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Resin-Extractable Phosphorus, Vanadium, Calcium and Magnesium as Factors in Maize (*Zea mays* L.) Yield

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With 5 figures and 3 tables

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Abstract

Resin extraction of soil permits evaluation of ratios of readily extracted elements and correlation of concentrations obtained with crop yield. This information provides guidance on potential genotype selection and fertility management. Two hybrids of maize (*Zea mays* L.), designated 2292 and 3895, were grown annually in rotational succession on a 3.2-ha site with soybean (*Glycine max* L.) and wheat (*Triticum aestivum* L.). Soil samples (0–15 cm) were extracted with ion-exchange resins and extracts were analysed with inductively coupled plasma. Data were regressed against crop yield using stepwise multiple correlation methods. Each hybrid was sensitive to unique combinations of extracted chemistries. Both hybrids of maize were sensitive to the resin-extractable V : (V + P) molar ratio and potential losses of ≥ 20 % were indicated as the ratio approached 0.2. A positive response to the Mg : (Mg + Ca) resin-extractable ratio was noted for maize hybrid 2292 in each of three successive years. Changes of yield potentials associated with the Mg : (Mg + Ca) ratio for hybrid 2292 ranged from none to ≥ 20 % as the ratio ranged from 0.2 to about 0.8. The results indicate that, in the presence of large extractable concentrations of competing or inhibitory ions, different approaches to nutrient management in the form of fertilizer nutrient analysis, application, and genotype selection are needed to overcome effects of competing ions.

Key words: calcium — maize — magnesium — phosphorus — resin extraction — vanadium — *Zea mays* L.

Introduction

Traditional examinations of crop yield have focused very intensively on nitrogen, phosphorus (P) and potassium as factors. To a lesser extent, nutrient elements such as sulphur, zinc, copper, boron, manganese and iron have received some attention. Of course, the 'heavy metals' of cadmium, lead, chromium, strontium and nickel have also received some attention. Several chemical elements are generally ignored because (1) they are detrimental to crop production or (2) the research has been conducted in such a manner that their effect on plant response was obscured or overlooked.

Using a resin-extraction (RE) technique, Olness and Rinke (1994) were able to obtain suites of readily extractable elements for a 3.2-ha site in western Minnesota in an experiment which had maize, soybean, and wheat grown in rotation. Resin-extraction of soils using this method obtains a suite of readily extractable elements, avoids microbial effects on soil redox potential and imposes a minimal chemical potential. An evaluation of soil samples collected during soybean production showed a strong correlation between the RE vanadium (V) : (V + P) ratio and seed yield (Olness et al. 2000). A distinct difference in sensitivity to the V : (V + P) ratio between varieties was also noted.

A survey of surficial materials conducted by Shacklette et al. (1971) found total V of > 120 $\mu g\ g^{-1}$ in 137 of 955 sites examined (Fig. 1). Thus, in some cases, the concentration of V may equal about 25–50 % that of inorganic P on a molar basis. The distribution of sites having V concentrations > 120 $\mu g\ g^{-1}$ does not seem to show distinct patterns. The Pacific north-west appears to have the greatest concentrations of V but concentrations > 120 $\mu g\ g^{-1}$ occur across the US.

While V has been given little attention, it has long been a source of controversy. As early as 1886, Witz and Osmond noted in a footnote that very small concentrations of V inhibited plant growth.

