Retronasal perception and flavour thresholds of iron and copper in drinking water

Pinar Omur-Ozbek and Andrea M. Dietrich

ABSTRACT

Drinking water flavour has a strong role in water quality perception, service satisfaction, willingness to pay and selection of water sources. Metallic flavours are often caused by the dissolved iron and copper, commonly found in groundwater or introduced to tap water by corroding infrastructure. Taste thresholds of iron and copper have been investigated by several studies; however, reported results and test methods vary considerably. This study determined the taste thresholds of ferrous and cuprous ions in room temperature reagent water by using the one-of-five test with multi-nation panellists in the United States. For ferrous and cuprous ions, individual thresholds ranged from 0.003 to >5 mg l^{-1} and 0.035 to >5 mg l^{-1}, respectively. Population thresholds were determined by logistic regression and geometric mean methods as 0.031 and 0.05 mg l^{-1} for ferrous ion, and 0.61 mg l^{-1} for cuprous ion by both methods. The components of metallic sensation were investigated by use of nose-clips while panellists ingested iron and copper solutions. Results showed that metallic sensation has a significant odour component and should be treated as a flavour instead of a taste. Ferrous, cuprous and cupric ions also produced weak bitter and salty tastes as well as astringent mouthfeel. In comparison, ferric ion produced no sensation.

Key words | copper, drinking water, flavour threshold, iron, metallic flavour, retronasal perception

Pinar Omur-Ozbek (corresponding author)
Andrea M. Dietrich
Civil and Environmental Engineering Department,
A207-D Engineering Bldg,
Colorado State University,
Fort Collins, CO 80523-1372,
USA
Tel.: +1-970-4916670
Fax: +1-970-4917727
E-mail: pinar@engr.colostate.edu

Andrea M. Dietrich
Civil and Environmental Engineering Department,
413 Durham Hall,
Virginia Tech,
Blacksburg, VA 24061,
USA

INTRODUCTION

Health-related and other effects of iron and copper in drinking water

Iron and copper are essential micronutrients and recommended daily intakes for adults aged above 18 years old for iron and copper were established as 15 and 2 mg, respectively. Although these values vary depending on gender and body weight, about 5% of the required values are supplied by most of the tap water in the US (World Health Organization 1996). Iron and copper participate in functioning of enzyme systems, are required for oxygen transport, and promote healthy growth. Anaemia, impaired immunity and development are common problems related to copper and iron deficiency. Reduced iron is commonly found in groundwater owing to lower dissolved oxygen levels. Although some of the treatment methods such as coagulation and precipitation remove iron and copper from the source water, corroding infrastructure may introduce them back to the drinking water.

Aesthetic guidelines for copper and iron have been established by many national and international drinking water agencies. For instance, the United States, the World Health Organization (WHO), the European Union (EU), and Australia have set standards for iron and copper. The USEPA established secondary maximum contaminant levels (SMCLs) at 0.3 and 1 mg l^{-1} for iron and copper, respectively, to prevent aesthetic problems such as metallic taste, coloured water or stains on clothes and fixtures (USEPA 1991, 1997). Similar levels are recommended by WHO and were

established by the Australian government at 0.3 and 1 mg l^{-1}; and by the EU at 0.2 and 3 mg l^{-1} for Fe and Cu, respectively. Doria (2010) has indicated that drinking water organoleptics, especially taste, plays an important role in public perception of water quality. Unpleasant taste and appearance of tap water will decrease the satisfaction of the consumers and their willingness to pay for it. Even though public perceptions of metals in drinking water is not well documented, a recent extensive study conducted with focus groups reported that consumers are aware of the presence of iron and copper in their tap water and suspect that they may cause adverse health effects (Doria 2005).

Because copper causes health problems when consumed at higher levels, including gastrointestinal distress and nausea, the USEPA established a regulatory action level (AL) of 1.3 mg l^{-1}, the European Union has a level of 1.0 mg l^{-1}, and World Health Organization guidelines indicate that the copper concentration should be below 2.0 mg l^{-1} Cu to avoid adverse health effects (WHO 1996; Australian Government National Health and Medical Research Council 2004). Incidents of copper toxicity from water have been reported in the literature. Ingestion of a single dose of 10 mg l^{-1} Cu^{2+} as cupric sulfate was shown to induce nausea in healthy adults (Araya *et al.* 2003). Distributed drinking water has been implicated in causing copper toxicity (Dietrich *et al.* 2004). Corrosion of residential copper pipes was implicated in an outbreak of abdominal pain, diarrhoea and vomiting among residents who were supplied municipal drinking water (Pizarro *et al.* 2007). When consumed at higher doses for longer periods, iron and copper may cause irreversible damage to the kidneys and liver, and may be lethal (National Research Council 1989; O'Donohue 1993).

