# Boric Acid as a Swimming Pool Buffer

Robert G Birch
The University of Queensland, Brisbane 4072 Australia

## 1.0 Summary

Boric acid in equilibrium with its conjugate base, the borate ion, has been applied increasingly in recent decades as a pH buffer system in swimming pools. This article provides a critical review of chemical and biological factors relevant to this application, based primarily on the refereed scientific literature. It examines basic chemistry, sources and conversion factors, safety and toxicology, pH buffering, and potential side-benefits including antimicrobial activity, anti-corrosive properties, photostabilisation of hypochlorite, and sensory effects such as water softening and colour. By highlighting some advantages of borate over bicarbonate as a buffer in salt-water pools, defining safety precautions in terms relevant to pool use, and noting the limits to scientific understanding of some potential side-benefits; the review should assist in science-based decision making about adoption of boric acid as a primary or adjunct buffer in swimming pools.

## 2.0 Introduction

Based on estimates from national pool associations, there are in the order of 20 million swimming pools on earth, maintained at an average cost of more than $500 per annum for chemical inputs, plus the costs of electricity for pumping and heating. Thus pool maintenance is a multi-billion dollar industry internationally. The number of pools, their combined operating cost, and their environmental footprint increase with average living standards. The vast majority of pools are now domestic, and managed by their owners with varying degrees of technical input from user forums, pool service providers, and the manufacturers and retailers of pool supplies. Advice from these sources is often conflicting. Therefore, a compelling case exists on financial and environmental grounds for far greater scientific input -- through research, critical analysis and dissemination of knowledge -- to support science-based decision making in swimming-pool management. The objective of this review is to contribute to that process, in relation to the use of boric acid in swimming pools.

## 3.0 Basics of boric acid chemistry

Boric acid, formula $B(OH)_3$, is a Lewis acid. It does not release a proton ($H^+$ ion) from its own structure, but it can acquire an $OH^-$ group from water: $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$. The final effect is still to increase the $H^+$ concentration in solution: the hallmark of an acid.

In solution, there is a equilibrium between the acid form (a planar molecule) and various borate ions, the simplest of which is tetrahydroxyborate $B(OH)_4^-$ (a tetrahedral molecule) (Fig. 1). So, in swimming-pool context "the boric acid buffer system" and "the borate buffer system" are exactly the same thing. Around pH 7, boric acid is the predominant form in aqueous solution.
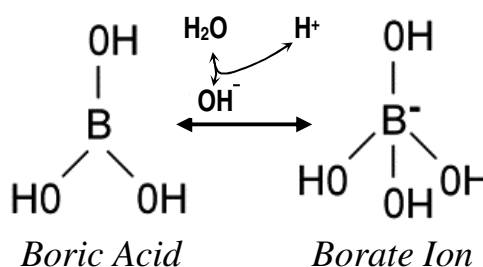
Boric acid is a weak acid. At 25C, its pKa (the pH at which buffering is strongest because the free



**Fig. 1.** Dissociation of water in the presence of boric acid to release a proton and a borate ion.

acid and borate ion are in equal concentrations) is 9.24 in pure water. But apparent pKa is substantially lower in swimming pool or ocean waters because of interactions with various other molecules in solution. It will be around 9.0 in a salt pool (see pH buffering below).

At high concentrations (above those used in swimming pools) various polyborate species may predominate at higher pH. For example, "Borax" used for various household purposes is a hydrated form of sodium tetraborate ($Na_2B_4O_7.10\ H_2O$), and sodium hexaborate is marketed for pool use. From another perspective, boric acid is sometimes considered as an aqueous form of boric oxide: $B_2O_3.3H_2O = 2\ B(OH)_3$.

No matter which form of soluble boron is added, within the acceptable range of pH and boron concentration for swimming pools, boric acid is the predominant form in aqueous solution (Fig. 2). This is important, because any of the side-benefits mentioned below that are mediated through the borate ion, as distinct from the boric acid molecule, will be pH dependent; and more evident in a pool at pH 8 than at pH 7.5.
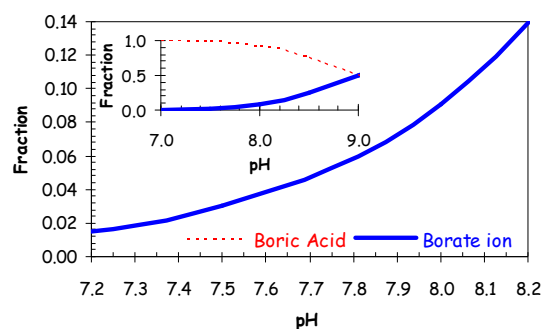


**Fig. 2.** Boric acid is the predominant form in aqueous solution across the swimming pool pH range.

Reviews of borate chemistry in other contexts are (Keren 1996; Hunt 2002; Schubert 2011).


## 4.0 Supply

Boric acid is used commercially for a wide range of industrial processes. Because boron is a micronutrient needed by crops, and some soils are deficient, boric acid may be purchased inexpensively (around $50 for 25 kg) in suitably pure form (>99.5%) from some farm supply stores. In some localities, borax is sold by supermarkets for domestic (laundry) use. Using borax to provide borate in a pool is typically more complex and expensive, because HCl must be added at the same time to maintain a satisfactory pool pH (Birnholz 2008). Some borate products marketed for swimming pool use are formulated near neutral pH for convenience.

The concentration of boric acid or borates is sometimes expressed in terms of the boron component. For example, pool recommendations are usually in ppm boron equivalents, whereas toxicology and chemistry reports more commonly use ppm of the compound tested, or molar units. When using units based on weight (like ppm, in contrast to molar units), the dose of a compound can be multiplied by that compound's boron content to obtain boron equivalents. For example, 1000 ppm boric acid (17.48% boron) is 174.8 ppm in boron equivalents and 1000 ppm borax (11.34% boron) is 113.4 ppm in boron equivalents.

To achieve 100 ppm boron equivalents in a 50 kl pool, a pool operator could add 100*50/0.1748/1000 = 28.6 kg of boric acid (572 ppm boric acid). Because it is a weak acid, no pH readjustment may be required, especially if the initial pool pH was on the high side or drifting upwards (for example through salt-water chlorinator action).

'Combination' products are also marketed. For example, some granular sanitizers contain trichlor and up to 30 % (w/w) sodium tetraborate pentahydrate. Unless the composition matches a ratio needed for some special purpose, (e.g. to replenish borate and cyanurate lost in pool overflow), combination products are likely to prove expensive, and to complicate the calculation of materials needed to maintain a preferred chemical make-up of pool water.

