

## Threshold flavor and odor concentrations of raw waters treated with peracetic acid or sodium hypochlorite

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Organoleptic properties of aliquots of surface and ground waters collected in Latium (Italy) from lake Bracciano and waterworks Peschiera, respectively, were compared before and after disinfection with sodium hypochlorite (NaClO) or peracetic acid (PAA). Every test was carried out according to the European Standard EN 1622 on the determination of threshold odor and flavor numbers. Assessors were selected by means of preliminary screening tests based on the evaluation of few reference compounds (citric acid, sodium chloride, and sucrose for flavor; *n*-butanol and NaClO for odor) added to a mineral water with a low content of salts. A series of successive dilutions were prepared and assessed by every candidate applying “paired test” and “forced choice” procedures. Afterwards, selected assessors were asked to perceive odor and flavor of the investigated surface and ground waters added with increasing concentrations of NaClO, PAA, acetic acid or hydrogen peroxide. In this case “paired tests” were evaluated by both “forced” and “unforced choice”. Organoleptic changes induced by the two disinfectants were independent of the aqueous matrix and were perceived when their concentrations became 0.04, 0.23, 6, and 11 mg L<sup>-1</sup> for NaClO odor, NaClO flavor, PAA odor, and PAA flavor, respectively.

**Keywords:** flavor; groundwater; odor; peracetic acid; sodium hypochlorite; surface water

### Introduction

Drinking water disinfection is a common practice applied to reduce the microbial load from raw water and to control algal re-growth in distribution systems. Its presence also guarantees consumers' health in case of water leaks in pipes and fittings. For a long time sodium hypochlorite (NaClO) has been preferred to other agents due to its good disinfectant properties and low cost. Recently, improvements in analytical techniques have highlighted the risk of by-product formation since NaClO reacts with humic or fulvic acids to form halogenated organic compounds, such as trihalomethanes, haloacids, and haloacetonitriles. In addition, it reacts with ammonium ion and amino compounds to form inorganic and organic chloramines, which are considered to be less effective disinfectants and suspected carcinogens.

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Moreover, NaClO imparts nasty odor and taste to drinking water when its concentration is in the range set up by the European Directive 98/83 (UE (European Union) 1998). This is why other chemicals, such as chlorine dioxide, ozone, and potassium permanganate, have frequently been tested as alternative or complementary water disinfectants. Their practical application has often been hindered by a number of drawbacks. Particularly, chlorine dioxide is responsible for the formation of inorganic by-products like chlorite and chlorate, which may lead to hemolytic anemia and methemoglobinemia at low and high concentrations, respectively. Ozone forms a variety of toxic organic and inorganic by-products such as aldehydes, ketones, and bromate. Potassium permanganate has a mild disinfectant power at neutral pH and may impart a violetish color to the treated water. Recently, another alternative disinfectant, that is peracetic acid (PAA), has proved to be a suitable agent from the toxicological point of view as no dangerous by-products have so far been identified. Moreover, its decomposition products (acetic acid (AA), hydrogen peroxide ( $H_2O_2$ ), and oxygen) do not affect water quality.

Although drinking water distributed in Europe is undoubtedly safe for human health, consumers express frequent reservations about its features. This is mainly due to its organoleptic properties, which have a considerable impact on their perception of the overall product quality. Complaints usually concern bad smell or taste produced by microorganisms, natural organic matter (NOM), and/or algal re-growth (Amoore 1986; Ettinger and Middleton 1956; McGuire et al. 1983; Young et al. 1996). In addition, some chemicals may change water flavor or odor even though their level is negligible from the toxicological point of view. Among them, metals like copper, iron, manganese, and zinc, which are released by pipes and fittings, affect water color, taste, and turbidity when their background concentration is increased by local corrosion processes. Finally, disinfection practice based on the use of chlorine compounds is often responsible for temporary organoleptic alterations, which may be perceived at some time of day (Young et al. 1996). These problems are caused by the presence of the disinfectant itself or by the occurrence of disinfection by-products formed by reaction with either NOM or some construction products. For example, the reaction of chlorine with certain nitrogen compounds dissolved in source water may lead to the formation of strong-smelling compounds such as aldehydes, nitriles, and some chloramines, which can cause pronounced chlorinous tastes and odors, sometimes even at very low levels (Bruchet et al. 1992; Daignault, Gac, and Hrudey 1988; Fabrellas, Matia, and Ventura 2004; Freuze et al. 2005; Froese, Wolanski, and Hrudey 1999; Hrudey 1989; Hrudey, Gac, and Daignault 1988; Hrudey, Huck, and Roodselaar 1990; Richardson 2001; Urbansky and Magnusson 2002). Chlorophenols, resulting from the reaction of chlorine with phenolic compounds, can be formed at the plant or in the distribution system and can impart "medicinal" taste and odor to the water (Mallevalle and Suffet 1987). It has been reported that these compounds may subsequently be converted to chlorinated anisoles in the distribution system via biomethylation (Nyström et al. 1992; Piriou et al. 2001; Suffet and Mallevalle 1995). They can impart an earthy-musty odor to water at low nanogram per liter concentration levels.

