Phytoavailability of Zinc in Postbloom Zinc Sprays Applied to 'Golden Delicious' Apple Trees

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Summary. **Postbloom zinc (Zn) sprays are replacing dormant and postharvest sprays as the primary means for applying Zn in commercial apple (*Malus ×domestica*) orchards. We conducted a multiyear field study comparing the phytoavailability of Zn in 11 commercially available Zn spray products, plus reagent-grade Zn nitrate and a water-sprayed control, applied postbloom at identical Zn concentrations to 'Golden Delicious' apple trees. Two sprays were applied per season (mid-May and mid-June), at per-spray rates of either 0.5 lb/acre in 2000 or 1.0 lb/acre in 2001 and 2002. No sprays were applied in 2003 in order to evaluate carry-over effects. The Zn sprays had no effect on fruit number, bitter pit or russeting, or on leaf green color. Zinc concentrations of detergent plus acid-washed leaves (a procedure used to remove surface residues of the Zn sprays) sampled in August and of unwashed winter buds sampled the following January were used as indices of tree Zn status. Leaf Zn concentration generally increased in the order: Zn phosphate < Zn oxide = Zn oxysulfate < chelated/organically complexed Zn ≤ Zn nitrate. There was little consistent difference among chelated and organically complexed Zn products. Leaf Zn concentration varied considerably between seasons, and was not related to Zn application rate. All of the Zn sprays increased leaf Zn concentrations to desirable levels. Because the inorganic Zn-based products typically are substantially less expensive per unit of Zn, it may be less costly and just as effective to use a higher rate of an inorganic Zn product as to use a lower rate of a more expensive chelated or organically complexed Zn product. On the other hand, use of low rates of highly phytoavailable Zn products minimizes release of the nutritionally essential but potentially ecohazardous metal into the environment. There was no detectable lasting effect of the three previous seasons of Zn sprays on leaf Zn in 2003. Similarly, there was no detectable effect in any year of the Zn spray treatments on bud Zn concentration the following winter. These results suggest that the amount of Zn supplied by the sprays at the tested rates was insufficient to promote substantial Zn accumulation within the trees, thereby validating the recommendation for annual application of Zn nutritional maintenance sprays.**

Zinc deficiency is widespread in apple orchards in the western United States and British Columbia (Luce and Bartram, 1947; Neilsen, 1988; Oberly and Boynton, 1966). It occurs naturally and visually is expressed as little leaf, rosetting, leaf chlorosis, blind wood, and shoot dieback (Woodbridge, 1954). Zinc deficiency can reduce the amount of marketable fruit in affected orchards because of its direct influence on the amount of viable fruiting wood. Dormant sprays of high rates of inorganic Zn salts traditionally used on apple trees usually eliminated Zn deficiency symptoms but often were found to have little or no effect on leaf Zn concentration (Benson, 1953a; Heeney et al., 1964; Neilsen and Hoyt, 1990). Postharvest Zn sprays sometimes were less effective than dormant sprays for controlling Zn deficiency symptoms on apple, and have been associated with delayed dormancy and possible winter injury (Benson, 1953a; Lindner and Luce, 1944; Neilsen and Hoyt, 1990).

Because of their greater effect on leaf Zn concentration, postbloom sprays of Zn applied at lower rates and as safer formulations are replacing dormant and postharvest Zn sprays (Hoffman and Samish, 1966; Neilsen and Hogue, 1983; Orphanos, 1975; Sanchez and Righetti, 2002; Swietlik, 2002). Movement of foliarly applied radiolabeled or heavy isotopic Zn into fruit and nut tree leaves and subsequent intra-plant transport of the absorbed Zn have been confirmed (Boaretto et al., 2002; Crowley et al., 1996; Wadsworth, 1970; Zhang and Brown, 1999a, 1999b). There are many commercially available Zn nutritional spray products labeled for postbloom use, which vary in Zn concentration, physical state, chemical composition, and cost. The chemistry of these sprays directly influences their effectiveness (Ferrandon and Chamel, 1988). Postbloom Zn sprays under some conditions can impair fruit finish, particularly the incidence and severity of russeting (Benson, 1953b). In addition to improving apple tree Zn nutrition, adopting spray practices and products that enhance fertilizer Zn phytoavailability can lower Zn application rates, thereby reducing environmental loading with this potentially ecohazardous heavy metal (Peryea, 2001).

