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Effect of Soil Applications of Sodium Molybdate on the Quality of Potatoes: Polyphenol Oxidase Activity, Enzymatic Discoloration, Phenols, and Ascorbic Acid

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The effect of soil applications of molybdenum on polyphenol oxidase activity, enzymatic discoloration, and total phenolic, chlorogenic acid, tyrosine, and ascorbic acid contents of Katahdin potatoes was investigated. Sodium molybdate was applied at rates of 0.0, 2.8, 6.7, and 10.1 kg/ha. Ascorbic acid increased significantly ($p < 0.01$) with increasing levels of molybdenum fertilization. No significant changes in polyphenol oxidase activity, enzymatic discoloration, or total phenolic, chlorogenic acid, and tyrosine contents were observed at 2.8 and 6.7 kg/ha applications of sodium molybdate. However, there was a highly significant ($p < 0.01$) decrease in polyphenol oxidase activity, enzymatic discoloration, and total phenolic, chlorogenic acid, and tyrosine contents in tubers from plants receiving 10.1 kg/ha of sodium molybdate.

Molybdenum, the only period 5 transition element of consequence to plants, is an essential nutrient for normal plant growth, metabolism, and reproduction. Although it is a mineral, usually occurring as Mo(IV), in aqueous solutions it is predominantly present as molybdate oxyanion, MoO_4^{2-} [Mo(VI)], the form available to plants. This form is the highest oxidative state of the metal. The functions of molybdenum as a plant nutrient are due to the valency changes it undergoes as a prosthetic moiety of certain enzymes, which are few in number and include nitrogenase, nitrate reductase, xanthine dehydrogenase, aldehyde oxidase and sulfate oxidase. Nicholas et al. (1962) showed that the protein component of all these enzymes was similar and speculated that molybdenum may have similar catalytic properties in all these enzymes. However, among these enzymes, only nitrogenase and nitrate reductase have been extensively studied and their functions in nitrogen metabolism are well documented. Agarwala et al. (1979),

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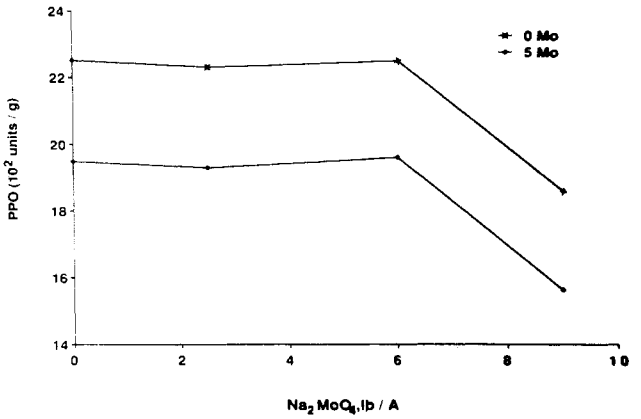

Figure 1. Polyphenol oxidase activity of Katahdin potatoes as affected by molybdenum before and after 5-month storage.

while working on maize plants, have demonstrated the requirement of molybdenum for normal pollen production and viability. Plants deficient in molybdenum showed a decrease in capacity for pollen production, and the pollen grains were smaller, contained no starch, showed poor germination, and had a significantly lower invertase activity than normal plants. Tanner (1978) observed an increase in premature sprouting of maize grains deficient in molybdenum.

Enzymatic discoloration and phenolic and ascorbic acid contents are some of the factors determining potato quality. Hewitt et al. (1950) have observed increases in the ascorbic acid content of tomatoes, Brussels sprouts, Marrowstem kale, cauliflower, rape, savoy cabbage, alsike clover, barley, and sugar beet with an increase in molybdenum supplementation and decrease in this compound under molybdenum-deficient conditions. However, no studies have been reported on the effect of molybdenum fertilization on the ascorbic acid content of potatoes, which provide as much as 25% of our daily requirement of the compound.

Mondy et al. (1967, 1979) have shown a highly significant positive correlation between total phenolic content of the tuber and the extent of enzymatic darkening. The effect of molybdenum status in potatoes on enzymatic darkening and phenolic content has not been reported in the literature. However, previous work on other crops has shown changes in amino acid composition due to molybdenum supplementation. Since tyrosine is one of the two main phenols in potatoes, the other being cholorogenic acid, changes in the amount of this amino acid and subsequent changes in discoloration are possible due to fertilization of the crop with molybdenum.

This investigation was undertaken in order to determine the effect of $NaMo_4$ fertilization on enzymatic discoloration and phenolic and ascorbic acid contents of Katahdin potato tubers.

