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# The occurrence of haloanisoles as an emerging odorant in municipal tap water of typical cities in China

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ABSTRACT

In this study, occurrence of the haloanisoles odorous compounds in tap water of Chinese cities, were investigated by solid-phase microextraction (SPME)-GC/MS analysis. This study revealed the occurrence of four kinds of haloanisoles in 22 cities of China in both summer and winter. Except 2,4,6-tribromoanisole (2,4,6-TBA), all studied haloanisoles showed higher frequency of detection. 2,3,6-Trichloroanisole (2,3,6-TCA) and 2,3,4-trichloroanisole (2,3,4-TCA) showed higher occurrence concentration; however, the relative odor values of them was lower. These values of 2,4,6-TBA and 2,4,6-trichloroanisole (2,4,6-TCA) in all samples were greater than zero in both summer and winter, indicating the odor from haloanisoles could be felt by human noise. This study further showed that Beijing exhibited most serious occurrence of haloanisoles that were depended on the season and drinking water distribution system (country and city). From this study, it was confirmed that haloanisoles was important taste and odor compounds in tap water of China. Based on the survey of occurrence of halophenol and residual chlorine, the possible source for the formation of haloanisoles in tap water was discussed. Furthermore, several suggestions on control the haloanisoles odor in drinking water treatment plant and water distribution system were provided.



## 1. Introduction

Taste and odours (T&O) in source water or drinking water have become an enhancing and universal problem (Zamyadi et al., 2015). The existing of T&O arises people's complaints on water quality for reducing the aesthetic aspect (Dietrich et al., 2014). Along with the improved living standard, the requirement of water quality also rises, including T&O and emerging pollutants. Generally, the typical T&O compounds in drinking water are 2-methyloisoborneol, geosmin, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine, which can produce earthy-musty odor (Wang et al., 2015b). Moreover, β-cyclocitral and β-ionone raise woody odor in algae bloom water environment (Antonopoulou et al., 2014). These odorant compounds produced by algae or microorganisms, mainly exposed in surface water including river (Wert et al., 2014), lake and reservoir (Su et al., 2015). However, some T&O compounds cannot be related to the classical algae metabolites, but are generated in water distribution system. According to an American survey, 65% of 300 water utilities reported that the distribution system is the main source of T&O problems (Brownlee et al., 2007). T&O from distribution system can mainly be subdivided into two categories: (1) T&O compounds that are leached and corrosion from pipes and sanitary installations can impart flavors to the tap-water (Heim and Dietrich, 2007), which contributed 37% problems; (2) the microbial activity in the distribution system (biofilms) can lead to the formation of a variety of T&O compounds, which contributed 40% problems (Piriou et al., 2007); (3) a third group caused by other unknown reason contributed about 23%. Much attention was drawn to haloanisoles as new odorants, because of the lower odour threshold concentrations (OTCs) (shown in Table 1) (McDonald et al., 2009), compared with the regular T&O compounds, such as 2-methyloisoborneol and geosmin. The relative importance of haloanisoles in earthy-musty off-flavors cases was pointed out, as it caused about 62% of the examined cases (Malleret et al., 2003). Most studies focused on the analysis method

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**Table 1**
Odorant properties and QA/QC for the analysis method of haloanisoles.

| Compounds | Abbreviation | Odour/Taste threshold (ng/L) in previous publication (McDonald et al., 2009) | Selected monitoring ions in GC-MS analysis method of this study | Method detection limit (MDL, ng/L) | Relative standard deviation from twelve measurement (RSD, %) | Detection frequency (%) in winter/summer | Frequency (%) the relative threshold values over 1.0 in winter/summer |
|---|---|---|---|---|---|---|---|
| 2,4,6-Trichloroanisole | 2,4,6-TCA | 0.03 | 167, 195, 210 | 0.098 | 2.79 | 77.5/93.8 | 100/100 |
| 2,3,6-Trichloroanisole | 2,3,6-TCA | 7.0 | 167, 169, 210 | 0.127 | 5.94 | 95.0/96.9 | 7.89/25.81 |
| 2,3,4-Trichloroanisole | 2,3,4-TCA | 5.0 | 197, 210, 212 | 0.109 | 4.24 | 87.5/100.0 | 2.86/3.13 |
| 2,4,6-Tribromoanisole | 2,4,6-TBA | 0.03 | 344, 346, 329 | 0.086 | 7.40 | 5.0/93.8 | 100/100 |