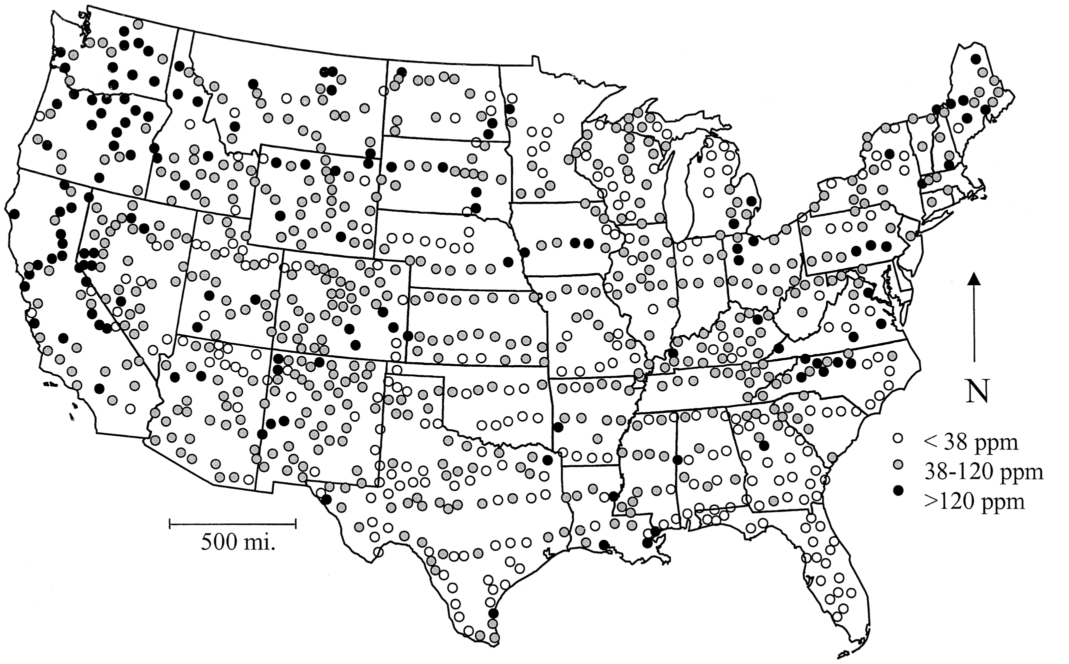

Fig. 1: The distribution of vanadium in surficial deposits (from Shacklette et al. 1971)

Bertrand (1950), in an excellent review, noted that in most studies V was toxic to plants; although several studies suggested growth enhancement at concentrations of about 10 ng g^{-1}. Results of most studies of V as a nutrient element for plants were negative until Arnon and Wessel (1953) stated that it was an essential element for green plants.

Work by Peterburgskii et al. (1977) suggested an increased protein content from applications of V to field crops. However, attempts to determine the relative need for V of crop plants generally failed. Work by Singh (1971), Hara et al. (1976), Wallace et al. (1977) and Davis et al. (1978) showed decreased plant growth as a function of added V. Their observations were in general agreement with earlier work by Warington (1954, 1956). In 1983, Bowman noted that P uptake was inhibited as the V concentration increased and that V uptake was inhibited as the P concentration increased for the common bread mould *Neurospora crassa*. These two elements apparently compete with each other for the same cell-membrane transport system. Thus, the uptake of either one in the presence of the other should be proportional (on a molar basis) to the ratio of the elements. Olness et al. (2000), using resin-extraction of soils, have shown that application of the ratio theory provided very close agreement for results obtained at different times and at widely separated locations for maize, kidney bean (*Phaseolus vulgaris* L.), cabbage (*Brassica oleracea*) and wheat.

Because V is a member of Group Vb in the periodic table of the elements, several authors had speculated that V might be incorporated in plants in much the same way as P, a member of Group Va. The two elements have similar chemical valences and ionic sizes (Crans 1994). However, $H_2VO_4^-$ is easily reduced by a variety of reductants to the vanadyl (VO^{2+}) form within the cell and both ions readily coordinate with a number of functional groups (see Crans and Tracey 1998). Internal cellular reduction of $H_2VO_4^-$ to VO^{2+} led us to speculate on the possibility of interactions with calcium (Ca^{2+}) and magnesium (Mg^{2+}) in a set of observations from soybean; an analysis of the data showed a strong seed yield increase as the Mg^{2+} : (Mg^{2+} + Ca^{2+}) molar ratio increased for an iron-chlorosis resistant variety (Olness et al. 2001).

