調べるため実験を行った。無臭水に臭気物質（トリクロラミン、ジェオスミン）を一定量加えた2種類の検体の臭気強度を測定した。パネルの人数は6人とした。希釈倍数は、3倍・10倍・30倍・100倍・300倍・1000倍で各パネルが無臭の判定（直接法）又は不正解（三点比較法）を出すまで実施した。1週間後に同一パネルに対して、同一の手順で作成した検体を用いて試験を実施し、測定値の変動を調べた。

3．2　水道水の臭気の測定

ある都市の同一配水区域内の10地点（a～j）から水道水を採取し、各地点同一の3人のパネルを用いて臭気強度を三点比較法（同一希釈倍数で2回試験を行い、2回とも的中で正解）により測定した。測定は、残留塩素を除去せずに行った。同時に、遊離塩素、トリクロラミン等の濃度をDPD/FAS法により測定した。

4．結果及び考察

4．1　人工付臭水を用いた実験

各パネル（A～E）の直接法と三点比較法の臭気強度の測定値（対数値）の比較を図1から図4に示す。また、同一パネルに対して1週間の間隔をおいて測定を行った際の初日と1週間後の測定値の比較を図5から図8に示す。表2には、臭気強度の対数値（平均）の差及び測定値に差異があった人数を整理した。直接法と三点比較法による臭気強度測定値（6人の平均値）の差異をみたところ、統計的には有意ではなかったが、計4回（2種類の検体・2日間）の測定において3人以上で直接法と三点比較法の結果が異なっており、特に初日のジェオスミンの測定では6人全員で異なっており、直接法では臭気の有無を判定するのに限界があることを示唆した。2回の測定における臭気強度の測定値の変化をみたところ、統計的に有意ではなかったが、直接法に比べ、三点比較法では、臭気強度の対数値（平均）の変化も小さく（0及び0.08）、測定値に変動があった人数も少なかった（2人及び3人）。

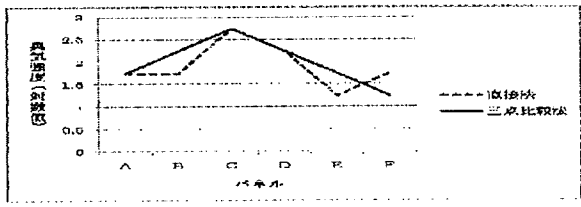

図1　直接法と三点比較法による臭気強度（初日・ﾄﾘｸﾛﾗﾐﾝ）

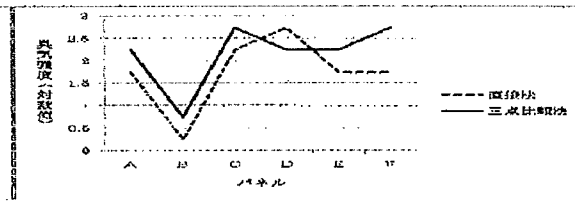

図2　直接法と三点比較法による臭気強度（初日・ｼﾞｪｵｽﾐﾝ）

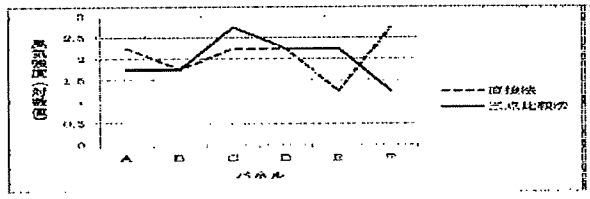

図3　直接法と三点比較法による臭気強度（1週間後・ﾄﾘｸﾛﾗﾐﾝ）

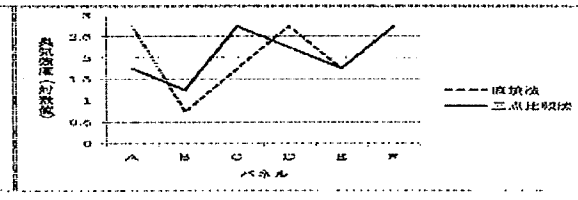

図4　直接法と三点比較法による臭気強度（1週間後・ｼﾞｪｵｽﾐﾝ）

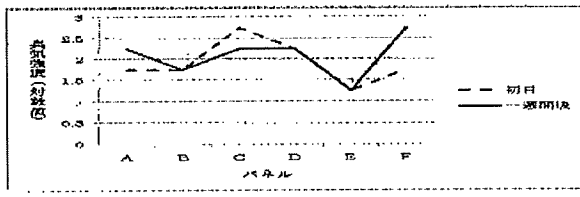

図5　臭気強度測定値の変化（直接法・ﾄﾘｸﾛﾗﾐﾝ）

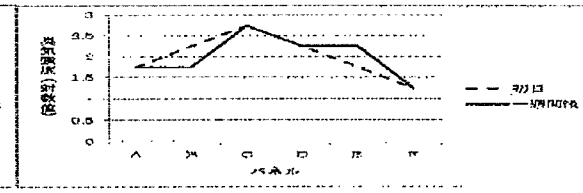

図6　臭気強度測定値の変化（三点比較法・ﾄﾘｸﾛﾗﾐﾝ）

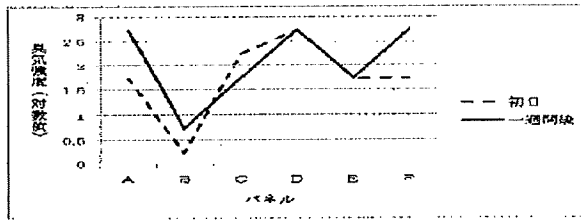

図7　臭気強度測定値の変化（直接法・ｼﾞｪｵｽﾐﾝ）

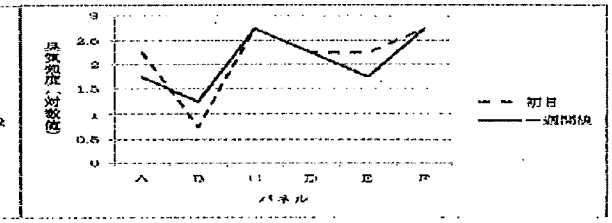

図8　臭気強度測定値の変化（三点比較法・ｼﾞｪｵｽﾐﾝ）

表2 臭気強度の対数値（平均）の差及び測定値に差異があった人数

	臭気強度の対数値(平均)の差	測定値に差異があった人数		臭気強度の対数値(平均)の差	測定値に差異があった人数
【直接法と三点比較法による臭気強度測定値の差異】					
初日・ﾄﾘｸﾛﾗﾐﾝ	0.08	3人	初日・ｼﾞｪｵｽﾐﾝ	0.41	6人
1週間後・ﾄﾘｸﾛﾗﾐﾝ	0.08	4人	1週間後・ｼﾞｪｵｽﾐﾝ	0	4人
【2回の測定における臭気強度測定値の変化】					
直接法・ﾄﾘｸﾛﾗﾐﾝ	0.17	3人	三点比較法・ﾄﾘｸﾛﾗﾐﾝ	0	2人
直接法・ｼﾞｪｵｽﾐﾝ	0.33	4人	三点比較法・ｼﾞｪｵｽﾐﾝ	0.08	3人

