Boron Fertilizer Product and Concentration Influence Spray Water pH

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ADDITIONAL INDEX WORDS. **mineral nutrition, micronutrient, pesticide, growth regulator, water quality, alkaline hydrolysis**

SUMMARY. Farmers often mix fertilizers, pesticides and other agricultural chemicals together in a spray tank to allow applications of multiple products in a single spray. Because polyborate-based B fertilizers may increase solution pH, adding B to tank-mixed sprays may impair the stability and efficacy of alkalinity-sensitive pesticides and growth regulators if an acidifier is not included. We conducted a laboratory experiment to determine the influence of 10 commercial B fertilizer sources in factorial combination with B concentrations ranging from 0 to 4 lb/100 gal (4.8 g·L⁻¹) on solution pH values of distilled water and two natural waters. Two boric acid-based compounds produced acidic reactions relative to background water pH at all tested B concentrations. Their pH responses were influenced by initial water composition. Seven B products produced moderately to strongly alkaline reactions at all but the highest B concentration, regardless of the form of B (polyborate vs. boric acid) initially present in the formulated products. One polyborate product formulated with an acidifier showed intermediate pH behavior. The dependence of

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Mention of a proprietary product does not constitute an endorsement or a recommendation for its use by Washington State Univ. This research was conducted under Project WNP0747, College of Agriculture and Home Economics, Washington State Univ., Pullman. Funding support was provided by the College and by the Washington Tree Fruit Research Commission. The cost of publishing this paper was defrayed in part by the payment of page charges. Under postal regulations, this paper therefore must be hereby marked *advertisement* solely to indicate this fact.

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solution pH on B rate of the polyborate-containing products was identical in all three waters. The maximum pH values generated by all products occurred in the B concentration range <0.1 to 0.25 lb/100 gal (0.12 to 0.3 g·L⁻¹). Solution pH values declined with increasing B concentration above this range. The pH responses qualitatively conformed to known aqueous chemical behavior of B and the product additives. The complexity of the interaction between initial water chemistry, B concentration, and B fertilizer product reinforces the need to measure the pH of B-amended spray water before adding pH-sensitive compounds.

Alkaline hydrolysis of pesticides in high pH spray water can reduce the stability and efficacy of many pesticides (Niessen, 1978; Seaman and Reidl, 1986). Pesticides and growth regulators sensitive to high pH include azinphos-methyl, parathion, carbaryl, dimethoate, and Promalin (Abbott Laboratory, Abbott Park, Ill.). Many natural waters have pH values high enough to affect some pesticides. Acidifying chemicals must be added to reduce pH in such waters or when alkalinity-generating chemicals are tank-mixed with susceptible pesticides.

Boron deficiency is a common problem of agricultural crops that can be corrected or prevented by foliar application of small quantities of B-containing fertilizer. Boron products often are mixed with other products in the spray tank to allow multiple applications of agricultural products in a single spray, thereby reducing cost of application.

Orthoboric acid was the first B com-

pound used for foliar sprays, starting about 1936 (Peryea, 1992). It was largely replaced about 1952 by sodium polyborate-based products which were as effective as boric acid in providing B to plants but dissolved more quickly in spray water. Orthoboric acid does not behave as a simple monoprotic acid; rather, it forms an acid-base adduct with water and ionizes to release a single hydrogen ion (Keren and Bingham, 1985), causing a decline in solution pH in poorly buffered waters:

In contrast, sodium polyborate compounds release hydroxyl ions upon hydrolysis and cause solution pH to increase (Colwell and Cummings, 1944). An alkaline reaction is not of consequence if the sodium polyborate-based product is to be applied as a single-product spray or tank-mixed with other compounds not sensitive to alkalinity. Tank-mixing sodium polyborate-based products with alkalinity-sensitive compounds may chemically degrade the compounds and impair their effectiveness. Adding acidifiers to aqueous solutions of sodium polyborate-based products can neutralize the induced alkalinity but increase overall spray cost.

Developments in fertilizer formulation have greatly expanded the composition of available B products used for spray applications. Some products contain B complexed with organic compounds claimed to enhance B phytoavailability. A recent advance is use of proprietary additives and processing techniques to enhance the rate of boric acid dissolution. Net changes in pH resulting from adding these B spray products to spray water are not well-characterized. The current laboratory study examines the effect of B spray

product source and B concentration on spray water pH.

