BORON

THE SOAP AND DETERGENT ASSOCIATION

BORON

INTRODUCTION

This monograph summarizes: 1) critical fate and effects data required for an environmental risk assessment on boron; and 2) conclusions drawn from a risk assessment of boron in the United States. The monograph addresses the environmental exposures to boron resulting from consumer use and disposal of the ingredient as a result of its presence in cleaning products. The monograph is written for a technical audience, but not necessarily one familiar with environmental risk assessment.

The monograph is formatted into five sections. The first section describes boron, its chemical structure and U.S. consumption volumes. The second section describes the function of boron in cleaning products. The third section describes its fate and exposure concentrations in the environment. The fourth section presents environmental effects information. The fifth section presents a comparison of exposure and effects concentrations in the framework of an environmental risk assessment.

This paper is made from 50% recycled fibers that include 10% post consumer waste.

Ingredient Identification

Chemical Description

Boron, a group III element, does not exist in the environment or in products in its elemental form but as boron-oxygen containing compounds called borates or borosilicates. Borates are used in consumer products. Borate compounds are sometimes compared in terms of their boron content or in terms of B_2O_3. Species of boron compounds used in cleaning products are listed in Table 1.

U.S. Consumption

The annual U.S. consumption of borates (as B_2O_3) is 297,000 metric tons (Will, Ishikawa, Riepl, Schneider and Willhalm, 1996). This represents a slight increase in consumption over 1990 data. Borates are used in a wide range of products. The major uses are in glass and related products (61%); cleaning products (9%); agrochemicals (5%); enamels, frits and glazes (3%); and miscellaneous, which includes fire retardants (22%) (Will *et al.*, 1996).

Ingredient Function

The functions of boric acid in cleaning products are as follows: 1) a source of non-alkali buffer; and 2) an enzyme stabilizer in liquid cleaning products. Typical concentrations of boric acid in products range up to 3%. Perborates (mono and tetrahydrates) are used as non-chlorine bleaching agents in granular detergents. Key attributes of perborates in detergents include: 1) high water solubility; 2) effective bleaching; 3) mild alkalinity; 4) ability to eliminate some unpleasant odors; 5) compatibility with other chemicals; and 6) good storage stability (Raymond and Butterwick, 1992). Typical concentrations of perborates in laundry detergents range up to 10%. Laundry bleach additives may have concentrations up to 50%. Borax functions as a cleaning/laundry aid, deodorizer and a buffer in consumer laundry products. Concentrations of borax in products range up to 100%.

Environmental Exposures

Boron is naturally present within silicates, which make up the bulk of the earth's mantle and crust. Boron enters the environment through the weathering of rocks, volatilization from sea water, atmospheric deposition, boron mining and processing, use in agriculture and disposal of boron-containing consumer products into municipal wastewater treatment systems (Butterwick, de Oude and Raymond, 1989; Raymond and Butterwick, 1992; Anderson, Kitto, McCarthy and Zoller, 1994). Of these, the weathering of borosilicate-containing rock to stable borate species and the discharge from municipal wastewater treatment systems of borate species described previously are the principal routes of entry into surface waters (Dyer and Caprara, 1997).

The predominant species of boron in surface waters (pH 6-9), regardless of its source, are undissociated boric acid and borate anion (Butterwick *et al.*, 1989; Raymond and Butterwick, 1992). These stable, highly soluble species are not easily removed from freshwater systems by natural mechanisms nor are they removed via conventional sewage treatment (Raymond and Butterwick, 1992: Dyer, Barnum and McAvoy, 1992). Hence, boron is largely associated with the water column. Importantly, these low molecular weight borate species are the most ecologically relevant (Eisler, 1990). In the marine environment (where boron concentrations are approximately 5 mg B/L), clays react and complex with borates, resulting in their removal from the water column to sediment. Therefore, mudstones of marine origin contain appreciable concentrations of boron in the clay mineral fraction (Butterwick *et al.*, 1989).