4．2 水道水の臭気の測定

10地点（a～j）の臭気強度、トリクロラミン等の測定結果を表3に示す。臭気強度（対数値）と他の測定項目の相関係数を求めたところ、トリクロラミンは0.76、遊離塩素は0.48で、他は負の値であった。

表3 各地点における臭気強度等の測定値

地点	a	b	c	d	e	f	g	h	i	j
遊離塩素	0.36	0.26	0.35	0.31	0.15	0.27	0.29	0.26	0.07	0.10
ﾓﾉｸﾛﾗﾐﾝ	0.05	0.06	0.05	0.05	0.06	0.04	0.06	0.06	0.05	0.06
ｼﾞｸﾛﾗﾐﾝ	0.02	0.04	0.03	0.02	0.06	0.03	0.03	0.03	0.04	0.04
ﾄﾘｸﾛﾗﾐﾝ	0.15	0.12	0.15	0.13	0.11	0.14	0.10	0.13	0.09	0.10
臭気強度	32	15	68	15	7	32	7	15	15	15

5．結論

本研究では、水道水の臭気の測定を定量的、客観的、安定的に実施するため、三点比較法の適用を目指して理論的考察、測定値の安定性に関する実験、実際の水道水の臭気の測定を行った。その結果、得られた主要な知見を以下に記す。

1) 三点比較法により複数のパネルで臭気強度を測定する場合、偶然の正解により測定値が本来の結果からずれてしまう確率は負の二項分布を示し、各パネルの平均に標準偏差を加えた数値を0.5未満とするためには、各希釈倍数の測定において1回の的中を正解とみなす方法ではその目標を満たすことはできず、2回の的中を正解とみなしパネルの人数を2人以上とすることが必要である。

2) 人工的にトリクロラミン、ジェオスミンで付臭した検体について、1週間の間隔をおいて同一パネルで三点比較法を用いた場合と用いない場合（直接法）で差をみたところ、計4回（2種類の検体×2日間）の測定において毎回3人以上で直接法と三点比較法の結果が異なっており、特に初日のジェオスミンの測定では6人全員で異なっており、直接法における臭気の有無の判定の限界を示唆した。1週間の間隔をおいて行った測定における臭気強度の測定値の変化をみたところ、直接法に比べ、三点比較法では、臭気強度の対数値（平均）の変化も小さく、測定値に変動があった人数も少なかった。

3) 三点比較法を用いて実際の水道水の臭気強度を測定したところ、同時に測定したトリクロラミン濃度とも高い相関のある測定値が得られ、実用性を裏付ける結果となった。

今後は、上水試験方法の臭気強度の測定方法に三点比較法を適用した場合の実験等を行い、三点比較法を用いた水道水の臭気の測定方法の確立を目指す予定である。

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Submicron-sized activated carbon particles for the rapid removal of chlorinous and earthy-musty compounds

Yoshihiko Matsui, Kenji Murai, Hiroshi Sasaki, Koichi Ohno and Taku Matsushita

ABSTRACT

Submicron-sized powdered activated carbon (PAC) was produced from a commercially available normal PAC by a bead mill. The submicron PAC decomposed dichloramine and nitrogen trichloride, impairing aesthetic quality with chlorinous odor, at a much faster rate than did normal PAC. Moreover, decomposition rates were faster for dichloramine and nitrogen trichloride than for monochloramine and free chlorine. Selective removal of chlorinous odors among chlorine compounds in a short time was thereby possible. The earthy–musty compound geosmin was also much more rapidly removed by adsorption on submicron PAC than on normal PAC. The increased removal rate was partly due to the adsorption capacity increase owing to the particle size reduction of PAC to submicron range, which accounted for 40% of the improvement of geosmin removal at a PAC contact time of 10 min.

Key words | adsorption, drinking water, flavor, particles

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INTRODUCTION

Adverse tastes and odors at the tap are the leading causes of consumer complaints and dissatisfaction with drinking water. Some of these tastes and odors are caused by chemical agents used for water treatment, such as chlorine (White 1999). Chlorine is sometimes added as a prechlorination agent to decompose ammonia, oxidize iron and manganese, and prevent algal growth in water treatment facilities. However, it often produces dichloramine and nitrogen trichloride, which have much greater chlorinous odors than does free chlorine. Naturally occurring compounds, such as geosmin, also impair aesthetic quality. These compounds are produced by cyanobacteria and add earthy and musty odors to water.

Adsorption by powdered activated carbon (PAC) is regarded as one of the best available technologies for removing dissolved contaminants such as taste-and-odor compounds from raw water in drinking water production. However, the adsorption capacity of PAC is not fully utilized because of slow uptake of adsorbates (slow adsorption kinetics). Although activated carbon decomposes dichloramine and nitrogen trichloride (Sontheimer *et al.* 1988), its application in removing these compounds has been limited. This could be also due to the slow decomposition kinetics, which previously rendered this use of activated carbon impractical.

Although PAC particles of smaller sizes would overcome the problems of slow adsorption and decomposition kinetics, the particle size of available PAC was previously limited to about 5 μm. However, recent advancements in nanotechnology enable pulverization of particles down to submicron and nanometre size ranges with reasonable costs. Membrane filtration technology should take advantage of the improved adsorption and decomposition capabilities of such fine particles in water and wastewater treatment (Matsui *et al.* 2005, 2006). In this study, we ground manufacturer-supplied PAC in a bead mill to produce submicron-sized PAC particles (less than 1.0 μm median diameter). We investigated the ability of the submicron PAC particles to decompose dichloramine and nitrogen trichloride and to adsorb geosmin.

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METHODS

A thermally activated wood-based PAC (Shirasagi, Japan EnviroChemicals, Ltd., Osaka, Japan) was obtained from its manufacturers. Submicron PACs were obtained by grinding this normal PACs in a bead mill. Particle-size distributions of PACs were determined using laser-light-scattering instruments (LMS-30; Seishin Enterprise Co., Ltd., Tokyo, Japan; Microtrac HRA; Nikkiso Co., Ltd., Tokyo, Japan), and nitrogen gas adsorption and mercury intrusion porosimetry were used to measure pore size distributions in the PAC particles (Prosorp VAS-3000, Seishin Enterprise Co., Ltd., Tokyo, Japan; Porosimeter 200; Carlo Erba, Milan, Italy).

Geosmin solution was prepared by diluting geosmin-MeOH liquid (Supelco, Sigma Aldrich Japan, Tokyo, Japan) with water. The solution was diluted to concentrations of 100 ngL^{-1} before use. Batch kinetic tests were conducted with efficient mixing in a stainless steel rectangular container containing 5 L of the solution. After addition of a certain amount of PAC, samples were withdrawn at intervals and filtered immediately through a 0.22-μm membrane filter for concentration analysis. The bottle-point technique was used to determine adsorption isotherms of geosmin. Sample waters (150 ml) containing PAC were transferred to 160-ml vials from 3-L solution and the vials were agitated on a shaker for 1 week. The liquid-phase concentrations were measured by filtering the water samples through a 0.22-μm membrane filter. The amount of geosmin adsorbed per unit mass of PAC (solid-phase concentration) was determined according to the mass balance equation. The concentrations of geosmin were analyzed with TDS- (Thermal Desorption System-) GC/MS and SBSE (Stir Bar Sorptive Extraction) methods (GERSTEL K.K., Tokyo, Japan; Agilent Technologies Japan, Tokyo, Japan).

