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SUMMARY AND CONCLUSIONS

The purpose of this review was to establish the safe environmental levels of borate in the ecosphere. The review covers the established methods for the analysis of borate, as boron. The natural occurrence, natural and anthropogenic distribution and balance of borate in the ecosphere are surveyed, including the borate content of waters, the lithosphere and the atmosphere. Finally, data are presented on the concentration of borate in individual parts of the biosphere, together with some critically evaluated no-effect and lowest-adverse-effect levels of borate on various representative species.

A variety of available analytical methods has been reviewed. Inductively-coupled plasma atomic emission spectrometry (ICP-AES) is currently the preferred screening method for the rapid analysis of samples, whereas inductively-coupled plasma mass spectrometry (ICP-MS) with a detection limit for boron of around 0.00015 mgB/l provides the most sensitive analytical results. The more traditional spectrophotometric method, in which a coloured complex of Azomethine-H with boron is assayed, is still in widespread use and has been incorporated into international standard methods.

The world's oceans have by far the greatest content of borate, with an average concentration of 5 mgB/l. Lakes and rivers in most parts of the world, except in areas of volcanic activity with more elevated concentrations, contain an environmental background content of <1 mgB/l, generally between 0.01 to 0.3 mgB/l. No typical concentration of borate can be cited for groundwater, which includes flowing springs (both hot and cold), geysers, aquifers (both flowing and confined), oilfield brines, etc. The recent review of the borate content of European groundwaters shows that values can vary from <0.1 to >1mgB/l and are dependent upon local geological circumstances, especially in areas of volcanic activity. Mineral waters contain a range from <0.02-4.3 mgB/l.

Igneous rocks generally have a low borate content. Sedimentary rocks have a higher borate content, which is related to the salinity of the water at the time of deposition. The borate content from such marine sediments ranges from 15-300 mgB/kg. The weathering of rocks, by rainfall and by erosion from rivers, provides a continuous small source of borate into the soil and the aqueous environment. Soils of low borate content (<10mgB/kg) are present on most of the earth. The average overall content of borate of all soils is 10-20 mgB/kg, with higher values (up to 100 mgB/kg) in the western USA and across the Mediterranean in Turkey, Iran and Kazakhstan.

Large deposits of borate minerals are rare. The only known massive deposits are located in the Mojave Desert of California, USA, and in Western Turkey. The four most important minerals are colemanite, kernite, tincal, and ulexite.

Although few data are available, the level of borate in the atmosphere is low and around 16 ngB/m³ according to a recent estimate. Its presence probably arises mainly from the vapour pressure of boric acid above the seawater. The tropospheric burdens for particulate and gas-phase boron (B) were recently estimated to be 6,000 tonnes and 60,000 to 110,000 tonnes, respectively.

There are industrial applications where the borate becomes fixed into a virtually water-insoluble matrix, but some localised aerial or aqueous discharges are likely to arise during production. In aqueous discharges, the borate passes unchanged through the sewage works and into river water and ultimately the sea. Examples of these include industries producing glass wool (insulation), enamels, ceramics and ferrous alloys. The use of boronated fertilisers in agriculture is a small but significant source of borate, arising from the fact that boron is a micronutrient required for healthy plant growth.

There are many other industrial and agricultural applications for the inorganic borates that result in discharges of borate to the environment. A significant contribution to European freshwaters in highly populated areas arises from the use of borates (including sodium perborate and other borates), where formulated in detergents.

Borate is required for the optimal growth of algae, but large concentrations (>20 mgB/l) inhibit growth. Pot experiments have shown that the reed plant *Phragmites australis* can tolerate a borate content in the aqueous nutrient substrate of up to 4 mgB/l, which may be extended to 8 mgB/l for a period of 2-3 months without noticeable damage. Concentrations of borate in domestic waste waters (up to 3.5 mgB/l) are much lower than those that would affect bacteria present in the sewage treatment processes. Bacteria, especially those present in sewage treatment plants tolerate concentrations >90 mgB/l. Chronic toxicity to protozoa and aquatic invertebrates is shown at ≥ 2.5 mgB/l. The toxicity of borate is low to terrestrial microorganisms and invertebrates ($LC_{50} \geq 17.5$ mgB/kg soil).

Boron is a required micronutrient for healthy plant growth, and is applied where necessary as a fertiliser at 0.5-3 kgB/ha. The borate content in all plants is in the range of 2-100 mgB/kg (based on dry weight). An inadequate supply of borate leads to symptoms of boron deficiency, whereas an excess leads to symptoms of boron toxicity.

