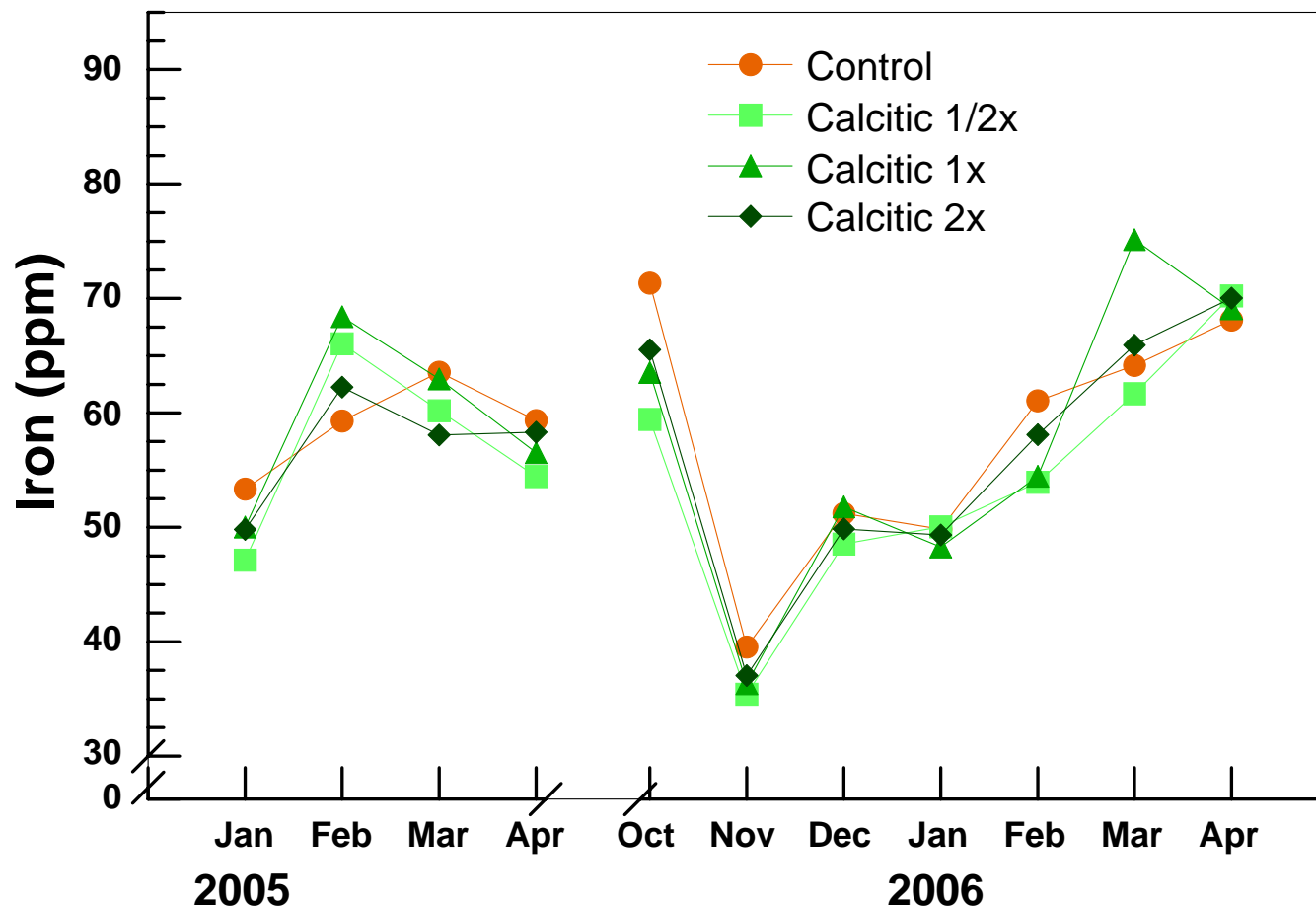


Figure 3-23. Iron concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means ($n=6$). LSD ($P<0.05$) = 8.97 for comparing treatments within a month and LSD ($P<0.05$) = 3.35 for comparing months within the same treatment.

Leaf Iron

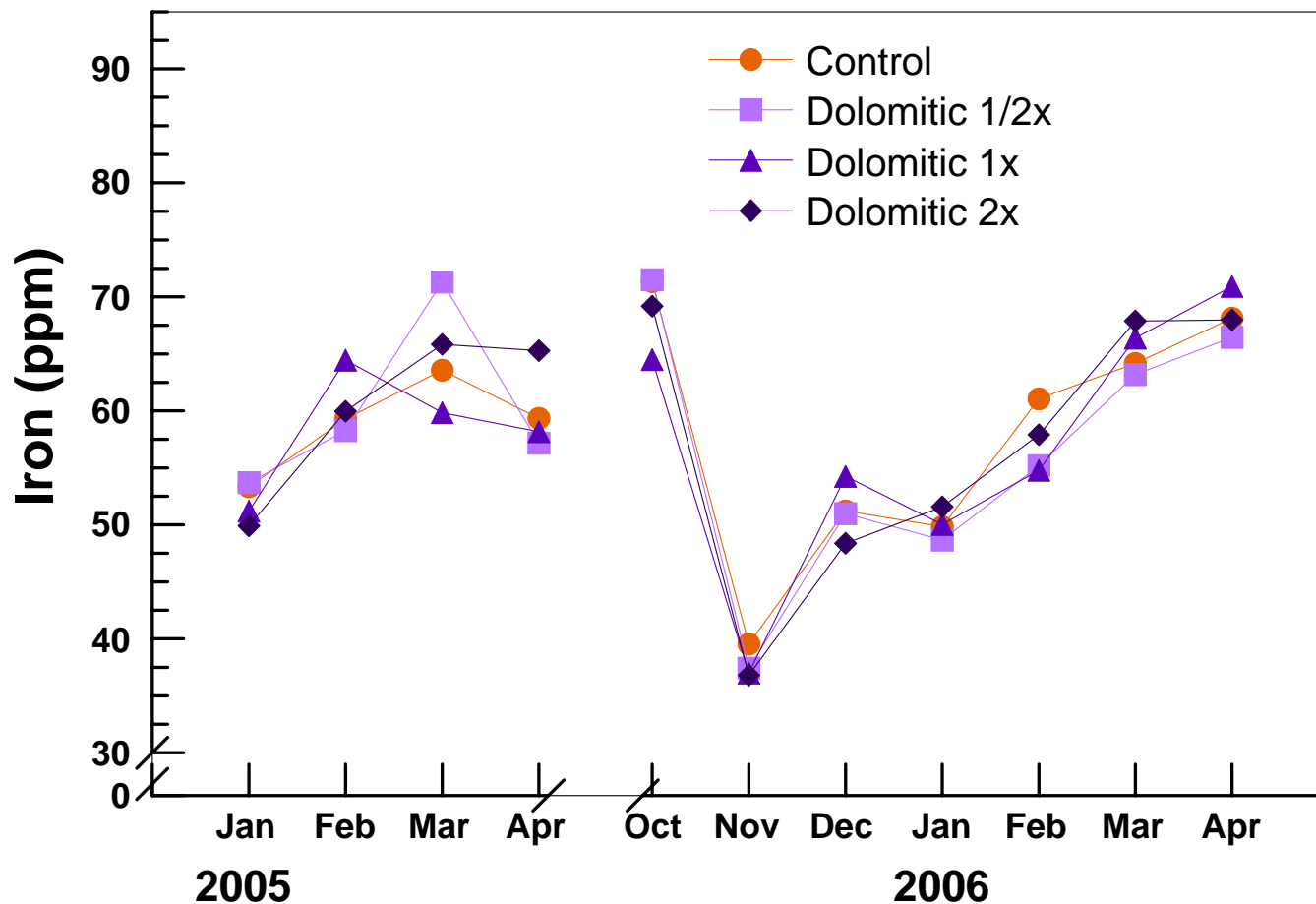


Figure 3-24. Iron concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 8.97 for comparing treatments within a month and LSD ($P < 0.05$) = 3.35 for comparing months within the same treatment.