Chloramine solutions were prepared by the batch aqueous reaction of sodium hypochlorite and ammonium (reagent grade chemicals, Wako Pure Chemical Industries, Ltd., Osaka, Japan) in a 3-L cylindrical glass beaker and then divided into 1-L solutions for activated carbon experiments. Monochloramine, dichloramine, and nitrogen trichloride were each dominantly formed at a different sodium hypochlorite/ammonium concentration ratio (Cl_2/NH_3—N ratio): concentrations of ammonia and sodium hypochlorite (as chlorine) and reaction temperature are described in "Results and Discussion" and figures. The concentrations of free chlorine, monochloramine, dichloramine, and nitrogen trichloride were separately analyzed by the diethyl-*p*-phenylenediamine method according to *Standard Methods for the Examination of Water and Wastewater* (2005).

RESULTS AND DISCUSSION

PAC particle-size distribution

The size distributions of the PAC particles revealed that the pulverized PAC had an effective particle size of 0.27 μm and a median size of 0.77 μm; 65% by volume of PAC particles were smaller than 1 μm (Figure 1).

Removal of chlorinous compounds

Chlorinous odor is caused by free chlorine and notably chloramine. Among chloramine compounds, nitrogen trichloride causes the strongest chlorinous odor, followed by dichloramine and monochloramine. The chloramine compounds were produced by the oxidation reaction of ammonia with hypochlorous acid, and the type of the prevailing chloramine compound formed was determined depending on reaction conditions including Cl_2/NH_3 ratio, pH, and temperature. In the experiment with dichloramine, which causes strong chlorinous odor, dichloramine was

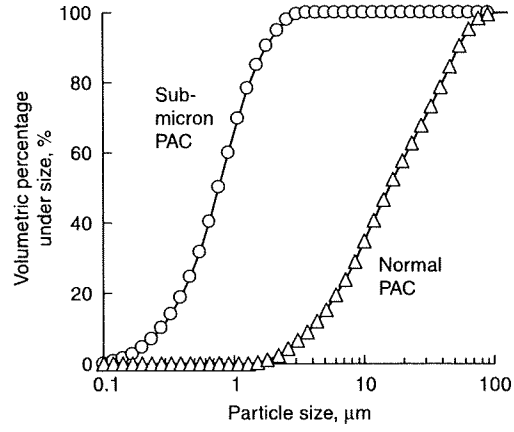

Figure 1 | Size distributions of PAC particles before and after grinding.

formed as the predominant and stable product among chloramines by the reaction condition of Cl_2/NH_3—N ratio of 9.6 at pH 6.7 and 5°C (a small but nonnegligible dichloramine decrease owing to natural decomposition was observed at 20°C, and therefore the dichloramine experiment was conducted at 5°C). After 20 min of the chlorine–ammonia reaction, 5 mg L^{-1} of normal PAC was added to the solution, and the dichloramine concentration decreased gradually over the following 60 min (Figure 2). On the other hand, very fast reduction of dichloramine was observed when 4.9 mg L^{-1} of submicron PAC was added (Figure 3). Even though we used the same dosage of submicron PAC as of normal PAC, the dichloramine concentration dropped by 90% in 10 min and chloramine was not detected 20 min after the PAC addition. Ammonia concentration was 1.0 mg L^{-1}-N before the chlorine–ammonia reaction, but ammonia was not detected above the detection limit of 0.02 mg L^{-1}-N when the dichloramine concentration dropped to almost zero after the PAC addition. This result suggests that dichloramine was converted to nitrogen gas and chloride, but not converted back to ammonia (Bauer & Snoeyink 1973). A very small portion of dichloramine could have been converted to free chlorine, as suggested by Figures 3 and 4, which show that free chlorine concentration increased when dichloramine concentration decreased. When dichloramine concentration dropped to zero at 40 min time (Figure 3), free chlorine concentration started to decrease. However, the rate of decrease seems to be slower than that of dichloramine.

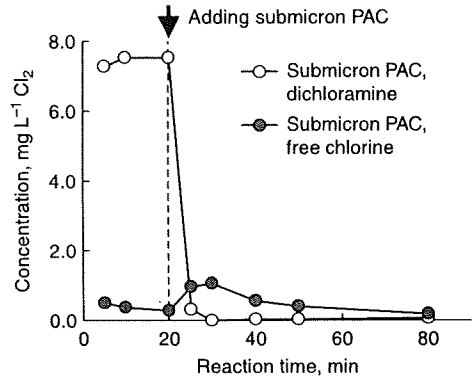

Figure 3 | Dichloramine concentration decay by addition of 4.9 mg L^{-1} of submicron PAC. Dichloramine was formed in the reaction of anmonia (1 mg L^{-1} as N) and sodium hypochlorite (9.6 mg L^{-1} as Cl_2) at 5°C, and the submicron PAC was added after 20 minutes of the reaction.

Next, monochloramine, which does not strongly impart chlorinous taste and odor, was produced as a dominant chloramine product after liquid sodium hypochlorite was added to ammonia solution (1 mg-NL^{-1}) at a Cl_2/NH_3—N ratio of 5, pH 7, and room temperature (20°C). After 30 min of the reaction, during which the stability of monochloramine concentration was confirmed, submicron PAC was added to the monochloramine solution, but the monochloramine concentration did not change (Figure 4).

Next, we conducted a decomposition experiment of nitrogen trichloride, the most chlorinous-odor-causing

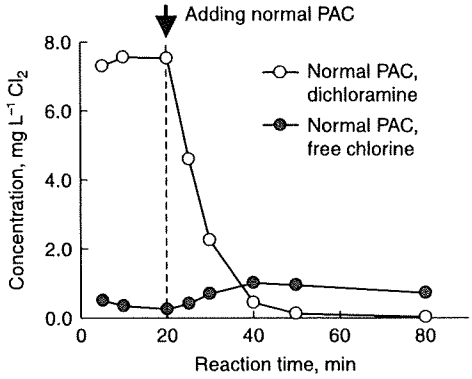

Figure 2 | Dichloramine concentration decay by addition of 5 mg L^{-1} of normal PAC. Dichloramine was formed in the reaction of anmonia (1 mg L^{-1} as N) and sodium hypochlorite (9.6 mg L^{-1} as Cl_2) at 5°C, and the normal PAC was added after 20 minutes of the reaction.