Boron, in the form of boron-oxygen compounds (primarily boric acid), is widely distributed in U.S. surface waters. The most widespread source of boron to surface waters is from natural weathering processes (Butterwick *et al.*, 1989). The median and 90th percentile U.S. surface water boron concentrations from over 55,000 samples collected are 0.076 and 0.387 mg B/L, respectively (Dyer

TABLE 1
Boron Compounds Used in Cleaning Products

Name	Structure	CAS Registry Number
Boric Acid	H_3BO_3	10043-35-3
Sodium Perborate Monohydrate	$NaBO_3CH_2O$	10332-33-9
Sodium Perborate Tetrahydrate	$NaBOC_4H_2O$	10486-00-7
Sodium Tetraborate Decahydrate (borax)	$Na_2B_4O_7C_{10}H_2O$	1303-96-4

and Caprara, 1997). Four localized areas of the U.S. have boron concentrations greater than the nationwide 90th percentile (0.387 mg B/L): 1) central and southern California; 2) eastern Oregon and western Nevada; 3) northern plains (eastern Montana and North Dakota); and 4) southern plains (Oklahoma and Texas) (Dyer and Caprara, 1997). For example, surface waters of California have a higher boron content, where the 90th percentile is 0.94 mg B/L (Dyer and Caprara, 1997). Surface water boron concentrations up to 150 mg B/L can occur in localities where the presence of boron-rich deposits becomes susceptible to weathering (Kopp and Kroner, 1970; Dyer *et al.*, 1992; Dyer and Caprara, 1997). Low concentrations (<0.1 mg B/L) were found in nearly all mountainous regions of the U.S. (Sierra Nevada/Cascade Ranges and Rocky Mountains) and east of the Mississippi River (Dyer and Caprara, 1997).

Localized sources of boron in surface water include municipal wastewater treatment plant (WWTP) discharges, boron-containing fertilizers, and the occurrence of boron in fly ash from coal fired power plants. The range of concentrations found in WWTP effluents is 0.1 to 2.8 mg B/L (Butterwick *et al.*, 1989; Raymond and Butterwick, 1992). Ninety percent of 38 U.S. WWTP effluents sampled for boron had concentrations less than 0.5 mg B/L (Dyer *et al.*, 1992).

Cleaning products are predicted to contribute between 50% and 60% of total boron measured in sewage effluent (Dyer and Caprara, 1997), consistent with Eisler's conclusion (Eisler, 1990). The median and 90th percentile contribution of cleaning products to measured boron concentrations in surface waters receiving WWTP effluent is 0.2 to 25%, respectively. The greatest contribution of cleaning products to surface water boron concentrations occurs at sites where WWTP effluents are minimally diluted in receiving waters having low ambient boron concentrations (Dyer and Caprara, 1997).

ENVIRONMENTAL EFFECTS

Terrestrial

Assessments of boron's role in the nutrition and toxicity to terrestrial plants have been reviewed extensively (Butterwick *et al.*, 1989; Eisler, 1990; Raymond and Butterwick, 1992; Bergmann, 1992). It is generally agreed that boron is an essential element for the growth of higher plants and that excess boron is phytotoxic. Also, it is agreed that plants vary greatly in their sensitivity to boron.

Boron concentration in plants is dependent on the content and availability of boron in the soil, season, plant health, and interactions with other substances, such as calcium, manganese and aluminum (Eisler, 1990; Lukaszewski and Blevins, 1992). Boron deficiency in plants is common and has been reported in at least 43 states (Gupta, 1979). It is most likely to occur in acidic, sandy soils in humid regions of the U.S. due to boron's tendency to leach (Eisler, 1990; Bergmann, 1992). However, in arid regions of the U.S. (e.g., the Southwest), boron may concentrate to toxic levels in soils due to high evapotranspiration rates (Gupta, Jame, Campbell, Leyshon and Nicholaichuk, 1985).

Since boron is transported in the plants mainly via transpiration flow, it accumulates at the leaf tips and margins of older leaves (Bergmann, 1992). Boron toxicity in plants is exhibited by stunted growth, leaf malformation, browning and yellowing of leaf tips, chlorosis, and necrosis (Eisler, 1990; Bergmann, 1992). Toxicity is augmented in low pH systems. As stated, there is considerable variation of boron tolerance between plant species.