**5.0 Safety**

This section considers safety in context of borate-buffered swimming pools. The underlying toxicological data are reviewed in other (pesticide, drinking-water) contexts in summary (Harper *et al.* 2012) and in more detailed analyses (WHO 1998; USDA 2006) which provide full citations to the primary scientific papers.

In solution, boron is found almost entirely as boric acid or borates, which are common at low concentration in our environment. Several common fruits and vegetables typically contain 160-300 ppm boron. Sea water contains about 4.5 ppm (0.43 mM) boron and some saline lakes contain above 300 ppm boron. It is generally recommended that drinking water should be below 1 ppm boron. Boric acid is classed as a low toxicity chemical. Reports of poisoning are rare, but symptoms from ingestion of large doses (more than could be plausibly swallowed while swimming - as discussed below) include nausea, vomiting, abdominal pain, diarrhoea, headaches, red skin rash, weakness, tremors, unconsciousness, respiratory depression, kidney failure, shock and death.

Boric acid and borates are poorly absorbed across intact skin. Estimated human consumption in food and drinking water is around 1-5 mg boron per day, with at least a 10-fold range around this amount depending on diet. At the low end of this range, boron may be an essential micronutrient.

Acute oral $LD_{50}$ for boric acid in laboratory animals is in the range 2.5-5 g/kg; about the same as table salt (NaCl: $LD_{50}$ 3-4 g/kg). For an individual weighing 50 kg, this would indicate more than 100 g of boric acid for lethal effect. From study of fewer individuals, dogs may be about 4-fold more sensitive. From accidental poisonings in humans, minimum oral lethal doses of boric acid have been estimated to be in the range of 5-20 g for adults, 3-6 g for children (>500 mg boron/kg/day, with sub-lethal effects above 180 mg boron/kg/day). The dose for acute toxicity depends on multiple factors including the form ingested (powder, concentrated solution) duration for ingestion and individual susceptibility. To obtain a 5 g dose of boric acid from a swimming pool at 100 ppm boron it would be necessary to swallow 10 litres of pool water.

There are no compelling data on doses causing chronic effects in humans, but studies have been performed in several animal species. In tested mammals, the most sensitive indicators of boron toxicity are testicular atrophy in males and effects on foetal development in pregnant females. Mice exposed over their lifetime to 0.95 mg boron/kg/day in their drinking water showed no adverse effect. Long-term studies on oral exposure in dogs and rats indicate that the lowest dose for testicular effects is around 17-30 mg boron/kg/day. In pregnant mice and rabbits, the lowest chronic dose for adverse effects on offspring was in the range 40-80 mg boron/kg/day. To obtain a dose of 10 mg boron/kg/day from a swimming pool at 100 ppm boron, an individual weighing 50 kg would need to swallow 5 litres of pool water every day. The World Health Organization recommends intake below 0.4 mg/kg/day (intended to avoid any possibility of harm to a foetus in a pregnant woman): under this scenario an individual weighing 50 kg should swallow less than 0.2 litres per day of pool water at 100 ppm boron.

In humans, reported half-life for urinary elimination of ingested boric acid ranges from 13-21 hours (> 90% elimination within 4 days).

In summary, it is inadvisable to use a borate-buffered pool as drinking water for any animal. It does not seem plausible that a swimmer could accidentally swallow enough pool water to

suffer any adverse effects - acute or chronic - from boric acid used anywhere in the range up to 100 ppm boron. A pregnant woman who swims every day might take particular care: to stay below the WHO-recommended maximum intake, don't swallow more than a half-cup of pool water (at up to 100 ppm boron) per session!

The most recent USA-EPA assessment (2006), based on a conservative 100-fold safety margin above average daily doses giving no adverse effects in mammalian species (and assuming ingestion of swimming pool water at up to 0.05 litres per hour by children), considers levels below 360 ppm boron safe for child or adult non-competitive swimmers.

## 6.0 Antimicrobial activity

The antimicrobial uses of boric acid - borate solutions have been explored since at least the early 1900's, including uses on foods (Winston 1935). About 1% boric acid is needed for broad antimicrobial activity (Borokhov and Schubert 2007). At swimming-pool concentrations, no adverse effect is expected on potentially pathogenic bacteria: *Pseudomonas putida* was unaffected at 290 ppm boron equivalents (ECETOC 1997).

There are few published scientific studies of borate toxicity to algae. For the green alga *Scenedesmus* and the cyanobacterium *Microcystis*, a 50% reduction in viable cell count within 72 hours required 34 -53 ppm boron equivalents (ECETOC 1997). A patent example (Girvan 1986) states no visible growth by the algae *Chlorella pyrenoidosa* and *Chlorococcum mustard* and the fungus *Aspergillus flavus* in a nutrient medium supplemented with 200 mg/l sodium tetraborate pentahydrate (i.e. 30 ppm boron equivalents), but there appear to be confounding variables relative to the control (absence of phosphate and altered pH). It is reasonable from this limited evidence to expect some inhibitory effect on the growth of some algal species at the levels (50-100 ppm) applicable in borate-buffered pools. Any operator of such a pool will know that some algal (and cyanobacterial) species are capable of rapid growth at these levels.

There appears to be no scientific support for the assertion sometimes made that borate starves algae of $CO_2$. Under some conditions borate can accelerate the slow step (hydration of dissolved $CO_2$ to form carbonic acid) in the aquatic carbonate equilibrium, but under typical swimming pool conditions the effect is trivial (Guo *et al.* 2011). Antibiotic activity is likely to involve multiple molecular targets, given the high affinity of boric acid to form complexes with various poly-hydroxyl compounds (Hunt 2002) .

Borax is used in the control of various wood-rotting fungi and insect pests, but the methods are expected to give very high local concentrations in treated wood (0.2% to 2% of sodium borate by weight in some industry estimates). Concentrations needed for antifungal activity have never been documented (USDA 2006).

In effect, the use of borate does not allow any reduction in free HOCl concentration needed for pool sanitation. There are no documented tests of additive or synergistic effects between boric and hypochlorous acids. It is perhaps ironic that in the (now-expired) patent which appears first to have recommended borate use in swimming pools, the claims are limited to control of algal growth through tetraborate addition (Girvan 1986). However, improved pH buffering and enhanced blue colour were also noted as benefits of the method.

## 7.0 pH buffering

A swimming pool is an aqueous solution of various acids, salts and other solutes.