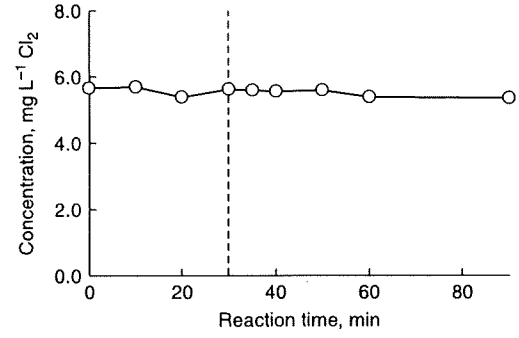

Figure 4 | Change of monochloramine concentration. Submicron PAC was added at 30 min time for a final concentration of 5.1 mg L^{-1}. Monochloramine was formed in the reaction of anmonia (1 mg L^{-1} as N) and sodium hypochlorite (5 mg L^{-1} as Cl_2) at a room temperature (about 20°C), and the submicron PAC was added after 30 minutes of the reaction.

compound. Nitrogen trichloride was formed at a high Cl_2/NH_3—N ratio, but the concentration of nitrogen trichloride at a neutral pH was very low and the concentration was unstable owing to natural decomposition (in practice, nitrogen trichloride causes perceptible chlorinous odor even at such low concentration). Therefore, in the experiment, nitrogen trichloride was formed as a dominant chloramine species with a stable form with reaction conditions of pH 3, 5°C, and a Cl_2/NH_3—N ratio of 12. Nitrogen trichloride was formed at the concentration of $1.44\,mg\,L^{-1}$, while free chlorine beyond the stoichiometric quantities of Cl_2/NH_3—N ratio remained at the concentration of $1.14\,mg\,L^{-1}$. After the submicron PAC addition, nitrogen trichloride decreased faster than free chlorine (Figure 5). It disappeared by 10 min. Nitrogen trichloride decrease was faster after submicron PAC addition than after normal PAC addition (Figure 6).

Figure 7 shows the concentration decay of free chloramine (hypochlorous acid) at pH 6.7 and pH 3.0; the nitrogen trichloride experiment was conducted at these low pH values. Free chloramine concentration also decreased after the S-PAC addition at a faster rate than after normal PAC addition. However, the concentration did not reach close to zero even after 90 min of contact time both for normal and submicron PACs.

In order to compare the concentration decay rate briefly but quantitatively, we described the decay curves by the first order reaction. Table 1 summarizes the decomposition

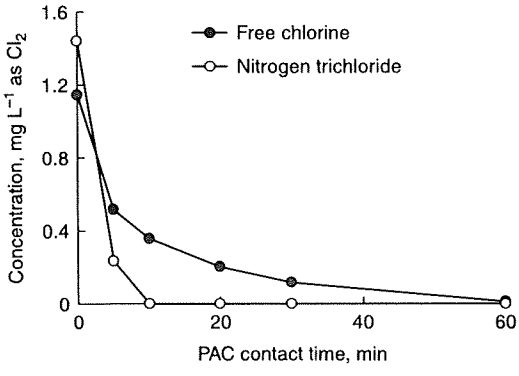

Figure 5 | Concentration changes of free chlorine and nitrogen trichloride after submicron PAC dose (PACs were dosed at zero time). Nitrogen trichloride was formed in the reaction of anmonia ($3\,mg\,L^{-1}$ as N) and sodium hypochlorite ($36\,mg\,L^{-1}$ as Cl_2) at 5°C, and the normal PAC was added after 100 minutes of the reaction (zero time in the *x*-axis) for a final concentration of $5.0\,mg\,L^{-1}$.

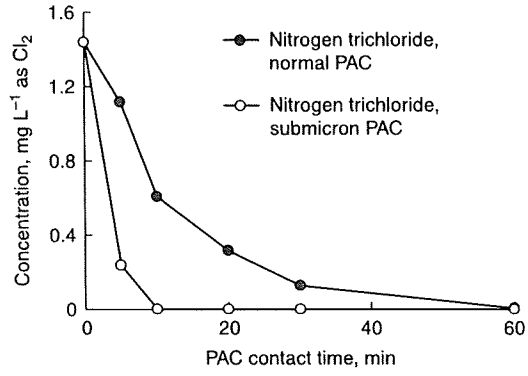

Figure 6 | Concentration change of nitrogen trichloride after PAC dose (PACs were dosed at zero time). Nitrogen trichloride was formed in the reaction of anmonia ($3\,mg\,L^{-1}$ as N) and sodium hypochlorite ($36\,mg\,L^{-1}$ as Cl_2) at 5°C, and the normal and submicron PACs were added after 100 minutes of the reaction (zero time in the *x*-axis) for final concentrations of 5.2 and $5.0\,mg\,L^{-1}$, respectively.

rate constants. For chlorine and chloramines, decay rate constants were in the following order:

nitrogentrichloride ≅ dichloramine > free chlorine

> monochloramine ≅ 0

This order is similar to one previously reported (dichloramine > hypochlorous acid > hypochlorous ion > monochloramine; Snoeyink & Suidan 1975).

Also, the decomposition rate constants of submicron PAC for dichloramine, monochloramine, and free chlorine is two times greater than those of normal PAC, respectively. For nitrogen trichloride, the decomposition rate constant of

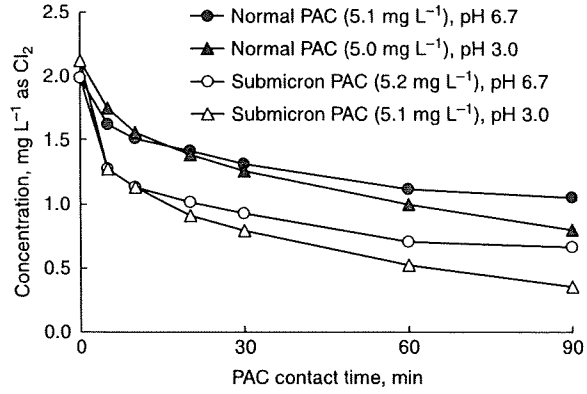

Figure 7 | Concentration change of free chlorine after PAC dose (PACs were dosed at zero time and reaction temperature was 5°C).

Table 1 | Decomposition rate constants

	Normal PAC	Submicron PAC
Nitrogen trichloride, pH 3.0	$2.2\,h^{-1}$	$9.4\,h^{-1}$
Dichloramine	$2.7\,h^{-1}$	$5.5\,h^{-1}$
Monochloramine	$0.0\,h^{-1}$	$0.0\,h^{-1}$
Free chlorine, pH 3.0	$0.32\,h^{-1}$	$0.59\,h^{-1}$
Free chlorine, pH 6.7	$0.23\,h^{-1}$	$0.41\,h^{-1}$

submicron PAC was almost 4 times greater than that of normal PAC. Finally, submicron PAC can quench chlorinous odor compounds, nitrogen trichloride and dichloramine, selectively among free and combined chlorine, and complete decomposition can be achieved in 10 min contact time with a dosage of only $5\,mg\,L^{-1}$.

Removal of earthy-musty compounds

An adsorption kinetic test for geosmin also showed the superiority of submicron PAC particles. The addition of submicron PAC to a geosmin solution decreased the geosmin concentration by more than 95% in 30 min, while normal PAC decreased the concentration by only 20% with the same dosage (Figure 8).