To date, water suppliers have met numerous difficulties in dealing with this kind of consumer complaints not only for the complexity of the described phenomena but also for the uncertainty of the organoleptic data acquired with nonstandardized protocols by untrained personnel. In 2006, the European Committee for Standardization published a standard (CEN 2006) to quantify the odor and flavor

of drinking water or reference waters from migration tests. The described methods enable an objective and reproducible determination of threshold levels below which odor or flavor are not perceived by the majority of the consumers.

In the present work, we have applied the European standard to evaluate the threshold odor and flavor numbers (TON and TFN, respectively) of waters destined for human consumption after disinfection with PAA or NaClO. Data so acquired have provided useful information on the organoleptic alterations produced by the two chemicals.

## Experimental

### Tested aqueous matrices

In this study, we have tested the organoleptic alterations produced by the disinfection of two different aqueous matrices collected at Bracciano lake and Peschiera river sources, respectively.

The Bracciano lake, also called lake Sabatino, is the largest volcanic lake with fresh water in the province of Rome and is characterized by a coastline of 31 km and a surface of 58 km<sup>2</sup>. It is at 164 m above sea level and is 160 m deep. Its water is currently used in agriculture, bathing, and fishing, and represents an important supply that may be used to satisfy the water requirement of Rome in case of emergency (ARPA (Regional Agency for Environment Protection) Lazio 2007). Water collected at a depth of 50 m in the middle of the lake flows through a 10 km long pipeline to a treatment plant where screening, settling, filtration through sand filters, and disinfection are generally applied. Table 1 lists its chemical and microbiological composition before final disinfection.

Table 1. Physico-chemical, chemical, and microbiological composition of Bracciano lake.

| Parameters                     |                                    | Mean  | Median | Min  | Max  |
|--------------------------------|------------------------------------|-------|--------|------|------|
| pH                             |                                    | 7.90  | –      | 7.63 | 8.24 |
| $\chi$ at 20°C                 | $\mu\text{S cm}^{-1}$              | 489   | –      | 480  | 503  |
| NPOC                           | $\text{mg L}^{-1}$                 | 1.91  | –      | 1.70 | 2.35 |
| $\text{Na}^+$                  | $\text{mg L}^{-1}$                 | 47.2  | –      | 45.3 | 48.3 |
| $\text{Mg}^{2+}$               | $\text{mg L}^{-1}$                 | 11.9  | –      | 11.2 | 12.8 |
| $\text{Ca}^{2+}$               | $\text{mg L}^{-1}$                 | 21.5  | –      | 20.3 | 22.1 |
| $\text{K}^+$                   | $\text{mg L}^{-1}$                 | 42.8  | –      | 41.4 | 43.7 |
| Alkalinity                     | $\text{mg L}^{-1}$ $\text{CaCO}_3$ | 163   | –      | 160  | 166  |
| $\text{SO}_4^{2-}$             | $\text{mg L}^{-1}$                 | 26.8  | –      | 26.2 | 27.9 |
| $\text{Cl}^-$                  | $\text{mg L}^{-1}$                 | 47.3  | –      | 46.0 | 49.6 |
| $\text{NO}_3^-$                | $\text{mg L}^{-1}$                 | 0.8   | –      | 0.1  | 0.6  |
| $\text{F}^-$                   | $\text{mg L}^{-1}$                 | 1.8   | –      | 1.6  | 1.9  |
| $\text{Br}^-$                  | $\text{mg L}^{-1}$                 | 0.12  | –      | 0.10 | 0.15 |
| $\text{NO}_2^-$                | $\text{mg L}^{-1}$                 | <0.01 | –      | –    | –    |
| $\text{NH}_4^+$                | $\text{mg L}^{-1}$                 | <0.03 | –      | –    | –    |
| Total coliform                 | UFC 100 mL <sup>-1</sup>           | –     | 3      | 0    | 22   |
| Faecal coliform                | UFC 100 mL <sup>-1</sup>           | –     | 0      | 0    | 12   |
| Faecal streptococci            | UFC 100 mL <sup>-1</sup>           | –     | 0      | 0    | 2    |
| Enterococci                    | UFC 100 mL <sup>-1</sup>           | –     | 0      | 0    | 1    |
| <i>Clostridium perfringens</i> | UFC 100 mL <sup>-1</sup>           | –     | 0      | 0    | 0    |