Leaf Iron

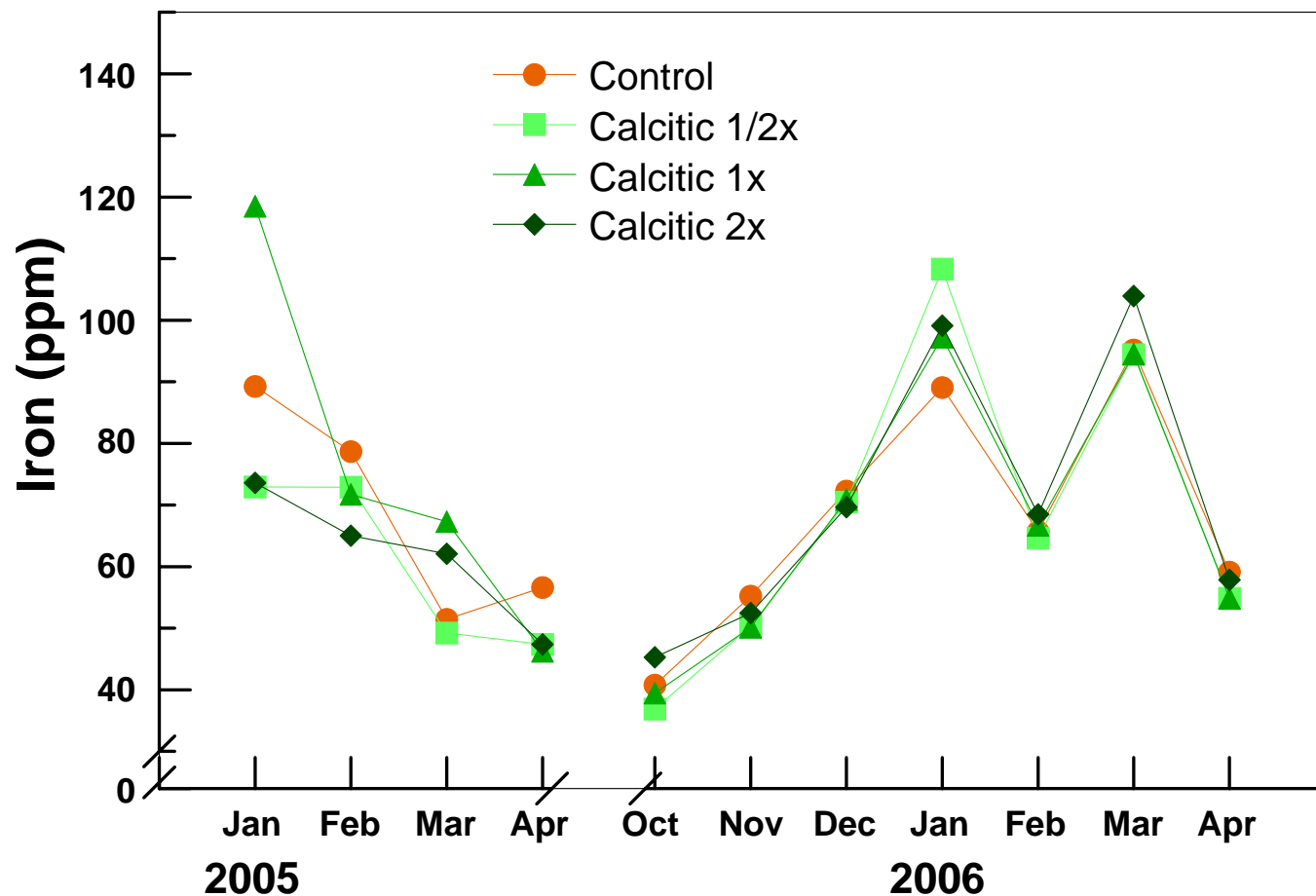


Figure 3-25. Iron concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 36.52 for comparing treatments within a month and LSD ($P < 0.05$) = 13.04 for comparing months within the same treatment.

Leaf Iron

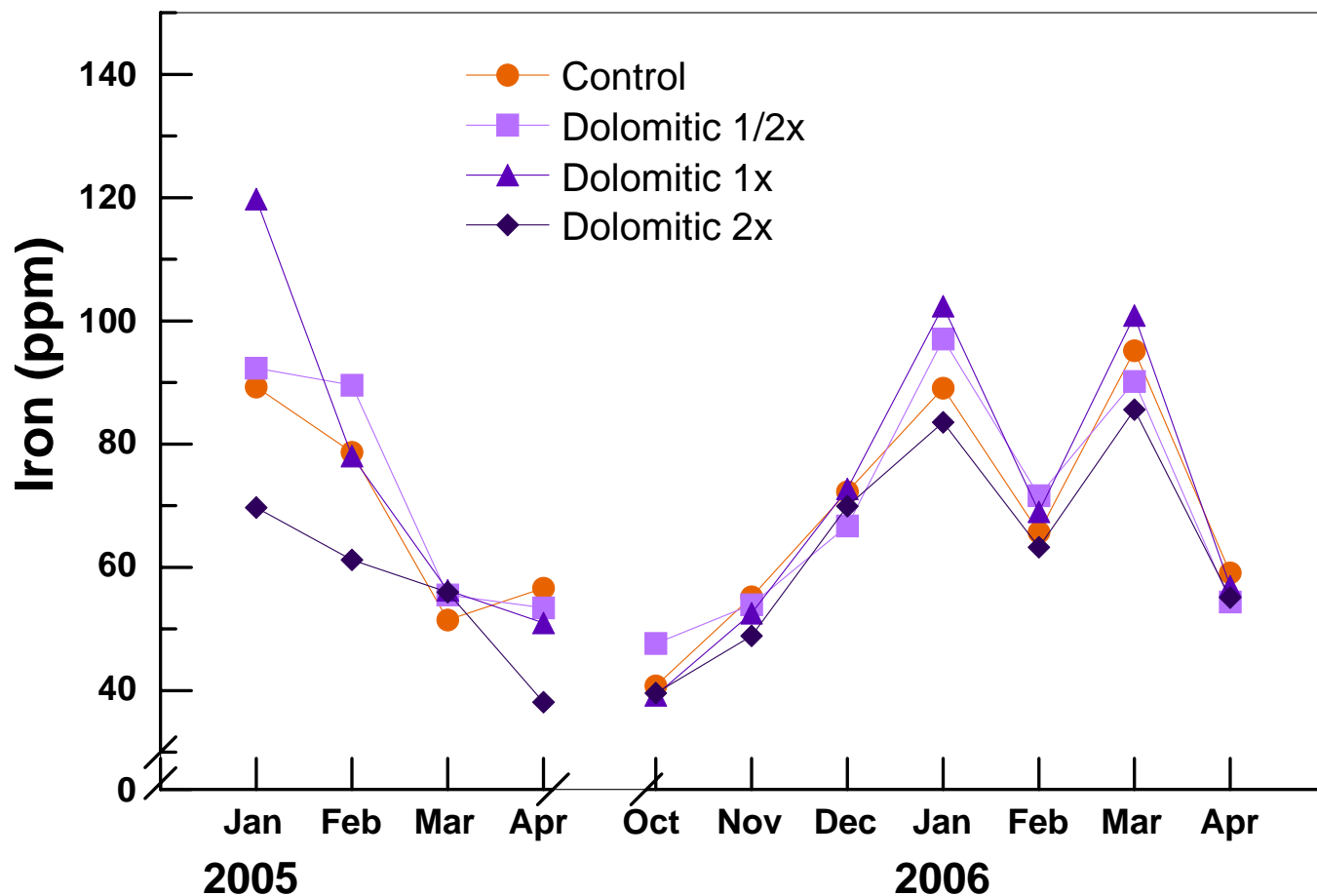


Figure 3-26. Iron concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 36.52 for comparing treatments within a month and LSD ($P < 0.05$) = 13.04 for comparing months within the same treatment.

Soil Iron

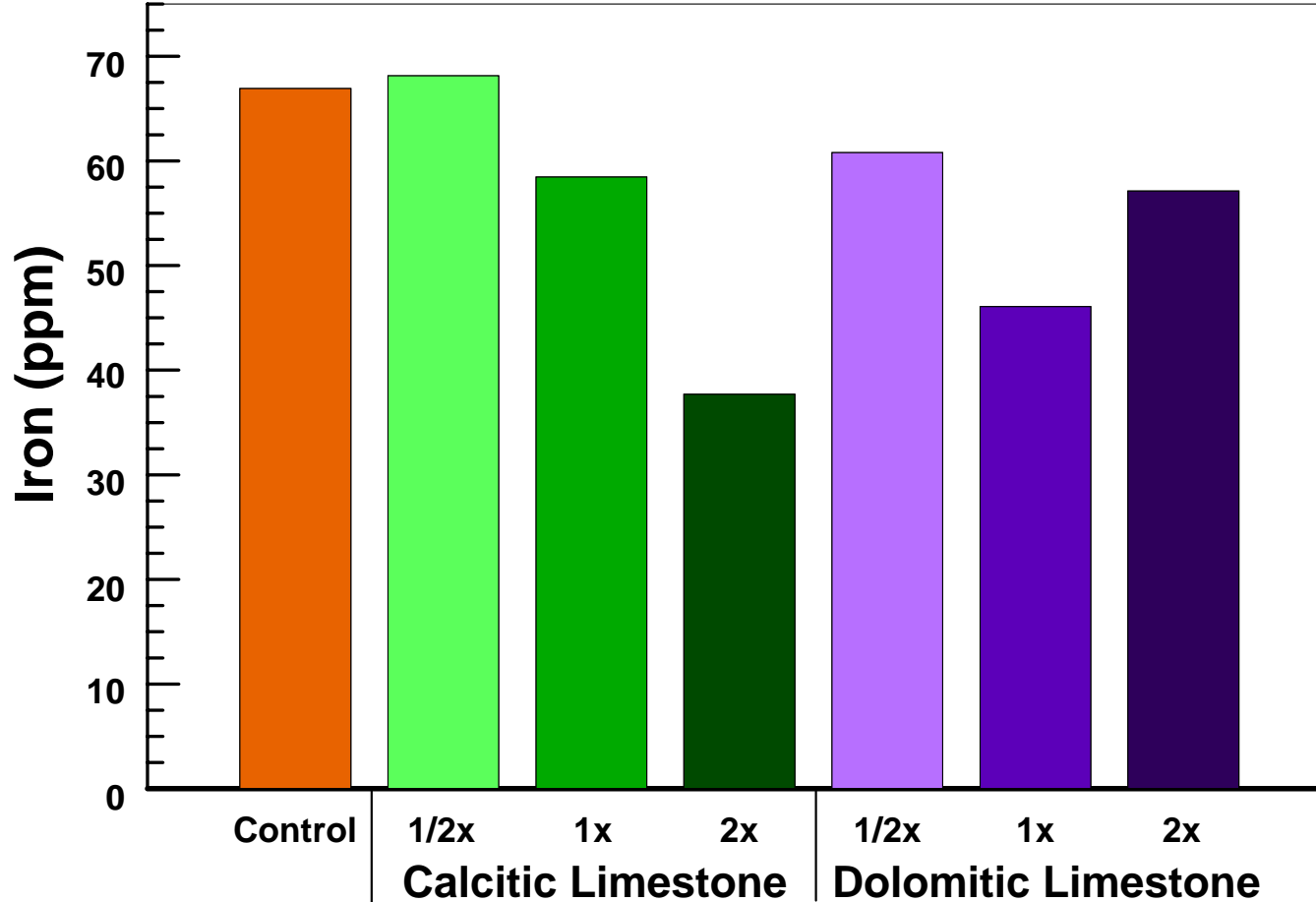


Figure 3-27. Soil iron concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 13.24 for comparing treatments.