Because V appears to be generally toxic at μmolar levels to a wide range of plants, we reviewed the soil analytical data and maize grain yield data. The objective of this study was to examine resin-extractable concentrations, obtained during soybean production, for evidence of sensitivity of two maize hybrids to V, P, Ca^{2+} and Mg^{2+}.

Materials and Methods

The experiment was conducted on the Barnes–Aasted Association's Swan Lake Research Farm located 24 km NNE of Morris, MN. The site consisted of about 3 ha measuring 108 m by 300 m. Soil mapping units within the site were Barnes loam (fine-loamy, mixed Udic Haploboroll), Buse loam (fine-loamy, mixed, Udorthentic Haploboroll), Hamerly clay loam (fine-loamy, frigid, Aeric Calciaquoll) and Parnell clay loam (fine, montmorillonitic, frigid typic Argiaquoll).

The field was divided into three equal portions and one portion was planted with soybean, maize or wheat; in the next year the crops were rotated so that maize followed soybean, soybean followed wheat and wheat followed maize. Each crop area was further subdivided into 360 plots measuring 3 m by 10 m. Each plot consisted of four rows of maize planted at a rate of 7.4 seeds m^{-2} at 0.75-m row spacing. Two maize hybrids (designated 3895 and 2292) were selected from among hybrids commercially grown in the area and planted continuously (that is, without subplot borders) over the 300-m length of the field. Grain yields were taken from the central 8 m of the two central rows of each plot with a plot combine and samples were withdrawn for further characterization. Plant population densities, barren plants and damaged plants were determined at harvest by counting all plants in 7.5 m of row in the two central rows of each plot.

Soil samples had been taken from plots on which soybean had been grown in the previous year (see Olness et al. 2000 for additional details and soil data). Five core samples (0–60 cm) were taken from the centre two rows of alternate plots, segmented into 15-cm increments, and each segment was composited into a single sample (about 540 samples over the 3.2-ha area). Soils were dried at about 60 °C and ground for chemical analyses. Resin extractions were conducted using the procedure described by Olness and Rinke (1994) with modifications described in Olness et al. (2000). Briefly, soil suspensions (6 g in 40 ml of 20 % ethanol) were equilibrated with cation and anion resin extractors ($NaNO_3$ saturation) for 5 days with slow continuous rotary mixing. Resins were subsequently washed with HCl and extracts were submitted to the Analytical Research Laboratory of the University of Minnesota, St. Paul for inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

Grain yields were plotted against various extracted chemical species and reviewed for evidence of curvilinearity before statistical analyses were conducted. Standard regression analyses were applied using SAS PROC REG with forward, backward and max R2 options and PROC GLM programs (SAS 1989).

Results and Discussion

Before evaluating the data for effects of various resin-extractable entities, the harvest data were examined for uniformity of plant population density (ppd) and evidence of insect damage (Table 1). Final harvest ppds were not measurably different between hybrids ($P > 0.1$) but did appear to vary slightly between years ($P < 0.05$). The ppds were lowest in 1997 (7.01 plants m^{-2}) and highest in 1998 (7.31 plants m^{-2}). The ppd differences were < 5 % and yields were not measurably affected by these differences, probably because interplant competition causes plants to produce less than the maximum number of seeds. The number of broken plants, and to a lesser extent dropped ears, indicates stress mainly due to European corn borer (*Lepidoptera pyrlidae*); these values were generally < 1 % except in 1996 when about 1–4 % of the plants were affected. Hybrid 2292 had measurably fewer dropped ears and barren plants than hybrid 3895 (both $P < 0.01$) but the number of affected plants was small and there was also no measurable effect on yield. Unlike the soybean yields, no plots were lost to excessive moisture (Olness et al. 2000).

