Bromine and Chlorine Disinfestation of Nursery Water Supplies

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INTRODUCTION

A wide range of plant pathogens are waterborne, and recycled irrigation water is recognised as a major source of inoculum. *Phytophthora, Alternaria, Aschochyta, Fusarium, Pythium,* and *Helminthosporum* are some of the nursery crop pathogens capable of entering water storages (Gill, 1970; Thomson and Allen, 1974).

Chlorination of nursery irrigation water from surface sources is currently the main method of disinfestation in Australia. Microfiltration, ultraviolet irradiation, bromination, ozonation, and the use of chlorine dioxide are lesser used methods.

A prior (unpublished) survey conducted by the authors indicated that chlorination was not being used successfully by nursery operators in most situations. A major reason for this was a general lack of appreciation by the survey participants of the need to routinely monitor chlorine demand and thus enable themselves to constantly maintain biocidal concentrations of residual free chlorine. The majority of operators included in the survey were calculating chlorine doses based on demand-free water and were not monitoring chlorine concentrations. That is, they were not catering to the changing chlorine demand needs resulting from seasonal water quality fluctuations.

Most microorganisms in water are inactivated at free available residual chlorine levels of 1 to 3 mg/litre (Clark and Smajstrla, 1992; Ewart and Chrimes, 1980; von Broembsen, 1990). In order to achieve these concentrations it is often necessary to add 5 to 10 mg of chlorine per litre of irrigant to ensure that 1 to 3 mg/litre is available as a biocide. This is because a large percentage of the added chlorine is lost in reacting with substances such as ferrous ions (0.6 mg/litre of chlorine will react with 1.0 mg/litre of ferrous ion), ammonium ions, and other inorganic and organic contaminants (Clark and Smajstrla, 1992). Field experience in Australia indicates that where water is high in organic substances, the chlorine demand can often be in the order of 25 to 30 mg/litre.

Bromine and chlorine are members of the same chemical family known as halogens and hence have similar actions in disinfesting water supplies. They rely on the formation in water of hypohalous acids for biocidal activity: for bromine it is hypobromous acid (HOBr) and for chlorine hypochlorous acid (HOCl). Both hypohalous acids are powerful oxidising agents which enter the cells and chemically react with proteins causing interruptions in the metabolic processes. This means they are toxic to all living organisms and that organisms can not become tolerant of their action.

Dissociation of these acids to their respective ions causes a marked drop in their ability to perform as disinfestation agents, possibly because they do not permeate the cell walls of organisms as readily (White, 1986). This dissociation is dependent on the pH of the water and as seen in Fig. 1, the active acid of bromine (HOBr) occurs in greater amounts over a much wider pH range, making the quality of water being treated less important.