Moreover, an adsorption equilibrium test showed that size reduction of PAC particles by pulverization increased the adsorption capacity of PAC for geosmin. Figure 9 shows

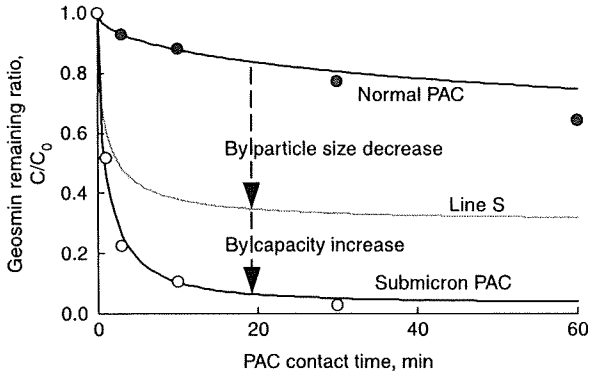

Figure 8 | Effects of particle size on batch adsorption kinetics of geosmin on PAC (initial geosmin concentrations were 104 and $94\,ngL^{-1}$ for normal and submicron PAC experiments, respectively; PAC dosages were $0.6\,mgL^{-1}$). Plots are observed data and lines are simulated by the branched pore adsorption model (surface diffusion coefficient = $4.3 \times 10^{-13}\,cm^2\,s^{-1}$, rate coefficient for mass transfer between macropores and micropore = $6.7 \times 10^{-9}\,s^{-1}$, and fraction of adsorptive capacity available in macropore region = 0.46).

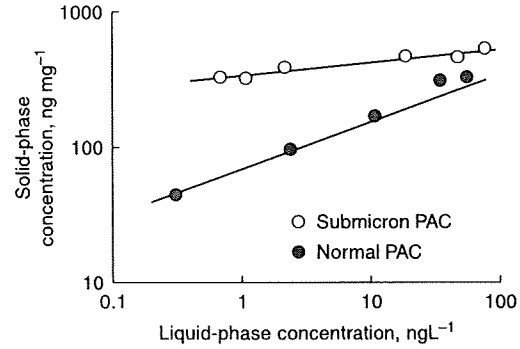

Figure 9 | Effects of particle size on geosmin adsorption isotherm for PAC.

adsorption isotherms of geosmin, in which the adsorption capacity of submicron PAC was higher than that of normal PAC. A similar phenomenon was reported for NOM adsorption on normal and submicron PACs (Matsui *et al.* 2004). Weber *et al.* (1983) reported the particle-size effect of granular activated carbon on NOM adsorption capacity, showing that smaller particles have greater capacity for adsorbing NOM. For low-molecular-weight (-MW) pure chemicals, however, the change of adsorptive capacity owing to carbon particle size has not been reported (Derick & Beckmann 1969; Letterman *et al.* 1974; Peel & Benedek 1980*a*; Najim *et al.* 1990; Matsui *et al.* 2004). The pore-size distribution data explained the adsorption capacity increase for adsorbates of high MW. The lack of adsorption capacity change for low-MW adsorbates showed that the volume of micro-pores, to which small molecules such as phenol (MW 98) adsorb, was not changed after the PAC pulverization produced submicron PAC, while the meso-pore volume for macro-molecule adsorption did increase (Matsui *et al.* 2004). However, geosmin is rather small molecules with MW 182, and the higher adsorption capacity of submicron PAC for these compounds was not explained by the pore-size distribution data. Although we have not yet determined the reason for the increased adsorption capacity, the experimental data clearly show that geosmin can be removed by submicron PAC at much lower dosages and much shorter PAC–water contact times than by normal PAC.

Besides the effect of the adsorption capacity increase, the particle size reduction of PAC should effectively increase its adsorption kinetics because more outer surface area is exposed to bulk water and because the diffusion pathway

from a particle's surface to its centre decreases in size. Therefore, the improvement of geosmin removal at a given PAC contact time should be due to the two effects caused by PAC particle size reduction: equilibrium and kinetic effects. Adsorption kinetic model analysis was conducted to separately evaluate the equilibrium and kinetic effects. We applied a branched pore adsorption model (Peel & Benedek 1980*b*), since normal adsorption kinetic models (homogeneous surface diffusion and pore-surface diffusion models) could not describe the adsorption kinetic data. Changing surface diffusivity (or liquid-filled pore diffusivity) was needed, depending on PAC particle size, to describe the adsorption kinetic data of both submicron and normal PACs.

The branched pore model successfully described the kinetic data of both submicron and normal PACs with the same kinetic parameter values; diffusion coefficient and other model parameters did not change with PAC particle size (Figure 7). Upon the successful application of the model, we conducted model simulation to investigate the equilibrium and kinetic effect. Line S in Figure 8 is a simulated result based on the hypothesis that PAC particle size was reduced but adsorption capacity did not increase (the PAC particle size was that of submicron PAC, but the adsorption isotherm parameter values were those of normal PAC). Therefore, the area between the normal PAC line and Line S represents improvement in geosmin removal owing to the adsorption kinetic effect of PAC particle size, whereas the area between Line S and the submicron PAC line represents improvement in geosmin removal owing to the adsorption capacity effect of PAC particle size. The result revealed that the 60% of improvement in removal percentage was due to the kinetic effect by PAC size reduction, while the remaining 40% was due to the increase in adsorption capacity (Figure 8). Therefore, the improved adsorptive removal resulting from the PAC particle size reduction to submicron range was due to increases in both adsorption capacity and kinetics.

CONCLUSIONS

1. Submicron PAC showed a very fast reaction rate in quenching chlorinous odors due to dichloramine and nitrogen trichloride. Dichloramine and nitrogen trichloride were decomposed, probably to nitrogen gas, in 10 min by submicron PAC at 5 mg L^{-1} dosage. The rates of decomposition by PAC were in the order of nitrogen trichloride ≅ dichloramine > free chlorine > monochloramine ≅ 0, and selective removal of dichloramine and nitrogen trichloride among free and combined chlorines was possible.
2. Submicron PAC showed a very fast adsorptive removal rate for the earthy–musty compounds geosmin. The improved adsorptive removal owing to PAC particle size reduction to submicron range was due to both kinetic and adsorption capacity increases. The former accounted for 60% and the latter 40% of the improvement, according to the branched pore model analysis.

ACKNOWLEDGEMENTS

The authors thank Mr. Toshiaki Tanaka of Tokyo Metropolitan Water Works Bureau, who instructed us in the analysis of chloramine concentrations. This study was partly conducted as a funded research of the Tokyo Metropolitan Water Works Bureau, and was also partially supported by research grants from the Ministry of Health, Labor, and Welfare and the Ministry of Education, Science, Sports, and Culture of the Government of Japan.

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Simultaneous removal of cyanobacteria and an earthy odor compound by a combination of activated carbon adsorption, coagulation, and ceramic microfiltration

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ABSTRACT

Engineers in drinking water treatment plants which employ activated carbon adsorption followed by microfiltration (MF) often ask why the removal ratio of compounds causing musty odors in real plants is smaller than that achieved in laboratory experiments. We investigated whether this difference in removal ratios was due to the release of intracellular geosmin under high pressure from cyanobacteria coexisting on the filter membrane surface. We conducted batch pressurization tests with a cyanobacterium-containing solution, laboratory-scale MF experiments, and pilot-scale experiments designed to remove both the geosmin and cyanobacteria in a hybrid system which used powdered activated carbon adsorption, coagulation, and ceramic microfiltration. Release of intracellular geosmin from cyanobacteria accumulated on the membrane surface was observed in both the laboratory-scale MF experiments and the pilot-scale experiments, but not in the batch pressurization tests. Geosmin was still observed in the MF permeate when the hybrid system was operated with commercially available powdered activated carbon (PAC), and its concentration increased with filtration time owing to the continued release of geosmin. In contrast, operation of the hybrid system with micro-ground PAC completely removed the geosmin.