Maize grain yields ranged from 6.03 to 14.0 megagrams (Mg) ha^{-1} and showed slight interannual variability (Table 2). While climate varied, the range

Table 1: Selected harvest plant population characteristics

		Population			
		plants m^{-2}	plants ha^{-1}		
Year	Hybrid	Harvest	Broken[1]	Barren[2]	Dropped[3]
1996	3895	7.09 ± 0.94	363 ± 335	69 ± 383	61 ± 87
	2292	7.14 ± 0.86	79 ± 92	14 ± 115	26 ± 43
1997	3895	7.04 ± 0.39	5 ± 8	11 ± 50	9 ± 9
	2292	6.98 ± 0.37	6 ± 10	7 ± 32	4 ± 6
1998	3895	7.31 ± 0.27	1 ± 3	20 ± 179	40 ± 69
	2292	7.31 ± 0.31	1 ± 3	9 ± 114	2 ± 12

[1]Values represent populations of plants whose stalk was broken below the ear and which, as a consequence, had greater risk of loss with mechanical harvesting.
[2]Ears had ≤ 5 kernels.
[3]Ears had abcissed from the plant.

Table 2: Maize grain yields in three consecutive years at the Barnes Aasted Research Farm

	Grain yield (Mg ha^{-1})		
Year	Minimum	Maximum	Mean
Hybrid 2292			
1996	6.71	14.0	9.73
1997	7.91	10.7	9.34
1998	9.10	12.9	11.3
Hybrid 3895			
1996	6.03	10.0	8.51
1997	7.85	10.3	9.73
1998	9.54	12.7	10.8

of variation was rather small; the 1996 growing season was cooler and drier than average and the 1998 growing season was warmer than the long-term average (Figs 2 and 3). Over the 3-year period, hybrid 2292 averaged 10.1 ± 1.04 Mg ha^{-1} and hybrid 3895 averaged 9.68 ± 1.16 Mg ha^{-1} (14.5 % moisture); these yields are regarded as slightly higher than average in the local area. Median yield values deviated from the means by < 0.15 Mg grain ha^{-1} for each hybrid in each year.

Maize yields were correlated with RE-V (resin-extractable vanadium), -Mg and -Ca, and the RE-V : (V + P) molar ratio ($P < 0.1$; Table 3).

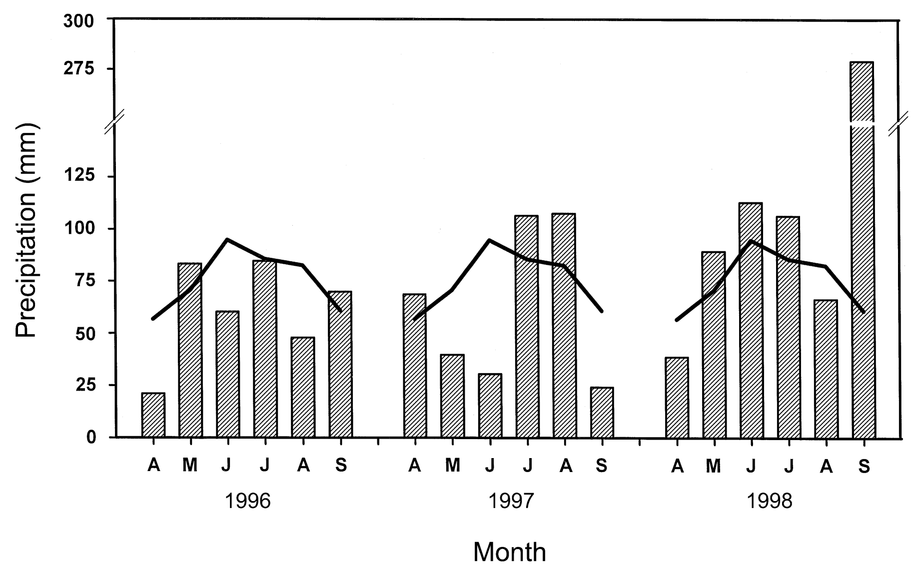

Fig. 2: Precipitation received during the growing seasons of 1996, 1997, and 1998 at the Barnes Aasted Research Farm, Morris, MN. The solid lines represent long-term mean values