Table 2. Physico-chemical, chemical and microbiological composition of river Peschiera.

| Parameters                     |                                  | Mean  | Median | Min  | Max  |
|--------------------------------|----------------------------------|-------|--------|------|------|
| pH                             | –                                | 7.19  | –      | 7.07 | 7.41 |
| $\chi$ at 20°C                 | $\mu\text{S cm}^{-1}$            | 607   | –      | 585  | 625  |
| NPOC                           | $\text{mg L}^{-1}$               | 0.28  | –      | 0.14 | 0.39 |
| $\text{Na}^+$                  | $\text{mg L}^{-1}$               | 2.8   | –      | 2.47 | 3.06 |
| $\text{Mg}^{2+}$               | $\text{mg L}^{-1}$               | 21.5  | –      | 20.4 | 23.0 |
| $\text{Ca}^{2+}$               | $\text{mg L}^{-1}$               | 112.8 | –      | 110  | 117  |
| $\text{K}^+$                   | $\text{mg L}^{-1}$               | 0.84  | –      | 0.68 | –    |
| Alkalinity                     | $\text{mg L}^{-1} \text{CaCO}_3$ | 357.5 | –      | 344  | 369  |
| $\text{SO}_4^{2-}$             | $\text{mg L}^{-1}$               | 12.1  | –      | 11.4 | 12.6 |
| $\text{Cl}^-$                  | $\text{mg L}^{-1}$               | 4.23  | –      | 3.55 | 4.56 |
| $\text{NO}_3^-$                | $\text{mg L}^{-1}$               | 2.4   | –      | 2.31 | 2.58 |
| $\text{F}^-$                   | $\text{mg L}^{-1}$               | 111.3 | –      | 100  | 190  |
| $\text{Br}^-$                  | $\text{mg L}^{-1}$               | <0.05 | –      | –    | –    |
| $\text{NO}_2^-$                | $\text{mg L}^{-1}$               | <0.01 | –      | –    | –    |
| $\text{NH}_4^+$                | $\text{mg L}^{-1}$               | <0.03 | –      | –    | –    |
| $\text{ClO}_2^-$               | $\text{mg L}^{-1}$               | <0.05 | –      | –    | –    |
| $\text{ClO}_3^-$               | $\text{mg L}^{-1}$               | <0.05 | –      | –    | –    |
| Total coliform                 | UFC 100 mL <sup>-1</sup>         | –     | 0      | 0    | 1    |
| Faecal coliform                | UFC 100 mL <sup>-1</sup>         | –     | 0      | 0    | 1    |
| Faecal streptococci            | UFC 100 mL <sup>-1</sup>         | –     | 0      | 0    | 0    |
| Enterococci                    | UFC 100 mL <sup>-1</sup>         | –     | 0      | 0    | 0    |
| Escherichia coli               | UFC 100 mL <sup>-1</sup>         | –     | 0      | 0    | 0    |
| <i>Clostridium perfringens</i> | UFC 100 mL <sup>-1</sup>         | –     | 0      | 0    | 0    |
| <i>Pseudomonas aeruginosa</i>  | UFC 250 mL <sup>-1</sup>         | –     | 0      | 0    | 0    |
| Pathogenic staphylococci       | UFC 250 mL <sup>-1</sup>         | –     | 0      | 0    | 0    |