Key words | cyanobacteria, geosmin, microfiltration, operation pressure

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INTRODUCTION

Consumers sometimes complain of a musty odor or taste in tap water, and the presence of such taints is still a big problem in the field of drinking water treatment. Musty odor and taste are due to the presence of geosmin or 2-methylisoborneol (2-MIB); these compounds are produced mainly by cyanobacteria in lakes or ponds in the upper parts of drinking water catchments and remain in the tap water, although at very low levels (less than $10\,ng\,L^{-1}$). The question of how to remove these compounds from water is of great interest to managers and engineers of drinking water treatment plants.

Powder activated carbon (PAC) adsorption has been applied widely for the removal of compounds causing the musty odor. Membrane technologies have also recently been developed and are now being used in drinking water treatment plants. A technology which combines PAC adsorption with microfiltration (MF) is already being employed in some experimental plants, with excellent results. However, the engineers at these plants often raise the question of why the removal ratio of the musty odor compound in real plants is smaller than that achieved in laboratory experiments. Thus, although the operational parameters used in real plants (e.g., the PAC dose and PAC contact time) are determined from the results of laboratory experiments, the performance of the systems in these plants is sometimes below the expected value.

There are two major differences in conditions between plant operation and laboratory experiments: (1) Whereas

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cyanobacteria are usually present along with the musty odor compounds in the raw water flowing into the plant, laboratory experiments are usually conducted with commercially available reagent chemicals of musty odor compounds in the absence of cyanobacteria. Because the cyanobacteria commonly incorporate musty odor compounds into their structures, under high pressure these intracellular compounds might be released from the cyanobacteria into the water during plant operation. It should be noted that the musty odor compounds have been already known to be released from the cyanobacteria by the addition of oxidative chlorine compounds such as hypochlorous acid (Ashitani *et al.* 1988; Ando *et al.* 1992), and accordingly the prechlorination process could cause the release of the odor compounds into the water. However, the difference in removal ratio of the odor compounds between real plants and laboratory experiments is observed even in the plants in which the prechlorination process is not employed. (2) Whereas musty odor compounds produced by cyanobacteria enter treatment plants, commercially available chemically synthesized musty odor compounds are used in most laboratory experiments. Thus, the adsorption properties of the compounds produced by cyanobacteria might be different from those of the chemically synthesized compounds.

Accordingly, our objectives were to investigate (1) the release of intracellular geosmin from cyanobacteria under high pressure in batch tests; (2) the release of intracellular geosmin from cyanobacteria in laboratory-scale MF operation; (3) the removal of both geosmin and cyanobacteria in pilot-scale experiments by using a hybrid system of PAC adsorption, coagulation, and ceramic MF; and (4) differences in adsorption of natural and chemically synthesized geosmin by PAC in batch tests.

METHODS

Cyanobacteria used

Three types of geosmin-producing cyanobacterium were used. Two of the three cyanobacteria, *Anabaena planktonica* (NIES 817) and *Anabaena smithii* (NIES 824), were provided by the National Institute for Environmental Studies (NIES, Tsukuba, Japan). These cyanobacteria were cultivated in 5-L glass vessels in cefixime and tellurite (CT) medium (Watanabe & Ichimura 1977). The other cyanobacterium, which was identified as *Anabaena* sp., was isolated from Lake Sagami (Yokohama, Japan) and then cultivated in 2-L flasks of CT medium.

Batch pressurization tests

Anabaena smithii in its three different growth phases (logarithmic phase, stationary phase, and decline phase) was used for the batch pressurization studies. Culture medium containing the cyanobacterium was diluted with river water (Toyohira River, Sapporo, Japan; DOC 1.1 mg L^{-1}, OD260 0.027 cm^{-1}) to obtain an extracellular geosmin concentration of approximately 100 ng L^{-1}. The solution was pressurized at 400 kPa for 4 h in a batch cell by introducing compressed air to the cell. After pressurization, the solution was gradually depressurized to normal pressure by using a ball valve to prevent volatilization of geosmin by rapid depressurization. Before and after pressurization, the intracellular and extracellular geosmin were separately quantified as described below.

Laboratory-scale MF experiments

Cyanobacterium *A. smithii* in its stationary phase was used for the MF experiments. Figure 1 is a schematic of the MF experiment. Culture medium containing the cyanobacterium was spiked into water from the Toyohira River in a raw water tank at the proportion of 1:9 (v/v). The cyanobacterium-spiked river water was directly fed into a

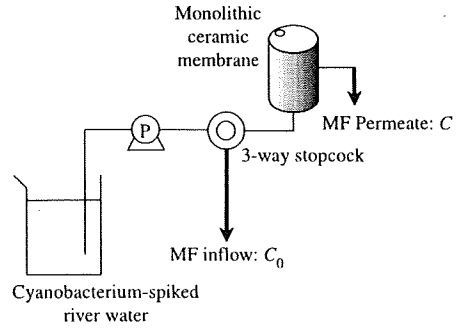

Figure 1 | Schematic of the laboratory-scale MF experiment.

monolithic ceramic MF module (single tubular, nominal pore size 0.1 μm, effective filtration area 0.0008 m^2; NGK Insulators, Ltd., Nagoya, Japan) at a constant flow rate (125 $L(m^2 \cdot h)^{-1}$) by a peristaltic pump in dead-end mode. The MF experiments lasted for 4 h with no backwashing. Geosmin concentrations in the MF inflow and in the MF permeate were measured periodically.

Pilot-scale experiments in a hybrid system with adsorption, coagulation, and microfiltration

Anabaena sp. isolated from Lake Sagami was used in the pilot-scale experiments (Figure 2). Culture medium containing the cyanobacterium was spiked into water from Lake Sagami in a raw water tank. The cyanobacterium-spiked lake water was supplemented with powdered activated carbon (PAC) at a dose of 2 mg L^{-1}. Two types of PAC were used: one was commercially available PAC (abbreviated here as N-PAC, d_{50} 7.6 μm, Futamura Chemical Industries Co., Ltd., Gifu, Japan) as received, and the other PAC (abbreviated here as S-PAC, d_{50} 0.65 μm) was obtained by micro-grinding of the N-PAC. After 2 min of PAC contact time with the water in the tube, the water was supplemented with coagulant (polyaluminum chloride, PACl, 10% (w/w), Hieisyouten Co., Ltd., Nagoya, Japan) at a dose of 25 mg L^{-1}. After 2 min of PACl contact time, the water was fed into a monolithic ceramic MF module (multichannel tubular, nominal pore sizes 0.1 μm, effective filtration area 0.48 m^2; NGK Insulators, Ltd.) at a constant flow rate (125 $L(m^2 \cdot h)^{-1}$) in dead-end mode. The experiments lasted for 4 h with no backwashing. Geosmin concentrations in the MF inflow and in the MF permeate were measured periodically.