The capacity of an aqueous solution containing an acid to resist change in pH due to $H^+$ or $OH^-$ addition increases with buffer concentration and is highest around the pKa of that acid (where the free acid and its dissociated base ion are in equal concentrations). Buffer capacity declines steeply as pH moves away from the pKa (Fig. 3), so ideally one would choose a buffer with a pKa close to the intended working pH; preferably +/- 1 pH unit. However, pKa depends on factors that vary between pools (and over time in the same pool) including temperature, overall ionic strength of the solution and the concentration of specific ions or other molecules that form complexes with the buffer molecules.

At 25 C, the apparent pKa of boric acid is 9.24 in pure water. pKa is expected to decrease with increasing ionic strength, as modelled using refinements of the Debye-Hückel equation (Pitzer 1991). But borate (and carbonate) buffers show much greater than predicted decrease in pKa in the presence of some ions (Fig. 4). This has been attributed to specific ion-pairing interactions. In the case of borate, the effect is absent with $K^+$, evident with $Na^+$, and even stronger with $Ca^{++}$ and $Mg^{++}$ (Owen and King 1943; Reardon 1976; Bassett 1980; Hershey *et al.* 1986).



**Fig. 3.** Buffer strength is highest when pH equals pKa (around 9.0 for borate in a salt water pool), and very low when pH is more than 2 units from pKa. Prepared using academic.pgcc.edu/~ssinex/buffer_cap.xls



**Fig. 4.** pKa of boric acid vs salinity in solutions containing NaCl alone (●), or NaCl plus 0.05 molal $MgCl_2$ (□) or $CaCl_2$ (Δ). From equations of Hershey *et al.* (1986). At typical swimming pool concentrations, the relationship would lie just below the NaCl curve.

Borate also forms low-pKa complexes with some organic compounds including sugars (a reaction used in some borate test kits). Therefore, it is not possible to predict the apparent pKa of borate in a pool from a measurement such as conductivity or total dissolved solids (TDS). It is necessary to know the precise composition of the water and to include the dissociation constants for each of the pairing ions (or other solutes) in the calculations to obtain a reasonable prediction.

While we can say that apparent pKa of boric acid will be around 9.0 in a salt water swimming pool (Fig. 5), it will vary with pool salt content and composition to an extent that is very noticeable in pool management. For example, the amount of acid required to adjust from pH 8.0 to pH 7.8 would approximately double with a decrease of 0.2 in the pKa.
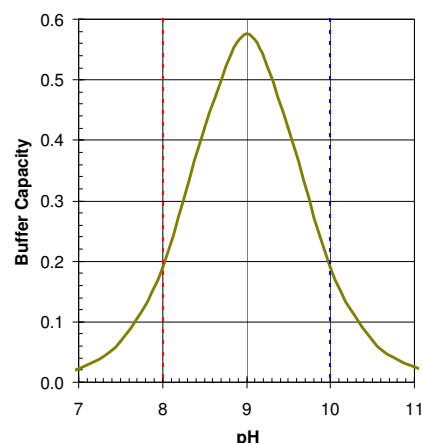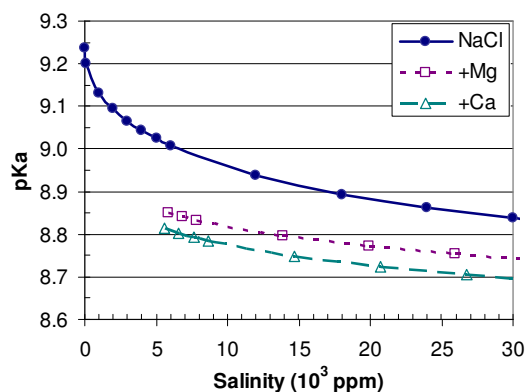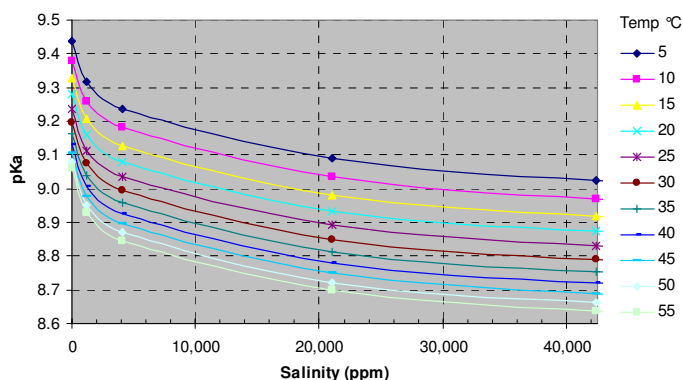


**Fig. 5.** The apparent pKa of boric acid decreases with salinity (from NaCl) and temperature. Plotted from experimental data of Owen & King (1943).

**7.1 Buffering and pH updrift in SWC pools**: Assuming the target range for pool pH is 7.5 - 8.2, boric acid is a more effective buffer in a salt-water pool than in fresh water; and its buffer strength will increase with salinity (which should be adjusted according to recommendations from the manufacturer of the electrolytic salt-water chlorinator - SWC) and hardness (which an SWC pool operator may prefer to keep low and mainly from $Mg^{++}$ to reduce problematic scaling of calcium salts in the SWC cell).

While buffering by borate will be stronger with increasing pH up to 9, a pool operator will need to consider other effects of pH including rate of chlorine photolysis and potential for scaling or staining at high pH. Increased loss of HOCl occurs at high pH through photolysis of $OCl^-$ ($2\ HOCl \rightleftharpoons 2\ H^+ + 2\ OCl^-$ --{UV}$\rightarrow 2\ H^+ + O_2 + 2Cl^-$). Loss via $Cl_2$ ($2\ HOCl + 2\ H^+ + 2\ Cl^- \rightleftharpoons 2\ Cl_2 + 2\ H_2O$ --{light, metal oxides}$\rightarrow 4\ HCl + O_2$) predominates below pH 5.

In any pool there are many interacting chemical reactions that affect and respond to pH, and all of these reactions are affected to differing extents by seasonal factors. Whether, where and when any particular pool tends to settle at an equilibrium pH, in the absence of deliberate intervention, is a matter for empirical observation. If a pool tends to equilibrate at a pH that is workable for other management needs, operating at the equilibrium pH will save costs of time and HCl. If a pool continuously drifts higher than the preferred operating pH, periodic adjustments by addition of HCl will be required.

Note that in this common scenario of up-drifting pH, buffering does not reduce the amount of HCl required: it just avoids the need for very frequent additions of small amounts of acid to correct rapid swings in pH that can occur without sufficient buffer. The buffer allows less frequent (but correspondingly larger) acid additions to counteract the same amount of $H^+$ depletion from the SWC process.