Several authors (Sprague, 1972; Keren and Bingham, 1985; Butterwick *et al.*, 1989; Eisler, 1990; Raymond and Butterwick, 1992) have divided plant species into three groups (sensitive, semi-tolerant and tolerant) according to their sensitivity to boron. Maximum tolerable boron concentrations in soil water for sensitive species (citrus, stone fruits, nut trees), semi-tolerant species (most vegetables, tubers, cereals and grains) and tolerant species (tomato, oat, parsley, cotton, asparagus) are 0.3-1.0, 1.0-2.0 and 2-10 mg B/L, respectively. The threshold concentration ranges are the maximum concentrations that a given plant species tolerates without manifesting visual injury symptoms and/or a decrease in yield (Raymond and Butterwick, 1992). If the pH of soil containing toxic concentrations of boron is low, boron toxicity in plants can largely be avoided by liming. However, in saline soils with high boron concentrations in arid and semi-arid regions, pH values are often high, and in such cases liming cannot prevent boron toxicity (Bergmann, 1993). In these soils, surplus boron can only be removed by leaching, if at all.

Aquatic

Plants

Algae and aquatic macrophytes are tolerant of boron in the absence of pH stress and nutrient deficiency. Studies summarized by Eisler (1990) indicate the no-observable effect concentrations (NOECs) for freshwater species *Anacystis nidulans* (blue-green algae), *Chlorella pyrenoidosa* (green algae) and *Lemna minor* (duckweed) to be 50, 10 and 10 mg B/L, respectively. Concentrations required for inhibition of growth and photosynthesis are between 50 and 100 mg B/L (Eisler, 1990).

Freshwater Invertebrates

Data are limited that describe boron toxicity to aquatic invertebrates. Available data suggest that chronic NOECs and lowest observable effect concentrations (LOECs) for *Daphnia magna* are 6 and 13 mg B/L, respectively (Lewis and Valentine, 1981; Gersich, 1984). Similar results were found with *Ceriodaphnia dubia* (Hickey, 1989).

Amphibians and Fish

A considerable number of acute and chronic toxicity tests have been performed to assess the effects of boron to aquatic vertebrates, amphibians and fish. Tests with embryo-larval stages of the channel catfish (*Ictalurus punctatus*), goldfish (*Carassius auratus*), largemouth bass (*Micropterus salmoides*), rainbow trout (*Oncorhynchus mykiss*), Fowler's toad (*Bufo fowleri*), and the leopard frog (*Rana pipiens*) have clearly demonstrated that the rainbow trout is the most sensitive species (Birge and Black, 1977; Black, Barnum and Birge, 1993).

Several tests with embryo-larval stages of rainbow trout yielded an extremely wide range of LOECs, 0.1 to >18.0 mg B/L. While the reasons for these differences are not established with certainty, the principal contributing factors may be related to: 1) a flat concentration-response curve (small changes in teratagenesis and mortality over a wide range of boron concentrations); 2) the effects of different types of dilution water (reconstituted vs. several different sources of natural waters); and 3) different sensitivities of the several strains of rainbow trout tested (Black *et al.*, 1993). Even so, the data clearly show the most consistent LOECs to be 1 mg B/L (Black *et al.*, 1993).

Experimental LOEC observations are consistent with field observations of viable trout populations in streams and hatcheries of California. Field surveys in California were compiled to determine the relationship between in-stream boron concentrations and the distribution of wild rainbow trout (Bingham, 1982; Black *et al.*, 1993). Boron concentrations of source water used in the 10 major trout hatcheries of California range from 0.02 to 1.0 mg B/L (Black *et al.*, 1993). Field surveys indicated that viable populations of wild trout were observed in 44 streams at 66 different locations ranging in concentrations from <0.01 to 13.1 mg B/L (Bingham, 1982; Black *et al.*, 1993).

In other western states (Montana, Nevada, New Mexico, North Dakota, Oregon and Wyoming), no instances were found where boron limited trout populations or hatchery production (EA, 1994). In fact, several locations with boron concentrations near, or above, 1 mg B/L were found to have successful rainbow trout populations. Important game species such as northern pike, sturgeon and catfish were also reported to live in streams with high boron concentrations, ranging up to 3.0 mg B/L. In these high boron concentration situations, rainbow trout were reported to be absent from the river due to unsuitable habitat and high water temperatures (EA, 1994).