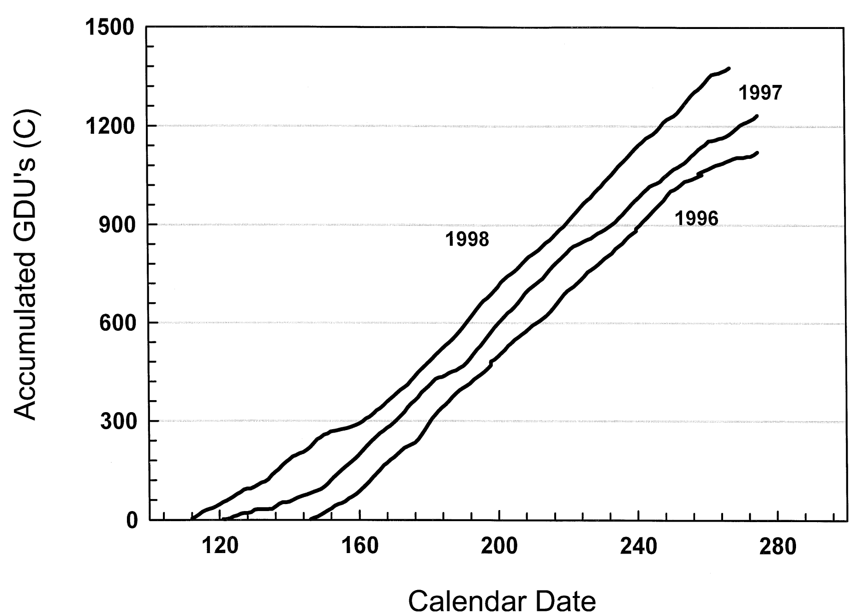

Fig. 3: Accumulated growing degree days during the growing seasons of 1996, 1997, and 1998 at the Barnes Aasted Research Farm, Morris, MN

Table 3: Statistical summary of eight variable coefficients affecting maize hybrid yields at the Barnes-Aasted Research Farm

	Regression analysis technique[1]					
	Forward selection		Backward Elimination		Maximum R^2	
REx[2] variable	Hybrid 2292	3895	Hybrid 2292	3895	Hybrid 2292	3895
Intercept	7.61	10.2	7.07	9.58	7.61	9.78
V	**-1.77×10^{-1}**	**-1.01×10^{-1}**	**-1.91×10^{-1}**	**-1.12×10^{-1}**	**-1.77×10^{-1}**	**-1.09×10^{-1}**
P	-3.81×10^{-4}	ns	ns	ns	-3.82×10^{-4}	-3.47×10^{-5}
Mg	**-2.79×10^{-1}**	**-1.20×10^{-1}**	**-2.87×10^{-1}**	**-1.50×10^{-1}**	**-2.79×10^{-1}**	**-1.40×10^{-1}**
Ca	**1.74×10^{-1}**	6.61×10^{-2}	**1.86×10^{-1}**	**1.07×10^{-1}**	**1.74×10^{-1}**	**9.77×10^{-2}**
V : (V + P)	−7.94	−5.23	ns	−4.84	−7.94	−5.15
Mg : (Mg + Ca)	7.79	−1.06	7.90	ns	7.79	-3.78×10^{-1}
Mg : (Mg + 1000V)	1.17	ns	ns	20.7	**1.17**	**20.3**
Ca : (Ca + 1000V)	−1.44	ns	ns	−20.6	**−1.44**	**−20.2**
R2	0.332	0.250	0.314	0.281	0.332	0.282

[1]Bold-faced coefficients are the most important factors in terms of regression analysis probabilities ($p < 0.10$).
[2]All variables given as resin-extractable concentrations in molar units (micro or nano) g^{-1} soil except intercept values which are given in megagrams ha^{-1}.
ns = non-significant; that is, the statistical technique omits these variables within a variety and considers them non-significant factors in explaining the variance in seed yield.