If the pH rise in an SWC pool is from $H^+$ depletion associated with $CO_2$ outgassing from bicarbonate added as a pH buffer, then there should be a saving if the addition of bicarbonate can be avoided through use of a suitable borate buffer concentration. As borate does not have the problem of a volatile component in its buffer system, this cause of $H^+$ depletion would be eliminated by leaving the carbonate system at equilibrium with atmospheric $CO_2$. Indeed borate can catalyse (albeit slightly at pool concentrations) the rate-limiting $CO_2$ hydration step in the natural carbonate buffer system (Guo *et al.* 2011).

This brings us to consider whether a borate concentration that is safe for swimmers (arguably up to 100 ppm boron equivalents) can - either alone or in combination with other pool buffer components such as CYA or bicarbonate - provide sufficient pH buffering for effective pool management.

Buffer capacity of an acid is directly proportional to the molar concentration of that acid in solution. When multiple acids are present, their buffer strengths at any specified pH are additive. Therefore, in a salt-water pool at 25 C and 6,000 ppm NaCl, considering capacity to resist upward drift of pH from a working target of pH 7.5 - 8.0: buffer strength from boric acid at 9.25 mM (100 ppm boron, pKa 9.0) will greatly exceed that from bicarbonate at a typical pool concentration of 2 mM ($pKa_1$ 6.0 and $pKa_2$ 9.4) or CYA at 0.39 mM (50 ppm, pKa < 6.9). Hypochlorous acid at 0.2 ppm (0.004 mM, pKa < 7.5) is too dilute to contribute useful pH buffering. The same is usually true of bicarbonate in equilibrium with the atmosphere (< 1 mM unless you are working at high salinity and high pH; Mook 2000).

From this analysis, and in practice, boric acid at 50-100 ppm boron provides more than sufficient pH buffering for efficient SWC pool management, without any need to add bicarbonate.

Note that "total alkalinity" (TA) commonly measured by pool test kits is an indicator of resistance to downward movement in pH (typically the amount of acid needed to titrate the pool water down to pH 4.0 or 4.5). It is a poor measure of buffering in the common SWC scenario of upward-drifting pH. When pH is changing because of addition or depletion of $H^+$ or $OH^-$ ions, TA will always increase with pH; whereas buffer capacity will decline steeply as pH moves away from the pKa of the buffer.

With pKa around 9 in a salt-water pool, borate provides increased buffer strength as pH rises in the usual working range of pH 7.5 - 8.0 (or above), but it has little buffer capacity against falling pH below that range. Because of its lower pKa (< 6.9 in a salt-water pool), CYA complements borate by buffering more against rapid falls in pool pH (rarely seen in SWC pools unless the operator mistakenly adds too much acid).

## 8.0 Reduced corrosion

Borate is used as a corrosion inhibitor in some industrial reticulation systems. Apart from buffering at alkaline pH, where corrosion is electrochemically less favoured, borate ions interact with metal surfaces and contribute to nonoxidizing anodic passivation (protective oxide film formation) at those surfaces (Schubert 2011). Depending on the metal involved, pool concentrations of borate may be sufficient to enhance passivation, but halides ($Cl^-$, $Br^-$) at SWC pool concentrations may still contribute to pitting corrosion (de Chialvo *et al.* 1985; Refaey 1996; Martini and Muller 1999).

## 9.0 Protection against photolysis of HOCl

Brady et al. (1963) made the curious observation that the extinction coefficient of $OCl^-$ is considerably lower in borate relative to carbonate buffer at the same pH. This has been attributed to reversible formation of a hypochloritoborate complex [$B(OH)_3OCl^-$] which does not absorb around 300 nm, and which reaches a maximum concentration at pH 8.3 (Bousher *et al.* 1987). Formation of this complex is expected to reduce both the photodegradation of $OCl^-$ and the HOCl (sanitizing chlorine) concentration. Therefore, borate will act as a photoprotectant and buffer of HOCl release from measured FC, with a pH sensitivity different from CYA.



**Fig. 6.** pH-dependent formation of photoprotected hypohaloborate complex in a pool with 100 ppm borate and 1 ppm 'free halogen' (without CYA), based on pKa values of 9.24 for $B(OH)_3$, 8.66 for HOBr, and 7.54 for HOCl, with stability constants of 68 for $B(OH)_3OBr^-$ and 178 for $B(OH)_3OCl^-$, as estimated by Bousher et al. (1987).

From the work of Bousher et al. (1987), it appears that borate has a much lower affinity than cyanurate for hypochlorite, and at typical pool concentrations (< 0.01 M $B(OH)_3$ and ~1 ppm FC excluding chlorocyanurates) the hypochloritoborate complex will comprise < 3% of FC; even lower at pH 7.5 (Fig. 6). This is not enough for substantial photoprotection. However, as for CYA, the estimations of stability constants were somewhat indirect and limited by the spectrophotometric methods of the time. It would be very interesting to see a follow-up study using direct measurements, to evaluate
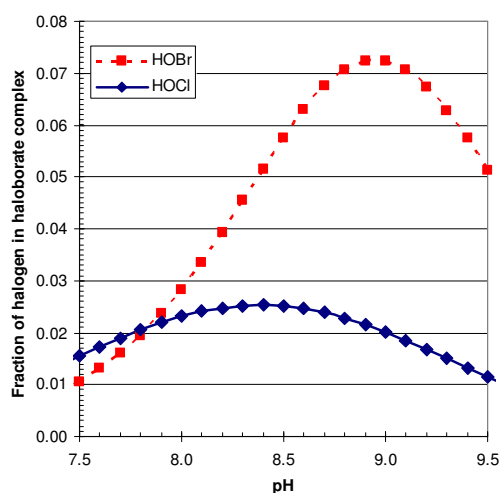
the extent to which borate might supplement CYA in the photoprotection of hypochlorite in swimming pools, and in rapid complexing of hypochlorite in SWC cells to minimise outgassing of $Cl_2$.

Wavelengths below 300 nm are almost completely blocked by ozone and oxygen in the earth's atmosphere (Madronich *et al.* 1998). Therefore, any solute with substantial absorption in the 300-400 nm range (where photolytic degradation of hypochlorite and hypobromite ions under sunlight is most severe, Fig. 7) has the potential to increase the half-life of sanitizer, particularly in deeper parts of a pool (Anbar and Dostrovsky 1954; Nowell and Hoigne 1992). As noted below, the absorbance of pure water is minimal whereas dissolved organic matter can absorb strongly in this range. While full UV-visible absorption spectra have never been published (or perhaps even measured with sufficient path length for this context) it appears from the published information that neither CYA nor boric acid has any absorption peak in this range (Berton 1938; Sancier *et al.* 1964).