Based on laboratory and field data, a boron concentration of between 0.75 and 1.0 mg B/L is protective of aquatic life (Black *et al.*, 1993). Field observations support laboratory derived toxicity LOECs for rainbow trout of 1 mg B/L. This is in agreement with conclusions of the U.S. Fish and Wildlife Service (Eisler, 1990) and Maier and Knight (1991) that support levels of <1.0 mg B/L and 1-2 mg B/L, respectively, as those protective of aquatic animal communities.

Risk Assessment

Terrestrial

The toxicity threshold concentration range for boron in irrigation water and typical irrigation regulations and guidelines are consistently between 0.5 and 1.0 mg B/L. Likewise, typical effluent regulations and guidelines permit discharges between 0.5 and 1.0 mg B/L. These levels have been set to protect sensitive crops, citrus and stone fruits, irrigated or potentially irrigated with wastewater effluent. Irrigation of boron sensitive crops with wastewater effluent has been used successfully worldwide. No adverse effects were reported on citrus crop growth or yield in California, Florida and Sicily with concentrations ranging up to 2 mg B/L, apparently exceeding sensitive plant tolerances (Butterwick *et al.*, 1989; Raymond and Butterwick, 1992).

Ninety percent of all WWTP effluents and surface waters sampled in U.S. boron monitoring studies have concentrations <0.5 mg B/L (Dyer *et al.*, 1992; Dyer and Caprara, 1997). However, of concern are arid regions of the U.S. where irrigation of crops is practiced. Here, excessive evapotranspiration may cause boron levels in soils to accumulate (Gupta *et al.*, 1985) and localized conditions may result in surface waters having high boron concentrations. The 90th percentile boron concentration for California surface waters is 0.94 mg B/L.

Given the distributions of U.S. and California effluent and surface water boron concentrations and observations of crops receiving irrigation waters with boron concentrations up to 2 mg B/L, which is in excess of reported adverse effect concentrations, crops irrigated with WWTP effluent or surface water are not likely to encounter toxicity problems. However, based upon reported localized median and 90th percentile concentrations (Dyer *et al.*, 1992; Dyer and Caprara, 1997), some areas may have surface waters with boron concentrations exceeding reported toxicity values. Where exceedances of regulatory limits are observed, natural geological sources override any anthropogenic influences.

Aquatic

As in the terrestrial situation, safety for aquatic organisms is assessed using the most sensitive species. For the aquatic environment, the embryo-larval stages of the rainbow trout are the most boron-sensitive of any aquatic organism tested to date. The most consistently observed rainbow trout LOEC is 1.0 mg B/L (Black *et al.*, 1993). Viable trout populations have been observed in western U.S. waters with boron concentrations near or above 1.0 mg B/L (EA, 1994). This is consistent with the observation that levels of <1.0 mg B/L and 1-2 mg B/L are protective of aquatic animal communities (Eisler, 1990; Maier and Knight, 1991).

Ninety-percent of U.S. WWTP effluents and surface waters have been shown to have boron concentrations <0.5 mg B/L (Dyer *et al.*, 1992; Dyer and Caprara, 1997). However, localized conditions may result in higher surface water boron concentrations. California surface waters have been shown to have a 90th percentile boron concentration of 0.94 mg B/L (Dyer and Caprara, 1997).

Based upon the reported median and 90th percentile boron concentrations for U.S. surface waters, 0.076 and 0.387 mg B/L, respectively, and the observation of healthy trout populations in streams with boron concentrations consistent with experimentally derived LOECs of 1 mg B/L, boron concentrations are not a concern for aquatic life. However, based upon reported localized conditions, such as the 90th percentile concentration of 0.94 mg B/L in California (Dyer *et al.*, 1992; Dyer and Caprara, 1997), some areas may reach or exceed toxic boron concentrations. In these localized situations, boron contributions from WWTP effluents are negligible (median and 90th percentile contributions of 0.2 and 25%, respectively), with the primary source being the natural weathering of borosilicate-containing rocks.

Conclusion

Based on overall U.S. surface water and WWTP effluent levels, boron concentrations are not a concern for terrestrial or aquatic life. However, some localized areas of the U.S. may approach or exceed concentrations of boron that are toxic. In these situations, the predominant contributor is weathering from the local geology, with a relatively insignificant amount attributable to detergent products.

REFERENCES

Anderson, D.L., M.E. Kitto, L. McCarthy and W.H. Zoller, 1994. Sources and atmospheric distribution of particulate and gas-phase boron, *Atmospheric Environment 28(*8):1401-1410.