Some differences between regression techniques are noted; for example, backward elimination accepted only V, Mg and Ca for both maize hybrids while forward selection included both the RE-V : (V + P) and RE-Mg : (Mg + Ca) molar ratios for both hybrids as factors determining grain yield. With backward elimination, the RE-V : (V + P) molar ratio was important for hybrid 3895 and the RE-Mg : (Mg + Ca) molar ratio was important for hybrid 2292.

In using multiple regression, several assumptions are made. Plots of the data indicated simple linear effects but this is probably due to the range of observations rather than the nature of the possible effects. At this point rather simple ratios have been explored without coefficients for the variables [except in the Mg : (Mg + 1000V) and the Ca : (Ca + 1000V) ratios]. More complex relationships may have been obscured because of the variances in the data and the limited range of the data. The ratios have been somewhat arbitrarily selected and only a few of the possible relationships have been explored. For example, because VO_4^- is easily reduced to VO^{2+} a more complex ratio effect with several cationic forms may and probably does exist. Finally, the size of specific coefficients depends somewhat on the suite of variables entered.

The RE-V and RE-V : (V + P) molar ratio effects appear to be general and rather unaffected by interannual climatic variability. The loss of yield potential was as great as 20 % as the RE-V : (V + P) molar ratio increased from 0.0 to about 0.2 for both hybrids (Fig. 4). The estimated regression coefficients for the V : (V + P) ratio effect ranged from −4.84 to −7.94 whereas the coefficients for RE-V alone ranged from about

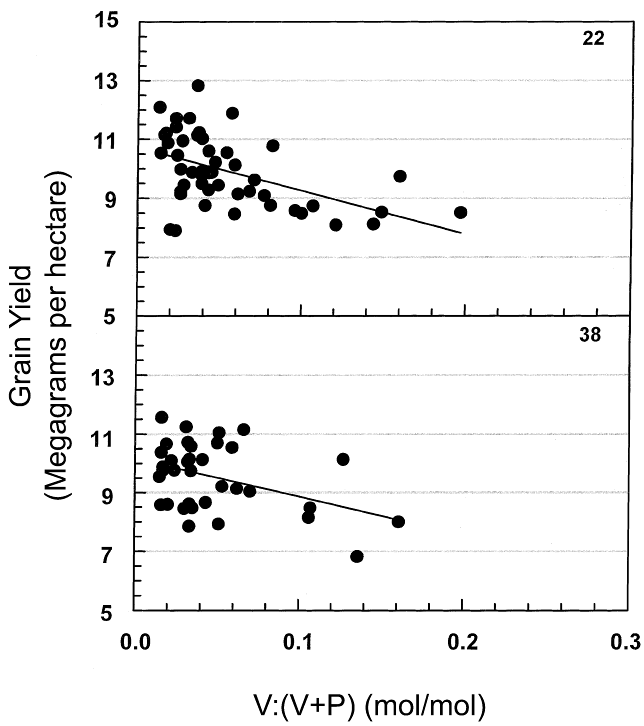

Fig. 4: The relative effect of the RE-V : (V + P) molar ratio on grain yield of maize over a 3-year period. Ratios of < 0.004 have been omitted

−0.10 to −0.18. Thus while the extracted V : (V + P) molar ratio is small, the relative effect makes it a more important factor of yield than either P or V alone. Grain yields of both hybrids seemed unresponsive to RE-P; this suggests that soil P was adequate for maximal seed yield (data not shown). The variance was too large to conclude that the V : (V + P) ratio effect was curvilinear. A curvilinear effect is reasonably expected in the light of growth chamber studies with soybean (data not shown). Although more complex models often provide improvements in many regression analyses, they were ignored here because no logical explanation of such an effect is apparent.

The increase in variance of yield as the V : (V + P) ratio decreases is due to error associated with very small concentrations of extracted V and occasionally of P. The RE concentrations at these ratios are in the nanomolar range. While V is toxic at elevated concentrations and this toxicity appears to be mitigated by the RE-P concentration, we cannot exclude V as an essential element at very dilute concentrations. Such a condition is consistent with the fact that V is essential or promotional for certain enzyme systems (Schwabe et al. 1979, Boer et al. 1986, Vilter 1995). If such is the case, then the simple linear regression techniques will obscure the essentiality of the element and the R^2 values will, of course, be rather small. In the absence of detectable amounts of RE-V, however, the mean grain yields were about 10–11 Mg ha^{-1} and no support for essentiality was obtained.