Materials and methods

Reagent-grade orthoboric acid and 10 commercial B spray products were evaluated (Table 1). Albion Liquid Boron, B-17, Borosol-10, MorBor-17, Solubor, and Solubor DF are specifically approved for use as fertilizers in organic farms in the state of Washington (Washington State Department of Agriculture, 2000).

Three water sources were used to prepare the B solutions: distilled water, Wenatchee canal water (WCW), and Tonasket well water (TWW). The WCW was collected from the Highline irrigation canal which carries water diverted from the Wenatchee River near Dryden, Wash. The TWW was collected from a well on an orchard in Tonasket, Wash. Both natural water sources are used to prepare spray tank solutions in commercial tree fruit orchards. Table 2 summarizes the concentrations of selected inorganic constituents of the two waters. Both waters were naturally alkaline. Estimated alkalinity was 12.3 times higher in the TWW than in the WCW, suggesting that the TWW had substantially greater buffering capacity against acidification. Both waters would be considered suitable as irrigation water except that use of TWW for overhead sprinkling likely would cause formation of lime deposits on wetted plant parts (Ayers and Wescot, 1976).

In the laboratory, solutions containing B concentration equivalent to 4 lb/100 gal (4.8 g·L⁻¹) were prepared using each product and water combination. This B concentration exceeds that likely to be used by commercial tree fruit growers (British Columbia Ministry of Agriculture

Table 1. Boron spray products evaluated in study.

Product name	Physical state ^z	B content ^y (%)	B form ^x	Additive	Manufacturer
Reagent-grade boric acid	S	17.5	BA	None	Mallinckrodt, Paris, Ky.
Albion Liquid Boron	L	5.0	NaB	Amino acids	Albion Lab., Clearfield, Utah
B-17	S	17.0	BA	Surfactant	Nutrient Technol., La Habra, Calif.
Borosol-10	L	10.0	BA	Ethanolamine	Clean Crop, Fremont, Nebr.
Greenleaf Boron	L	1.75	Unspecified	Carbohydrates	SafeScience, Boston, Mass.
Mor-Bor 17	S	17.3	BA	Surfactant	G.S. Long, Yakima, Wash.
N-Boron	L	5.4	BA	Urea, polysaccharides	Plant Health Technol., Boise, Idaho
Solubor	S	20.5	NaB	None	U.S. Borax, Los Angeles, Calif.
Solubor DF	S	17.4	NaB	None	U.S. Borax, Los Angeles, Calif.
SprayBor	S	16.5	NaB	Acidifier	Plaaskem, Gauteng, South Africa
Tech-Spray Liquibor	L	2.5	BA, NaB	Surfactant	Nutrient Technol., Dinuba, Calif.

^zS = solid; L = liquid.

^yPercent B by weight.

^xBA = boric acid, NaB = sodium polyborates of varying composition.

Table 2. Chemical characteristics of Wenatchee canal water (WCW) and Tonasket well water (TWW) used in study.

Water source	pH	Chemical (ppm) ²								Estimated alkalinity ³ (mmol _c ·L ⁻¹)
		Ca	Mg	K	Na	SO ₄	Cl	B	PO ₄	
WCW	7.63	8.26	1.85	1.20	1.53	1.2	<0.5	<0.1	<0.07	0.6
TWW	7.90	136	76	8.92	49.4	354	136	<0.1	<0.07	7.4

²1.0 ppm = 1.0 mg·L⁻¹.

³Sum of CO₃²⁻ and HCO₃⁻, calculated as the difference between the summations of measured concentrations of cations and anions expressed in mmol_c·L⁻¹ (meq·L⁻¹).

and Food, 1998; Smith, 2000). The pH values of these initial solutions were measured using a temperature-compensated combination glass electrode. The solutions were then diluted by adding a known volume of the same water used to prepare the starting solutions. The diluted solutions were allowed to equilibrate and pH was again measured. This procedure was continued with increasing amounts of dilution to a final B concentration equivalent to 0.1 lb/100 gal (0.12 g·L⁻¹), which is lower than that usually recommended as a maintenance rate for deciduous tree fruit orchards (e.g.; Smith, 2000; Stiles and Reid, 1991). Each B product-water combination was tested in duplicate.