Bergmann, W., 1992. *Nutritional Disorders of Plants.* Gustav Fischer Verlag Jena, Stuttgart/New York.

Bingham, F.T., 1982. *The Boron Concentration of Wild Trout Streams in California*, report to The Procter & Gamble Company, Cincinnati, OH.

Birge, W.J. and J.A. Black, 1977. *Sensitivity of Vertebrate Embryos to Boron Compounds*, Report No. EPA-560/1-76-008, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC.

Black, J.A., J.B. Barnum and W.J. Birge, 1993. An integrated assessment of the biological effects of boron to the rainbow trout, *Chemosphere 26*(7):1383-1413.

Butterwick, L., N. de Oude and K. Raymond, 1989. Safety assessment of boron in aquatic and terrestrial environments, *Ecotox. Environ. Safety 17*:339-371.

Dyer, S.D., J.B. Barnum and D.C. McAvoy, 1992. Aquatic Safety Assessment for Boron, *Proceedings from the First International Symposium on the Health Effects of Boron and Its Compounds*, University of California at Irvine.

Dyer, S.D. and R. J. Caprara. 1997. A method for evaluating consumer product contributions to surface and drinking water: boron as a test case, *Environ. Toxicol. Chem. 16*(10):2070-2081.

EA, 1994. *Boron Concentrations and Rainbow Trout Populations in Seven States in the Western United States*, report to The Procter & Gamble Company, Cincinnati, OH, EA Engineering, Science, and Technology, Sparks, MD.

Eisler, R., 1990. Boron Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review, U.S. Fish and Wildlife Service, Biol. Rep. 85 (1.20), Washington, DC.

Gersich, F.M., 1984. Evaluation of a static renewal chronic toxicity test method for *Daphnia magna* Straus using boric acid, *Environ. Toxicol. Chem. 3*:89-94.

Gupta, U.C., 1979. Boron nutrition of crops, *Adv. Agron. 31*:273-307.

Gupta, U.C., Y.W. Jame, C.A. Campbell, A.J. Leyshon and W. Nicholaichuk, 1985. Boron toxicity and deficiency: a review, *Can. J. Soil Sci. 65*(3):381-409.

Hickey, C.W., 1989. Sensitivity of four New Zealand cladoceran species and *Daphnia magna* to aquatic toxicants, *New Zealand J. Mar. Freshwat. Res. 23*:131-137.

Keren, R. and F.T. Bingham, 1985. Boron in Water, Soils and Plants, *Advances in Soil Science*, Vol. 1, Springer-Verlag, Berlin/New York.

Kopp, J.F. and R.C. Kroner, 1970. *Trace Metals in Waters of the United States*, U.S. Department of the Interior, Cincinnati, OH.

Lewis, M.A. and L.C. Valentine, 1981. Acute and chronic toxicities of boric acid to *Daphnia magna* Straus, *Bull. Environ. Contam. Toxicol. 27*:309-315.

Lukaszewski, K. and D.G. Blevins, 1992. Possible Biochemical Functions of Boron in Plants That May Be Related to the Function of Boron in Animals and Humans, *Proceedings from the First International Symposium on the Health Effects of Boron and Its Compounds*, University of California at Irvine.

Maier, K.J. and A.W. Knight, 1991. The toxicity of waterborne boron to *Daphnia magna* and *Chironomus decorus* and the effects of water hardness and sulfate on boron toxicity, *Arch. Environ. Contam. Toxicol. 20*:282-287.

Raymond, K. and L. Butterwick, 1992. Perborate, *The Handbook of Environmental Chemistry: Detergents, Volume 3, Part F* (O. Hutzinger, ed.), Springer-Verlag, Heidelberg, pp. 288-318.

Sprague, R.W., 1972. The Ecological Significance of Boron. U.S. Borax and Chemical Research Corporation, Anaheim, CA.

Will, R., with M. Ishikawa, J. Riepl, J. Schneider and R. Willhalm, 1996. Boron minerals and chemicals, *Chemical Economics Handbook*, SRI International, Menlo Park, CA.

The Soap and Detergent Association
475 Park Avenue South
New York, NY 10016

http://www.sdahq.org