The sources of river Peschiera, a minor tributary of river Velino, are at the side of Mount Nuria, a few kilometers from the municipality of Cittaducale in the province of Rieti. Water gushes at a flow rate of 17–18 m<sup>3</sup> s<sup>-1</sup> from the sides of an extensive calcareous massif affected by karst and numerous fracture systems. Since 1937, these sources have fed the waterworks Peschiera–Capore that distributes drinking water to Rome at a flow rate of 9.5 m<sup>3</sup> s<sup>-1</sup> after disinfection with NaClO (Wikipedia 2008, [http://it.wikipedia.org/wiki/Sorgenti\\_del\\_fiume\\_Peschiera](http://it.wikipedia.org/wiki/Sorgenti_del_fiume_Peschiera)). Table 2 lists the chemical and microbiological compositions of nonchlorinated water. Before the following use in the organoleptic tests, both Bracciano and Peschiera water samples were filtered to remove suspended solids. Filtration was performed through a sintered-glass crucible with porosity rank of 4 (5–1  $\mu\text{m}$  pore size). The crucible was carefully cleaned with concentrated HNO<sub>3</sub> and abundantly rinsed with ultrapure water.

### Chemicals

Ultrapure water at 18.2 M $\Omega$  cm resistivity was obtained directly from a Milli-Q Plus 185 Millipore Corp. water-purification system. Mineral water Levissima collected in Valtellina (province of Sondrio, Italy) and supplied by Sanpellegrino Nestlè Waters Italia was selected as odor and flavor free water and used for rinsing, dilution, and reference water. Its chemical composition is listed in Table 3.

Table 3. Chemical composition of mineral water Levissima.

| Parameters                     |                       | Label value       |
|--------------------------------|-----------------------|-------------------|
| $T$ at the source              | $^{\circ}\text{C}$    | 5.5               |
| pH                             | –                     | 7.8               |
| $\chi$ at $20^{\circ}\text{C}$ | $\mu\text{S cm}^{-1}$ | 119               |
| Total dissolved solids         | $\text{mg L}^{-1}$    | 78.2              |
| NPOC                           | $\text{mg L}^{-1}$    | 0.32 <sup>a</sup> |
| $\text{Na}^{+}$                | $\text{mg L}^{-1}$    | 1.8               |
| $\text{Mg}^{2+}$               | $\text{mg L}^{-1}$    | 1.7               |
| $\text{Ca}^{2+}$               | $\text{mg L}^{-1}$    | 20.8              |
| $\text{K}^{+}$                 | $\text{mg L}^{-1}$    | 1.7               |
| $\text{SO}_4^{2-}$             | $\text{mg L}^{-1}$    | 16.5              |
| $\text{NO}_3^{-}$              | $\text{mg L}^{-1}$    | 1.6               |
| $\text{HCO}_3^{-}$             | $\text{mg L}^{-1}$    | 56.5              |
| $\text{NO}_2^{-}$              | $\mu\text{g L}^{-1}$  | <2                |
| $\text{F}^{-}$                 | $\text{mg L}^{-1}$    | 0.2               |
| Silica                         | $\text{mg L}^{-1}$    | 5.6               |

Notes: <sup>a</sup>Value determined by the authors of the present article.