The acute toxicity of borate to juvenile fish is relatively low, as median lethal concentrations range from 14 to 3,400 mgB/l. The data suggest that *Oncorhynchus mykiss* (rainbow trout) and *Brachydanio rerio* (zebra fish) are the most sensitive species. Chronic toxicity studies with early life stages of several fish species in reconstituted water clearly indicate that rainbow trout is the most sensitive species. By means of a combination of laboratory studies and field observations in natural waters, the determination of a safe concentration for borate in freshwater systems can be based on rainbow trout information exclusively. No effect concentrations of 0.75 mgB/l have been reported in tests with natural waters. The

observations of borate toxicity from field surveys show that healthy trout populations may occur in streams and lakes of the western USA at concentrations of near or slightly above 1 mgB/l.

These observations need to be consolidated by more observations linking occurrence of trout with measured boron concentrations. A study is planned, which may be expected to show that current NOEC values established in the laboratory are representative for the observations made in the USA for high boron streams. If this is the case the need to use a conservative assessment factor to extrapolate from laboratory to field data will disappear, supporting the NOEC to trout in aquatic systems of 1 mgB/l.

Data are available to show that borate does not bioaccumulate in algae, reeds, salmon and oysters.

The early life stages of amphibians, such as the frog and toad, had no effect concentrations of 3 mgB/l.

High concentrations of boron and selenium were found in waterfowl exposed to agricultural drainwaters in California. Diets containing 13 mgB/kg fresh weight showed no effects on mallards, but 30-100 mgB/kg produced growth reduction.

Environmental borate levels are not considered to be a concern for domestic animals. No effect concentrations in cattle were found at 120 mgB/l in drinking water and at 157 mgB/kg in feed.

It is concluded that boron is an ubiquitous element, present naturally as borate in seawater, freshwater, rocks, soil and all plants. Boron neither accumulates in any environmental compartment nor bioaccumulates, but is transported into the oceans, which have a high natural environmental background level of borate. Boron is an essential micronutrient for the healthy growth of all plants, and boronated fertilisers are used in agriculture to improve yields and to correct the symptoms of boron deficiency in crops. At the concentrations generally monitored in river water, borate causes no adverse effects to either land plants by irrigation or to water plants and aquatic life. Similarly, borate levels generally detected in soil cause no effects to land plants or soil organisms. Organisms in freshwater are the most sensitive to borate. The NOEC of borate to all freshwater aquatic life is at least 1 mgB/l.

1. INTRODUCTION

The element boron (B) is widely distributed in nature. Because of its high affinity for oxygen, boron always occurs in nature bound to oxygen in the form of inorganic borates. Apart from their occurrence in a few commercially exploitable deposits (mainly as sodium or calcium borate minerals), the borates are present everywhere at low concentrations in rocks (15-300 mgB/kg), soils (<10-20 mgB/kg), fresh waters (<1 mgB/l) and sea water (5 mgB/l).

Throughout this review the term "borate" is used as an abbreviation for the boron-oxygen substance under consideration. The term "boron" is used to express data as the equivalent boron (B) content of a borate, and is not intended to mean elemental boron. The term is also used to compare the effect of an equivalent B content of one borate with another when discussing doses applied in animal studies (details for conversion are given in section 2.4). Except for sodium perborate, the environmental effects are likely to result from the ultimate chemical species in aqueous solution, namely undissociated boric acid (see section 2.1).

Borates are in extensive commercial use. The nature of the product or end use will determine the extent of exposure to consumers and the environment. In some of the larger applications such as glass wool (insulation), enamels, ceramics and borosilicate glass, the borate becomes fixed into a water-insoluble matrix with little or no environmental impact. Applications where slow leaching into the environment will occur include adhesives, flame retardants and timber preservatives. The borates enter the aqueous environment most readily when used or discharged directly in the form of water-soluble inorganic borates. These include perborate-containing detergents, run-off from boronated fertilisers, additives to corrosion inhibitors in anti-freeze formulations, biocides for cutting fluids, insecticides and as buffers/preservatives for cosmetic and pharmaceutical preparations.

Borates are taken up naturally in all life forms and are found especially in fruit, vegetables, nuts and wine. Although borates are essential plant micronutrients, their essentiality for animals is not proven, but it does appear that borates may be nutritionally important for animals and man. During the past 5 years, largely through dietary studies made by the US Department of Agriculture, there has been renewed interest in the nutritional importance of boron. For example, Nielsen (1992) suggested that inadequate dietary boron (≤ 0.2 mgB/d) may be one factor that contributes to susceptibility to bone loss or osteoporosis. Further work is still required to establish whether there is an essential requirement for boron in human beings.