**Fig. 7.** Absorption spectra of aqueous hypochlorite and hypobromite species, relative to earth surface radiation. Data from Anbar & Dostrovsky (1954), Madronich et al. (1998) and references therein.

## 10.0 Sensations

*10.1 Blue colour.* It is sometimes asserted that addition of borate (to about 50 ppm boron equivalents) confers either or both of an attractive blue tint or a sparkling appearance to pool water. Probably unrelated is the observation that symptoms of acute borate poisoning include blue-green tinted vomiting and diarrhoea. Some suppliers of borate for pesticide use add a blue dye, perhaps to convey an (incorrect) impression of higher potency. Borate does form blue-coloured complexes with some chemicals (Juza *et al.* 1966; Ma and Boo 1976), but it is not apparent that any of these should commonly form in swimming pools.

Blue colour (under white light) arises from preferential absorption of other wavelengths, with the effect that those perceived in the blue colour range are preferentially reflected or transmitted. Outdoor bodies of water change in colour and intensity depending on viewing angle and reflected sky colour. Clear sky is blue for most of the day, because shorter (blue) wavelengths are preferentially scattered by molecules in the atmosphere. When we look at the

sky, or at a reflection of the sky in a body of water, we are seeing mostly scattered light; except around dawn and dusk (Gibbs 1997). This component of colour due to reflection from the pool water surface does not depend much on pool solute composition, but many times (depending on viewing angle and disturbance to the surface mirror effect) we are seeing a substantial proportion of light that has been transmitted through the pool water and reflected back to us from the pool floor or walls, or by scattering from dissolved molecules or suspended particles in the pool water.
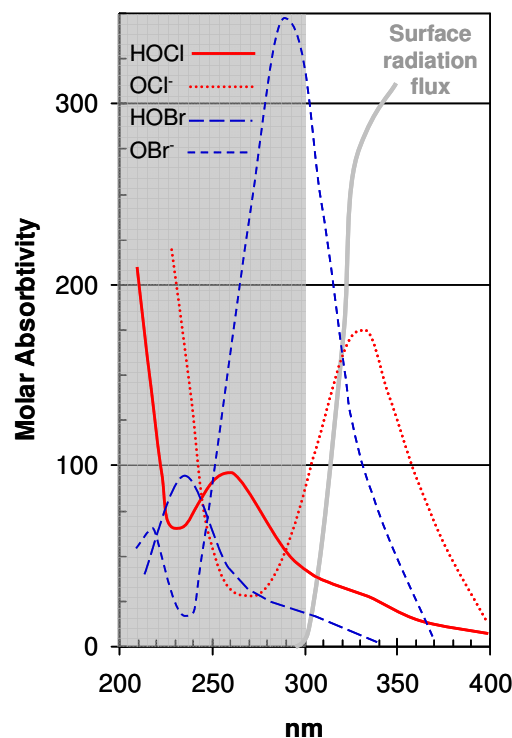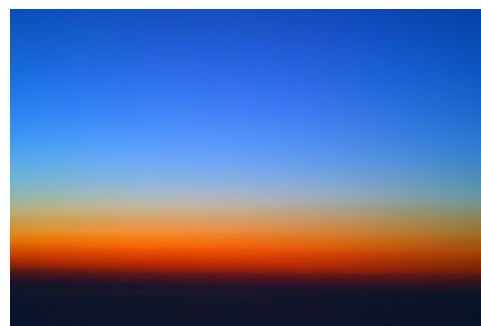


**Fig. 8.** Scattered (blue) and transmitted (red) light in the sky at sunset. Photograph by Rodrigo da Cunha ( http://en.wikipedia.org/wiki/File:SDIM0241b.jpg).

Pure water is nearly transparent throughout the visible spectrum, but when the light path is long enough (a metre or more) water has a blue tint, due to higher absorbance at the red end of the visible spectrum (Braun and Smirnov 1993; Chaplin 2013). The red : blue absorbance ratio of about 100 : 1 in ultra-pure water is reduced by common trace impurities (Pope and Fry 1997) but it remains high enough to cause a blue tint in many clean natural water bodies. Coloured dissolved organic matter shifts the colour towards green or yellow (Green and Blough 1994). Light absorption in pure water is substantially due to vibrational effects in the OH



**Fig. 9.** Absorption of radiation by pure water is very low across visible wavelengths, and minimal in the near UV - blue range. From Chaplin,2013.

bond. Colourless salts can have measurable effects on the absorption spectrum when dissolved in water at high concentrations (Wolszczak *et al.* 2002) but at swimming-pool concentrations no discernable effect seems likely above traces of chromogenic organic substances in the water (Morel *et al.* 2007). No direct evidence has been published in support of absorption of visible light by boric acid in solution, whereas infra-red absorbance is characterized (Mao *et al.* 2005; NIST 2011).
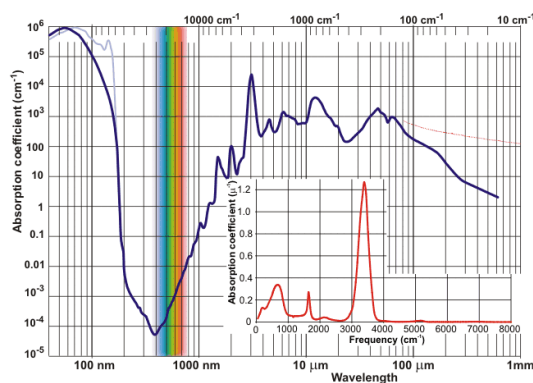
Dissolved salts can also affect the perceived tint of water due to increased light scattering. This is a complex phenomenon (partly explained theoretically by luminaries including Rayleigh and Einstein). In summary, bigger molecules (and ion pairs) increase scattering, which is greater at shorter wavelengths. Within the typical SWC pool concentration range, effects of different solutes may be more than additive and molecular scattering of blue wavelengths would be around $10^{-2}$ per metre  (Zhang *et al.* 2009). This is comparable in magnitude to absorption of blue, but >30-fold less than absorption of red which confers the blue tint in pure water (so a visible effect seems unlikely). Whether greater scattering of shorter wavelengths increased or decreased a perceived blue tint would depend on the proportion of the light scattered or transmitted on its course to the observer. It seems barely plausible that borate could have an effect through this mechanism on perceived water tint, depending on overall solute composition. No direct experiments on borate have been published, but comparisons of natural and artificial seawater indicate no likely visible effect (Ravisankar *et al.* 1988; Sullivan *et al.* 2006). Another indirect test is that molecular scattering tends to polarize light scattered perpendicular to the original direction of travel. The vector of polarization is then in a plane perpendicular to the plane formed by the light source, the point of scattering and the observer. The degree of polarization decreases with consecutive scattering events. The sum of these effects can be seen in the sky viewed through polarizing sunglasses (Hall 2010). Ocean solutes can also cause a high degree of polarization to underwater light (You *et al.* 2011). When viewing pools through a polarizing filter, there is an obvious and expected effect on reflection from the water surface. But I have not observed any polarizing effect that would support a solute molecular scatter model for pool colour. More critical scientific testing is needed to support a light scattering mechanism for any effect of borate on pool colour.