Results and discussion

The pH value of the B-free distilled water was 5.65, as expected for pure water in thermochemical equilibrium with atmospheric CO₂. The pH values of the experimental B solutions ranged from moderately acidic to strongly alkaline (Fig. 1). The relative pH ranking of

the products averaged over all concentrations was: reagent-grade boric acid ≤ B-17 < MorBor-17 < Spraybor < Greenleaf Boron < Albion Liquid Boron, Solubor DF, Liquibor < Solubor < N-Boron < Borosol-10.

Solution pH values for a given concentration of the boric acid-based compounds tended to be higher in the order: distilled < WCW < TWW, consistent with the measured pH and estimated alkalinity of the three waters. The sodium polyborate-based products and the N-containing boric acid-based Borosol and N-Boron showed similar responses in all three waters, suggesting that some component of the formulations was buffering solution pH at levels specific to the individual products.

Reagent-grade boric acid and B-17, a boric acid-based product, decreased pH at all B concentrations, in reference to the background pH, in all three waters. Although MorBor-17 also is a boric acid-based product, it increased pH in distilled water and decreased pH

in the two natural waters. It generated slightly to substantially higher pH values than did its analog B-17, presumably because the surfactant in its formulation has more alkaline properties than that used in B-17.

All of the remaining products caused solution pH to increase with product-specific pH maxima occurring in the B concentration range of <0.1 to 0.25 lb/100 gal (<0.12 to 0.3 g·L⁻¹). Solution pH declined with increasing B concentration above the pH maxima. This behavior conforms to known B solution chemistry. Boron occurs principally as the uncharged B(OH)₃ molecule and B(OH)₄⁻ anion at B concentrations below about 0.23 lb/100 gal (0.28 g·L⁻¹) (Keren and Bingham, 1985). At higher B concentrations, these monomeric species begin to polymerize into polyborate molecules and release H⁺ ions and water.

The pH values of several alkalinity-generating B product and water combinations approached or declined below B-free

Fig. 1. Interaction of B fertilizer product, B rate and water source on spray solution pH; 1 lb/100 gal = 1.2 g·L⁻¹.

water pH at the highest B concentrations (Spraybor in all three waters; Greenleaf Boron in WCW and TWW; and Albion Liquid Boron in TWW). Five products (Solubor, Solubor DF, Borosol, Liquibor, N-Boron) caused pH to increase at all tested B concentrations.

The additives in some of the B products qualitatively explain the differential pH effects. The acidifier incorporated into Spraybor was effective at partially neutralizing the pH increase caused by polyborate hydrolysis. The possible presence of residual processing acid in Greenleaf Boron makes it a less alkaline product than the polyborate-only products, as does the presence of amino acids in Albion Liquid Boron. Hydrolysis of amino compounds and urea and consequent release of ammonium likely accounts for the high pH values generated by the boric acid-based N-Boron and Borosol-10. The small amount of sodium polyborate in the boric acid-dominated Liquibor appears to increase and maintain solution pH in the range characteristic of the polyborate-only products.

Conclusions

Of 10 tested products formulated for use in B nutritional sprays, only the boric acid-based B-17 and MorBor-17 did not increase solution pH over background levels in natural waters; rather, they reduced pH. For many spray waters, using these products as the B source for tank-mixes would eliminate the requirement for adding an acidifier to counterbalance B product-induced alkalinity. In waters that are naturally alkaline and highly pH-buffered, the acidity generated by boric acid-based products alone may be insufficient to reduce final solution pH to values low enough to preclude alkaline hydrolysis. Addition of an exogenous acidifier may still be required in such waters. It is possible that adding boric acid-based products to poorly buffered naturally acid waters could reduce pH to values low enough to influence the chemistry of acid-sensitive tank-mixed compounds, thereby requiring addition of an acid-neutralizing agent. Diazinon is an example of a pesticide that degrades rapidly in low pH solutions (Bailey et al., 1996).

All of the remaining products caused pH to increase, sometimes substantially, at the B spray concentrations likely to be used in agricultural settings, typically less than 1 lb/100 gal (1.2 g·L⁻¹). Tank-mixing of these latter B products with alkalinity-sensitive crop protection chemicals

and growth regulators therefore would require addition of an acidifier to reduce solution pH to an acceptable level. Less acidifier may be required for Spraybor because it produced a smaller pH increase than did the other sodium polyborate-based products. The difference in pH performance between the six most alkaline B products was small enough to be of little practical significance; hence, other properties, such as organic certification, handling characteristics, and cost may distinguish which of these products is best suited for a particular spray application.

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