Plastic tastes in drinking water: factors affecting the chemistry of bromophenol formation

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Abstract A "plastic" or "chemical" taint, has recently emerged as a problem in drinking water in Perth, Western Australia. The taste occurs intermittently in zones receiving blends of treated groundwaters from several sources, generally only in boiled water. The compound primarily responsible is 2,6-dibromophenol (taste threshold concentration 0.5 ng/L). It was established that the relative ratios of phenol, bromide and chlorine, and pH are important determinants in whether the taste would or would not form and that the primary sources of phenol are plastic appliances, especially kettles and refrigerators (Heitz *et al*., 2001). However, bromophenol formation varied widely between waters from different sources, even though reaction conditions were ostensibly identical, and it was concluded that another, as yet unknown, factor must influence the reaction rate. This could account for observations that plastic taste only occurred in some groundwaters, but not in others. In the present study the effects of organic and inorganic nitrogen-containing compounds on phenol bromination rates were examined, with the view that this might give some insights into the nature of the unknown factor discussed above. These compounds slowed the rate of bromophenol formation, and results suggested that disinfection using chloramine, rather than chlorine, could prevent plastic taste problems.

Keywords Amines; bromophenols; drinking water; halophenols; off-tastes

Introduction

A taint in drinking water described as "plastic", "medicinal" or "chemical" has recently emerged as a problem affecting consumers in Perth, Western Australia. The "plastic taste" problem has been under investigation since July 1999, when complaints were first received from consumers in a zone receiving a blend of treated groundwaters from several sources. The taste was never present at the outlet of groundwater treatment plants, or at the outlets of storage reservoirs, but usually only formed in water after it had been boiled (e.g. as in beverages such as coffee or tea). Although the taste occurred relatively infrequently, it was often very strong, unpleasant, and was of considerable concern to the affected consumers. The taste occurred intermittently, and this presented some difficulties in studies of the problem.

Investigations of the causes of the taste problem revealed that the compound primarily responsible for the taste was 2,6-dibromophenol (2,6-DBP), which has a taste threshold concentration of 0.5 ng/L. These investigations (Heitz *et al*., 2001) also confirmed that bromophenols could be readily formed in simple aqueous solutions containing amounts of phenol, bromide and chlorine that might realistically be present in drinking waters. However, the solution pH and the relative ratios of these precursor compounds were shown to be important determinants in whether the taste would, or would not, form.

Initially, studies focussed on determining sources of phenol unique to plastic taste-prone waters, especially phenol derived from natural organic matter (NOM) in source waters. These studies did not reveal any major sources of phenol related to NOM, but it was demonstrated that many plastic and rubber materials had the potential to contaminate water with phenol. Items that were shown to be directly involved in taste formation were plastic kettles and refrigerators. Other items shown to be potential sources of phenol were tap washers,

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polyethylene and polybutylene pipes and water meters, but it could not be demonstrated that these significantly affected plastic taste formation, and consumer complaints.

The above observations indicated that traces of phenol are probably often present in potable water contacting common plastic kitchen appliances, and this suggests that plastic taste problems should be more commonplace than appears. The concentrations of chlorine (up to 0.6 mg/L) and bromide (0.2 to 0.3 mg/L), and pH values (7–9) in the waters described in the present study are by no means exceptional, and if these are the only critical factors in whether or not bromophenols form, then problems associated with these compounds should occur more frequently, and in more water types. The broad aims of the present study were to examine the chemistry of bromophenol formation in various water types (plastic taste-prone and non-plastic taste-prone), in an attempt to determine whether other, as yet unidentified, factors exist that are important in the generation of plastic tastes.

Experimental

Analysis of phenol and halophenols

A method suitable for routine analysis of large numbers of halophenols at the sub-ng/L concentrations required in the present study was not available at the commencement of the study. A new method was developed, which enabled rapid in-situ derivatisation, isolation and pre-concentration of bromophenols from water samples as their acetyl derivatives, followed by analysis by GC-MS. Details of this method will be published elsewhere.

Results and discussion

As discussed above, the observation that phenol, in sufficient concentration to form plastic taste, can be leached from many common plastic items, showed that the potential for the formation of bromophenols, and therefore plastic taste, was probably much more widespread in drinking waters than was initially thought. The reactants required to form bromophenols (bromide, chlorine and phenol) are likely to be present in many chlorinated water supplies worldwide, not just in the few groundwater sources described in the present study. Tastes and odours caused by halophenols have been reported previously, and these have involved circumstances such as halogenation of phenolic compounds naturally present in raw waters (e.g. humic substances, p-hydroxybenzoic acid associated with humic substances; Horth *et al*., 1990), or halogenation of phenolics leached from synthetic materials in distribution systems (e.g. Rigal and Danjou, 1999). However, in the present study, the taste could not be generated by boiling water sampled directly from the distribution system (i.e. without adding phenol to the sample), and it therefore appeared that the phenol was not present in distributed water, as in these previous studies, but was introduced into the water after it had entered consumers' service pipes.