Use of postbloom sprays complicates interpretation of leaf Zn analysis by creating a possibility of leaf surface contamination. Numerous researchers have addressed this issue by evaluating or recommending a sequential detergent and hydrochloric acid (HCl) washing procedure to remove surface Zn spray residues. Adding an acid wash step to the normal detergent washing procedure usually but not always removed an additional amount of Zn

Units

To convert U.S. to SI, multiply by	U.S. unit	SI unit	To convert SI to U.S., multiply by
10	%	$g \cdot kg^{-1}$	0.1
0.4047	acre(s)	ha	2.4711
0.3048	ft	m	3.2808
3.7854	gal	L	0.2642
25.4000	inch(es)	mm	0.0394
1.1209	lb/acre	$kg \cdot ha^{-1}$	0.8922
28.3495	oz	g	0.0353
1	ppm	$mg \cdot kg^{-1}$	1
(°F – 32) ÷ 1.8	°F	°C	(1.8 × °C) + 32

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compared to detergent washing alone. Ashby (1969) and Smith and Storey (1976, 1979) felt that leaf Zn remaining after detergent plus acid washing was located within the leaf tissue; however, most authors concluded that some external residues were likely to remain on or embedded in the detergent plus acid-washed leaf surfaces (Chamel et al., 1982; Labanauskas, 1966; Orphanos, 1975, 1977; Smith et al., 1950). Unwashed, detergent-washed, and detergent plus acid-washed leaves from unsprayed fruit trees exhibited identical Zn concentrations, suggesting that the washing procedure does not remove internal leaf Zn (Ashby, 1969; Crowley et al., 1996; Smith and Storey, 1976).

Movement of fertilizer Zn into tree leaves has been confirmed when the Zn is soil-applied (Sparks and Payne, 1982) or foliarly applied (Boaretto et al., 2002; Crowley et al., 1996; Zhang and Brown, 1999a, 1999b). The last-mentioned authors demonstrated that transport of absorbed Zn within and out of Zn-treated leaves increased concurrently with a decline in leaf Zn recalcitrant to detergent plus acid washing, suggesting that, even if some of the Zn recalcitrant to detergent plus acid washing has not been absorbed, it may continue to be phytoavailable. This result was consistent with that of Boaretto et al. (2002), who showed that leaf Zn recalcitrant to detergent plus acid washing increased with residence time of radiolabeled Zn solution on the leaf surface, followed by movement of radiolabeled Zn into other portions of the plants not directly contacted by the Zn solution.

Given these circumstances, it will be difficult to ascertain that the Zn concentration measured in detergent plus acid-washed leaves does not overestimate the concentration of metabolically active Zn in Zn-sprayed leaves; however, it should provide a more accurate estimate than does Zn analysis of unwashed or detergent-only-washed leaves. Zinc concentration in detergent plus acid-washed leaves was used to diagnose Zn nutritional requirements (Herrera, 2000; Smith and Storey, 1976) or to quantify the relative effects of Zn spray products or spray adjuvants on leaf Zn status (Boaretto et al., 2002; Crowley et al., 1996; Hoffman and Samish, 1966; Labanauskas and Puffer, 1964; Orphanos, 1975, 1977, 1982; Smith and Storey, 1979).

The current study was conducted to evaluate the relative phytoavailability and some secondary effects of commercially available Zn spray products applied postbloom to apple trees grown under field conditions. The detergent plus acid washing procedure was used to operationally partition leaf Zn between potentially phytoactive and inert surface residue pools.