Altered refractive index of the pool water is sometimes proposed as a mechanism for an effect of borate on colour, with the idea that the effect arises from altered path length or direction of the light reflected back to the viewer from the pool floor. This seems implausible considering that refractive index increases from 1.3330 for pure water (at 20 C and 589 nm) to 1.3335 with NaCl at 3,000 ppm or 1.3340 with NaCl at 6,000 ppm (spanning the range in

most SWC pools). To increase the refractive index of water to 1.3335 using borate would require 100 mM of $B(OH)_4$ (Galleguillos *et al.* 2001), or more than 1,000 ppm expressed as boron equivalents. Any effect on refractive index of borate at recommended concentrations (< 100 ppm boron equivalents) will be trivial in a SWC pool. Variations in refraction within a solution do contribute at the molecular level to the scattering mechanism mentioned above.

Sparkling appearance of a pool is generally a reference to water clarity, in contrast with a dull or turbid appearance arising from a fine suspension such as a nascent $CaCO_3$ precipitate in the pool water. It is possible that through improved pH buffering or ion-pairing with $Ca^{++}$, the addition of borate might help in a pool at the brink of $CaCO_3$ precipitation (scaling). This condition is not common, and in the longer term it would likely indicate a need for better filtration, attention to pH, and/or reduced calcium and carbonate levels in the affected pool. It is sometimes suggested that the effect might be related to algaestasis. This is not consistent with 'instant' sparkle on borate addition, but it might follow a period of effective filtration in a pool at the brink of failure to control borate-sensitive algae. Again this condition is not common, and in the longer term it would likely indicate a need for better filtration and attention to chlorine, pH, and/or CYA levels in the affected pool.

In summary, there is no published evidence in physical science for a mechanism of enhanced blue colour or sparkle in otherwise well-maintained pools (particularly SWC pools) through addition of boric acid; but data are scant or lacking in some areas such as long-path UV-visible absorption spectra. Other treatments (such as filtration that increased pool water clarity, or chlorination that removed coloured dissolved organic matter) applied around the same time as borate addition could clearly have an effect in some cases.

*10.2 Water softening.* Another comment sometimes made is that the water in a borate-buffered pool "feels softer". Water "hardness" is associated with divalent cations ($Ca^{++}$ and $Mg^{++}$) that form precipitates with some other ions, soaps, or lipids on human skin and hair surfaces - resulting in a sticky feel after swimming. Water "softening" involves removal of divalent cations from solution, commonly by ion exchange with a monovalent cation such as $Na^+$. Unless there is precipitation on addition of borax, this mechanism (which would reduce both measured hardness and boron concentration) does not seem to be involved: $Ca^{2+}_{(aq)} + Na_2B_4O_{7(aq)} \rightarrow CaB_4O_{7(ppt)} + 2 Na^+_{(aq)}$. Borate does form ion-pairs with divalent cations at higher affinity (higher pK for dissociation) than with $Na^+$ (Reardon 1976). Therefore borate can function as a "non-precipitating water softener", by forming soluble complexes with divalent cations and thereby reducing the subsequent formation of the above-mentioned sticky precipitates (Borax Co. 2013). These ion-pairs are reversible interactions: they do not alter hardness (CH or TH) measured in common test kits, but it is plausible that they affect reactions perceived by human 'skin tests' in some pools.

While some boron compounds are important for lubricity in some industrial settings (Shah *et al.* 2013), it is not clear how they could form under swimming pool conditions. The assertion is sometimes made that borate gives pool water a soft feel through saponification of skin lipids. Saponification (hydrolysis of triglycerides into glycerol and fatty acids) requires a high concentration of $OH^-$ ions. It will not proceed at a detectable rate at the hydroxide concentration in swimming pool water (below pH 9), with or without buffering by borate. More likely, the propensity of borate to crosslink conjugated hydroxyl groups (Hunt 2002) contributes to a 'soft' feel by emulsifying compounds at the skin surface.

Despite anecdotal reports to the contrary, dissolved boric acid does not directly alter the surface tension of water (Nakath *et al.* 2013). Borate can protect some surfactants from

depletion by precipitation with $Ca^{++}$ (Borax Co. 2013), and it can form complexes with surfactant properties (Zhang *et al.* 2008) , but it is not clear that either of these effects is expected within the usual range of swimming pool solute compositions.

*10.3 Sound absorption.* Boron is a contributor to the sound-absorbing property of sea water (Francois and Garrison 1982). But this effect operates over long distances and even at the higher boron concentrations used in swimming pools, there is unlikely to be any substantial sound-muffling (for example against nuisance noise from a pool cleaning device).

## 11.0 Measuring concentration

Colour tests are used for boron (as boric acid or borates) in drinking water, and in soil extracts (Keren 1996). Several suppliers have produced strip or drop-based tests for use with swimming pools and aquaria. Opinions vary about the accuracy, precision, readability and stability of different products (e.g. Poolforum 2011). For current versions, search the web for 'pool borate test' and check that the tested concentrations suit your need. Test strips generally have fairly large borate concentration steps between distinguishable colours. The designs are proprietary, and the extent of interference by other SWC pool solutes is difficult to guess. Titration based on the lowered pKa of boric acid when complexed with a sugar alcohol seems to provide finer resolution, but kits based on this method may not be widely available.