It has previously been shown that plastic kettles and refrigerators could contaminate water with phenol at concentrations up to several thousand ng/L, and these plastic items were shown to be key sources (but not the only sources) of phenol in the plastic taste problem (Heitz *et al*., 2001). A chromatogram showing the distribution of phenol and bromophenols typically detected in water samples (i.e. consumer complaints; Figure 1) shows that phenol is far more abundant than halophenols. Phenol was always detected in relatively high abundance in water samples that had the plastic taste, suggesting that contamination of water by phenol was a significant factor in the production of bromophenols. In other words, it is likely that phenol itself, rather than a more complex phenolic compound (e.g. humic-bound phenol, or a plastic additive, such as triphenylphosphate), was probably brominated directly to produce bromophenols.

Higher concentrations of phenol were released from plastic kettles after boiling water in the kettles, than after simply leaching the kettles with cold water, suggesting that phenol is
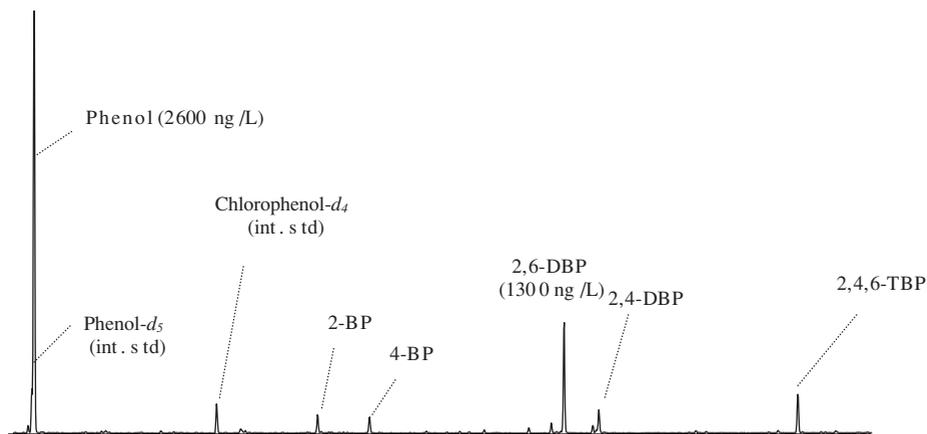
Figure 1 Chromatogram (GC-MS) of phenol and bromophenols isolated from a water sample that exhibited a strong plastic taste. BP = bromophenol; DBP = dibromophenol; TBP = tribromophenol

bound within the plastic in the form of a compound that can be hydrolysed, at high temperature and/or pH, to produce phenol (Blythe, 2000). Phenol (0.3 µg/L) was leached from a plastic kettle after 24 hours of contact with cold water, but a much greater amount was released after boiling the same water in the kettle for only a few minutes (2.3 µg/L). Analysis by Fourier Transform Infrared Spectroscopy (FTIR) of the plastic kettle body showed that it was most probably constructed from polypropylene (Blythe, 2000). Phenolic stabilisers such as butylated hydroxytoluene (BHT, antioxidant) and phenyl salicylate (UV stabiliser) are added to polypropylene to prevent degradation of the polymer (Seymour and Carraher, 1992): phenyl salicylate could readily form free phenol at the temperature and pH (8–9) of water during and after boiling. Laboratory experiments to determine the yields of bromophenols from treating free phenol and bound phenols, including phenyl salicylate, with chlorine and bromide at various pHs, found that yields were by far the highest with free phenol. Although not conclusive, these observations do suggest that phenol was first released from the plastic matrix into the water, and the free phenol was then brominated to produce bromophenols.

The "high-phenol" plastic items, such as kettles and refrigerators, identified previously as potential sources of phenol in causing plastic tastes (Heitz *et al*., 2001), are likely to be in widespread use, certainly in Australia, and possibly worldwide. It is therefore surprising that plastic taste problems similar to those experienced in Perth are not more commonplace than has been reported thus far. Consequently, it is possible that, although only phenol, chlorine and bromide at pH 7–9, are required to form bromophenols. Further crucial, as yet unidentified, factors exist which determine whether bromophenols form and persist to cause the plastic taste problems, and that these may be peculiar to some of the waters described in the present study.