Materials and methods

The study was conducted in an irrigated ‘Golden Delicious’/‘Malling 9’ apple orchard planted in 1985 in Wenatchee, Wash. The natural environment is semi-arid sagebrush-steppe. Annual precipitation averages 265 mm. Average January and July temperatures are –1.7 and 22 °C, respectively. The soil is classified as a Burch loam, a coarse-loamy, mixed, superactive, mesic Aridic Haploxeroll. The trees were planted at a 4 × 12-ft spacing (907.5 trees/acre) and were supported by a metal conduit-wire trellis system. The trees were irrigated using a permanent undertree high pressure/high volume sprinkler system. Herbicides were used to maintain a weed-free strip within tree rows. Chemical and hand-thinning of fruit, and control of insect and disease pests were carried out using commercial practice (Smith, 2000).

Thirty-nine experimental plots of single ‘Golden Delicious’ apple trees were identified in four adjacent tree rows. Plots are physically separated within-row by five guard-trees, while experimental trees in adjacent rows are offset by three guard-trees. Thirteen spray treatments, including water, reagent-grade Zn nitrate, and 11 commercially available Zn spray products of varying composition, were imposed on the 39 plots using a randomized complete-block design with three replications (Table 1). Zinc sulfate and Zn chloride were not included in the study. While they are highly soluble in aqueous solution, both have been shown to cause fruit phytotoxicity and therefore are not used commercially on bearing trees postbloom (Benson, 1953a; Boaretto et al., 2002). Solutions or suspensions of the 12 Zn-containing spray products were prepared in polyethylene containers, with individual containers prepared for each experimental plot. Each container contained a constant quantity of actual Zn (0.25 g in 2000 and 0.5 g in 2001 and 2002) and 1.2 L tap water (average amount established empirically on guard trees as that required to bring the single tree of each experimental plot to drip). The entire content of each container was applied to each plot

Table 1. Zinc products used to compare tree responses to and zinc phytoavailability from postbloom zinc sprays applied to ‘Golden Delicious’ apple trees.

Product name	Physical state	Zinc content (% by wt)	Principal ligand accompanying zinc[z]	Manufacturer
Zinc nitrate	solid	22.0	nitrate	J.T. Baker, Phillipsburg, N.J.
Nutra-Phos 0-24-0	solid	12.0	phosphate	Pace International, Seattle, Wash.
Nutra-Phos Zn-K	solid	31.0	phosphate	Pace International
Tech-Flo Zeta Zinc 22	liquid	10.0	oxysulfate	Nutrient Technologies, La Habra, Calif.
Nutra-Spray Zn	solid	50.0	sulfate, oxide	Pace International
Keylate Zinc	liquid	9.0	carboxylate	Stoller Enterprises, Houston, Texas
Zinc Polyamine	liquid	5.8	glucosamine	PhytoChem Laboratories, Pasco, Wash.
ZincMax	liquid	10.2	carbohydrate	NutriAg, Toronto, Ontario
Biomin Zinc	liquid	7.0	glycine	JH Biotech, Ventura, Calif.
Zinc X-tra	liquid	10.0	fulvic acid	Custom Agricultural Formulations, Fresno, Calif.
CM Liquid 9% Zinc	liquid	9.0	lignosulfonate	Custom Agricultural Formulations
Metalosate Zinc	liquid	6.8	amino acids	Albion Advanced Nutrition, Clearfield, Utah

[z] Some products contain additional minor components.

using a portable hand-pump sprayer. The nominal Zn rate was 0.5 lb/acre per spray in 2000 and 1.0 lb/acre per spray in 2001 and 2002, applied twice per season. The first spray was applied in mid-May about 1 week after petal-fall, and the second about 4 weeks later. No sprays were applied in 2003 to evaluate possible carry-over effects of the sprays applied during the previous three seasons.