Kits designed to measure the contribution of borate to alkalinity in marine aquaria are more widely available. However, kits sold for aquarium use may run into problems such as interference from HOCl, CYA or other chemicals in pool water at concentrations well outside of their range in sea water. For example, a kit by Seachem uses strontium to complex bicarbonate and carbonate, then titrates to pH 6 to measure alkalinity attributed to borate. For pool use, HOCl must first be eliminated using thiosulphate, to avoid bleaching of the indicator dye. Then (non-carbonate) alkalinity measured by titration must be corrected for CYA (subtract 0.19 to 0.31 meq/L for 30 to 50 ppm CYA in pool water at pH 8). Then remaining (assumed borate) alkalinity in meq/L can be multiplied by 119 to compare with ppm boron equivalents measured by some pool kits, assuming pool pH = 8. The correction factors depend on the proportions of boric and cyanuric acids in base form, and therefore on both pH of the pool and the pKa of these acids as influenced by the exact solute composition of the particular pool water. Errors in the estimated correction factors are compounded in the final estimate of borate concentration. Users without knowledge of these factors will likely obtain greater satisfaction from a borate test designed for salt-water swimming pools, if available.

## 12.0 Conclusions

Boric acid can be conveniently and safely applied in the concentration range 50 - 100 ppm boron equivalents as a primary or adjunct pH buffer system in swimming pools. It is most likely to be useful as a primary buffer system (substituting for the bicarbonate system) in pools with salt-water chlorine generators that tend to show upward drift in pH from a working range of pH 7.5 - 8.2 (Birch 2013). While these boron concentrations are exceeded in some common foods, swimmers should be advised not to swallow more than a cup of pool water per day, to remain below the WHO-recommended maximum rate of chronic intake. Precise concentration is not critical, but 200 ppm would call for dilution as a precaution against excessive ingestion with pool water by daily swimmers. The use of boric acid in this concentration range does not allow any reduction in free HOCl concentration needed for pool sanitation, but it may add marginally to the photoprotective effects of cyanuric acid. There is

some scientific support for other marginal benefits through anti-corrosive activity or perceived water softness, depending on overall pool solute composition. On current evidence, effects on water colour or clarity seem unlikely in otherwise well-maintained pools. Direct scientific tests are needed to establish the extent (if any) of these potential marginal benefits under various swimming pool conditions. In contrast, the pH buffering chemistry is thoroughly established. Like any other pool solute, boric acid will be lost through overflow or back-flushing; and several test kits exist with sufficient resolution to manage replenishment to the desired concentration range.

## 13.0 References

**Anbar M, Dostrovsky I** (1954) Ultra-violet absorption spectra of some organic hypohalites. *Journal of the Chemical Society* **1954 (MAR)**, 1105-1108.

**Bassett RL** (1980) A critical evaluation of the thermodynamic data for boron ions, ion pairs, complexes, and polyanions in aqueous solution at 298.15K and 1 bar. *Geochimica et Cosmochimica Acta* **44**, 1151-1160.

**Berton A** (1938) Étude comparée de la couleur visible et ultraviolette des oxydes minéraux et de leurs hydroxydes et hydrates. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences* **207**, 625-627.

**Birch RG** (2013) BABES: a better method than "BBB" for pools with a salt-water chlorine generator. http://members.iinet.net.au/~jorobbirch/BABES.pdf (Accessed 30NOV2013)

**Birnholz EH** (2008) So you want to add borates to your pool -- why and how (waterbear). www.troublefreepool.com/so-you-want-to-add-borates-to-your-pool-why-and-how-t4921.html (Accessed 25NOV2013)

**Borax Co.** (2013) Borates in detergency. www.borax.com/docs/euf_pdfs/euf-borates-boratesindetergency.pdf (Accessed 15NOV2013)

**Borokhov O, Schubert D** (2007) Antimicrobial properties of boron derivatives. In 'New Biocides Development'. (Ed. P Zhu) pp. 412-435. (American Chemical Society: Washington, DC)

**Bousher A, Brimblecombe P, Midgley D** (1987) Stability constants for hypochloritoborate and hypobromitoborate complex ions in aqueous solution. *Journal of the Chemical Society-Dalton Transactions* **1987 (4)**, 943-946.

**Brady AP, Sirine G, Sancier KM** (1963) Equilibria in solutions of cyanuric acid and its chlorinated derivatives. *Journal of the American Chemical Society* **85 (20)**, 3101-3104.

**Braun CL, Smirnov SN** (1993) Why is water blue. *Journal of Chemical Education* **70 (8)**, 612-615.

**Chaplin M** (2013) Water absorption apectrum. http://www1.lsbu.ac.uk/water/vibrat.html#c (Accessed 25NOV2013)

**de Chialvo MRG, Salvarezza RC, Vasquez Moll D, Arvia AJ** (1985) Kinetics of passivation and pitting corrosion of polycrystalline copper in borate buffer solutions containing sodium chloride. *Electrochimica Acta* **30 (11)**, 1501-1511.

**ECETOC** (1997) Ecotoxicology of some inorganic borates. pp. 97. (European Centre for Ecotoxicology and Toxicology of Chemicals: Brussels)

**Francois RE, Garrison GR** (1982) Sound-absorption based on ocean measurements. 2. Boric-acid contribution and equation for total absorption. *Journal of the Acoustical Society of America* **72 (6)**, 1879-1890.

**Galleguillos HR, Flores EK, Aguirre CE** (2001) Density and refractive index for boric acid plus potassium chloride plus water and disodium tetraborate plus potassium chloride plus water systems at (20, 25, and 30) degrees C. *Journal of Chemical and Engineering Data* **46 (6)**, 1632-1634.

**Gibbs P** (1997) Why is the sky blue?
http://math.ucr.edu/home/baez/physics/General/BlueSky/blue_sky.html (Accessed 25NOV2013)

**Girvan JW** (1986) Borate algaecide and fungicide. USA Patent US4594091-A

**Green SA, Blough NV** (1994) Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. *Limnology and Oceanography* **39**, 1903-1916.

**Guo D, Thee H, da Silva G, Chen J, Fei W, Kentish S, Stevens GW** (2011) Borate-catalyzed carbon dioxide hydration via the carbonic anhydrase mechanism. *Environmental Science & Technology* **45 (11)**, 4802-4807.

**Hall SW** (2010) Rayleigh sky model. http://en.wikipedia.org/wiki/Rayleigh_sky_model (Accessed 25NOV2013)

**Harper B, Gervais JA, Buhl K, Stone D** (2012) Boric acid technical fact sheet. (NPIC: Corvallis, Oregon)

**Hershey JP, Fernandez M, Milne PJ, Millero FJ** (1986) The ionization of boric acid in NaCl, Na-Ca-Cl and Na-Mg-Cl solutions at 25 degrees C. *Geochimica Et Cosmochimica Acta* **50 (1)**, 143-148.