Nonionic surfactants, nitric acid  $14 \text{ mol L}^{-1}$ , hydrochloric acid  $2.0 \text{ mol L}^{-1}$ , and  $\text{H}_2\text{O}_2$   $2.0 \text{ mol L}^{-1}$  were used to clean glassware as described below. Stock solutions of *n*-butanol  $0.10 \text{ g L}^{-1}$ , citric acid  $5.0 \text{ g L}^{-1}$ , sucrose  $20 \text{ g L}^{-1}$ , sodium chloride  $5.0 \text{ g L}^{-1}$ , AA  $1.5 \text{ g L}^{-1}$ , NaClO  $25 \text{ mg L}^{-1}$ ,  $\text{H}_2\text{O}_2$   $330 \text{ g L}^{-1}$ , and PAA  $0.50 \text{ g L}^{-1}$  were employed to prepare test solutions in mineral water Levissima, in Bracciano surface water or in Peschiera groundwater. NaClO, PAA, and  $\text{H}_2\text{O}_2$  concentrations were checked by iodometric titration (Veschetti et al. 2003). All chemicals used were of analytical reagent grade.

Test dilutions of NaClO and PAA were prepared 5 min before each panel assessment and were discharged at the end of every session after colorimetric analysis (Veschetti et al. 2003). This procedure avoided significant decomposition of the two disinfectants.

### Glassware

Glassware employed for TON and TFN assessment was made up of two series of six 250 mL conical flasks with glass stoppers and two series of six 100 mL beakers, respectively. It was reserved solely for organoleptic tests and was stored in clean conditions far from laboratory reagents. Before use, it was carefully cleaned separately from other laboratory items with nonperfumed detergent, HCl  $2.0 \text{ mol L}^{-1}$ , and  $\text{H}_2\text{O}_2$   $2.0 \text{ mol L}^{-1}$ . Afterwards, it was abundantly rinsed with ultrapure water and heated at  $100^{\circ}\text{C}$  for a few hours in a drying oven to remove residual odors.

### Selection of the assessors

The test panel was constituted by choosing a sufficient number of assessors who had undergone a period (not less than 1 month) of training and experience.

Potential candidates were preliminarily interviewed to disqualify the individuals suffering from respiratory diseases, such as allergies or unusual insensitivity. People who passed this selection had undergone screening tests consisting in comparative organoleptic evaluations of known solutions in mineral water Levissima to which increasing quantities of reference compounds (*n*-butanol and NaClO for odor; citric acid, sucrose, and sodium chloride for flavor) were added. These latter tests, carried out as described below, enabled the exclusion of very sensitive or insensitive individuals compared to the average.

### Flavor testing

Selected assessors were asked to refrain from having food or drinks no less than 1 h before every test session in order not to prejudice their own skills.

Two beakers containing 25 mL of Bracciano or Peschiera samples with and without a known quantity of tested compound (NaClO, PAA, H<sub>2</sub>O<sub>2</sub>, or AA), respectively, were randomly presented to each panelist (paired test). After tasting, without swallowing, a suitable volume of water from both beakers, the assessor was asked a comparative opinion on the flavors. This procedure was repeated six times while increasing the quantity of the added compound on the basis of the geometric progression 2<sup>*n*</sup> (with *n* = 1, 2, . . . , 6). The evaluation of every couple in the series was carried out in the order of ascending concentration of the compound to avoid possible fatigue or saturation phenomena. Temporary lowering of sensitivity was recovered by supplying the assessor with a biscuit of mineral water Levissima. Glassware and room temperatures were kept to 25 ± 1°C during each test session.

Panelist decisions were evaluated twice according to the following different criteria (CEN 2006):

- The individual threshold number (TN<sub>*i*</sub>) of an assessor was assumed to be equal to the concentration level of the compound present in the latest solution perceived different from the corresponding blank (unforced choice). The cumulative threshold number (TN) of the whole test panel was the geometric average of the TN<sub>*i*</sub> values, after excluding individual TN<sub>*i*</sub>, which differed more than one concentration level from TN.
- Even if the assessor was unable to perceive a difference between a solution and the corresponding blank, he/she was asked to choose one of them as having the greater flavor (forced choice). The whole set of decisions taken by the test panel for a concentration level was used to calculate the percentage *R*<sup>+</sup> of the panelists who guessed the beaker containing the compound solution. This value was then corrected from the results obtained by chance (50% in paired test) with the following equation:

$$S = \frac{R^+ - 50}{100 - 50} \cdot 100,$$

where *S* represents the percentage of the corrected positive answers for a particular concentration level. The cumulative TN was equal to the point of inflection in the sigmoid plot of *S* versus concentration level.