In addition to the experimental treatments, all of the trees received a foliar spray of 0.55 lb/acre boron (B) in late May 2000. In 2001, they received foliar sprays of 0.55 lb/acre B at delayed dormant, 4 lb/acre nitrogen (N) and 8.7 lb/acre sulfur (S) at petal-fall, and 1.5 lb/acre per spray of calcium (Ca) in the first through third cover sprays. In 2002, all of the trees received nutrient sprays of 0.25 lb/acre B at delayed dormant, 4 lb/acre N and 8.7 lb/acre S at petal-fall, 0.5 lb/acre copper (Cu) in the first cover spray, and 1.5 lb/acre per spray of Ca in the second through fourth cover sprays. In 2003, all of the trees received the N, S, and Ca sprays at the 2002 rates and timings. The B sources were organically complexed boric acid or sodium (Na) polyborate products. The source of N and S was foliar-grade ammonium thiosulfate. The Ca source was organically complexed Ca oxide.

PLANT TISSUE ANALYSES. In early Aug. 2000 and 2001, 20 leaf samples were sampled randomly from each experimental tree, selecting mid-shoot leaves on current season's growth. The leaf samples were split randomly into two subsamples of 10 leaves each. The first subsample leaves were oven-dried at 65 °C without washing. The second subsample leaves were individually washed by hand using sequential 0.5% (v/v) detergent wash, tap water rinse, washing in 8 L of 0.1 M HCl, flowing tap water rinse, and flowing deionized water rinse. Both the adaxial and abaxial leaf surfaces were gently rubbed by the operator's gloved fingers in the detergent and acid baths during the cleaning process. The acid solution was changed after every 10 samples to reduce likelihood of cross-contamination. This cleaning procedure is similar to that used for pecan (*Carya illinoinensis*) leaves by Smith and Storey (1976) except that Liquinox was used in place of Alconox (both Alconox, Inc., White Plains, N.Y.) to avoid phosphorus (P) contamination. The detergent plus acid-washed leaves then were oven-dried at 65 °C. In 2002 and 2003, 10 leaf samples were sampled randomly from each tree, subjected to the detergent plus acid washing procedure only, dried, and ground. In Jan. 2001–04, 10 buds were sampled randomly from each experimental tree and oven-dried at 65 °C without washing.

All dried plant tissue samples were ground in a stainless steel Wiley mill and analyzed for N, P, potassium (K), Ca, magnesium (Mg), S, Zn, B, manganese (Mn), iron (Fe), Cu, aluminum (Al), and Na concentrations. Nitrogen was determined by total Kjeldahl digest and flow injection colorimetry, and the other mineral elements by wet-digestion, followed by assay using inductively coupled plasma-atomic emission spectroscopy. Plant tissue analytical data are reported on a dry weight basis.

FRUIT RESPONSES AND LEAF COLOR. The percentage of fruit with bitter pit was determined by visually inspecting every apple in each plot at commercial harvest in Sept. 2000 and 2002–03. A fruit was considered to have bitter pit if one lesion was present. The percentage of fruit that failed to meet the russeting standard for Washington Grade C or higher, "… the aggregate area of an apple which may be covered by smooth net-like russeting shall not exceed 25 percent; and the aggregate area of an apple which may be covered by smooth solid russeting shall not exceed 10 percent" (Washington State Legislature, 2003), was determined visually. The fruit response data for 2001 could not be calculated because of a data collection error. Leaf green color was measured nondestructively in late July 2001–04 on 20 randomly selected leaves per plot using a SPAD-502 chlorophyll meter (Minolta Camera Co., Osaka, Japan).

STATISTICAL ANALYSES. Treatment response data were analyzed by year using analysis of variance. Mean separation was done using Duncan's multiple range test when the analysis of variance indicated a significant main treatment effect. Statistical analyses were carried out using SAS (release 8.0 TS Level 00M0 for Windows; SAS Institute, Cary, N.C.). Statistical significance was defined at $P \leq 0.05$.