development of haloanisoles in drinking water or tap water (Ma et al., 2012). The formation of haloanisoles were found in tap water, including chloroanisole, bromoanisole and chloro-bromoanisole (Maggi et al., 2008; Maillet et al., 2009; Peter and von Gunten, 2009), and the concentration was reported from 6.27 to 23.6 ng/L in different county with different water sources. In recent, research found that the biological process in wastewater treatment would form haloanisoles, leading to the occurrence in effluent of wastewater treatment plant (Urase and Sasaki, 2013) or the reclaimed water (Agus et al., 2011). Generally, there was three kinds source for the formation of haloanisoles in aqueous environment: (1) biotransformation of halophenol by actinomycetes (Zaitlin and Watson, 2006) and fungi (Urase and Sasaki, 2013) at the presence of halophenol in water distribution system or biological treatment process of wastewater, releasing to accepted water body such as surface water or reclaimed water, respectively; (2) biotransformation by biofilm in waterworks from halophenol as a regular disinfection by-products (DBPs) (Benanou et al., 2003; Copete et al., 2009); (3) the presence of materials of pipeline such as polyethylene that would provide the precursor (Maillet et al., 2009). To satisfy the users' requirement, several drinking water treatment method and advanced reclaimed water treatment was employed (Wang et al., 2015a), such as powder active carbon adsorption, ozonation, membrane filtration and UV based advanced oxidation process. However, the occurrence of T&O including haloanisoles in the municipal tap water was ignored. These T&O compounds generated in distribution systems showed more serious problem to water utilities than the algal or microorganisms source T&O compounds that could be removed by the drinking water treatment or the advanced method, because the respective T&O compounds cannot be retained through water treatment, but are directly delivered to the customers without any treatment technology (Proulx et al., 2007). In these cases, it is of utmost importance to identify these compounds that cause problems and also track their origins and formation mechanism. Based on this, some technology, design method or management strategy could be employed to remove the precursor of these T&O or prevent the formation in distribution system. In China, the research on T&O was carried out recently, only limiting on earth-musty odor (Sun et al., 2014) and T&O compounds containing sulfur (Guo et al., 2015). Only less publication was focused on the occurrence of haloanisoles in tap water (Chen et al., 2013) and limited on 2,4,6-TCA. In this study, the aims are identifying the occurrence of haloanisoles in municipal tap-water in typical cities of China and evaluating the variation of haloanisoles during several months in Beijing as the capital of China.

## 2. Materials and methods

### 2.1. Chemicals

The mixed standard of the four typical haloanisoles (2,4,6-trichloroanisole, 2,3,6-trichloroanisole, 2,3,4-trichloroanisole, 2,4,6-tribromoanisole) in methanol was purchased from Sigma-Aldrich (USA) as 1.0 μg/mL for each compound and was stored in −4 °C. Stock solutions were prepared in Milli-Q water at the scene. Sodium chloride used in extraction of haloanisoles was reagent grade after calcination at 450 °C in muffle oven for 4 h.

### 2.2. Sample site and collection

Samples from the municipal tap water over 22 cities in China were collected in winter and summer. 80 samples were collected on 40 sites (two samples at one site as the parallels) in Jan. 2011 as winter samples, and 64 samples were collected on 32 sites (two samples at one site) in Aug. 2011 as summer samples. The sampling distribution was shown in Table 2. All water samples in this study were collected from the outlet of the residence water taps directly to avoid the emission of haloanisoles. During sampling, samples of the first 5 min were abnegated to avoid the effect of residual impurity. Each integrated water sample was mixture of three subsamples that were collected at 8:00, 14:00 and 20:00 in one day, after each sampling obtained the dechlorination reagents was added to quench the residual chlorine. Duplicate water sample were collected in 100 mL narrow necked glass bottles, leaving no headspace to avoid the volatilization, stored immediately in a portable refrigerator at about 4 °C until being analyzed. A detailed study was carried out in Beijing city that exhibited more serious occurrence of haloanisoles in tap water all over China. Four sites were set up, in which 2 sites were sited in city, the other 2 sites were located in a country nearby this city. Samples collected from the city were supplied by a water distribution system; samples collected from the country were only supplied from a well as source of underground water. The municipal tap water was obtained after enhanced drinking water treatment (reservoir-coagulation- sediment-ozonation- activated carbon-sand filtration-chlorination- city distribution system). Country samples of two user located in Beijing Country were collected at the outlet of tap directly. The source water of this country sample was underground water. After being intaked, raw water was treated by sand filtration and chlorination, and distributed to users by a small distribution system. The survey study lasted for six months (one sampling per months, from July to Dec.) to discuss the variation of the occurrence concentration of haloanisoles. Duplicate water samples were collected as the above method, but were analyzed in 24 h.

### 2.3. Sample preparation and analysis for haloanisoles

Water sample (50 mL) was filtered through a fiberglass filter (0.22 μm). After that, the filtrate was analyzed for haloanisoles in the samples. PDMS/DVB/CAB fibre (Supelco, USA) was chosen for solid phase microextraction (SPME) (Watson et al., 2008). In