Iron and copper chemistry

Iron may be present in ferric or ferrous ion forms in drinking water. Complexation and speciation of iron depends on the pH, dissolved oxygen, pE and minerals in the water. Owing to the anaerobic conditions, ferrous ion, the reduced form of iron, is the dominant species in groundwater, and has no colour. Ferric ion, the oxidized form of iron, is more commonly found in surface waters, has a yellow to rusty orange colour depending on concentration, and is much less soluble than ferrous ion (Nealson & Saffarini 1994). Copper may also be found in cupric or cuprous ion forms in drinking water. As for iron, pH, dissolved oxygen, pE and minerals in water play an important role in speciation and complexation of copper. Cuprous ion is colourless whereas cupric ion, which is the dominant species in surface waters, has a blue-green colour. Cuprous and cupric oxides are common on the surfaces of copper drinking water pipes (Zhang *et al.* 2002). So far no work has studied taste thresholds for cuprous ion; hence this research is the first to compare threshold values of cupric and cuprous ions.

Retronasal perception of iron and copper

Although historically researchers have focused mainly on taste thresholds of metals, recent studies evaluating the effect of olfaction on metallic sensation discovered that the metallic sensation is really a combination of taste and odour, which is described as 'flavour' (Hettinger *et al.* 1990; Lawless *et al.* 2004; Dietrich 2009). These studies have conducted oral perception tests by occluding the panellists' noses with nose-clips and reported a significant decrease in perceived perception for ferrous and cupric ions even when they were tested at very high concentrations (Hettinger *et al.* 1990; Lawless *et al.* 2004). Epke & Lawless (2007) determined taste thresholds with and without occluding olfaction of the panellists by nose-clips and reported that sensory thresholds were 2 to 30 times higher when the olfaction was occluded. For example, with the nose occluded, the sensation thresholds, calculated by logistic regression, of ferrous sulfate and cupric sulfate were 13.7 mg l^{-1} Fe^{2+} and 37.6 mg l^{-1} Cu^{2+}, respectively, while with the nose open the thresholds were 0.46 mg l^{-1} Fe^2 and 1.2 Cu^{2+} mg l^{-1}, respectively. Threshold values for sulfate and chloride salts were generally, but not always, similar. The focus of these studies was metals in foods and thus lowest concentrations tested were near or above the drinking water aesthetic or health standards, depending on the metal. However, the data presented by the researchers above indicate that metallic sensation has an important odour component. A recent study investigated the metallic odour of skin and analysed the carbonyls in the headspace above the skin after ferrous or cupric ion solutions were rubbed on it. A series of aldehydes and ketones were reported, including n-hexanal and 1-octen-3-one, that resulted from oxidation of lipids in the skin (Glindemann *et al.* 2006).

'Taste/flavour' thresholds of iron and copper

Metallic sensation has been an issue for the drinking water industry because of aesthetical issues. Iron corrosion in water distribution systems is known to cause metallic taste and musty odours (Kirmeyer 2000) and metallic-tasting drinking water is a complaint that customers report to their utilities (Whelton et al. 2007). Metallic was also a common descriptor used by a utility flavour profile analysis team to describe the drinking water from one of the three rivers that supply water to Barcelona, Spain (Fabrellas et al. 2004). Recently it has gained attention in the medical industry as cancer patients receiving chemotherapy suffer from malnutrition because of the metallic taste dysfunction (Comeau et al. 2001; Hong et al. 2009). Until the last decade, researchers have only focused on taste thresholds of iron and copper and have overlooked retronasal odour perception that combines with taste to produce a metallic 'flavour'. Thus, many of the studies on metallic taste were actually conducted with the nose open and are flavour studies.

The first study was conducted in 1960 by Cohen et al. Since then, numerous sensory methods have been used including one-of-five forced choice test, modified triangle test and paired difference test. Cohen et al. (1960) reported that ferrous sulfate was tasted by 5 and 50% of the population at concentrations as low as 0.04 and 3.4 mg l^{-1} Fe^{2+}, respectively, in distilled water. The values change to 0.12 and 1.8 mg l^{-1} Fe^{2+} for spring water. Another study reported a taste threshold value of 0.6 mg l^{-1} Fe^{2+} in distilled water that was detected by 50% of the population (Zacharias & Tuorila 1979). More recent studies reported higher values for ferrous ion as 1.58 mg l^{-1} Fe^{2+} in mineral water (Gonzales Vinas et al. 1998); and as 5.54 mg l^{-1} Fe^{2+} in deionized water by using the geometric mean method (Lim & Lawless 2006). The reported taste threshold values are higher for cupric ion than ferrous ion. Cohen et al. (1960) also studied cupric ion and reported the taste thresholds that can be detected by 50% of the population as 2.46 and 4.73 mg l^{-1} Cu^{2+} in distilled and spring water, respectively. Recent studies, however, determined lower values for cupric ion taste threshold. It was reported that cupric ion may be detected by 50% of the population at 0.61 mg l^{-1} (Zacarias et al. 2001). Another work reported taste thresholds for cupric ion as 0.48 and 0.77 mg l^{-1} Cu^{2+} in distilled water and as 0.39 and

0.75 mg l^{-1} Cu^{2+} in mineralized water by using the geometric mean and logistic regression methods, respectively (Cuppett et al. 2006). Similar values were obtained by a recent study for cupric ion as 0.49 and 1.2 mg l^{-1} Cu^{2+} in deionized water by using the geometric mean and logistic regression methods (Epke & Lawless 2007).