Results and discussion

No Zn deficiency symptoms appeared on any of the experimental trees at any time. The Zn spray treatments had no effect on crop yield, bitter pit incidence, the percentage of fruit failing to meet the Washington Grade C or higher russeting standard, or leaf SPAD value (data not shown). Experiment-wide fruit responses varied between years. For the years 2000, 2002, and 2003, yield averaged 47.3, 19.7, and 94.5 fruit per tree; bitter pit incidence averaged 1.6%, 0.6%, and 2.8%; and russeting incidence averaged 15%, 78%, and 47%. The low fruit numbers in 2002 resulted from chemical overthinning. Interveinal and marginal chlorosis often appears on Zn-deficient apple trees before other symptoms (Neilsen and Hoyt, 1990; Woodbridge, 1954). Chlorosis was absent in the current experiment. Leaf greenness, averaged across treatments, ranged from 43.5 to 46.4 SPAD units during the experiment. These values are consistent with those reported for 'Golden Delicious'/'Malling 9' orchards in northern Italy (Porro et al., 2001). These results suggest that the Zn status of the experimental trees, although sometimes low (Fig. 1; Table 2) was sufficient to preclude Zn deficiency-related symptoms, and that Zn sprays could be safely applied postbloom at the tested rates.

All of the Zn sprays produced high Zn concentrations in the unwashed leaves, with Zn nitrate having the highest mean Zn concentration. Products containing sticky components or additives, such as Zeta Zinc 22 and Zinc-Max, tended to generate high unwashed Zn concentrations. Adjuvant stickers and surfactants can help reduce loss of sprayed Zn during application and subsequent weathering (Crowley et al., 1996). The detergent plus acid washing procedure substantially lowered the Zn concentration of the Zn-sprayed leaves (Fig. 1), suggesting that a considerable portion of the Zn associated with the unwashed leaves was not phytoactive. The detergent plus acid washing caused no reduction in Zn concentrations of unsprayed leaves, suggesting that the procedure did not remove internal leaf Zn.

The applied fertilizer Zn can be partitioned into three hypothetical classes: non-retained, loosely held surface residue, and tightly bound/internal. Assuming that the Zn nitrate-sprayed leaves represent the best possible retention outcome, the difference between Zn concentrations