The concentration of borates in fresh waters is under scrutiny because the World Health Organisation (WHO, 1993) has recently published a new guideline value for boron in drinking water of 0.3 mgB/l, following a risk assessment based on reproductive toxicology. Because of more recent toxicological

data, this new guideline will be subject to further review and WHO has indicated that boron will be given top priority for re-evaluation at the first opportunity. The European Commission is now revising its guideline values for drinking water, which for boron is currently set at 1 mgB/l. The toxicological aspects of the borates have already been reviewed in a companion document (ECETOC, 1995). This report also covered current human exposures to boron via food and drinking water (see terms of reference below).

The objective of this Task Force has been to establish critically evaluated environmental levels of borate in the ecosphere, in order to provide appropriate guideline values for environmental safety. The terms of reference were:

- Review the ecotoxicology of boron and its derivatives;
- Identify the natural and consumer routes by which boron reaches the environment;
- Evaluate the current exposure to boron by man via food and drinking water (see above);
- Determine acceptable surface and drinking water concentrations.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, PRODUCTION, USES AND DISCHARGES TO THE ENVIRONMENT

2.1 IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES

Borax, the principal naturally occurring commercial source of the element boron, with the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, can be considered as the basis of inorganic borates. Borates are odourless white crystalline granules or powders. Identity and physical/chemical properties of the seven major inorganic borates discussed in this report are summarised in Table 1.

Of particular interest is an understanding of the nature of the active chemical species and how it interacts with biological tissues. Because boric acid is stable and a very weak acid (pK_a 9.15), the undissociated acid (H_3BO_3) is the predominant species in aqueous solution at physiological pH. This conversion into undissociated boric acid applies also to boric oxide and the sodium borates. As a consequence, the ecotoxicology of all these substances is likely to be similar on an equivalent boric acid basis (as boron). Furthermore, it is known that boric acid can form complexes with carbohydrates and proteins (Kliegel, 1980). For the series of boron-containing compounds identified in Table 1 (except sodium perborate), it is assumed that the final species will be either the undissociated boric acid or a complex of boric acid with a carbohydrate or protein.

Boric acid (H_3BO_3) can be steam distilled from its aqueous solutions (Levi and Curti, 1938). This is a physical property of some environmental significance, because it indicates that boric acid will exert a small partial vapour pressure over seawater. The presence of small quantities of boric acid vapour observed in the atmosphere probably originates because of its reported vapour pressure of ca. 260 Pa (2 mm Hg) at 20°C (Schachtschabel et al, 1989). The volatility of boric acid can be suppressed, either by the addition of strong alkali, or by the complexation of the boric acid with mannitol (Feldman, 1961).

Different considerations apply to sodium perborate, a peroxygen compound, that readily generates hydrogen peroxide in addition to sodium borate in biological systems.

Table 1: Identity, Physical and Chemical Properties

Physical/Chemical Properties	Boric Acid ¹⁾	Borax ¹⁾	Borax Pentahydrate ¹⁾	Anhydrous Borax ¹⁾	Boric Oxide ¹⁾	Sodium Perborate tetrahydrate ²⁾	Sodium Perborate Monohydrate ³⁾
Chemical Formula	H ₃ BO ₃	Na ₂ B ₄ O ₇ ·10H ₂ O	Na ₂ B ₄ O ₇ ·5H ₂ O	Na ₂ B ₄ O ₇	B ₂ O ₃	NaBO ₃ ·4H ₂ O	NaBO ₃ ·H ₂ O
Chemical Name	Orthoboric acid	Disodium tetraborate decahydrate	Disodium tetraborate pentahydrate	Disodium tetraborate	Diboron trioxide	Sodium perborate tetrahydrate	Sodium perborate monohydrate
Synonyms	Boracic acid	Borax decahydrate, Borax 10 Mol	Sodium tetraborate pentahydrate, Borax 5 Mol	Sodium tetraborate, Borax Glass	Boron trioxide, Anhydrous boric acid	PBS4, PBST	PBS1, PBSM
CAS Registry No.	10043-35-3	1303-96-4	12179-04-3	1330-43-4	1303-86-2	10486-00-7	10332-33-9
EINECS No.	233-139-2	215-540-4	215-540-4	215-540-4	215-125-8	234-390-0	234-390-0
Physical Form	White crystalline granules or powder	White crystalline granules or powder	White crystalline granules or powder	White vitreous granules	White vitreous granules	White crystalline powder	White crystalline powder
Mol. Weight	61.83	381.37	291.35	201.27	69.62	153.9	99.8
Spec. Gravity (20°C)	1.51	1.73	1.81	2.37	1.83		
Bulk Density (kg/m ³)	880	935	1,000-1,150	1,075-1,380	975-1,090	700-900	500-650
Melting Point (°C)	171	> 62	<200	742 (Crystal)	450 (Crystal)	Decomposes	Decomposes
Closed Space							
Anhydrous Form (°C)	450 (Crystal)	742 (Crystal)	742 (Crystal)				
Boron Content (%)	17.48	11.34	14.85	21.49	31.06	7.03	10.8
Available Oxygen (% wt)	N.A.	N.A.	N.A.	N.A.	N.A.	10.0	15
Water Solubility (% w/w)	4.72 (20°C) 27.53 (100°C)	4.71 (20°C) 65.63 (100°C)	3.6 (20°C) 50.15 (100°C)	2.48 (20°C) 34.5 (100°C)	Rapidly hydrates to boric acid	23 g/l (20°C) 37 g/l (30°C)	15g/l (20°C) 24 g/l (30°C)
pH of Aqueous solution (20°C)	6.1 at 0.1% 3.7 at 4.7%	9.24 (constant)	9.24 (constant)	9.24 (constant)	Rapidly hydrates to boric acid	10 at 1.5%	10 at 1.5%
pK _a (pK ₁) (20°)	9.15 ⁴⁾						
Pow (25°C)	0.175 ⁵⁾	N.A. (dissociates)	N.A. (dissociates)	N.A. (dissociates)	N.A. (Rapidly hydrates to boric acid)	N.A. (decomposes)	N.A. (decomposes)