Regression analysis also suggests that the RE-Mg : (Mg + Ca) molar ratio is an important factor in grain yield for hybrid 2292 (Table 3 and Fig. 5). Again, the coefficients were rather large and ranged between 7.79 and 7.90, while the molar ratio ranged from about 0.2 to 0.7; thus, this ratio had a rather important effect on yield. The slopes of the ratio effect appeared to vary slightly with year. The slope for 1997 was shallow and only a 10 % yield difference was indicated over the Mg : (Mg + Ca) molar ratio range, whereas the effect was about a 20 % yield difference over a similar range in 1998. The molar ratio effect appeared to be about 25 % in 1996; however, the efficiency of extraction was poorer and the variance greater than in the other two years.

The indicated RE-Mg : (Mg + Ca) molar ratio effect is particularly interesting because the coefficient for RE-Mg is consistently negative and the coefficient for RE-Ca is consistently positive when considered independently; both coefficients are rather small. Thus, the opposite molar effect, a negative molar ratio coefficient, might logically be expected. Soils in this region are very rich in both Mg and Ca so any indication of a positive effect was rather unexpected. Plots of similar data for hybrid 3895 appeared weak, inconsistent and negative and lacked significance (data not shown). The negative effect of Mg may be an indication of marginal drought stress in this region; Mg is more soluble than Ca. Drought stress at flowering can occur even though excessive amounts of moisture are received shortly after planting. Considered by itself, the data indicate that additions of Mg would decrease grain yield slightly.

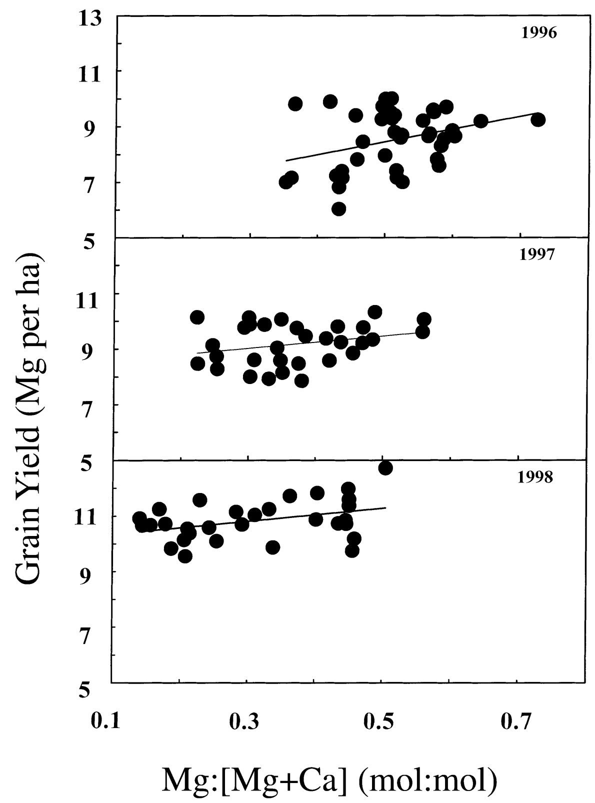

Fig. 5: The relative effect of the RE-Mg : (Mg + Ca) molar ratio on grain yield of maize hybrid 2292

The RE-Mg : (Mg + 1000V) and RE-Ca : (Ca + 1000V) molar ratios were generally inconsistently included in the regression analyses as factors of grain yield determination. When included, however, the RE-Mg : (Mg + 1000V) molar ratio was consistently negative and the RE-Ca : (Ca + 1000V) molar ratio was consistently positive. Thus, as Mg increased relative to V, the grain yield increased; this is consistent with observations in other fields of study that show inhibition of Mg-activated enzymes by V (see review by

Stankiewicz et al. 1995). The apparent positive effect of the RE-Ca : (Ca + 1000V) molar ratio is less easily resolved.