As can be concluded by comparing the values reported in literature, taste thresholds vary significantly by the sensory methods employed, the experimental water that the samples were prepared in, concentrations of the metals tested and data analysis method used. It should also be noted that sensitive people (who represent 5% of the population) may be able to detect metals in water at 100 to 1,000 times lower concentrations compared with less sensitive people (Cohen et al. 1960). Hence, even though the iron and copper concentrations are very low in drinking water, consumers may still detect their presence. One challenge in detecting and reporting the sensation of copper is that its metallic flavour, bitter taste and astringent mouthfeel reach their maxima in 20–40 seconds after ingestion. In a study of Cu^{2+} (as cupric sulfate) in a low mineral tap water, the soluble copper concentration, therefore the copper sensation were affected by both pH and concentration, and lingered for up to 2 minutes (Hong et al. 2010).

The objectives of this research were: 1) to determine flavour thresholds for ferrous and cuprous ions in deionized water at concentrations compatible with levels of these metals in drinking water, and then compare the results to water quality standards; and 2) to assess the magnitude of the taste and odour components of the metallic flavour sensation for ferrous, ferric, cuprous and cupric ions through tasting metal-containing solutions under two settings: with nose open and with nose occluded with nose-clips.

MATERIALS AND METHODS

Reagents

High purity ferrous sulfate, ferric sulfate, cuprous chloride and cupric chloride were purchased from Fisher Scientific (Pittsburgh, PA). Deionized reagent water was obtained from the Barnstead Nanopure® filter (NJ). Nose-clips were purchased from Speedo™ (7530015). The metal salt solutions

were prepared fresh daily prior to testing. The concentrations of the metal salt solutions were verified by either flame atomic adsorption spectrometry (Perkin Elmer 5100, Norwalk, CT) or inductively coupled plasma/mass spectroscopy (Thermo Scientific X-Series, Waltham, MA). For the threshold studies the concentrations tested for ferrous sulfate were 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4 and 5 mg l^{-1}; and the concentrations tested for cuprous chloride were 0.025, 0.05, 0.075, 0.125, 0.2, 0.325, 0.5, 0.75, 1, 1.3, 2, 3, 4 and 5 mg l^{-1}. These concentrations were selected to provide an ample range of results within those already reported in the literature. For the nose-clips studies, ferrous sulfate, ferric sulfate, cuprous chloride and cupric chloride were prepared at 20 mg l^{-1} concentrations. In deionized reagent water, these salts were soluble at the selected concentrations.

Subjects

Free and informed consent of the participants was obtained prior to testing and the study protocol was approved by the Institutional Review Board at Virginia Tech for the protection of human participants (VA, USA, Protocol # 06-395, approved on 14 July 2006). Healthy subjects with no problems in taste or smell perceptions were selected from the faculty, staff and students at Virginia Tech. The data were collected over a two year period. The panellists participating in the flavour threshold testing were untrained and were not informed about the specific aims of the study. Before each test panellists confirmed that they could breathe and smell properly and had no allergies or a cold. For ferrous ion threshold testing 27 panellists (14 females and 13 males) were tested, with an age range of 18 to 60 (mean 30.4) years old. Another group of 27 panellists (12 females and 15 males) participated in cuprous ion threshold testing with an age range of 19 to 72 (mean 35.2) years old. For the nose-clips studies, 25 panellists (12 males and 13 females) with an age range of 22 to 53 (mean 32.6) years old participated in ferric and ferrous ion studies. Seventeen (7 males and 10 females) and 21 (9 males and 12 females) panellists with an age range of 18 to 53 (mean 28.8) years old participated in the cupric and cuprous ion tests, respectively. The countries of origin for the panelists included the USA (~75%), Turkey, Korea, Honduras, Mexico, China, Russia, Germany and Switzerland.

Flavour thresholds of ferrous and cuprous ions

The same protocol as Cuppett et al. (2006), the one-of-five forced choice test, was selected for this research, which is a modified version of the triangle test. It is a stronger discriminative test as it has only 20% of chance of guessing correct. For each session panellists received 5 cups: four containing reagent water and one containing the metal salt solution (at ~pH 6); 30 ml of samples were presented at room temperature (~22°C) in 3 oz Solo cups coded with randomly selected 3-digit numbers. The panellists were asked to taste the samples from left to right without going back, swishing each sample for 15 seconds in their mouths, and then to expectorate. They were asked to take a 2 minute break in between samples in case of a delayed taste development. After all the samples were tasted, panellists selected the odd (metallic tasting) sample and marked it on their scorecard. Discussions were not allowed between panellists during the testing. Order of the samples was randomly selected, meaning that the sample containing metal salt solution could be placed anywhere in the row. Testing was complete for a subject when an incorrect answer was followed by three correct answers.