MATERIALS AND METHODS

Katahdin potatoes grown at the Cornell Vegetable Research Farm, Freeville, NY, were used in this study. Soil type was Howard gravely loam. Sodium molybdate was sprayed with use of a hand sprayer (MAT-OSU Plot Sprayer, Mater International, Inc.) onto the soil at rates of 0.0, 2.8(2.5), 6.7(6.0), and 10.1(9.0) kg/ha (lb/acre) 1 day prior to the planting of seed potatoes. Each treatment was replicated twice. The soil was adjusted to pH $\approx$6.7 to facilitate maximum availability of molybdenum to the plants. The tubers were harvested 21 weeks after planting and stored at 5 °C until analysis. Analysis was done after periods of 0- and 5-month storage.

The tubers were cut longitudinally from bud to stem end and the slices separated into cortex and pith sections. Since cortex tissue is the region highest in metabolic activity, it was used for the determination of enzymatic discoloration and phenolic and ascorbic acid contents. The periderm was removed during the determination of enzymatic discoloration. Ascorbic acid determinations were also carried out on the pith section. Eight tubers were used in each determination, and duplicate determinations were made on each replicate (two replicates/treatment).

Polyphenol Oxidase Activity. Polyphenol oxidase activity was assayed on an acetone extract of fresh tubers as described by Flurkey and Jen (1978). Poly(ethylene glycol) 8000 (5%, w/w) was used as phenolic scavenger.

Determination of Enzymatic Discoloration. Color measurements were made on potato tissue with the Hunter color difference meter as described by Mondy et al. (1967).

Determination of Total Phenolic Content. The spectrophotometric method described by Mondy et al. (1966) was employed using tannic acid as the standard.

Determination of Chlorogenic Acid. Chlorogenic acid content was determined spectrophotometrically on lyophilized tissue as described by Mapson et al. (1963). Chlorogenic acid was used as the standard.

Determination of Tyrosine Content. The tyrosine content of tubers was determined by a modified Millon's reaction as described by Samotus et al. (1982b). Purified tyrosine was used as the standard.

Determination of Ascorbic Acid Content. Ascorbic acid analysis was carried out by a modified iodate titration method (Samotus et al., 1982a).

Statistical Analysis. Complete random design was utilized for statistical analysis, and statistical significance was determined by analysis of variance with protected LSD test as described by Steel and Torrie (1980).

RESULTS AND DISCUSSION

Polyphenol Oxidase Activity. There was a significant ($p < 0.01$) decrease in polyphenol oxidase activity at the 10.1 kg/ha application of sodium molybdate (Figure 1). The 2.8 and 6.7 kg/ha applications did not result in any significant changes in the enzyme activities. These findings appear to be in agreement with those of Nason (1952) who found that polyphenol oxidase activity increased during molybdenum deficiency.

Enzymatic Discoloration and Total Phenolic Content. No significant changes were observed in discoloration at 2.8 and 6.7 kg/ha rates of molybdate application (Figure 2). Total phenolic content also showed no significant changes at 2.8 and 6.7 kg/ha rates of molybdenum fertilization. However, there was a significant ($p < 0.01$) decrease in enzymatic discoloration and total phenolic content at 10.1 kg/ha application of molybdenum fertilization.

Chlorogenic Acid. There was no significant change in the chlorogenic acid content at 2.8 and 6.7 kg/ha levels of molybdenum application (Figure 3). A significant ($p < 0.01$) decrease in chlorogenic acid content was observed in tubers from plants receiving 10.1 kg/ha sodium molybdate.

Tyrosine. No significant change in the tyrosine content of tubers from plants receiving 2.8 and 6.7 kg/ha of molybdenum was observed (Figure 4). Application of 10.1 kg/ha resulted in a significant ($p < 0.01$) decrease in the tyrosine content of tubers.

Ascorbic Acid. There was a highly significant ($p < 0.01$) increase in ascorbic acid content with increasing levels of molybdenum fertilization (Figure 5). This finding is in agreement with that of Hewitt (1950) who also found