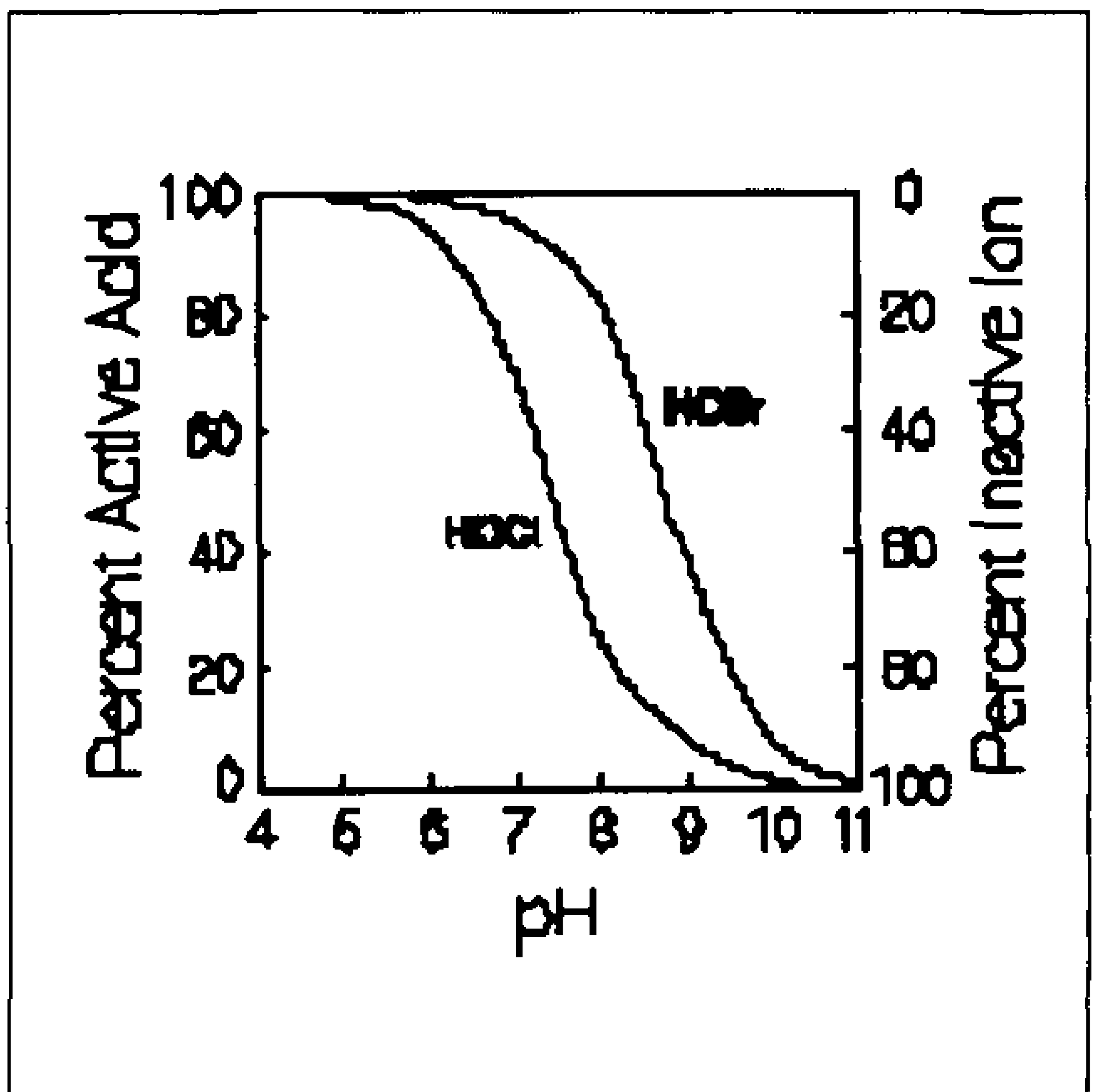

Figure 1. Dissociation curves of hypohalous acids (Adapted from Conley et al., 1987, with permission).