The regression analyses showed very different responses of two maize hybrids to the RE chemical environment. The response of hybrid 2292 to increased Mg relative to Ca was similar to the response of a soybean variety to the same molar ratio (Olness et al. 2001). It is not clear, however, that the Mg : (Mg + Ca) effect represents a direct interaction of Mg with the plant and it is entirely possible that increased relative Mg concentrations may be enhancing auxiliary rhizosphere biota in both the soybean and maize seed yield results. The results suggest that hybrid-variety compatibility in rotations may be worthy of consideration and that fertilizer forms such as $MgSO_4$ and $MgHPO_4$ will provide better economic returns when the appropriate genotype is used.

Conclusions

Resin extraction appears promising for elucidation of complex soil chemical effects on crop production. Resin-extracts of soil showed a correlation between yield decrease in maize as the V : (V + P) molar ratio increased. The intensity of the effect varied with hybrid but appeared to be as great as 20 % in sensitive hybrids.

A clear and repeatable correlation between the RE-Mg : (Mg + Ca) molar ratio and grain yield was obtained for hybrid 2292 but it was not evident with hybrid 3895. The nature of the effect is unclear and surprising because the soils were relatively rich in both Mg and Ca.

The results reveal some of the complexity of the response of hybrids to the environment. They also provide insights as to possible management approaches for fertility applications. For example, banded applications would seem to offer advantages over broadcast applications when the availability of one element is inhibited by the presence of another. Further, changing fertilizer formulation may be beneficial for specific genotypes.

Zusammenfassung

Mit Harz-extrahierbares Phosphor, Vanadium, Kalzium und Magnesium als Faktoren des Maisertrages (*Zea mays* L.)

Harz-extraktionen aus Böden ermöglichen die Auswertung der Verhältnisse bereits extrahierter Elemente und die Korrelation der mit dem Ernteertrag erzielten Konzentrationen. Diese Information liefert eine Anleitung für die potentielle Auswahl der Genotypen und das Fruchtbarkeits-Management. Zwei mit 2292 und 3895 bezeichnete Maiskreuzungen (*Zea mays* L.), wurden in jährlich wechselnder Folge mit Sojabohnen (*Glycine max* L.) und Weizen (*Triticum aestivum* L.) auf einem 3,2 ha großen Feld angebaut. Bodenproben (0 bis 15 cm) wurden mit Ionenaustauschharzen extrahiert und die Extrakte mit induktiv gekoppeltem Plasma analysiert. Mit mehrfachen schrittweisen Korrelationsmethoden wurde eine Datenregression gegenüber dem Ernteertrag durchgeführt. Jede Kreuzung reagierte empfindlich auf bestimmte Kombinationen extrahierter chemischer Stoffe. Beide Maiskreuzungen regagierten empfindlich auf das harz-extrahierbare V : (V + P)-Molverhältnis Potentielle Verluste von ≥ 20 % waren angezeigt, als sich das Verhältnis auf 0,2 zu bewegt. In jedem der drei aufeinanderfolgenden Jahre war für die Maishybride 2292 ein positive Reaktion auf das harz-extrahierbare Mg : (Mg + Ca)-Verhältnis festzustellen. In den Ertragspotentialen ergaben sich in Verbindung mit dem Mg : (Mg + Ca)-Verhältnis der Maiskreuzung 2292 Änderungen im Bereich von 0 bis ≥ 20 %, als das Verhältnis 0,2 bis etwa 0,8 betrug. Die Resultate zeigen, dass beim Vorhandensein großer extrahierbarer Konzentrationen konkurrierender und hemmender Ionen unterschiedliche Ansätze erforderlich sind hinsichtlich des Nährstoffmanagements – in der Form von Düngemittelnährstoff-Analysen-, in der Anwendung und in der Genotypenauswahl, um die Wirkung konkurrierender Ionen zu bewältigen.

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