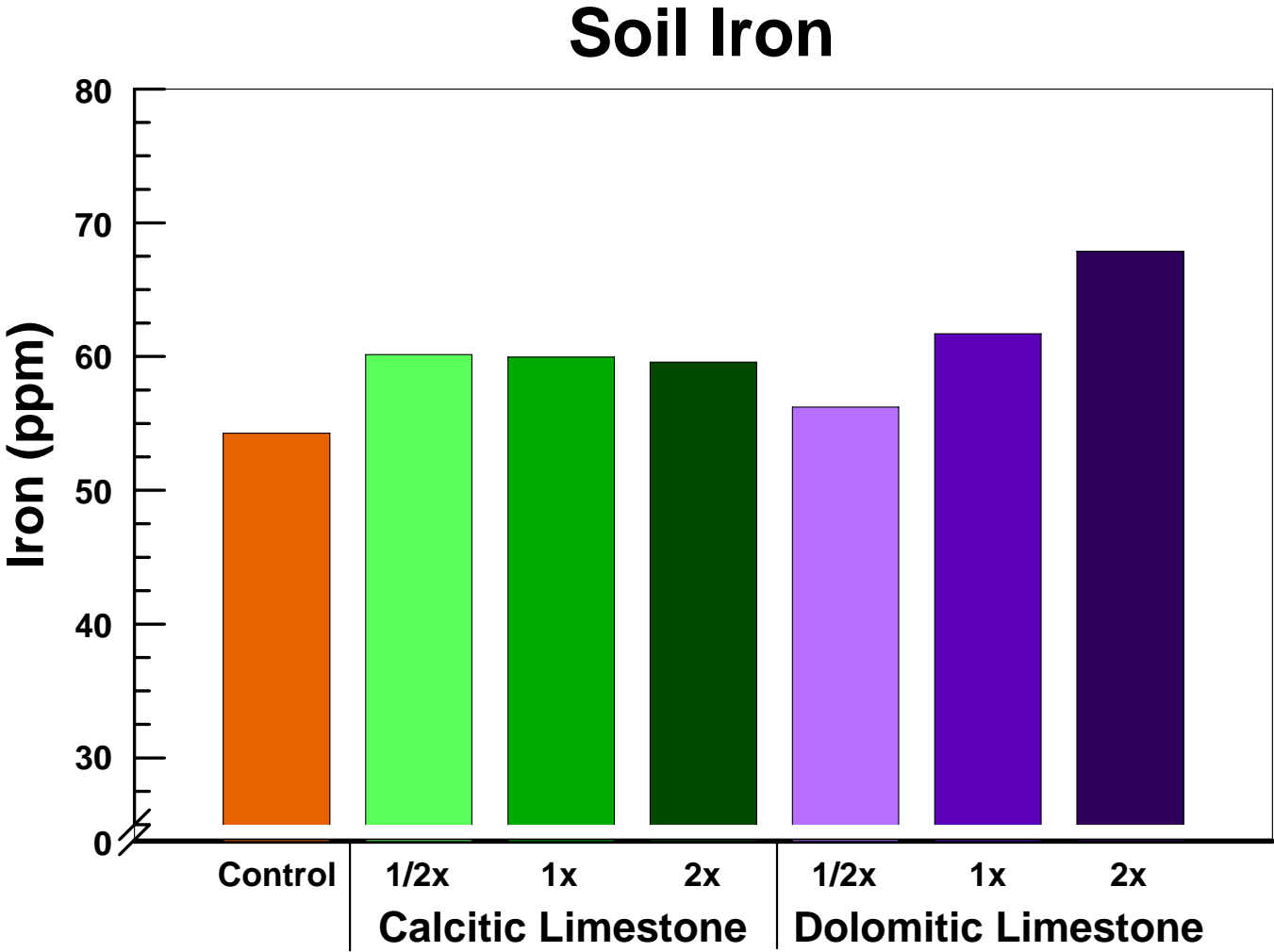


Figure 3-28. Soil iron concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P<0.05$) = 8.26 for comparing treatments.

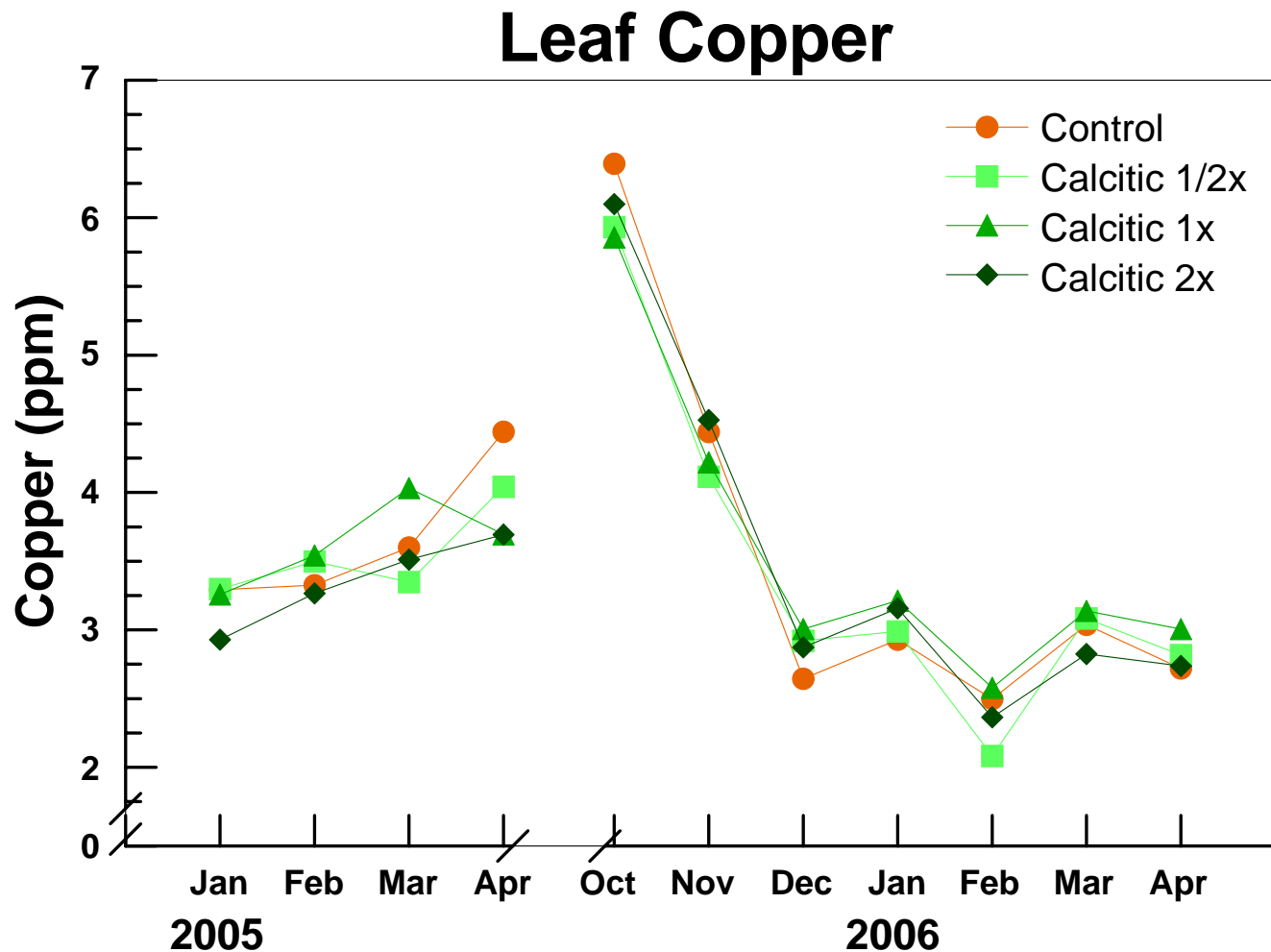


Figure 3-29. Copper concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.524 for comparing treatments within a month and LSD ($P < 0.05$) = 0.195 for comparing months within the same treatment.