Evidence to support the suggestion that factors other than those already discussed (i.e. concentrations of chlorine, bromide and phenol and pH) affect bromophenol formation were demonstrated by variations in the rates of formation of these compounds in waters from various sources. Halogenation of phenols occurs via a stepwise mechanism: monobromophenols (MBPs) are formed initially, bromination of MBPs forms dibromophenols (DBPs), and tribromophenol (TBP) forms from bromination of DBPs. The relative concentrations of these bromophenol congeners can therefore give an indication of differences in reaction rates between samples. This is demonstrated in Figure 2, which shows the concentrations of these bromophenol congeners formed in two different water types; a

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groundwater sample from a source that was prone to plastic taste complaints; and a surface water sample from a source where plastic taste complaints had never been received.

Both samples had been spiked with an identical quantity of phenol (2,000 ng/L), and reaction conditions for each sample were ostensibly identical (see caption to Figure 2), but bromophenols appeared to be formed much more rapidly in the plastic taste-prone sample than in the non-plastic taste-prone sample. In the latter sample, phenol was recovered, essentially unreacted, with only a small amount of MBP formed, indicating that the bromination reaction had not progressed to any significant extent. However, all of the phenol and MBPs in the plastic taste-prone sample had reacted completely to form the higher bromophenols (DBPs and TBPs), indicating that in this sample the reaction progressed almost to complete bromination of phenol. Similar experiments at longer reaction times (results not shown) confirmed that while the bromophenol products for each water type were similar, the reaction rates varied significantly between these two waters. These and other experiments showed conclusively that a component in the water that had not been previously considered had a significant effect on the rate of bromophenol formation and, consequently, was potentially important in the plastic taste problem. These observations explained, to some extent, why plastic taste occurred in some waters from some sources, but not others, even though it was possible to form the tastes in all waters under appropriate conditions (i.e. all waters contained sufficient bromide, chlorine and phenol).

Factors that are known to affect halogenation of phenols are the presence of some organic compounds, especially organic nitrogen compounds such as amines (Fujisaki *et al.*, 1993; Higuchi and Hussain, 1967; Smith *et al.*, 1987, 1988, 1989). The presence of high valence metal cations such as ferric and ferrous iron can also affect reactions involving phenol, by forming organometallic complexes. The effects of selected organic and inorganic nitrogen compounds on the rate of bromophenol formation under conditions similar to those employed in the above samples (described in Figure 2) were investigated. The compound groups tested were: (a) quaternary ammonium compounds; (b) amides; (c) amino acids; (d) amines; and (e) ammonia and monochloramine. The compounds (0.5 mg/L N) were spiked into water samples from three different sources, that contained identical concentrations of bromide (0.3 mg/L), free chlorine (0.1 mg/L) and phenol (2,000 ng/L) at pH 7.5 and pH 9.0. Reaction times (i.e. the time between adding phenol and termination of the halogenation process by adding thiosulfate) were 5 seconds or 30 seconds, depending on the water being tested.
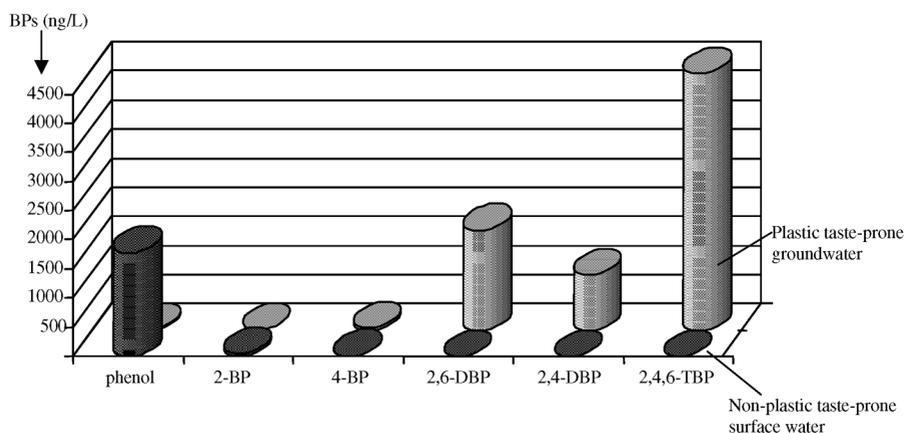

Figure 2 Concentrations of phenol and bromophenol congeners (BPs) formed after addition of phenol (2,000 ng/L) to: (a) a plastic taste-prone groundwater sample; and (b) a non-plastic taste-prone surface water sample. The reaction time (10 seconds), pH and concentrations of bromide and free chlorine were identical in both samples ($Cl_2 = 0.1$ mg/L; $Br^- = 0.3$ mg/L; pH = 9.0)