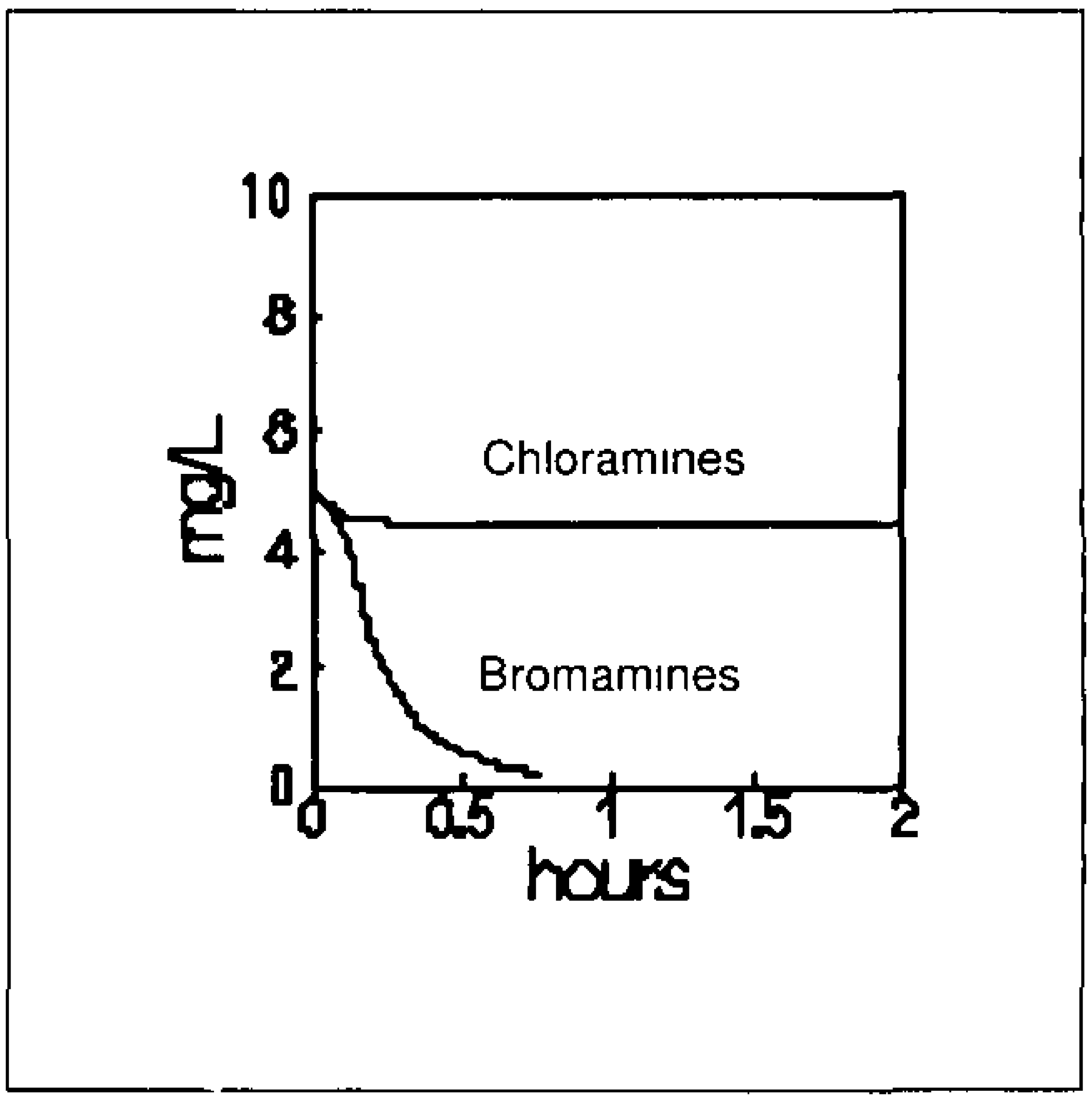

Figure 2. Relative decay of haloamines (Adapted from Conley et al., 1987, with permission).

Most surface waters, and in particular, recycled waters commonly used in nurseries, contain various and fluctuating levels of ammonium and/or other nitrogen-based compounds. Both bromine and chlorine react with these compounds readily to form haloamines. The chloramines formed are relatively poor biocides with the activity of monochloramine being eighty times less than that of free chlorine (White, 1986), while bromamines show disinfection properties comparable to free bromine (Johnson and Overby, 1971). Typically, breakpoint chlorination requires 10 mg/litre of chlorine for every 1 mg/litre of ammonia (Conley and Puzig, 1987; Conley et al., 1987; Degremont, 1991), but because bromamines are very effective biocides, breakpoint bromination is not relevant.

In the application of chlorine or bromine to water it is necessary to ensure that a sufficient amount has been added to achieve the desired result in terms of pathogen control. In practice, this control consists of frequent determinations of residual active agent in the water after a given contact time. The amount of chemical used up by reaction with living organisms, organic contaminants, and nitrogen compounds depends upon the actual dose applied and the time of contact (dwell time in a tank or length of pipe from injection point to spray head) with the chemical. Situations where the water will be in contact with the chemical agent for a short period of time will require a larger initial dose to bring about the required disinfestation (White, 1986; Smith, 1977).

Given the problems experienced with chlorination, bromination appears to offer a number of advantages. The great majority of Australian nursery operators who sanitise water are already using chlorine and therefore have experience relevant to bromine use. The methods of applying and monitoring it are very similar to the techniques used for chlorine, and capital costs in changing over to bromine are therefore minor.

In most situations where 10 to 25 mg of chlorine per litre of irrigation water is needed to produce an excess of 1 to 2 mg/litre of free available residual chlorine, the use of bromine would appear to offer distinct economic advantages.

As byproducts of chlorine and bromine (particularly chloramines and halomethanes) have been implicated as environmental and human health hazards (Office of Water Regulations and Standards, 1986; Division of Environment, 1992; Anon, 1992, 1993, D'Onofrio, 1988) the use of bromine, which produces less long-lived halogenated residuals than chlorine, (Fig. 2) has additional benefits in terms of reduced environmental impact.