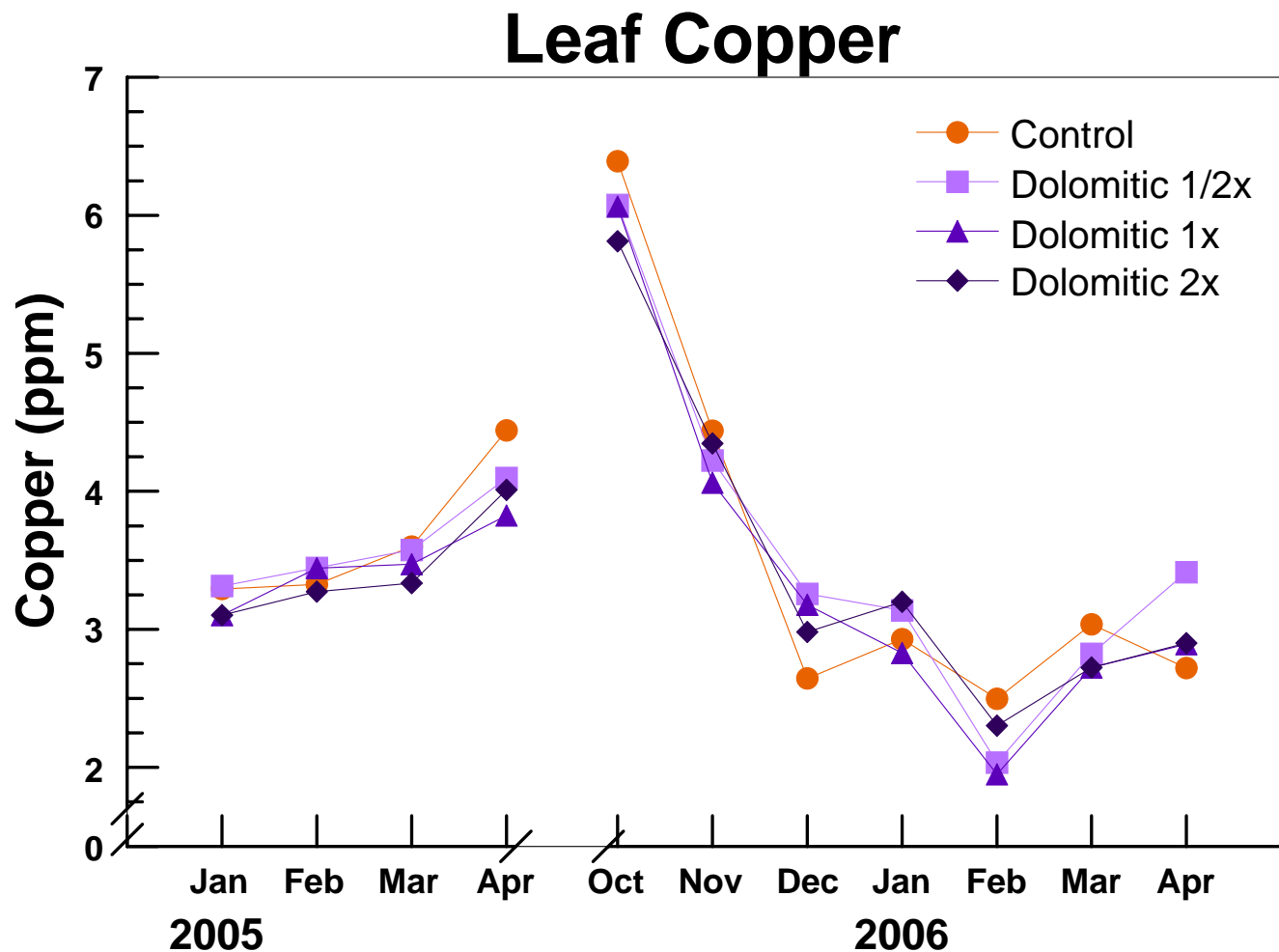


Figure 3-30. Copper concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.524 for comparing treatments within a month and LSD ($P < 0.05$) = 0.195 for comparing months within the same treatment.

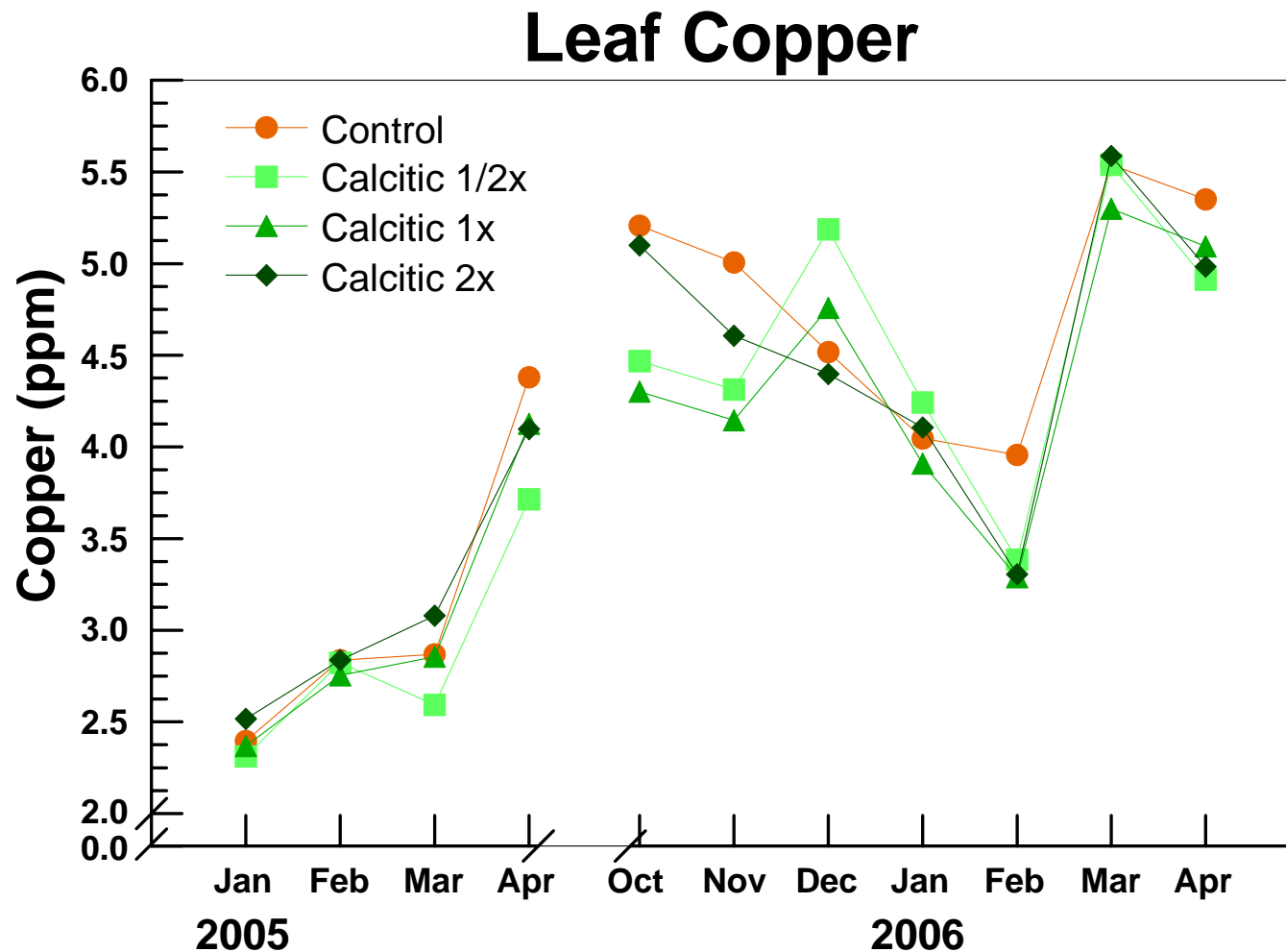


Figure 3-31. Copper concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 3.29 for comparing treatments within a month and LSD ($P < 0.05$) = 1.19 for comparing months within the same treatment.