Individual taste thresholds for the panellists were calculated as the geometric mean of the highest incorrectly picked concentration and the lowest correctly identified concentration. The population thresholds were determined by using the geometric mean method and logistic regression method as the threshold value detectable by 60% of the population according to Abbott's formula (Gallagher & Cuppett 2007).

Components of metallic sensation from iron and copper

To separate the taste and odour perceptions, noses of the panellists were occluded by nose-clips. For nose-clips testing the panellists were presented with only one sample at each time. Panellists first placed the nose-clips on their noses and made sure no airflow through their noses was permitted. They were asked to sip and swish the sample around their mouth for 15 seconds and then to expectorate. This procedure was repeated after they removed the nose-clips. Right after each tasting panellists were asked to report their taste and flavour perceptions. Discussions were not allowed between panellists during the testing. A scale from 0 to 12, as used in flavour

profile analysis (*Standard Methods* 2006), was used to rate the taste, flavour and mouthfeel perceptions, '0' corresponding to 'no perception' and '12' corresponding to 'strong perception'. Some of the panellists were trained in this method; others were guided with examples of food items for taste intensities. A guideline for basic tastes (sweet, salty, sour, bitter, umami) and mouthfeelings (astringent, tingling, drying) was supplied at the bottom of the scorecards.

RESULTS AND DISCUSSION

Flavour thresholds of ferrous and cuprous ions

During the sensory sessions panellists described the taste of iron mostly as metallic and bloody, and copper as metallic and penny-like. However, these descriptors were also interchangeably used for both iron and copper by some panellists. Individual nose-open 'flavour' thresholds, as determined by the geometric mean method for ferrous ion, ranged from 0.003 to >5 mg l^{-1} Fe^{2+}. The population thresholds determined by geometric mean method and logistic regression for ferrous ion were 0.052 and 0.031 mg l^{-1} Fe^{2+}, respectively. Figure 1 shows the distribution of flavour threshold values for ferrous ion. It should be noted that 2 out of 27 panellists could not detect the metallic flavour of ferrous ion at 5 mg l^{-1} Fe^{2+} concentration.

Individual flavour thresholds determined with the nose open and calculated by the geometric mean method for

cuprous ion ranged from 0.035 to >5 Cu^{2+} mg l^{-1}. The population threshold determined by geometric mean method and logistic regression for cuprous ion was 0.61 mg l^{-1} Cu^{+} for both methods. Figure 2 shows the distribution of taste flavour threshold values for cuprous ion. Figure 2 also contains data from Cuppett *et al.* (2006) for cupric ion to illustrate the correlation of cuprous and cupric ion thresholds. It should be noted that 5 out of 27 panellists could not detect the metallic flavour of cuprous ion at 5 mg l^{-1} Cu^{+} concentration.

The study by Cuppett *et al.* (2006) reported similar threshold values for cupric sulfate. The determined nose-open flavour threshold values varied from 0.04 to >8 mg l^{-1} for 36 panellists (15 males and 21 females) with an age range of 22 to 54 years old. The population threshold concentrations were 0.48 and 0.77 mg l^{-1} Cu^{2+} as calculated by geometric mean and logistic regression, respectively. Data from Cuppett *et al.* (2006), as shown in Figure 2, indicated that detection of cuprous and cupric ions by the population parallel each other very closely and often coincide. When population thresholds were compared by the geometric mean method, cupric and cuprous ions both had similar flavour threshold concentrations, 0.48 and 0.61 mg l^{-1}, respectively. Thus, either species would be equally detectable by consumers when drinking water.

When Figures 1 and 2 are observed, it may be noted that about 90% and more than 75% of the panellists can detect ferrous and cuprous ions in water at or below their respective SMCLs set by the USEPA as 0.3 mg l^{-1} and 1.0 mg l^{-1} for iron and copper. These results should be taken into consideration by policymakers when revising existing drinking
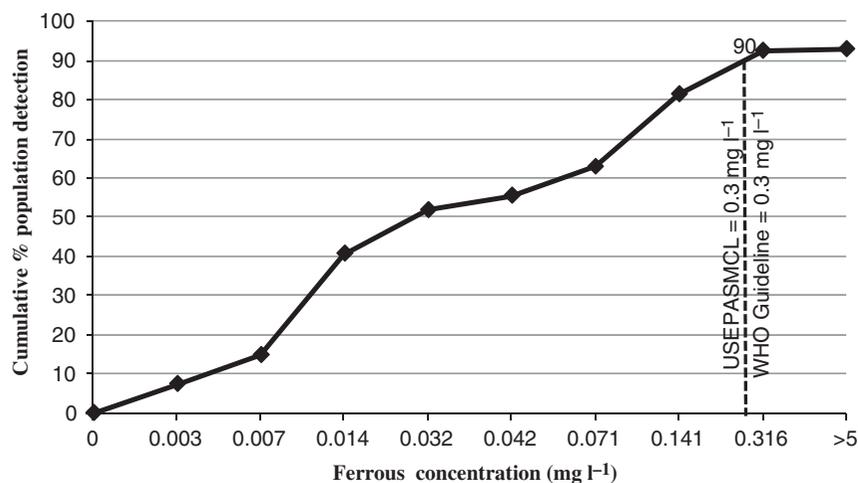

Figure 1 | Cumulative distribution of individual ferrous threshold values, mg l^{-1} Fe^{2+} in distilled water (n = 27 panellists).