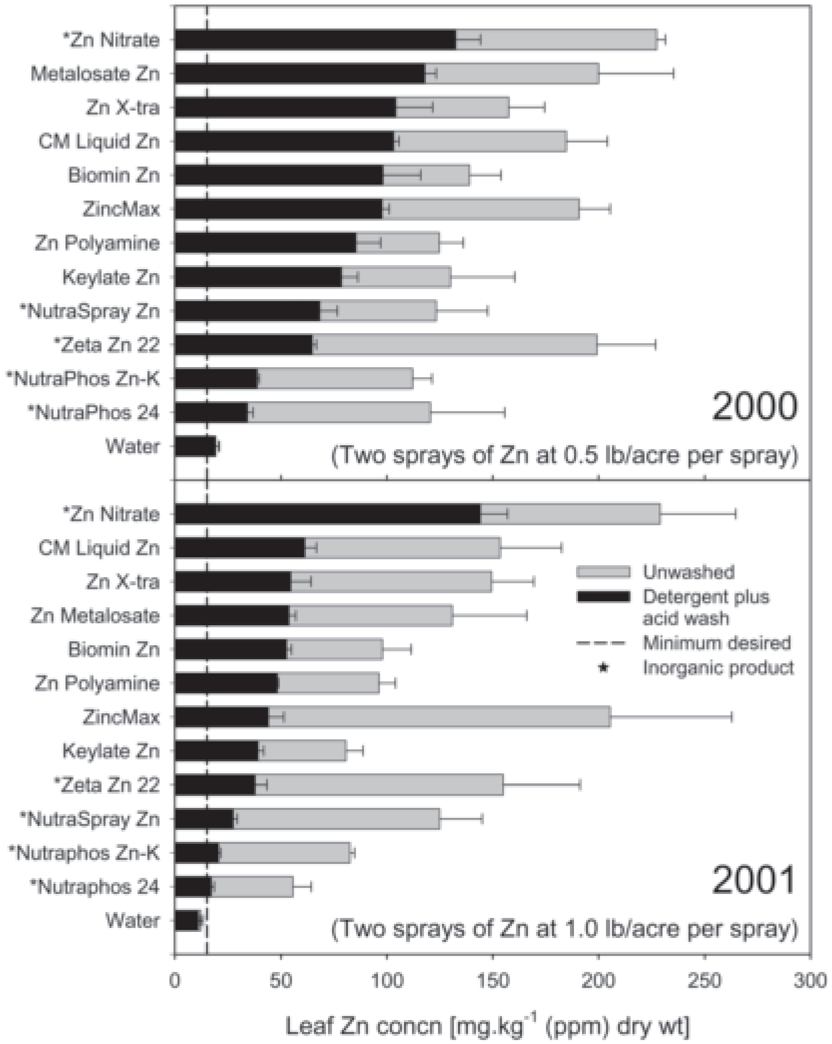

Fig. 1. Zinc (Zn) concentration of unwashed and detergent plus acid-washed midsummer leaves of 'Golden Delicious' apple trees receiving two postbloom sprays per season of water, reagent-grade Zn nitrate, and 11 commercial Zn spray products in 2000 and 2001. The vertical dashed line represents the minimum leaf Zn concentration recommended by Washington State University. The product names preceded by a star contain Zn as inorganic compounds; the others contain chelated or organically complexed Zn. Each point is an average for three replicates. The error bars represent SE (1 lb/acre = 1.1209 kg·ha^{-1}).

of the unwashed leaves of any product and Zn nitrate represents applied fertilizer Zn that is missing at the time of leaf sampling. The missing Zn was presumably lost from the leaves because of poor adhesion during application or after subsequent physical weathering. Leaf Zn removable by detergent plus acid washing (gray portion of bars in Fig. 1) appears to represent weakly held surface residues of Zn derived from the applied Zn products. They probably have undergone some chemical transformations due to reaction with the leaf surface, rain and irrigation water, dust, other foliar sprays of pesticides and nutrients, and leaf surface-dwelling organisms. Some of the residue Zn likely would be available for absorption by the leaf if the Zn is present as or can be transformed to a soluble form when the leaf surface is wetted. Leaf Zn recalcitrant to detergent plus acid washing (black portion of bars in Fig. 1) includes background Zn derived from tree reserves and soil uptake, Zn absorbed by the leaf from the foliar sprays, and probably some precipitated or strongly bound Zn surface residues.

In the following discussion, the term "leaf Zn_{d+a}" refers to the measured leaf Zn concentration after the detergent plus acid washing procedure. In most cases, the Zn nitrate and Zn products that contained chelates and organic complexes produced higher leaf Zn_{d+a} than did the Zn products that contained inorganic forms (Table 2; Fig. 1). There was little difference among the chelated and organically complexed products. While Zn nitrate appears to be an effective Zn source for pecans (Smith and Storey, 1979), it does not appear to have ever been used commercially on apple. Zinc nitrate was not marketed as a fertilizer before the early 1970s (J.B. Storey, unpublished) and probably was not considered for apple because less expensive Zn products were available and effective (Luce and Bartram, 1947). The Zn phosphate-based products consistently produced the lowest mean leaf Zn_{d+a} values, reflecting the low solubility of Zn phosphate minerals. The Zn oxysulfate and Zn oxide-based products tended to demonstrate intermediate phytoavailability. These results are generally consistent with predicted Zn solubility based on geochemical equilibrium models (Lindsay, 1979).

There was considerable inter-year variation in leaf Zn_{d+a} (Table 2), and no correlation between Zn spray rate and leaf Zn_{d+a}. These results are consistent with those reported for other Zn-sprayed apple orchards in the Pacific Northwest (Neilsen and Hoyt, 1990). Background mineral element concentrations in apple leaves vary naturally between seasons (Bould, 1966), and additional variability is introduced by differential adherence, absorption, and loss of foliarly applied nutrients (Swietlik, 2002). All of the Zn spray treatments produced leaf Zn_{d+a} concentrations that fell within or above the 15 to 60 mg·kg^{-1} desirable range used by Washington State University (WSU) (Tukey and Dow, 1979). Orphanos (1982) and Neilsen and Hoyt (1990) reported Zn toxicity symptoms of leaf burn and death associated with leaf Zn concentrations above 120 and 133 mg·kg^{-1}, respectively. Although these values were approached and exceeded in some cases in the current experiment, no such symptoms appeared. Leaf Zn_{d+a} in the water-sprayed control treatment in 2001 and 2002, and in all experimental trees in 2003, was at or below the minimum desirable concentration of 15 mg·kg^{-1}. There is considerable variability in the critical value for leaf Zn above which Zn deficiency is not expected to be expressed (Bould, 1966). While the presence of deficiency symptoms and not low leaf Zn