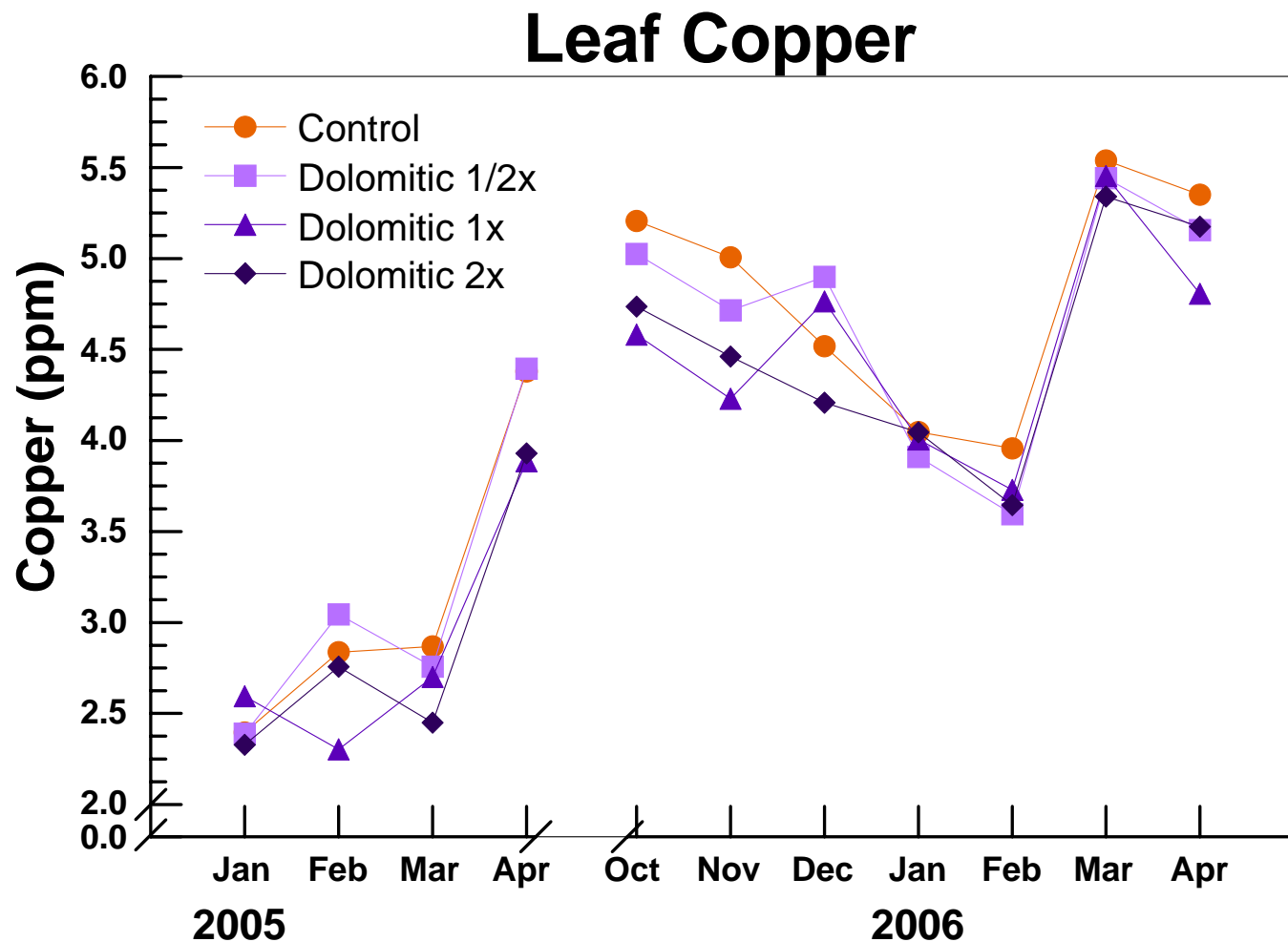


Figure 3-32. Copper concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 3.29 for comparing treatments within a month and LSD ($P < 0.05$) = 1.89 for comparing months within the same treatment.

Soil Copper

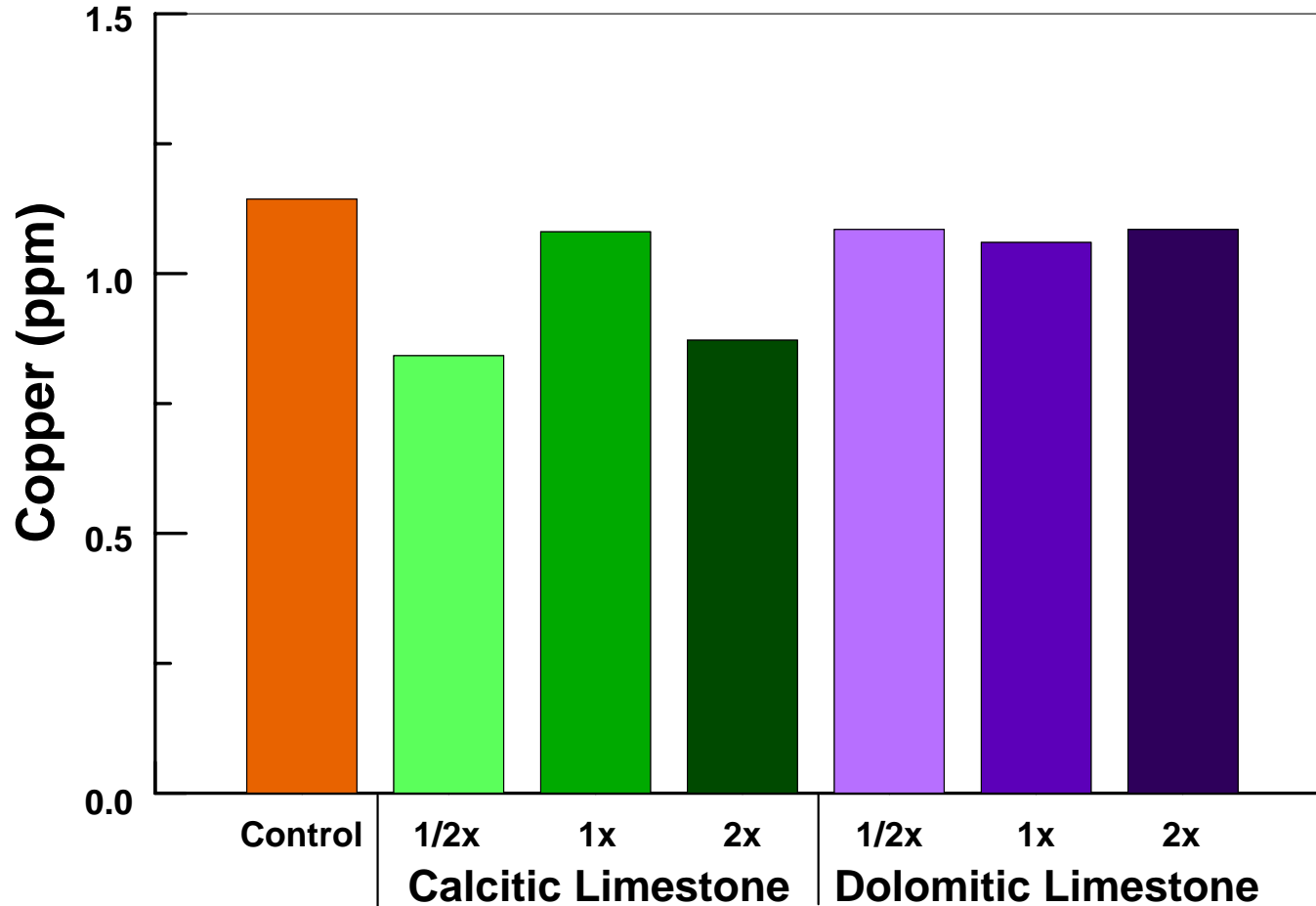


Figure 3-33. Soil copper concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 0.202 for comparing treatments.

Soil Copper

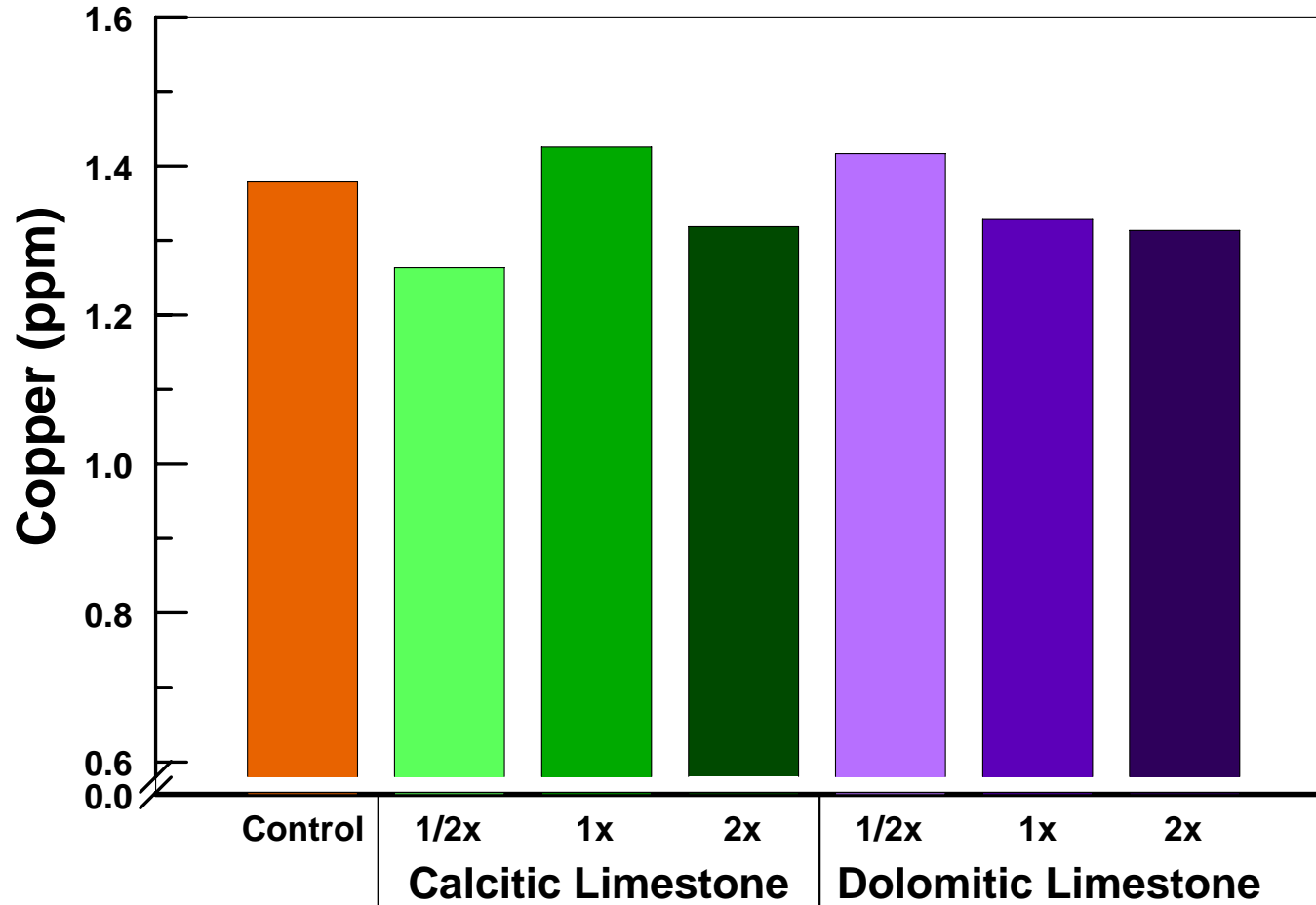


Figure 3-34. Soil copper concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.187 for comparing treatments.