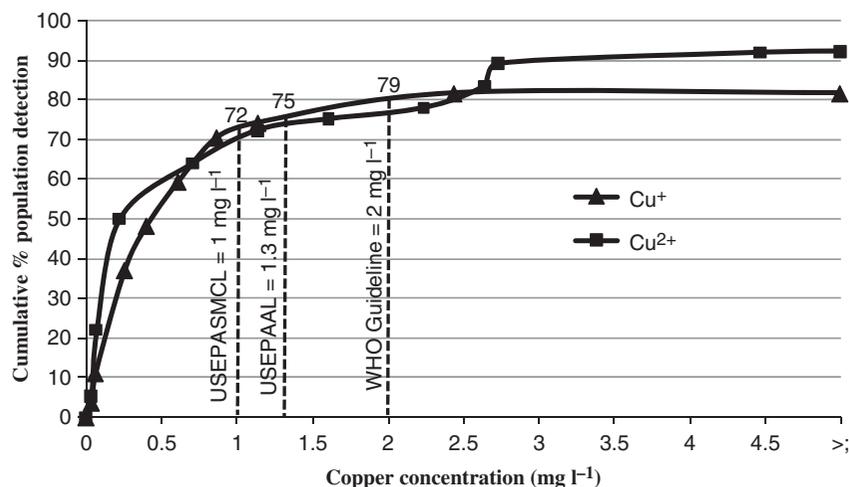**Figure 2** │ Cumulative distribution of individual cuprous (Cu$^+$) and cupric (Cu^{2+}) threshold values, mg l^{-1} Cu in distilled water (n = 27 and 36 panellists, respectively); data for cupric threshold values were obtained from Cuppett et al. (2006).

water standards. Although sensory studies conducted over a decade ago reported higher threshold values for iron and copper, recent studies which tested lower concentrations of metal species using more powerful sensory tests indicate that iron and copper are detected at much lower concentrations than previously reported.

Components of metallic sensation from iron and copper

The panellists did not report a 'metallic' sensation for any of the 20 mg l^{-1} iron or copper ion solutions when they tasted the samples with noses closed. Taste perceptions such as bitter and salty were reported at very weak intensities as well as mouthfeel factors such as astringent and drying for ferrous, cuprous and cupric ions. Ferric ion did not cause taste or mouthfeel perceptions at the levels tested.

Upon removal of the nose-clips, panellists reported a moderate-strong bloody/metallic flavour for ferrous ion, a moderate penny-like/metallic flavour for cupric ion, and a weak-moderate metallic flavour for cuprous ion. Panellists expected a strong taste when they noticed the yellow-coloured solution of ferric ion and were surprised to perceive no flavour. Doria (2010) has indicated that when people are used to drinking water at a certain quality, they react to or reject any water that is different. This may be the case when our panellists were biased about the yellow-coloured ferric ion solutions. Detection of metallic flavour of ferrous ion was

instantaneous whereas the flavour development took about 10 to 15 seconds for cuprous and cupric ions and got stronger with time. Final intensity ratings for cupric and cuprous ions were always lower than intensity ratings for ferrous ion. The results for ferrous ion are presented in Figure 3. The combined results for ferrous, ferric, cuprous and cupric ions each at 20 mg l^{-1} concentration are presented in Table 1.

Iron and copper are known to have different gustatory and tactile components such as astringent, drying, bitter, salty and sour, and the intensities and descriptors depend on the concentrations and anions (Hettinger et al. 1990; Lawless et al. 2005; ; Hong et al. 2010). In this study, the mouthfeel and taste descriptors were similar for cupric and cuprous ions and ferrous ion. These descriptors could be distinguished and reported when the noses of the panellists were occluded. Ferrous ion was more often perceived as astringent, while cupric ion was more often perceived as bitter. However when the nose-clips were removed, the panellists focused solely on the strong metallic flavour for all three cations.