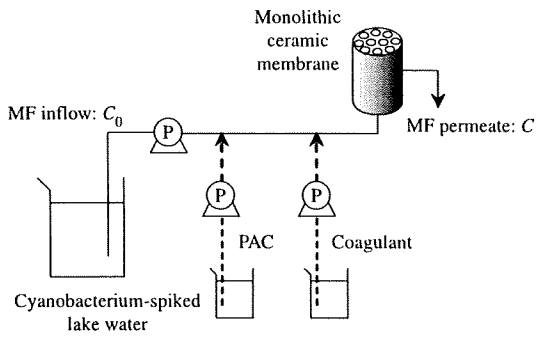

Figure 2 | Schematic of the pilot-scale hybrid system with PAC adsorption, coagulation, and microfiltration.

Batch adsorption tests

Geosmin produced by *A. planktonica* was used for the batch adsorption tests. Culture medium containing the cyanobacterium was filtered through a glass fiber filter with a 1-μm pore size (Toyo Roshi Kaisha, Ltd., Tokyo, Japan) to remove any cyanobacterium cells, and then the filtrate was stored as a stock solution of natural geosmin. After appropriate dilution of the stock solution with ultrapure water to obtain a geosmin concentration of approximately 100 ng L^{-1}, chemically synthesized d_3-geosmin was injected into the diluted solution at the same concentration as that of the natural geosmin. The solution was supplemented with sodium bicarbonate at 16.8 mg L^{-1}, and then the pH was adjusted to 7.0 by the addition of HCl. N-PAC was then added to the solution at a dose rate of 0.7 mg L^{-1}. Samples were periodically withdrawn from the solution at predetermined times, and geosmin and d_3-geosmin were quantified after the samples had been passed through a membrane with a 0.2-μm pore size (PTFE, Toyo Roshi Kaisha, Ltd.).

Measurement of intra- and extracellular geosmin

Each sample was divided and placed into two beakers: one for quantification of total geosmin, and the other for quantification of extracellular geosmin. For quantification of total geosmin, sodium hypochlorite was added to the sample solution at 20 mg L^{-1} to release the intracellular geosmin into the water by breaking down the cell walls of the cyanobacteria. After the mixture had been kept for 30 min at room temperature for reaction, an excess amount of sodium thiosulfate was added to the mixture to quench the unreacted sodium hypochlorite. Quantification of the geosmin in the mixture after the mixture had been passed by gravity through a glass fiber filter with a 1-μm pore size gave the total geosmin concentration (intracellular + extracellular geosmin). For quantification of extracellular geosmin, cyanobacterial cells were removed from the sample solution by passing the solution by gravity through a glass fiber filter with a 1-μm pore size. Quantification of the geosmin in the filtrate gave the extracellular geosmin

concentration. Subtraction of the extracellular geosmin concentration from the total geosmin concentration gave the intracellular geosmin concentration.

Method of geosmin analysis

Geosmin was extracted from the sample solutions by the stir bar sorptive extraction (SBSE) method with a Twister stir bar (Gerstel GmbH, Mülheim, Germany), and then quantified by gas chromatography – mass spectrometry (GC–MS, 6890N gas chromatograph, 5973 mass spectrometry detector, Agilent Technologies, Palo Alto, CA, USA) equipped with a thermal desorption apparatus (TDSA, Gerstel). GC–MS was performed in selected ion monitoring (SIM) mode. d_3-Geosmin was used as an internal standard, except in the batch adsorption experiments on d_3-geosmin, in which 2-MIB was used as an internal standard. Detection of ion fragments of geosmin, d_3-geosmin, and 2-MIB occurred at m/z 112, 115, and 95, respectively.

RESULTS AND DISCUSSION

Batch pressurization tests

Figure 3 shows the changes in geosmin concentrations before and after pressurization at 400 kPa for 4 h. In the logarithmic and stationary phases, more geosmin was retained in the cells than was found outside the cells.

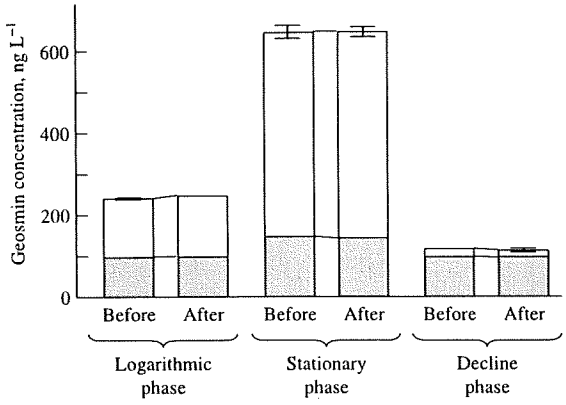

Figure 3 | Changes in geosmin concentration before and after pressurization (400 kPa, 4 h). White and gray columns represent intra- and extracellular geosmin concentrations, respectively. Error bars represent standard deviation ($n = 3$).

This distribution tendency was similar to that in *Anabaena macrospora* (Negoro *et al.* 1988), *Fischerella muscicola* (Wu & Jüttner 1988*a*), and *Oscillatoria tenuis* (Wu & Jüttner 1988*b*). In contrast, the intracellular geosmin concentration was much smaller than the extracellular geosmin in the decline phase: most of the geosmin existed outside the cell.

No changes were observed in the concentrations of either extra- or intracellular geosmin at any growth phase after pressurization of the cyanobacterium-containing solutions up to 400 kPa for 4 h, indicating that geosmin was not released from the cyanobacteria under high pressure at 400 kPa in static conditions.

Laboratory-scale MF experiments

Figure 4(a) shows the changes in extracellular geosmin concentration in the MF inflow and in the MF permeate. The extracellular geosmin concentration in the MF inflow (white circles) did not change substantially during the filtration. In the early stage of filtration the extracellular geosmin concentration in the MF permeate (gray circles) was almost the same as that in the MF inflow, meaning that the MF membrane alone could not remove the extracellular geosmin because its pores were much larger than the

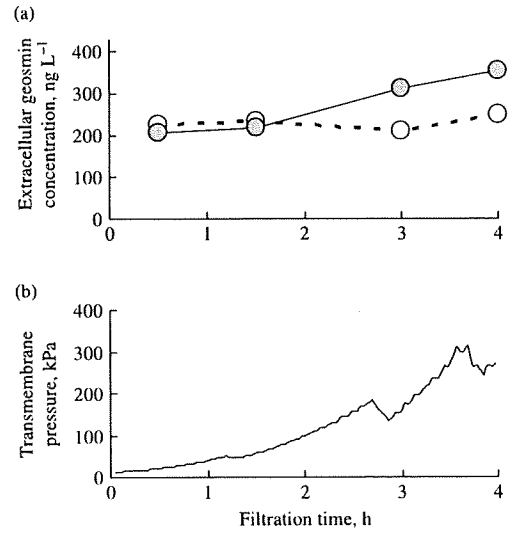

Figure 4 | Changes in extracellular geosmin concentration in the MF inflow and in the MF permeate (a), and transmemebrane pressure (b), in laboratory-scale MF experiments. White and gray circles represent the extracellular geosmin concentrations in the MF inflow and in the MF permeate, respectively.

geosmin molecules. In contrast, approximately 800 ng L^{-1} of the intracellular geosmin in the MF inflow (data not shown) was completely removed by the membrane, because the cyanobacterium, which incorporated part of the geosmin in its structure, was so much larger than the membrane's pores that it was rejected by the membrane. Bottino *et al.* (2001) reported that a ceramic MF membrane with pores of 0.2 μm almost completely rejected eight types of algae.