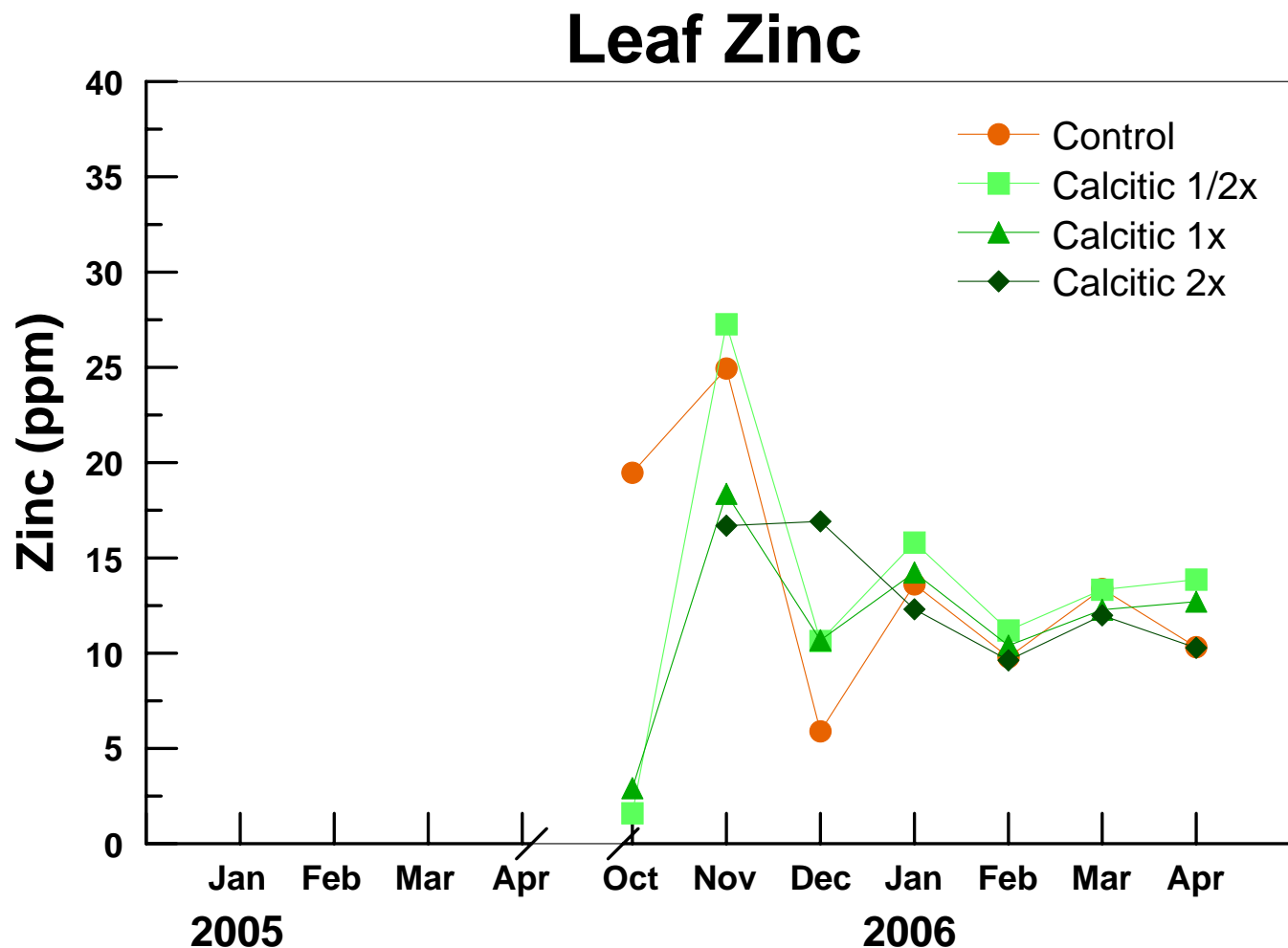


Figure 3-35. Zinc concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at SWC. Means ($n=6$). LSD ($P<0.05$) = 19.47 for comparing treatments within a month and LSD ($P<0.05$) = 6.57 for comparing months within the same treatment. Data from Jan to Apr 2005 harvests were removed due to large variations.

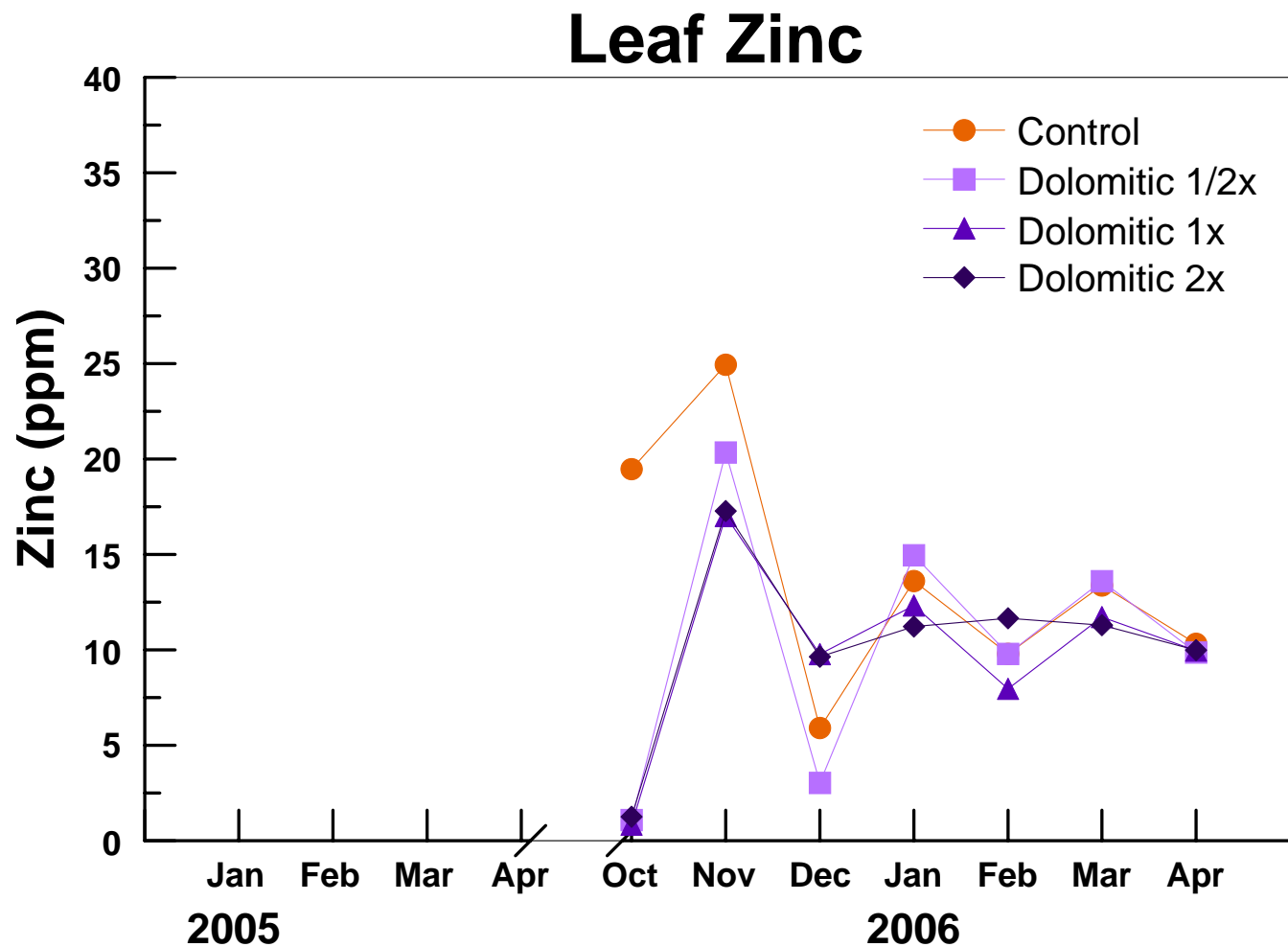


Figure 3-36. Zinc concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at SWC. Means (n=6). LSD ($P < 0.05$) = 19.47 for comparing treatments within a month and LSD ($P < 0.05$) = 6.57 for comparing months within the same treatment. Data from Jan to Apr 2005 harvests were removed due to large variations.