The difference between the perceptions of panellists with and without nose-clips agrees with the retronasal component of metallic flavour reported by Hettinger et al. (1990), Lawless et al. (2004), and Epke & Lawless (2007). It should be noted that in these studies panellists still reported metallic perception even when their noses were occluded; however, the concentrations of the iron and copper were about 10-fold higher than the concentrations tested for the current study. A recent study reported that at very high concentrations, iron
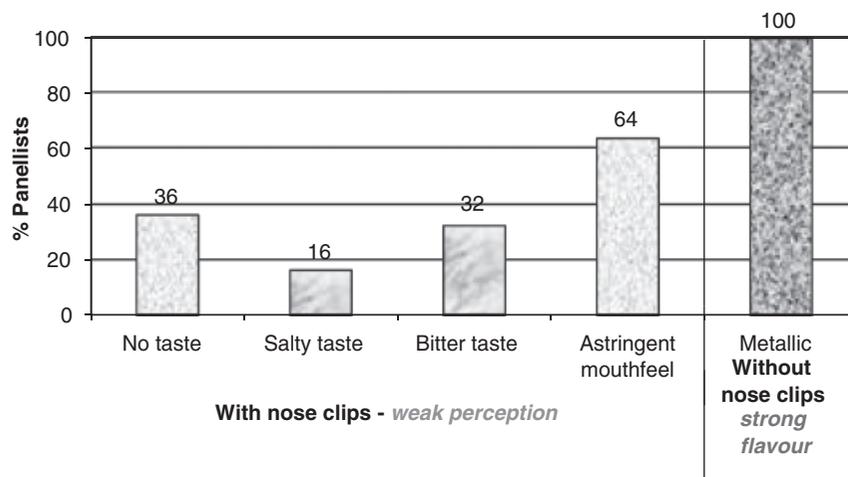
Figure 3 │ Taste, mouthfeel and flavour perceptions reported for ferrous at 20 mg l^{-1} Fe^{2+} by 25 panellists.

and copper (~600 mg l^{-1} for both Cu and Fe, which are 30-fold higher concentrations than tested here) activate TRPV1 taste receptors and suggest that these receptors may be related to metallic taste perception (Riera *et al.* 2007). Nevertheless, it should again be noted that the concentrations tested by Riera *et al.* (2007) were at unrealistically high levels and the sulfates may have activated these receptors instead.

The redox pair ferrous and ferric ions demonstrated a very different flavour relationship from that of cuprous and cupric ions. Ferrous ion is very flavourful with a population threshold of 0.051 mg l^{-1} Fe^{2+} as calculated by the geometric mean method; ferric ion is nearly tasteless and flavourless. A factor to be considered is that ferric ion can be readily reduced to ferrous ion in the oral cavity by salivary antioxidants (reducing agents) such as ascorbic acid (Vitamin C) (Gumus *et al.* 2009). Thus, under oral conditions

where ferric ion can be reduced, it could produce the flavour associated with ferrous ion.

This study found a delay of about 10 to 15 seconds before panellists detected a sensation for cuprous or cupric ions. This delay is similar to that reported for a 'time to intensity' study of the metallic flavour, bitter taste, and astringent mouthfeel for cupric ion at 2.5 and 5 mg l^{-1} Cu^{2+} in a low mineral tap water at pH 5.5 and 7.5 using a tasting with nose-open format (Hong *et al.* 2010). In that study, the onset of the oral sensation began at about 10 seconds and was most intense between 20 and 40 seconds. Cupric ion concentration significantly influenced metallic flavour but had less effect on the detection of bitter taste. Astringent mouthfeel was found to be most prominent at acidic pH values.

Similar to Cuppett *et al.* (2006), Hong *et al.* (2010) also reported that soluble cupric ion produced more flavour than

Table 1 │ Taste and flavour sensory response for reduced and oxidized iron and copper

| Test Conditions | Sensory response | % Panellists Responding* | | | |
		Ferrous, Fe^{2+}	Ferric, Fe^{3+}	Cuprous, Cu$^+$	Cupric, Cu^{2+}
***Nose closed* – taste/mouthfeel** perception	No taste	36	100	52	16
	Bitter taste, **weak**	32	0	33	47
	Salty taste, **weak**	16	0	14	29
	Astringent mouthfeel	64	0	33	24
	Drying mouthfeel	0	0	24	12
***Nose open* – flavour** perception	Metallic flavour, **strong**	100	0	100	100
	Common descriptors	Metallic bloody	None	Metallic penny-like	Metallic penny-like

*Results for ferrous (n = 25), ferric (n = 25), cuprous (n = 21) and cupric (n = 17) each at 20 mg l^{-1} concentration

the particulate copper. Several researchers have shown that metals catalyse the oxidation of phospholipids in the cell membranes (of food products, skin) and cause production of several carbonyls that have metallic flavours (Buettner & Schieberle 2001; Venkateshwarlu et al. 2004; Glindemann et al. 2006; Mielnik et al. 2006). Therefore it should be noted that, rather than taste receptors, carbonyls produced as a result of lipid oxidation may be the cause of the metallic flavour. As the soluble forms of iron and copper are more available than the particulate species, carbonyl production will be higher and this relates well to the stronger flavour perception by the panellists.

The actual perception of the metal sensation by consumers would be influenced by water quality factors of pH and metal concentration. Water utilities and regulatory agencies should consider these factors when interpreting complaints of 'metallic' and when developing procedures to address the issue. Although treated water may comply with the standards, corrosion of infrastructure may increase the iron and copper concentrations at the tap. It may also be noted that, regardless of the constituents of a typical tap water, the conditions in the mouth (buffers and electrolytes in saliva) (Tenovuo 1989; Gandara & Truelove 1999) may override the drinking water conditions and hence control the speciation which may result in similar results for taste and flavour perception.