**Hunt CD** (2002) Boron-binding-biomolecules: a key to understanding the beneficial physiologic effects of dietary boron from prokaryotes to humans. In 'Boron in Plant and Animal Nutrition'. (Eds HE Goldbach, B Rerkasem, MA Wimmer, PH Brown, M Thellier and RW Bell) pp. 21-36. (Kluwer: New York)

**Juza R, Seidel H, Tiedeman J** (1966) Color centers in alkali borate glasses containing cobalt, nickel, or copper. *Angewandte Chemie-International Edition* **5 (1)**, 85-94.

**Keren R** (1996) Boron. In 'Methods of Soil Analysis. Part 3 - Chemical Methods'. (Eds DL Sparks, AL Page, PA Helmke, RH Loeppert, PN Soltanpour, MA Tabatabai, CT Johnston and ME Sumner) pp. 603-626. (Soil Science Society of America: Madison, Wisconson)

**Ma TS, Boo HK** (1976) A simple method for determining ammonia in water at the ppm level. *Mikrochimica Acta* **II (5/6)**, 515-523.

**Madronich S, McKenzie RL, Bjorn LO, Caldwell MM** (1998) Changes in biologically active ultraviolet radiation reaching the Earth's surface. *Journal of Photochemistry and Photobiology B-Biology* **46 (1-3)**, 5-19.

**Mao DS, Lu GZ, Chen QL** (2005) Deactivation and regeneration of the $B_2O_3$/$TiO_2$-$ZrO_2$ catalyst in the vapor phase Beckmann rearrangement of cyclohexanone oxime. *Journal of Molecular Catalysis A-Chemical* **240 (1-2)**, 164-171.

**Martini EMA, Muller IL** (1999) Passivation of iron in solutions containing borate using rotating ring-disc measurements. *Journal of the Brazilian Chemical Society* **10 (6)**, 505-511.

**Morel A, Gentili B, Claustre H, Babin M, Bricaud A, Ras J, Tieche F** (2007) Optical properties of the "clearest" natural waters. *Limnology and Oceanography* **52 (1)**, 217-229.

**Nakath R, Schuster C, Hurtado A** (2013) Bubble size distribution in flow boiling of aqueous boric acid under high pressure. *Nuclear Engineering and Design* **262**, 562-570.

**NIST** (2011) Boric acid. http://webbook.nist.gov/cgi/inchi/InChI%3D1S/BH3O3/c2-1(3)4/h2-4H (Accessed 25NOV2013)

**Nowell LH, Hoigne J** (1992) Photolysis of aqueous chlorine at sunlight and ultraviolet wavelengths.1. Degradation rates. *Water Research* **26 (5)**, 593-598.

**Owen BB, King EJ** (1943) The effect of sodium chloride upon the ionization of boric acid at various temperatures. *Journal of the American Chemical Society* **65**, 1612-1620.

**Pitzer KS** (1991) 'Activity Coefficients in Electrolyte Solutions.' (CRC Press: Boca Raton, Florida)

**Poolforum** (2011) Drop based borate test kit www.poolforum.com/pf2/showthread.php?12710-Drop-Based-Borate-Test-Kit. (Accessed 25NOV2013)

**Pope RM, Fry ES** (1997) Absorption spectrum (380-700 nm) of pure water .2. Integrating cavity measurements. *Applied Optics* **36 (33)**, 8710-8723.

**Ravisankar M, Reghunath AT, Sathianandan K, Nampoori VPN** (1988) Effect of dissolved NaCl, MgCl$_2$, and Na$_2$SO$_4$ in seawater on the optical attenuation in the region from 430 to 630 nm. *Applied Optics* **27 (18)**, 3887-3894.

**Reardon EJ** (1976) Dissociation constants for alkali earth and sodium borate ion pairs from 10 to 50°C. *Chemical Geology* **18**, 309-325.

**Refaey SAM** (1996) The corrosion and passivation of tin in borate solutions and the effect of halide ions. *Electrochimica Acta* **41 (16)**, 2545-2549.

**Sancier KM, Brady AP, Lee WW** (1964) Absorption spectra of solutions of cyanuric acid and its chlorinated derivatives. *Spectrochimica Acta* **20 (3)**, 397-403.

**Schubert D** (2011) Boron Oxides, Boric Acid, and Borates. In 'Kirk-Othmer Encyclopedia of Chemical Technology' pp. 1-68. (John Wiley & Sons, Inc.)

**Shah FU, Glavatskih S, Antzutkin ON** (2013) Boron in tribology: from borates to ionic liquids. *Tribology Letters* **51 (3)**, 281-301.

**Sullivan JM, Twardowski MS, Zaneveld JRV, Moore CM, Barnard AH, Donaghay PL, Rhoades B** (2006) Hyperspectral temperature and salt dependencies of absorption by water and heavy water in the 400-750 nm spectral range. *Applied Optics* **45 (21)**, 5294-5309.

**USA-EPA** (2006) Boric acid / sodium borate salts: HED chapter of the tolerance reassessment eligibility decision document (TRED). http://federal.eregulations.us/rulemaking/document/EPA-HQ-OPP-2005-0062-0026 (Accessed 30NOV2013)

**USDA** (2006) 'Human Health and Ecological Risk Assessment for Borax (Sporax®).' (USDA Forest Service: Arlington, VA)

**WHO** (1998) Boron. (World Health Organization: Geneva)

**Winston JR** (1935) Reducing decay in citrus fruits with borax. *Technical Bulletin. United States Department of Agriculture* **488**, 32 pp.

**Wolszczak M, Wypych M, Tomczyk M, Kroh J** (2002) Water structure and electron trapping in aqueous ionic solutions. *Research on Chemical Intermediates* **28 (6)**, 537-549.

**You Y, Tonizzo A, Gilerson AA, Cummings ME, Brady P, Sullivan JM, Twardowski MS, Dierssen HM, Ahmed SA, Kattawar GW** (2011) Measurements and simulations of polarization states of underwater light in clear oceanic waters. *Applied Optics* **50 (24)**, 4873-4893.

**Zhang X-L, Ma Q-K, Zhang H-D, Cen T-Q** (2008) The synthesis and properties of borate surfactant. *Journal of Hebei Polytechnic University (Natural Science Edition)* **2008 (4)**.

**Zhang X, Hu L, Twardowski MS, Sullivan JM** (2009) Scattering by solutions of major sea salts. *Optics Express* **17 (22)**, 19580-19585.