Bromine reacts more quickly than chlorine and this may provide some benefits in reducing the required contact periods between the biocide and the pathogen (Great Lakes Chemical Corporation, 1989). Because of the good biocidal properties of bromamines and the consequent reduced need to achieve the breakpoint concentrations and free residual halogen requirements of chlorine, halogen phytotoxicity problems may be reduced with bromine use. This could have important implications with regard to the continuous disinfestation of hydroponic solutions, where chlorine toxicity may be the major limitation to an otherwise significant reduction in some pathogens (Runia, 1988). Runia (1988) found that 1 to 5 mg litre^{-1} of chlorine reduced the activity of *Fusarium oxysporum*, however 3 to 10 mg of chlorine per litre of nutrient solution was phytotoxic to plants in hydroponics. Containerised stock, even in propagation areas would appear to be tolerant of levels of hypohalous acid of 5 to 10 mg litre^{-1} (Hammen, 1989; Powell and Ashley Smith, 1989). These levels reduced algal growth and some foliage and flower pathogens such as *Colletotrichum* and *Botrytis*. Chase (1990) and Chase (1992) using Agribrom under continuous mist reduced the effect of pathogens such as *Alternaria panax* and *Rhizoctonia solani* using hypohalous acid concentrations up to approximately four times greater than the above, but with phytotoxicity problems at the highest rates.

Therefore it appeared to be of value to investigate the use of bromine as a substitute or replacement for chlorine, in situations where there are water quality and other constraints to the effective use of the latter. The first phase of the study was to install and monitor bromination systems and compare them with chlorinators in term of halogen delivery (particularly the constancy of biocidal doses). Methods of quantifying free available residual halogen and combined available residual halogen in the field were also tested. The effect of several different water qualities was also considered when comparing chlorination with bromination.

MATERIALS & METHODS

Application Methods. There are many methods for applying both chlorine and bromine to water supplies. For chlorine the most common is the in-line feeding of sodium hypochlorite solution. Other methods such as chlorine gas injection, calcium hypochlorite, or sodium dichloro isocyanurate (swimming pool dry chlorine) are not commonly used because of safety and injection difficulties (Degremont, 1991) and are not studied in this paper.

The three most practical methods of delivering bromine are bromine chloride (BrCl), activated bromide (Br^-), and bromochlorodimethylhydantoin (BCDMH) (Conley and Puzig, 1987; Conley et al., 1987). The feed systems for using BrCl and BCDMH are quite complicated and somewhat expensive. The activated bromide method relies on the reaction of the bromide ion with hypochlorous acid in the pH range of 7-9, to form hypobromous acid (White, 1986). This is done by adding a sodium bromide (NaBr) solution to bulk sodium hypochlorite (NaOCl) solution at a stoichiometric ratio of 1:1 or slightly higher (Conley et al., 1987). The added advantage of this system is that present chlorine-based feeders can easily be modified to bromine feeders.

Six nurseries utilising either chlorine or bromine disinfestation techniques were observed over a longer than 12 month period:

Nurseries A & B. Both nurseries used activated bromine systems. The combined chemicals were injected into the passing dam water supply (sand filtered) which was stored in holding tanks, before going out onto the nursery. Nursery B had a water quality which fluctuated considerably more than A, both in terms of organic matter and pH. This was because excess water from the nursery was immediately drained back into the storage dam. The metered pumps of both nurseries were switched on and off with the main irrigation pump from the dam, with Nursery A having added regulation from a flow meter. Both nurseries carried a wide range of outdoor and greenhouse crops.

Nursery C. This nursery had an in-line chlorine feeder using sodium hypochlorite solution. The chlorine was injected at the pump station from the dam, some distance from the sprinkler heads. This distance ensures an approximate 20 min contact time before the water is used on the nursery. The nursery grew both outdoor and greenhouse crops.

Nursery D. This nursery employed a modern, sophisticated, self-regulating chlorine feeder. Before entering the irrigation system a sodium hypochlorite solution was injected into a recirculating water flow (from a holding tank) to a predetermined residual level for a precise period of time. This nursery recycles this water. The nursery produced both outdoor and greenhouse crops.