CONCLUSIONS

Recently determined sensory threshold values in the literature and our findings indicate that ferrous, cupric and cuprous ions are detected at concentrations that are much below the current aesthetic guidelines of about 0.3 mg l^{-1} Fe and 1 mg l^{-1} Cu. As demonstrated with the nose-occluded and nose-open studies, metallic flavour perception has a significant odour component that is perceived retronasally and also a weak taste perception. The strong metallic flavours of ferrous, cuprous and cupric ions are dominated by the retronasal perception of odours, while their taste perceptions have weak qualities of bitter, salty and astringent.

Using standard statistical approaches, population flavour thresholds were determined to range from 0.031 to 0.05 mg l^{-1} Fe^{2+} for ferrous ion and 0.61 mg l^{-1} Cu^{2+} for cuprous ion. For ferrous ion, individual flavour thresholds ranged from 0.003 to >5 mg l^{-1} Fe^{2+} and for cuprous ion, from 0.035 to >5 mg l^{-1} Cu^{2+}. Sensitive people readily detect these metals at low μg l^{-1} levels in drinking water and hence may complain. Cupric and cuprous ions have similar flavour thresholds for individuals and for the population. Ferric ion had no taste or flavour perception even at 20 mg l^{-1} Fe^{3+}.

Implications of this research are that current standards for metals, based on taste and discoloration, may not prevent complaints about off-flavours of iron and copper in drinking water.

REFERENCES

Araya, M., Pena, C., Pizarro, F. & Olivares, M. 2003 Gastric response to acute copper exposure. Sci. Total Environ. **303**(3), 253–257.

Australian Government National Health and Medical Research Council 2004 Australian Drinking Water Guidelines (ADWG), http://www.nhmrc.gov.au, accessed 23 November 2010.

Buettner, A. & Schieberle, P. 2001 Characterization of the most odor active volatiles in fresh hand-squeezed grapefruit juice by quantitation and flavor reconstitution experiments. J. Agric. Food Chem. **49**(3), 1358–1363.

Cohen, J., Kamphake, J., Harris, K. & Woodward, R. 1960 Taste threshold concentrations of metals in drinking water. J. Am. Wat. Wks Assoc. **52**, 660–670.

Comeau, T. B., Epstein, J. B. & Migas, C. 2001 Taste and smell dysfunction in patients receiving chemotherapy: a review of current knowledge. Support. Care Cancer **9**, 575–580.

Cuppett, J. D., Duncan, S. E. & Dietrich, A. M. 2006 Evaluation of copper speciation and water quality factors that affect aqueous copper tasting response. Chem. Senses **31**, 689–697.

Dietrich, A. M. 2009 The sense of smell: contributions of orthonasal and retronasal perception applied to metallic flavor of drinking water. *J. Water Suppl.: Res. & Technol.-AQUA* **58**(8), 562–570.

Dietrich, A. M., Glindemann, D., Pizarro, F., Gidi, V., Olivares, M., Araya, M., Camper, A., Duncan, S., Dwyer, S., Whelton, A., Younos, T., Subramanian, S., Burlingame, G., Khiari, D. & Edwards, M. 2004 Health and aesthetic impacts of copper corrosion on drinking water. *Water Sci. Technol.* **49**(2), 55–62.

Doria, M. F. 2005 *Water Quality and Risk: A Cross-national Study on Perception*, PhD Dissertation, University of East Anglia, Norwich, UK.

Doria, M. F. 2010 Factors influencing public perception of drinking water quality. *Water Policy* **12**, 1–19.

Epke, E. M. & Lawless, H. T. 2007 Retronasal smell and detection thresholds of iron and copper salts. *Physiol. Behav.* **92**, 487–491.

Fabrellas, C., Cardenoso, R., Devesa, R., Flores, J. & Matia, L. 2004 Taste and odor profiles (off-flavors) in the drinking waters of the Barcelona area (1996–2000). *Water Sci. Technol.* **49**(9), 129–135.

Gallagher, D. & Cuppett, J. 2007 Comparison of threshold limit methods for sensory data. *Water Sci. Technol.* **55**(5), 69–75.

Gandara, B. K. & Truelove, E. L. 1999 Diagnosis and management of dental erosion. *J. Contemp. Dental Pract.* **1**, 16–23.

Glindemann, D., Dietrich, A. M., Staerk, H. J. & Kuschk, P. 2006 The two smells of touched or pickled iron (skin) carbonyl-hydrocarbons and organophosphines. *Angew. Chem. Int. Edit.* **45**, 7006–7009.

Gonzales Vinas, M. A., Slavador, M. D. & Martin Alvarez, P. J. 1998 Comparison of two simple methods for the measurement of detection thresholds for basic, umami and metallic tastes. *J. Sens. Stud.* **13**, 299–314.