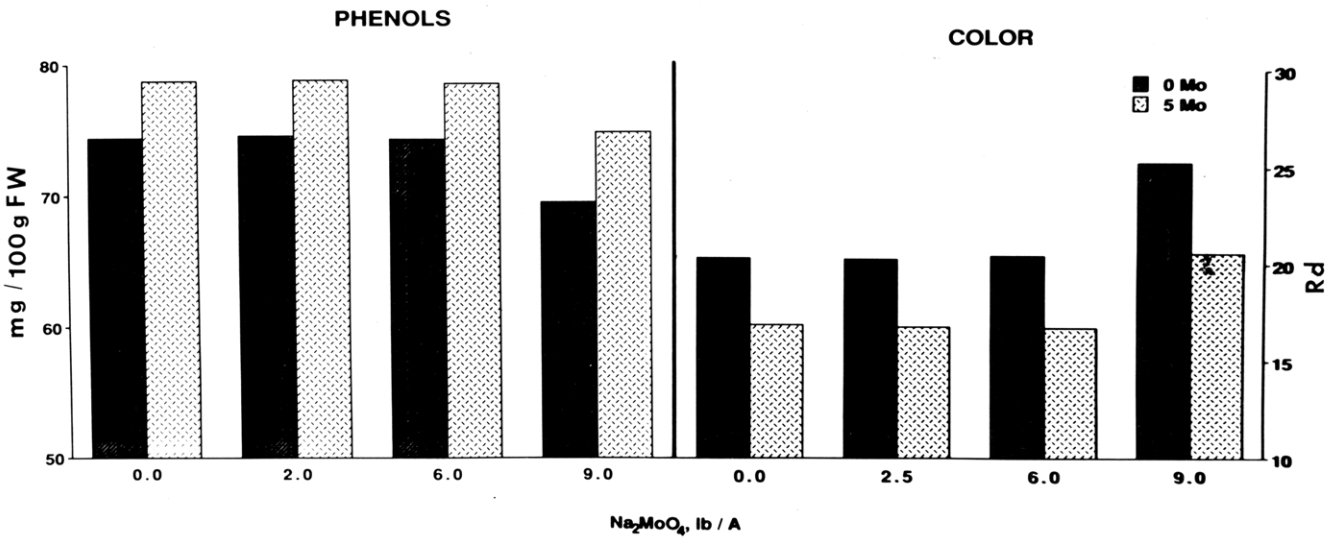

Figure 2. Effect of molybdenum on total phenolic content and enzymatic discoloration of Katahdin potatoes before and after 5-month storage.

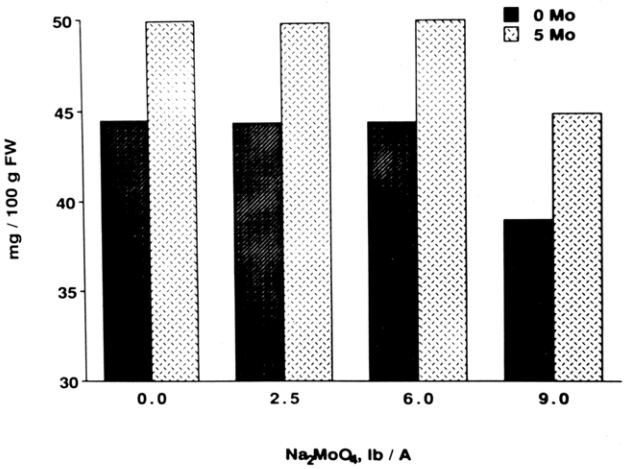

Figure 3. Chlorogenic acid content of Katahdin potatoes as affected by molybdenum before and after 5-month storage.

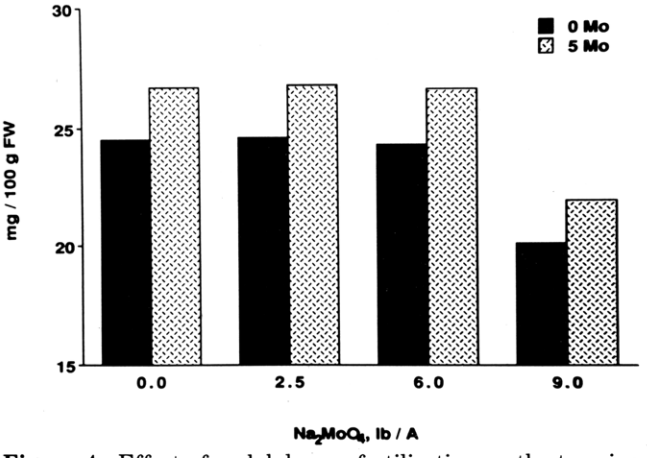

Figure 4. Effect of molybdenum fertilization on the tyrosine content of Katahdin potatoes before and after 5-month storage.

an increase in ascorbic acid content of several vegetables upon application of sodium molybdate.