### Odor testing

Two conical flasks containing 100 mL of Bracciano or Peschiera samples with and without a known quantity of tested compound (NaClO, PAA, H<sub>2</sub>O<sub>2</sub>, or AA), respectively, were randomly presented to each panelist (paired test). After shaking, removing the stopper, and smelling inside both vessels, the assessor was asked a comparative opinion on the odors.

All other details of the procedure were as described previously for flavor testing.

### Results and discussion

Sixteen out of 20 candidates passed the preliminary screening tests carried out to select the eligible assessors. Only 13 of them were regularly included in the test panel while the remaining three panelists were convened as substitutes. The identity of each assessor in the test sessions was masked and protected by assigning a letter to the file containing his/her decisions.

Afterwards, changes in the organoleptic properties of fresh waters disinfected with PAA were examined and compared to the corresponding alterations produced by NaClO. In order to evaluate the effect produced by H<sub>2</sub>O<sub>2</sub> and AA, which are always co-present in PAA solutions, panelists were also asked to test pure solutions of these two chemicals in the same fresh waters. Table 4 shows the maximum concentrations of the compounds examined by the assessors at the end of the appropriate test session (concentration level = 6). The individual decisions coming from unforced choices were represented in bar charts (Figure 1) to identify and exclude any outliers (i.e., TN<sub>*i*</sub> out of the range TN - 1 ÷ TN + 1). The remaining values were combined in the overall geometric averages (Table 5). On the contrary, the percentages of corrected positive answers calculated from the forced choice results were plotted against the corresponding concentration levels (Figure 2). Cumulative TNs (Table 5) were interpolated from the sigmoid curves at their inflection point. Data sets resulting from the application of these two different approaches differ from each other by 3–30% in terms of relative standard error. Considering that human answers are generally affected by a strong variability, these differences do not appear to be significant. Similarly, threshold concentrations obtained by disinfecting Bracciano water resulted quite similar to the corresponding values recorded for Peschiera water although the two aqueous matrices had different levels of not-purgeable organic compounds (NPOC) as shown in Tables 1 and 2. This suggests that the production of odorous and/or tasty disinfection by-products was

Table 4. Maximum concentration of compounds tested by panelists (concentration level = 6).

| Chemicals                     |                    | Bracciano water |        | Peschiera water |        |
|-------------------------------|--------------------|-----------------|--------|-----------------|--------|
|                               |                    | Odor            | Flavor | Odor            | Flavor |
| PAA                           | mg L <sup>-1</sup> | 40              | 40     | 40              | 40     |
| NaClO                         | mg L <sup>-1</sup> | 0.2             | 1.6    | 0.2             | 0.8    |
| H <sub>2</sub> O <sub>2</sub> | g L <sup>-1</sup>  | 6.7             | 0.4    | 13.3            | 0.8    |
| AA                            | mg L <sup>-1</sup> | 60              | 120    | 120             | 240    |



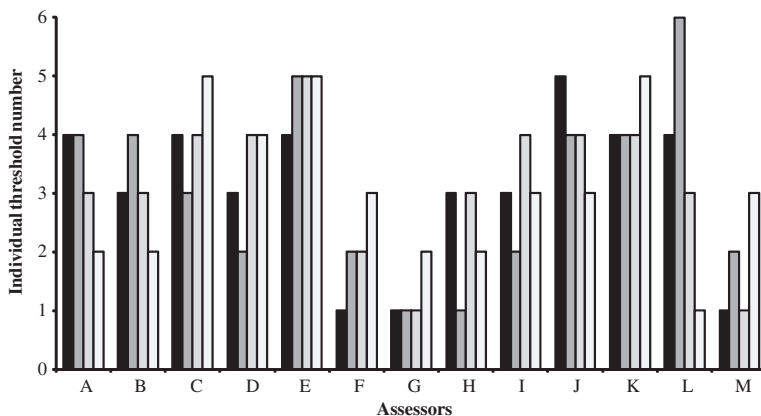


Figure 1. Example of individual threshold numbers of PAA (■), NaClO (■), H<sub>2</sub>O<sub>2</sub> (■), and AA (□) obtained during unforced choice tests: Flavor trends for chemicals in Peschiera water.