Nursery E. Sodium hypochlorite was fed into the water supply and held in tanks. This nursery had several water sources from good quality bores to a recycling dam high in nitrogenous compounds, tannins, and organic matter. The nursery produced both open-grown and greenhouse crops.

Nursery F. Water was treated with a flocculating agent in a storage tank and pH adjusted and chlorinated by injection of sodium hypochlorite and then it passed into a second treatment tank. The water quality on this site fluctuated considerably. The nursery produced only greenhouse crops.

Analytical Methods

Chemical Analysis. Residual bromine and chlorine levels were monitored using a modified DPD titrometric method (Anon 1980; APHA, WPCF, AWWA, 1985; White, 1986). Hach® "free chlorine reagent pillows" were selected as a source of DPD and buffer for field analysis because of ease of transport and reagent stability. The DPD method was chosen because of ease of use in the field, as well as simulating commercially available test kits which would normally be used to monitor levels in the nursery.

Water quality analyses for pH, electrical conductivity, major cations and anions, and iron were carried out broadly following the standard methods of water analysis (APHA, WPCF, AWWA, 1985).

Phytotoxicity Determinations. Control plants could not be maintained under the same conditions as treated stock, and this limited the validity of assessments of plant damage due to the treatments. Situations existed where plants were irrigated with untreated bore or town water, however, these were in propagating or holding areas only.

However, comparisons were made between crops which were not irrigated with treated water, prior to the installation of treatment facilities, and later crops.

Any loss of foliage and flower quality not later found to be due to other causes was noted. Overall crop performance was also considered.

Disease Control Determinations. Surveys of soil-borne and water-borne pathogens were made on all nursery sites. The methods used in sampling and for the laboratory determinations are described by Bodman and Forsberg (1994).

RESULTS

Chemical Analysis. The quality of the water used for irrigation on the various nurseries differed considerably in such things as mineral content, clarity, and pH. During the period of investigation the quality of the individual supplies also fluctuated greatly. As an example of this the pH values recorded at one nursery can be seen in Fig. 3. In general during drier periods the mineral content increased and after rain periods biological activity increased in surface supplies.

Residual levels of chlorine/bromine were also observed to change greatly and at times the required amount greatly exceeded the doses being applied. The test kits used by the nurseries showed good agreement with results we obtained and therefore would be quite acceptable for routine monitoring of residual levels. Some supplies contained potentially troublesome levels of iron which were eliminated by both chlorine and bromine. Neither chlorination nor bromination caused any adverse increase in mineral salt levels, even at the highest application rates.

Phytotoxicity Determinations. There were no, or no easily detectable, problems with flower and foliage quality in the majority of crops treated with brominated water. *Cyathea cooperi* at one site suffered from a marginal and tip necrosis of the lower fronds, but similar age plants on the other brominated water site did not. No other possible cause for the problem was determined. Two *Calathea* species at one brominated water site experienced similar symptoms. A number of other causes were possible but the problem was not ultimately resolved.