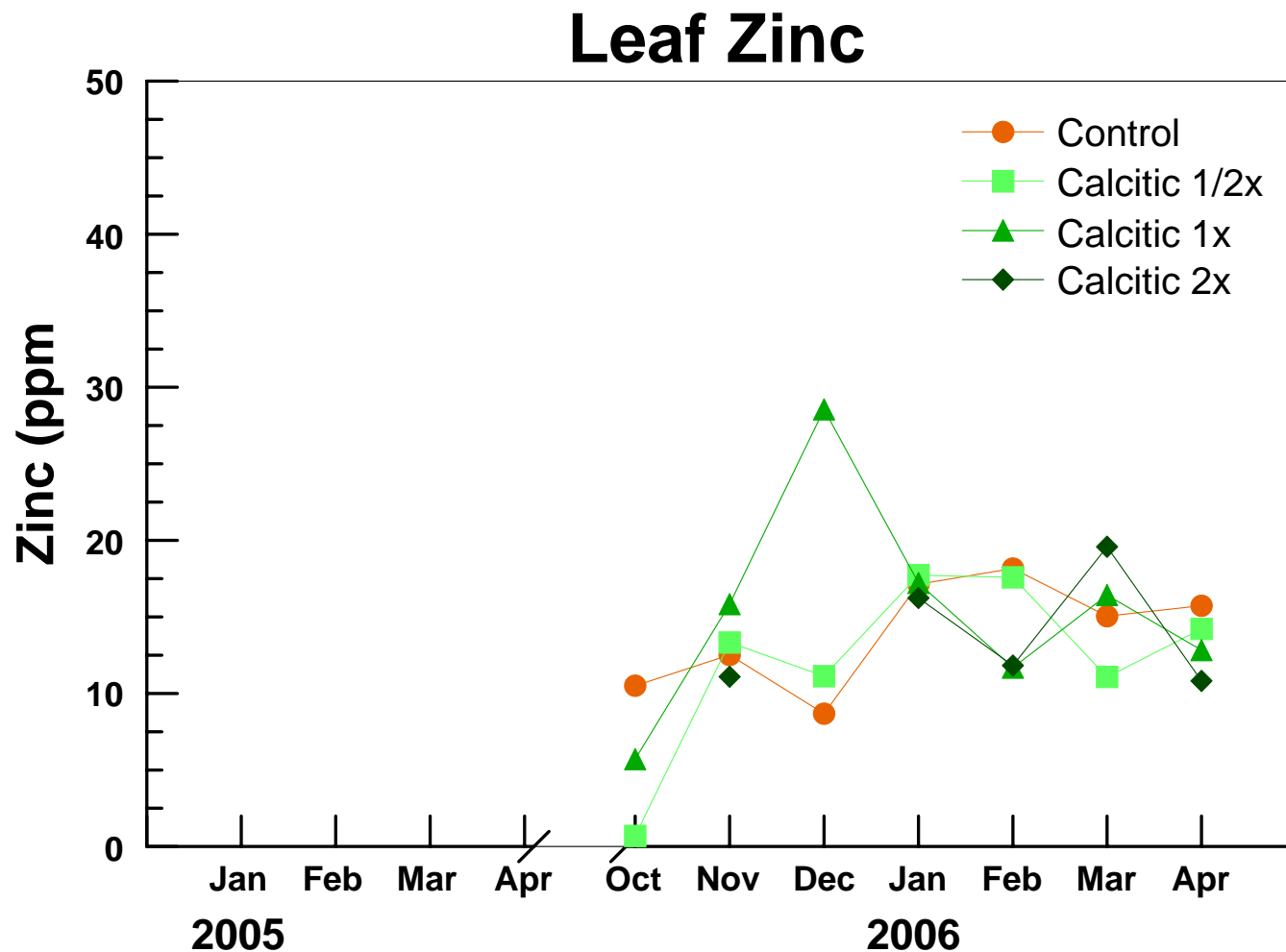


Figure 3-37. Zinc concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of calcitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 25.75 for comparing treatments within a month and LSD ($P < 0.05$) = 8.78 for comparing months within the same treatment. Data from Jan to Apr 2005 harvests were removed due to large variations.

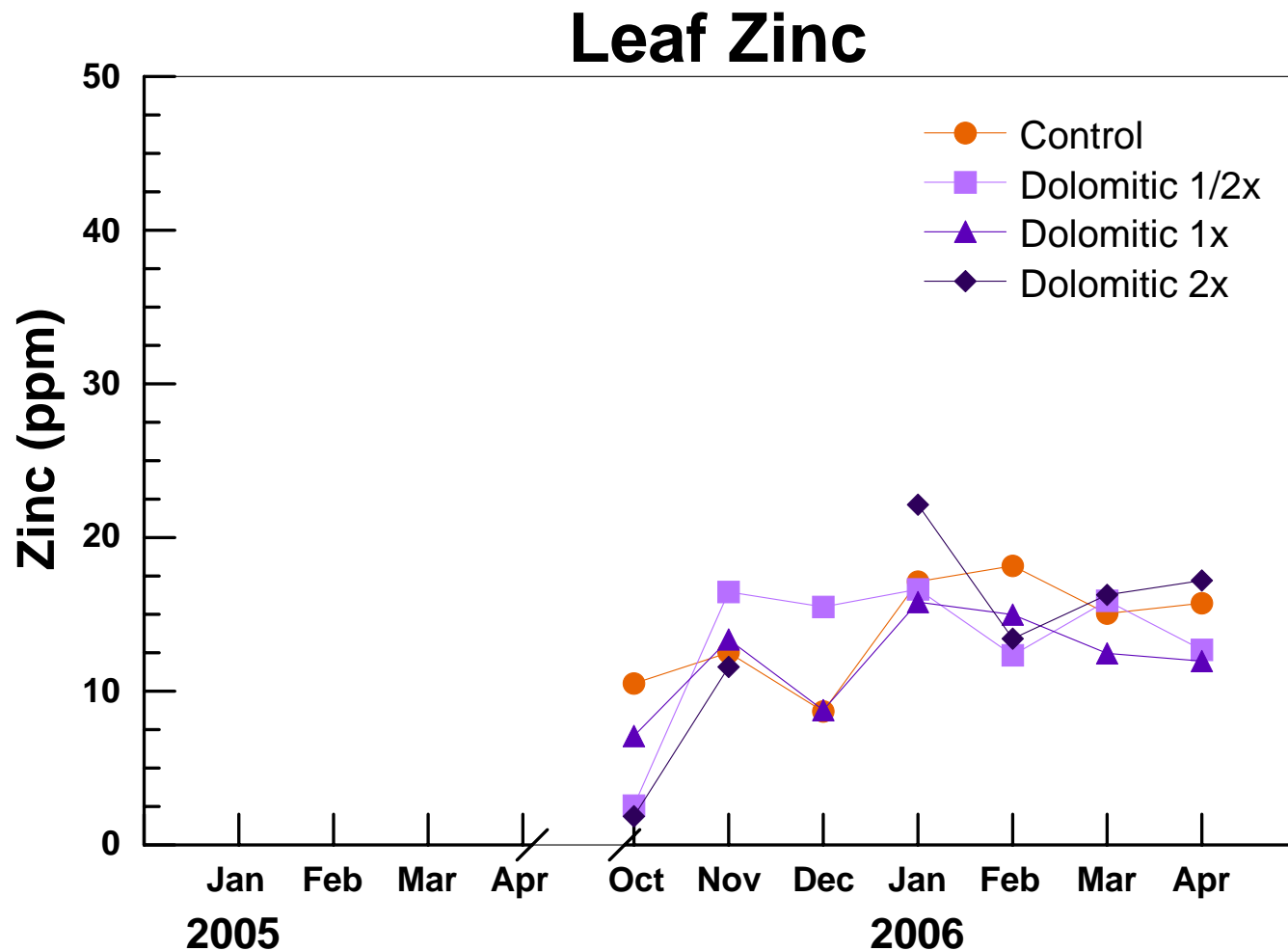


Figure 3-38. Zinc concentrations in stockpiled tall fescue leaves harvested monthly from plots treated with 0x, 1/2x, 1x, and 2x the recommended rate of dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 25.75 for comparing treatments within a month and LSD ($P < 0.05$) = 8.78 for comparing months within the same treatment. Data from Jan to Apr 2005 harvests were removed due to large variations.