N.A. Not Applicable;

¹⁾ Borax Consolidated, 1992;²⁾ Intertox Chemicals, 1982a;³⁾ Intertox Chemicals, 1982b; ⁴⁾ Dawber and Matusin, 1982;⁵⁾ Barrès, 1967.

2.2 PRODUCTION

Limited published data are available on production statistics of the inorganic borates, as follows:

- the estimated total world production of boron minerals and compounds in 1991 was almost 3 million tonnes (Lyday, 1992);
- the world's annual capacity (expressed in tonnes per annum B_2O_3) to make the major boron chemicals in 1989 (CEH, 1993) was:

USA, 750,000 of sodium borates and 195,000 of boric acid,

Western Europe, 30,000 of sodium borate and 56,000 of boric acid.

- The European consumption of sodium perborate tetrahydrate in 1993 was 620,000 tonnes (CEFIC, 1994).

2.3 USES

Borates are in widespread use in industrial, agricultural and consumer products. The specific end uses of each substance are outlined below (Borax Consolidated, 1992).

2.3.1 Boric Acid

Boric acid is an important source of soda-free boric oxide (B_2O_3) in vitreous systems such as glass, enamels and ceramic glazes. It is a flame retardant with effective anti-smoulder characteristics. The high-purity form is used in the production of capacitors, and for the control and emergency shutdown of nuclear reactors (absorption of neutrons by ^{10}B isotope). Boric acid is also used as a preservative in some cosmetic and pharmaceutical preparations. In admixture with borax it is a useful buffer in eye lotions.

2.3.2 Borax

Borax is generally the sodium borate selected for applications in aqueous solutions, e.g., anti-corrosion additive in vehicle cooling systems or in cutting fluids. Borax is also used for cosmetic/pharmaceutical applications.

2.3.3 Borax Pentahydrate

Borax pentahydrate is the major borate raw material for the glass, ceramics and enamel industries. It is used as the feedstock for the production of sodium perborate bleach.

2.3.4 Anhydrous Borax

Anhydrous borax is borax from which the water of crystallisation has been removed by fusion. The resultant molten glass is cooled and crushed to form a granular product, but the glassy nature of the particles can still be discerned. The finished product has a higher bulk density than either borax or borax pentahydrate and is preferred to these materials in the glass, ceramic and enamel industries if furnace capacity and/or storage capacity is at a premium.

2.3.5 Boric Oxide

Boric oxide is prepared by the dehydration of boric acid. As in the case of anhydrous borax, the water is removed by fusion and the glassy product is crushed to form a coarse granular or a powder product. The glassy nature of the material can be discerned in the coarse form.

Boric oxide is used in the manufacture of ferroboron and other master alloys. It is used for heat treatment in the metallurgical industries.

Boric oxide is hygroscopic, absorbing moisture from the atmosphere to form boric acid.

2.3.6 Sodium Perborate Tetrahydrate

Sodium perborate tetrahydrate is produced commercially from the oxidation of aqueous sodium metaborate by hydrogen peroxide. It is used primarily as a bleaching agent in detergent powders and in bleaching powders, but also to a smaller extent as a mild disinfectant and deodorant in cosmetic and pharmaceutical preparations (Martindale, 1977).

2.3.7 Sodium Perborate Monohydrate

Sodium perborate monohydrate is prepared by the partial dehydration of sodium perborate tetrahydrate. It is used primarily as a bleaching agent in detergent powders.