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All of the groups of nitrogen-containing compounds that were tested appeared to inhibit reactions involving phenol in all three water types tested (including Milli-Q water). The presence of the N compounds decreased the amounts of total phenol that could be recovered from the sample, either as phenol, or as halophenols, but this was to some extent dependent on reaction time. This is demonstrated in Figure 3, which shows the concentrations of bromophenol produced in a groundwater sample to which phenylalanine had been added. Results from three experiments are shown: (a) groundwater with no added phenylalanine; (b) groundwater plus phenylalanine, after a reaction time of 5 seconds; and (c) groundwater plus phenylalanine, after a reaction time of 30 seconds. In the sample containing no added phenylalanine, all of the added phenol was recovered as bromophenols after 5 seconds of reaction, mostly as 2,4,6-TBP (98% recovered). However, where phenylalanine had been added only 3% was recovered after a reaction time of 5 seconds and 67% was recovered after 30 seconds of reaction.

Similar results were obtained for other N compounds, with the most marked effects observed in the case of amines, such as butylamine, phenylalanine and leucine, and ammonia (effectively halamines). Betaine, a quaternary ammonium compound, had the least effect of all the N compounds tested. Under comparable conditions, phenol was usually well recovered from mixtures that had not had N compounds added to them. It should be noted that although only one set of results for one N compound are shown in Figure 3, all experiments were conducted in duplicate, and that generally reproducible and consistent results were obtained.

These observations suggest that the N containing compounds react with phenol to form a weak complex, effectively slowing, but not preventing, halogenation. Amines and ammonia form halamines in the presence of chlorine or bromine, and upon reaction with phenol, these compounds then go on to form indophenol complexes (Ngo *et al*., 1982). The formation of indophenol complexes could explain the absence of phenol and the low recovery of total phenols in solutions containing N compounds. Bromination of phenol, once it is in the form of indophenol, probably still occurs, but at a slower rate than in the case of free phenol. The brominated indophenol complex is probably unstable, and breaks up to form the DBPs and TBP, as observed in the experiment after 30 seconds (Figure 3). It should be noted that these reactions, where N compounds hinder bromophenol formation, only occur where the N-compounds are present as halamines. In chlorinated waters in which the concentrations of combined chlorine are negligible, it is unlikely that these reactions would occur.
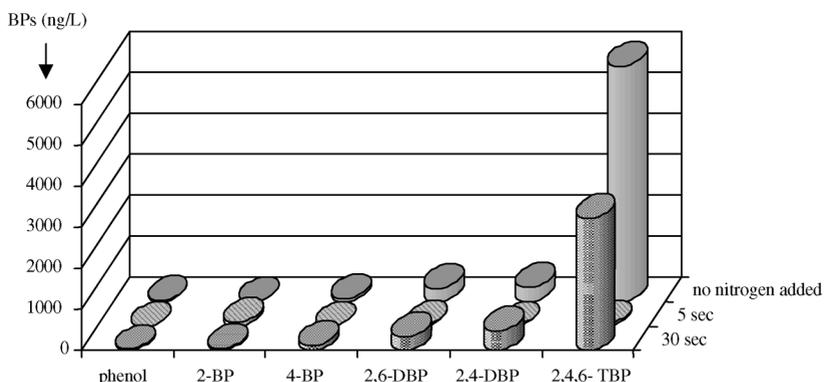

Figure 3 Effect of phenylalanine (0.5 mg/L N) on bromination of phenol in a groundwater sample. Concentrations of phenol and bromophenol congeners formed: (a) without added phenylalanine (5 second reaction time); with phenylalanine added (0.5 mg/L N) after (b) 5 seconds reaction time; and (c) 30 seconds reaction time. Concentrations of other reactants were identical for all experiments. They were: phenol 2,000 ng/L; free chlorine 0.1 ng/L; bromide 0.3 ng/L; pH = 7.5

Conclusion

It was shown that rates of bromination of phenol in water varied significantly, depending on the source of the water, even though reaction conditions such as concentrations of phenol, bromide and chlorine and pH were apparently identical. This suggested that, in addition to these latter four factors, another component affected the production of bromophenols. It was shown that organic and inorganic nitrogen containing compounds, especially amines, have a significant retardant effect on halogenation of phenols. It has not yet been possible to determine whether, or how, the observed variations in bromophenol formation rate in various waters are related to plastic taste complaints, but from our studies to date, it appears that those waters in which the rate is fastest are generally plastic taste-prone. Since many N containing compounds, including monochloramine, inhibit bromophenol formation, chloraminated waters might be less prone to forming the taste, and indeed, chloramination may be a potential treatment solution for the plastic taste problem.

Other factors that affect bromophenol, and plastic taste formation have recently been observed in both laboratory and field studies. These new results, and those in the present paper, will be discussed further elsewhere.

Acknowledgements

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