negligible during the time elapsed between the preparation of test dilutions and their assessment (10–15 min on the whole). In addition, NOM in Bracciano surface water did not mask or alter flavor perceptions of the two disinfectants despite its strong earthy-musty taste. The latter finding was completely unexpected as it contrasts sharply with the results acquired by Piriou et al. (2004). Indeed, they observed an antagonist positive shift of chlorine flavor threshold as the NOM background taste was increasing. On the basis of these evidences, data acquired for the two aqueous matrices by means of forced and unforced choices were combined into a general mean per tested compound and sensorial assessment (Table 5).

A threshold value of  $0.23 \pm 0.02 \text{ mg L}^{-1}$  was found for chlorine flavor. This result agrees with the range  $0.25\text{--}0.30 \text{ mg L}^{-1}$  reported by Krasner and Barrett (1984) and with the value of  $0.20 \pm 0.05 \text{ mg L}^{-1}$  found by Piriou et al. (2004) using untrained panelists. However, it is significantly different from the threshold concentration of  $0.05 \pm 0.02 \text{ mg L}^{-1}$  detected by a French well-trained panelist (Piriou et al. 2004) and from the sensitivity limit of  $0.8 \text{ mg L}^{-1}$  shown by the average American population (Mackey et al. 2004). The latter strong discrepancy is probably due to high residuals of chlorine (near  $1.0 \text{ mg L}^{-1}$ ) in drinking waters distributed in US (Piriou et al. 2004) compared to those present in European potable waters ( $0.1\text{--}0.2 \text{ mg L}^{-1}$ , on average), which determine a considerable drop in perception sensitivity.

In the present study, the average odor threshold for chlorine in water ( $0.04 \pm 0.01 \text{ mg L}^{-1}$ ) was statistically less than the corresponding data currently available in literature. In this connection, a study by Krasner and Barrett (1984) suggested an odor threshold of  $0.28\text{--}0.36 \text{ mg L}^{-1}$ , while the Australian National Health and Medical Research Council reported a concentration of  $0.6 \text{ mg L}^{-1}$  (Australian NHMRC 2004). It is evident that there is a wide variability in chlorine odor threshold, probably depending on individual sensitivities.

As regards PAA, threshold concentrations of  $6 \pm 1 \text{ mg L}^{-1}$  and  $11 \pm 1 \text{ mg L}^{-1}$  were obtained for odor and flavors, respectively. To date no reference values are available from the scientific literature for comparison with our findings.

It is interesting to note that organoleptic changes produced by NaClO are clearly more intense than those induced by PAA. In particular, disinfectant odor and taste



Table 5. Threshold odor and flavor concentrations<sup>a</sup> of tested compounds in Bracciano and Peschiera waters.

| Chemicals                     | Parameter | Bracciano water |       |       |                 |       |       | Peschiera water |       |       |                 |      |       |      |      |
|-------------------------------|-----------|-----------------|-------|-------|-----------------|-------|-------|-----------------|-------|-------|-----------------|------|-------|------|------|
|                               |           | Forced choice   |       |       | Unforced choice |       |       | Forced choice   |       |       | Unforced choice |      |       |      |      |
|                               |           | choice          | Mean  | SE    | choice          | Mean  | SE    | choice          | Mean  | SE    | choice          | Mean | SE    |      |      |
| NaClO                         | Odor      | 0.04            | 0.06  | 0.01  | 0.05            | 0.01  | 0.03  | 0.03            | 0.04  | 0.01  | 0.05            | 0.04 | 0.01  | 0.04 | 0.01 |
|                               | Flavor    | 0.21            | 0.28  | 0.03  | 0.25            | 0.03  | 0.19  | 0.25            | 0.22  | 0.03  | 0.25            | 0.23 | 0.03  | 0.23 | 0.02 |
| PAA                           | Odor      | 5               | 7     | 1     | 6               | 1     | 5     | 8               | 6     | 2     | 8               | 6    | 2     | 6    | 1    |
|                               | Flavor    | 10              | 13    | 2     | 12              | 2     | 7     | 12              | 10    | 3     | 12              | 11   | 3     | 11   | 1    |
| AA                            | Odor      | 10              | 18    | 4     | 14              | 4     | 14    | 18              | 16    | 2     | 18              | 15   | 2     | 15   | 2    |
|                               | Flavor    | 26              | 49    | 11    | 37              | 11    | 56    | 69              | 62    | 6     | 69              | 50   | 6     | 50   | 9    |
| H <sub>2</sub> O <sub>2</sub> | Odor      | 0.9             | 1.1   | 0.1   | 1.0             | 0.1   | 1.4   | 1.6             | 1.5   | 0.1   | 1.6             | 1.2  | 0.1   | 1.2  | 0.2  |
|                               | Flavor    | 0.093           | 0.087 | 0.003 | 0.090           | 0.003 | 0.132 | 0.141           | 0.137 | 0.005 | 0.141           | 0.11 | 0.005 | 0.11 | 0.01 |