Table 2. Zinc (Zn) concentration of detergent plus acid-washed mid-summer leaves and unwashed winter buds of 'Golden Delicious' apple trees receiving differential zinc spray treatments. The treatments are arranged in order of increasing zinc concentrations of detergent plus acid washed leaves in 2000.

	Plant tissue Zn concn [mg·kg^{-1} (ppm) dry wt]							
Spray material	Leaf Zn[z] Aug. 2000[y]	Bud Zn Jan. 2001	Leaf Zn Aug. 2001	Bud Zn Jan. 2002	Leaf Zn Aug. 2002	Bud Zn Jan. 2003	Leaf Zn Aug. 2003	Bud Zn Jan. 2004
Water control	19.4 f[x]	54.3	11.1 e	37.1	15.0 e	38.3	12.0	40.7
Nutra-Phos 0–24–0	34.1 f	57.7	17.0 e	54.6	40.3 cde	62.6	11.7	45.9
Nutra-Phos Zn-K	38.7 ef	74.0	20.4 e	51.2	35.2 de	65.1	12.4	37.7
Tech-Flo Zeta Zinc 22	64.7 de	64.4	37.7 cd	48.3	58.5 bcd	57.3	10.8	40.5
Nutra-Spray Zinc	68.2 d	55.5	27.4 de	46.5	67.9 bc	58.8	13.5	41.3
Keylate Zinc	79.8 cd	59.3	39.1 cd	46.8	54.6 bcd	73.6	10.7	39.0
Zinc Polyamine	85.3 cd	69.5	48.2 bc	56.2	69.2 bc	52.2	14.1	37.1
ZincMax	97.7 bc	66.9	44.0 cd	58.0	67.4 bc	55.5	11.8	39.0
Biomin Zinc	100.6 bc	60.5	52.6 bc	51.5	79.0 b	57.3	10.6	35.9
Zinc X-tra	104.2 abc	60.1	54.6 bc	67.4	70.7 bc	61.9	11.9	40.2
CM Liquid 9% Zinc	107.8 abc	55.6	64.2 b	53.4	141.4 a	63.6	9.8	44.0
Zinc Metalosate	117.9 ab	63.1	53.7 bc	46.6	66.0 bc	63.2	12.4	38.8
Zinc nitrate	132.5 a	53.6	144.2 a	56.2	76.2 b	53.7	11.0	35.5
F statistic[v]	14.66	1.07	39.52	1.06	9.61	1.23	1.02	0.98
Probability[u]	<0.0001	0.4275	<0.0001	0.4288	<0.0001	0.3169	0.4638	0.4898

[z] Two sprays applied at nominal rates of 0.5 lb/acre per spray in 2000 and 1.0 lb/acre per spray in 2001 and 2002. No sprays were applied in 2003; 1 lb/acre = 1.1209 kg ha^{-1}.

[y] Plant tissue sampling date.

[x] Within-column treatment means followed by different letters are significantly different by Duncan's multiple range test (*P=0.05*).

[v] *F*-test statistic (12, 24 df)

[u] Level of significance for *F*-test.

concentration appears to be the better predictor of tree Zn need (Sanchez and Righetti, 2002; Swietlik, 2002), there is a recent tendency to recommend higher minimum values to eliminate risk of inadvertent development of Zn insufficiency (e.g., 30 mg·kg^{-1} in Agnello et al., 2005). Adoption of a higher minimum value also helps to compensate for the error introduced when using composite leaf samples (Sparks and Payne, 1982).