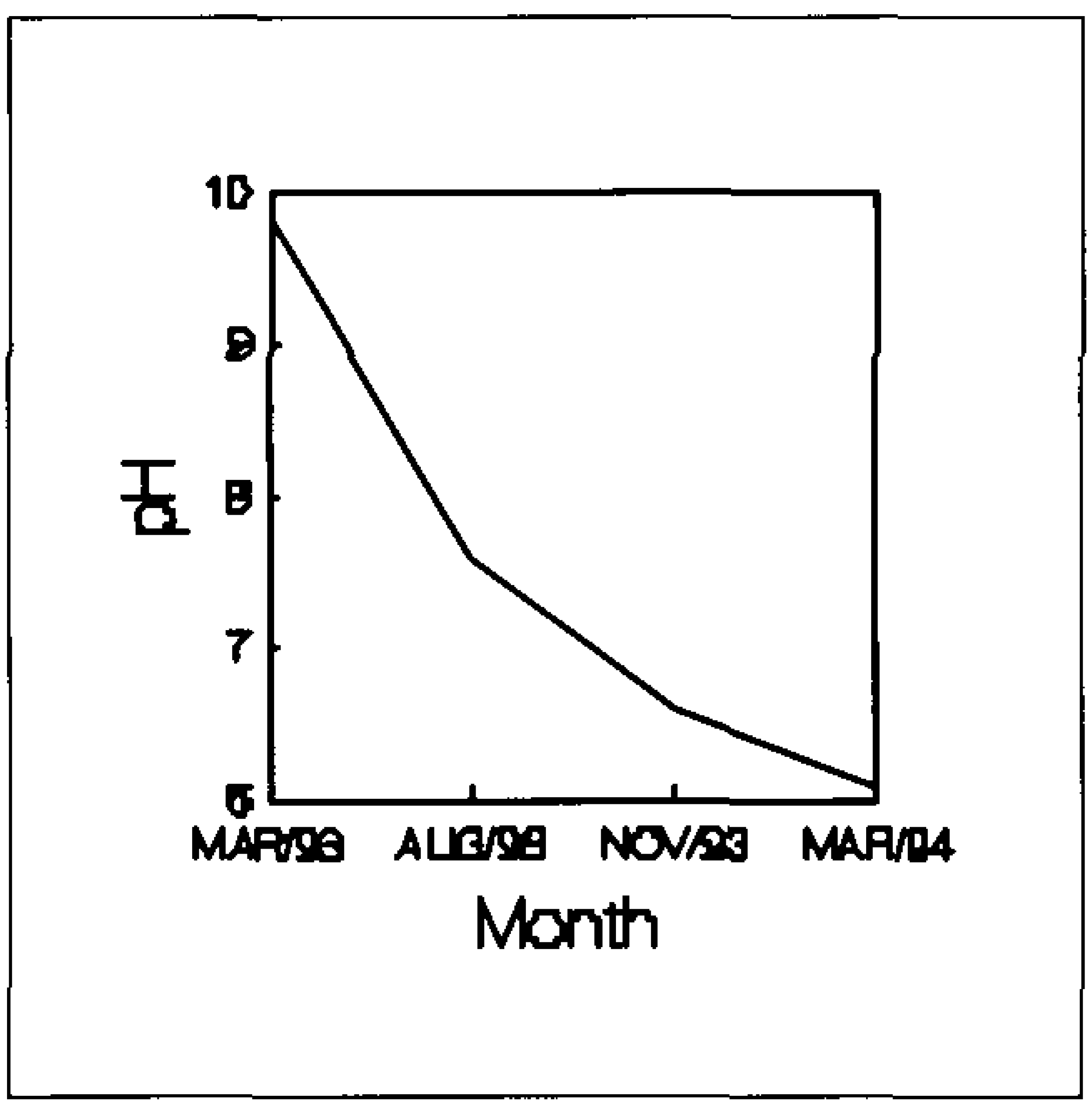

Figure 3. pH values of water supply at nursery B.

Two *Anthurium andraeanum* cultivars experienced an irregular etching of new leaves during the period when the highest bromine rates were used. An unidentified thrips was associated with the plants but damage appeared to persist after this was controlled. Another three *A. andraeanum* cultivars in the same production area remained asymptomatic.

Disease Control Determinations. *Phytophthora cryptogea* was baited from two dams on two sites. It was not isolated from crops on these sites during the observation period.

Operator error allowed a disruption to chlorination on one site, but there was no evidence of a subsequent change to the status of *Phytophthora* as determined by lupin baiting 1 and 3 weeks after the disruption.

DISCUSSION

The repeated fluctuations in water quality emphasised the need to carefully and regularly monitor the systems being operated to maintain proper levels for disinfestation. To this end, bromination may have a slight advantage as it performs better over a wider range of water qualities. In situations where water quality is suboptimal in terms of pH and organic and inorganic contaminants, the advantages of using bromine become greater.

From our observations treatment should take place after filtration. This can considerably lower the chemical demand of the water by taking out a lot of the microorganisms and organic matter which would use up the chlorine or bromine. Adding nutrients to the water supply for fertigation purposes is best done after a sufficient dwell time to allow disinfestation to take place, as some nutrients (e.g., ammonium) react with the treatment chemicals.

Possible phytotoxicities to two cultivars of *Anthurium andraeanum* and two species of *Calathea* occurred at one nursery using brominated water. If resources are available this will be evaluated later, under controlled conditions. At the doses used, there was no evidence that bromination was less or more effective than chlorination in preventing waterborne disease at the sites tested, however this needs to be determined by further work.

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