Soil Zinc

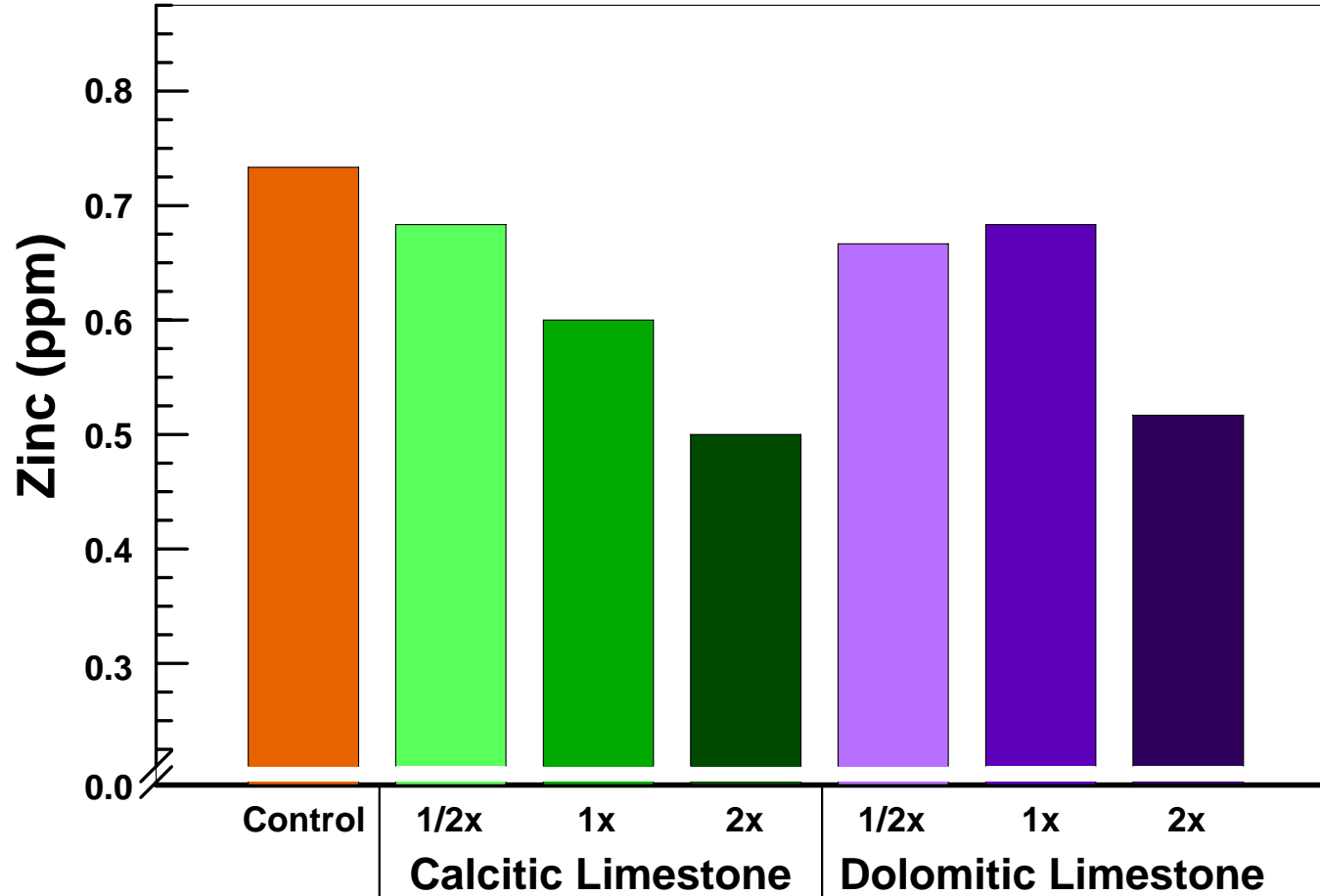


Figure 3-39. Soil zinc concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at SWC. Means (n=6). LSD (P<0.05) = 0.175 for comparing treatments.

Soil Zinc

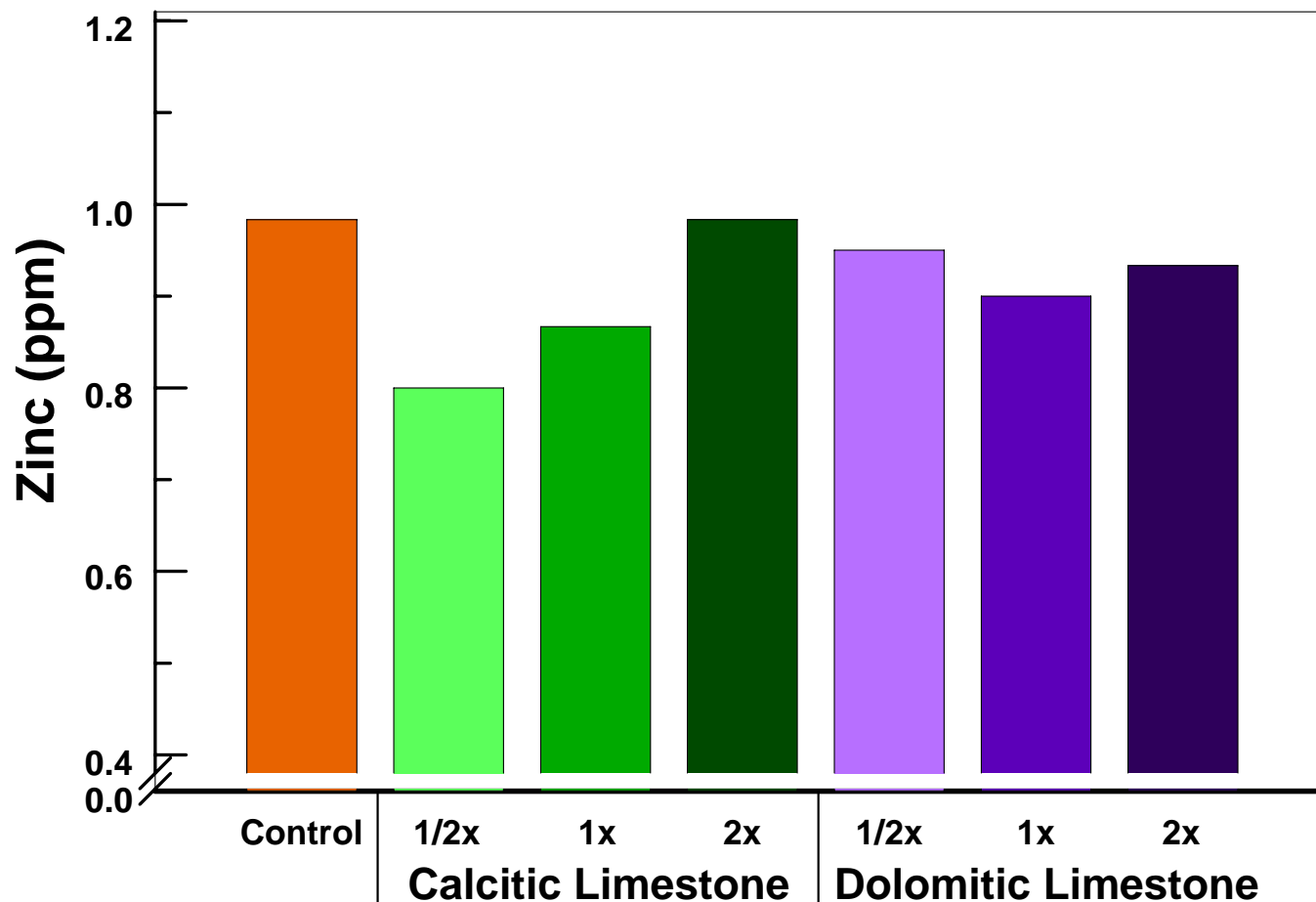


Figure 3-40. Soil zinc concentrations 19 months after application of 0x, 1/2x, 1x, and 2x the recommended rate of calcitic and dolomitic limestone at BREC. Means (n=6). LSD ($P < 0.05$) = 0.244 for comparing treatments.

CHAPTER 4

Summary

The aim of this study was to examine the impacts of dolomitic and calcitic limestone on the elemental concentrations of stockpiled tall fescue leaves and the underlying soil. Of particular interest, was the effect of limestone on the availability of P, Mg, and Al in the soil and the subsequent leaf concentrations. It was hypothesized that lime would increase the availability of soil P and decrease the availability of soil Al; consequently leaf Mg concentrations would increase, lowering the likelihood of grass tetany.

However, liming did not decrease the availability of soil Al in either the Gerald or Mexico/Leonard silt loams. Additionally, liming did not increase the availability of soil P in these soils. As a result, the calcitic limestone did not have a large effect on leaf Mg concentrations; because dolomitic limestone is essentially a Mg fertilizer, it increased the Mg concentrations in tall fescue leaves. Although it was not via the proposed mechanism, both limestone sources positively affected the grass tetany cation ratio of the forage; both limestone types substantially decreased K concentrations of the forage while dolomitic limestone increased leaf Mg concentrations and calcitic limestone increased leaf Ca concentrations. The impact of limestone on the concentrations of these macronutrients in tall fescue leaves was explained by the effects of limestone on the soil availability of the elements.

The increase in soil pH and the addition of Ca and Mg to the soil as a result of limestone application also altered the dynamics of many other elements in the soil, and, consequently, the availability of the elements to plant roots growing in the soil. Limestone had very little effect on Fe, Cu, and Zn

concentrations in tall fescue leaves and the underlying soils albeit liming is often associated with decreases in availability of all of these elements. However, leaf N and B decreased with increasing limestone applications. Furthermore, extractable soil Mn concentrations decreased, and leaf Mn concentrations followed suit, decreasing by as much as 61% at SWC and 45% at BREC with 2x treatment of calcitic limestone. Extractable soil sulfate increased as did leaf Mo concentrations with increasing limestone rates. Additionally, soil CEC decreased while OM content remained relatively unaltered.

Limestone is applied with the intent of decreasing soil acidity, but there are also important changes in soil and leaf macro-, micro-, and beneficial nutrient concentrations. Liming positively affected plant growth and has the potential to impact the health of grazing animals.