There was no detectable effect of the three previous seasons of Zn sprays on leaf Zn_{d+a} in 2003, when no Zn sprays were applied (Table 2). Similarly, there was no detectable effect in any year of the Zn spray treatments on bud Zn concentration the following winter (Table 2). While the available evidence indicates that foliarly applied Zn is taken up by leaves, little of the absorbed Zn appears to be mobilized from the leaves and redistributed to winter storage organs for remobilization the following season (Sanchez and Righetti, 2002). These results validate the current WSU recommendation for annual application of Zn nutritional maintenance sprays.

The Zn spray treatments had no influence on the leaf and bud concentrations of the elements other than Zn, except for a few inconsistent significant effects attributed to statistical randomness (data not presented). The Zn products containing N, K, S, or P did not enhance leaf or bud N, K, S, or P concentrations (data not presented). Concentrations in the detergent plus acid-washed leaves, averaged over the four years of the experiment, were (expressed in g·kg^{-1} dry weight): N, 21; P, 1.4; Ca, 17; Mg, 3.2; S, 1.6; and (expressed in mg·kg^{-1} dry weight): Mn, 71; Fe, 67; Al, 61; Na, 45. These values would be considered within normal ranges. Leaf K concentration averaged 18 g·kg^{-1} but was elevated at 21.5 g·kg^{-1} in 2002 as a result of fruit overthinning. Leaf B concentration directly reflected the foliar B spray program: 38 mg·kg^{-1} in 2000 when B was applied in late May; 29 to 30 mg·kg^{-1} in 2001 and 2002 when B was applied at delayed dormant; and 15 mg·kg^{-1} in 2003 when no B was applied. Leaf Cu concentration was marginally low at 5 to 6 mg·kg^{-1} (Agnello et al., 2005; Tukey and Dow, 1979) except in 2002, when it increased to an acceptable value of 14 mg·kg^{-1} due to use of the Cu nutritional spray. Visual symptoms of Cu deficiency, such as wither-tip and chlorosis, were absent at all times.

Conclusions

The research results confirm that postbloom Zn sprays applied to apple trees generate substantial amounts of Zn residues on leaf surfaces. Detergent plus acid washing appears to remove a considerable proportion of these residues. The physical location and physiological activity of the Zn remaining after washing are unclear. Previous research indicates that some of the Zn probably is adsorbed to cuticular tissue; however, a portion of this adsorbed Zn appears to be available for uptake into the leaf. While leaf Zn_{d+a} likely provides a closer estimate of the "true" concentration of phytoactive Zn in leaves, lack of confidence in the efficiency of residue removal likely will limit its use to that of a correlative index. Applications could include comparing relative Zn uptake, such as is done in the current study and some of those previously cited, as well as a practical aid for diagnosing inadequate tree Zn status (i.e., Zn_{d+a} lower than a chosen critical value can confidently be said to indicate Zn insufficiency, while Zn_{d+a} higher than the critical value is uninterpretable).

Assuming that phytoactive Zn concentration is proportional to Zn_{d+a}, the experimental results generally support commercial claims of high phytoavailability of Zn in chelated or organically complexed Zn foliar spray products. Differences among the chelated and organically complexed forms were small and inconsistent between seasons. Zinc in Zn nitrate was highly phytoavailable, whereas Zn in the other tested inorganic forms often but not always was less phytoavailable than in the chelated or organically complexed products. None of the Zn spray products applied postbloom at rates of 0.5 to 1.0 lb/acre caused any fruit or foliage damage. All of the products were capable of increasing leaf Zn_{d+a} to values that are considered desirable. Because the inorganic Zn-based products usually are substantially less expensive per unit of Zn, it may be less costly and just as effective to use a higher rate of an inorganic Zn product as to use a lower rate of a more phytoavailable but more expensive chelated or organically complexed Zn product. The latter practice does confer the added benefit of reduced release of Zn into the environment. Failure to find evidence for a measurable increase in tree Zn reserves validates the current WSU recommendation for annual application of Zn maintenance sprays to ensure proper apple tree nutrition.

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