Gumus, P., Buduneli, N., Cetinkalp, S., Hawkins, S. I., Renaud, D., Kinane, D. F. & Scott, D. A. 2009 Salivary antioxidants in patients with type 1 or 2 diabetes and inflammatory periodontal disease: a case-control study. *J. Periodontol.* **80**(9), 1440–1446.

Hettinger, T. P., Myers, W. E. & Frank, M. E. 1990 Role of olfaction in perception of non-traditional 'taste' stimuli. *Chem. Senses* **16**, 755–760.

Hong, J. H., Duncan, S. E. & Dietrich, A. M. 2010 Effect of copper speciation at different pH on temporal sensory attributes of copper. *Food Qual. Prefer.* **21**, 243–249.

Hong, J. H., Ömür-Özbek, P., Stanek, B. T., Dietrich, A. M., Duncan, S. E., Lee, Y. W. & Lesser, G. 2009 Taste and smell abnormalities in cancer patients. *J. Support. Oncol.* **7**(2), 58–65.

Kirmeyer, G. J. 2000 Guidance Manual for Maintaining Distribution System Water Quality. *AWWA Research Foundation and American Water Works Association*, Denver, CO.

Lawless, H. T., Shlake, S., Smythe, J., Lim, J., Yang, H., Chapman, K. & Bolton, B. 2004 Metallic taste and retronasal smell. *Chem. Senses* **29**, 25–33.

Lawless, H. T., Stevens, D. A., Chapman, K. W. & Kurtz, A. 2005 Metallic taste from electrical and chemical stimulation. *Chem. Senses* **15**, 755–760.

Lim, J. & Lawless, H. T. 2005 Oral sensations from iron and copper sulfate. *Physiol. Behav.* **85**, 308–313.

Lim, J. & Lawless, H. T. 2006 Detection thresholds and taste qualities of iron salts. *Food Qual. Prefer.* **17**, 513–521.

Mielnik, M. B., Olsen, E., Vogt, G., Adeline, D. & Skrede, G. 2006 Grape seed extract as antioxidant in cooked, cold stored turkey meat. *LWT – Food Sci. Technol.* **39**(3), 191–198.

Nealson, K. H. & Saffarini, D. 1994 Iron and manganese in anaerobic respiration: environmental significance, physiology, and regulation. *Ann. Rev. Microbiol.* **48**, 311–343.

NRC (National Research Council) 1989 *National Research Council, Food and Nutrition Board Recommended dietary allowances*, 10th edn. National Academy Press, Washington, DC.

O'Donohue, J. W. 1993 Micronodular cirrhosis and acute liver failure due to chronic copper selfintoxication. *Eur. J. Gastroen. Hepat.* **5**(7), 561–562.

Pizarro, F., Araya, M., Vasquez, M., Lagos, G., Olivares, M., Mendez, M. A., Leyton, B., Reyes, A., Letelier, V. & Uauy, R. 2007 Case study of complaints on drinking water quality. *Biol. Trace Elem. Res.* **16**, 131–145.

Riera, C. E., Vogel, H., Simon, S. A. & le Coutre, J. 2007 Artificial sweeteners and salts producing a metallic taste sensation activate TRPV1 receptors. *Am. J. Physiol. – Regul., I.* **293**, R626–R634.

Standard Methods for the Examination of Water and Wastewater 2006 21st edition, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.

Tenovuo, J. O. 1989 *Human Saliva: Clinical Chemistry and Microbiology*, Vol. I. CRC Press, Boca Raton, FL, pp. 75–94.

USEPA (United States Environmental Protection Agency) 1991 *Maximum Contaminant Level Goals and National Primary Drinking Water for Lead and Copper*. Final Rule, Federal Register 56, 26460–26564.

USEPA 1997 *National Secondary Drinking Water Regulations*. Final Rule, Federal Register 44(140), 42195.

Venkateshwarlu, G., Let, M. B., Meyer, A. S. & Jacobsen, C. 2004 Modeling the sensory impact of defined combinations of volatile lipid oxidation products on fishy and metallic off-flavors. *J. Agric. Food Chem.* **52**, 1635–1641.

Whelton, A. J., Dietrich, A. M., Gallagher, D. L. & Roberson, J. A. 2007 Using customer feedback for improved water quality and infrastructure monitoring. *J. Am. Wat. Wks Assoc.*, **99**(11), 62–76.

WHO (World Health Organization) 1996 *Guidelines for Drinking Water Quality*, Vol. 2, 2nd edn. Health Criteria and Other Supporting Information, Geneva, Switzerland.

Zacarias, I., Yanez, C. G., Araya, M., Oraka, C., Olivares, M. & Uauy, R. 2001 Determination of the taste threshold of copper in water. *Chem. Senses* **26**, 85–89.

Zacharias, R. & Tuorila, H. 1979 Taste thresholds for metallic salts in different media. *LWT – Food Sci. Technol.* **12**, 36–40.

Zhang, X., Pehkonen, S. O., Kocherginskya, N. & Ellis, G. E. 2002 Copper corrosion in mildly alkaline water with the disinfectant monochloramine. *Corros. Sci.* **44**(11), 2507–2528.