No visible signs of molybdenum toxicity were observed in any of the plants even at the highest level of molybdenate application. The molybdenum content of the tubers from plants receiving molybdenum fertilization were not significantly higher than the controls. The level of molybdenum in the tuber at the highest level of fertilization and the control was 0.598 ppm. No toxicity studies

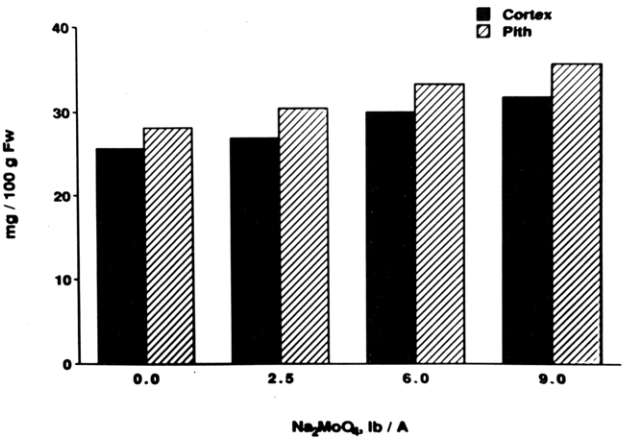

Figure 5. Effect of molybdenum fertilization on the ascorbic acid content of Katahdin tubers.

of molybdenum on humans have been reported in the literature, but Underwood (1971) reported that intake of molybdenum levels greater than 10–20 ppm has been shown to be harmful to animals such as horses, pigs, and cattle. Clearly, the levels reported in our study were far below the levels considered to be toxic to the animals.

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Registry No. Na_2MoO_4, 7631-95-0; ascorbic acid, 50-81-7; L-tyrosine, 60-18-4; chlorogenic acid, 327-97-9; polyphenol oxidase, 9002-10-2.

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Separation of Immunoglobulins from Bovine Blood by Polyphosphate Precipitation and Chromatography

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Mapping super-simplex optimization was applied to separation of crude immunoglobulins (Ig) from blood plasma by polyphosphate precipitation. The best conditions found were pH 3.95, NaCl 0.132 M, polyphosphate 1.04%, and temperature 12.7 °C. Cu-loaded immobilized metal affinity chromatography yielded almost pure IgG when the crude Ig was applied after residual polyphosphate was removed by ion exchange. DEAE-Sephacel also purified the crude Ig to about the same purity. The purified IgG separated from blood plasma and from cow's colostrum both became unstable at temperature above 70 °C and pH below 3 and were almost equally degraded by pepsin and trypsin hydrolyses. The leftover plasma proteins can be used as a food ingredient.

Recently the utilization of animal blood has been of growing interest because it contains biologically active compounds, e.g., immunoglobulins, transferrin, fibronectin, fetuin, and heme, that are believed to play important roles in a wide variety of biological activities including passive immunity, oncogenic transformation, growth-promoting function, etc. (Gaillard et al., 1985), and also is a source of nutritional and functional proteins that are not alien in meat products (Crenwelge et al., 1974).

In newborn pigs, the protective value of orally administered immunoglobulins is well documented (Kohler et al., 1975; Hoerlein, 1957). Weaning piglets fed blood immunoglobulin (Ig) preparations had a faster daily weight gain, lower incidence of scours, and reduced mortality (Kennelly et al., 1979), probably due to a passive immunity (McCallum et al., 1977).

In humans, the importance of Ig in infant feeding was well proven by clinical test results in India (Narayanan et al., 1983). Successful treatment of *Escherichia coli* gastroenteritis of infants by feeding immunized cow colostrum was reported by Packard (1982) and Ballabriga (1982).

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Bovine blood contains approximately 18% protein, and plasma contains about 6% protein. Concentrations of bovine immunoglobulins are 22.0, 58.8, and 0.85 mg/mL in the serum, colostrum, and milk, respectively (Butler, 1974).

At present, however, little blood protein is recovered for human consumption in Canada. Most of the blood from meat- and poultry-processing plants is used in the production of blood meal or other byproducts for animal feeding (Jones et al., 1982) or as a fertilizer.

Most popular methods for plasma protein isolation entail precipitation with ammonium sulfate or ethanol. However, these precipitation methods have problems in the disposal of solvent, removal of high salt, production of heterogeneous protein mixture, and potential denaturation of proteins during isolation.

Polyphosphates have been extensively used as additives in food processing. Sofas (1986) has stated that the meat industry may use polyphosphates in low-NaCl meat formulations with the potential of improving the quality of low-salt products and of using as antimicrobial agents in meats at reduced NaCl levels. McKee and Tucker (1966) found that the metaphosphate complex of lactalbumin was useful as a substitute for milk solids in cake and cookie formulations. Also sodium hexametaphosphate has been used as an anticoagulant (Gunstone, 1980). Etheridge et al. (1981) demonstrated the functional and chemical

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