Notes: <sup>a</sup>NaClO, PAA, and AA threshold concentrations in mg L<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub> threshold concentration in g L<sup>-1</sup>.

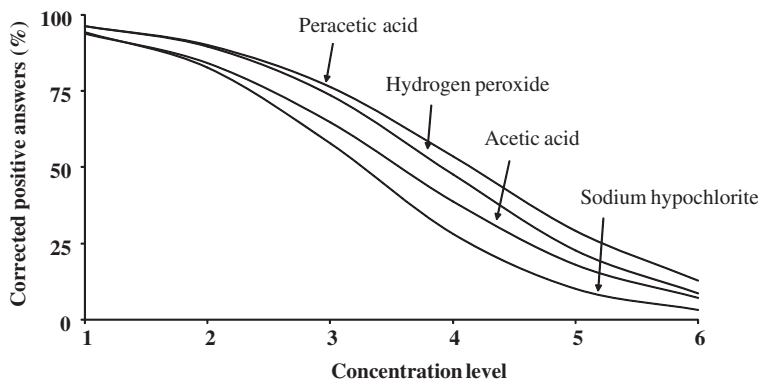


Figure 2. Example of corrected positive answers vs. concentration levels of PAA, NaClO, H<sub>2</sub>O<sub>2</sub>, and AA obtained during forced choice tests: Odor trends for chemicals in Bracciano water.

become detectable when NaClO concentration is, respectively, 150 and 50 times less than PAA concentration. Moreover, the alterations produced by the latter are not influenced by the concomitant presence of H<sub>2</sub>O<sub>2</sub> and AA as their threshold concentrations are significantly higher (Table 5).

In a previous research, some authors of the present article compared PAA with NaClO actions on seven microorganisms (Veschetti et al. 2003). The obtained results showed that PAA dosage should be eight times as big as NaClO concentration to reduce the most resistant microorganism in the study to 10% of its initial population. This means that it would be necessary to reach a residual concentration of 0.8–1.6 mg L<sup>-1</sup> for PAA to obtain a biocide effect equivalent to 0.1–0.2 mg L<sup>-1</sup> of chlorine. Such a concentration range is sufficiently below the threshold values of PAA odor and flavor. Moreover, no high-level production of dangerous by-products has so far been detected (Booth and Lester 1995; Veschetti et al. 2003) when PAA has been used as water disinfectant. At the moment, the only drawback is its unit cost, which is approximately three times higher than NaClO cost. In the near future, it will be necessary to seek possible interactions between water containing PAA residuals and construction products installed in distribution systems in order to evaluate technological and toxicological effects.

## Conclusions

No significant differences were detected between the threshold concentrations of each examined compound in the two aqueous matrices. NaClO was perceived much more strongly than PAA (TON: 0.04 and 6 mg L<sup>-1</sup>, respectively; TFN: 0.23 and 11 mg L<sup>-1</sup>, respectively). The two chemicals which are present in PAA (i.e., AA and H<sub>2</sub>O<sub>2</sub>) did not contribute considerably to the organoleptic properties of the two waters disinfected with PAA. The use of the latter could eliminate nasty odors and tastes imparted to drinking water by residual free chlorine at 0.2 mg L<sup>-1</sup> level.

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