After 3 h of filtration, the geosmin concentration in the MF permeate exceeded that in the MF inflow, and at the end of filtration it was still increasing. This result evidently indicated that the geosmin was released from cyanobacterial cells that had been accumulated on the membrane surface, possibly by the increased operation pressure; transmembrane pressure (TMP) gradually increased during the filtration and peaked at approximately 300 kPa (Figure 4(b)). When release of geosmin from the cyanobacteria was observed at 3-h filtration, the TMP was approximately 160 kPa. This value was smaller than the pressure (400 kPa) at which release of intracellular geosmin did not occur in the batch pressurization tests described above. One possible explanation for the discrepancy is as follows: the cyanobacterial cells were isotropically pressurized under stationary conditions in the batch pressurization tests. In contrast, each cell on the membrane was pressurized on one of its sides, but vented to the atmosphere on the other. This gradient in pressure might have forced the cells to compress and release the intracellular geosmin. Another explanation is that when the cyanobacterial cells were pressed against the disturbed, rough surface of the membrane on which foulant was accumulated, the particles of foulant trapped between the membrane and the cells might have acted as fulcrums in the water flow, exerting shear forces on the cells and thus breaking them open. No morphologic differences between the cyanobacteria before and after filtration were observed under an optical microscope; further study with an electron microscope (i.e. under higher magnification and resolution than with the optical one) is needed.

Regardless, under high pressure intracellular geosmin was not released in static conditions but was released in dynamic conditions. However, the precise relationship between TMP and the release of geosmin is not clear and further study is needed. Nonetheless, the difference in geosmin removal between actual plant operations and laboratory experiments with reagent geosmin is apparently due to the release of geosmin from cyanobacterial cells accumulated on the membrane.

Pilot-scale experiments with a hybrid system of adsorption, coagulation, and microfiltration

The MF inflow contained approximately 40 ng L^{-1} of the intracellular geosmin as well as 55 ng L^{-1} of extracellular geosmin (data not shown). The extracellular geosmin concentration in the MF permeate was 20 ng L^{-1} at the beginning of filtration when the system was operated with N-PAC (Figure 5), meaning that the geosmin was removed to a certain extent by N-PAC addition. However, the geosmin concentration in the MF permeate gradually increased with filtration time. The increase was probably due to the release of intracellular geosmin from cyanobacteria accumulated on the MF membrane, because coagulant dosing has been reported not to cause lysis of cyanobacterial cells and not to increase the geosmin concentration in the water (Velzeboer *et al.* 1995). The amount of N-PAC dosed to the system was insufficient for geosmin removal. In contrast, geosmin was completely removed from the water over the entire filtration period when the system was operated with S-PAC, even though the dose of S-PAC was exactly the same as that of N-PAC. This is

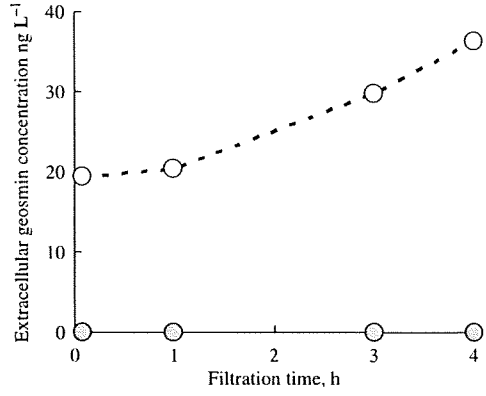

Figure 5 | Change in extracellular geosmin concentration in pilot plant experiments with a hybrid system that used PAC adsorption, coagulation, and microfiltration. White and gray circles represent N-PAC and S-PAC addition, respectively.

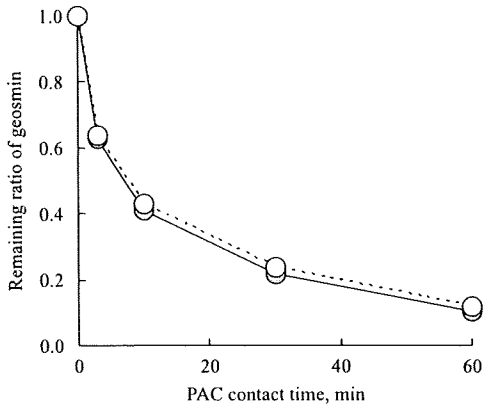

Figure 6 | Changes in concentrations of natural and synthesized geosmin. Solid and open symbols represent natural and synthesized d3-geosmin, respectively.

because the specific surface area and adsorption capacity of the S-PAC were much better than those of the N-PAC, thanks to the micro-grinding (Matsui *et al.* 2004, 2005, 2006). The hybrid system using S-PAC adsorption, coagulation, and microfiltration could simultaneously and effectively remove both the cyanobacteria and the geosmin from the water.

Batch adsorption tests

Figure 6 shows changes in the concentrations of natural and synthesized d_3-geosmin. The concentrations of natural geosmin and d_3-geosmin decreased similarly with N-PAC contact time. No difference was observed between the remaining ratios of the two compounds, indicating that natural and synthesized geosmin behaved in the same manner with respect to PAC adsorption. Therefore, the difference observed in geosmin removal between actual plant operations and laboratory experiments does not result from a difference in adsorption characteristics between natural and chemically synthesized geosmin.

CONCLUSION

1. Intracellular geosmin was not released from cyanobacterial cells under the static conditions of the batch pressurization tests, but it was released under the dynamic conditions of the laboratory-scale MF experiments.
2. Extracellular geosmin was partly removed by the hybrid system with N-PAC dosing, but its removal rate decreased with filtration time, probably because of the release of intracellular geosmin. In contrast, the hybrid system with S-PAC dosing simultaneously and effectively removed both the cyanobacteria and the geosmin from the water.
3. No difference was observed in adsorption characteristics between natural and chemically synthesized geosmin.
4. The difference in geosmin removal between actual plant operations and laboratory experiments with reagent geosmin is probably caused by the release of geosmin from the cyanobacterial cells accumulated on the membrane under high pressure.

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「論　文」

臭気強度（TON）の測定における三点比較法の適用

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要旨：水道水の臭気の測定を定量的、客観的に実施するため、臭気強度（TON）の測定に三点比較法を適用した。まず、三点比較法で必然的に生ずる偶然の正解について確率論的考察を行い、各測定で2回以上の的中を正解としパネル人数が2人以上必要であることを示した。ついで、三点比較法と従来法を比較したところ、三点比較法では臭気強度の変化が小さく、また測定値に大きな変動があった人数も少なく、再現性に優れていた。さらに、実際の水道水を採取して、残留塩素を除去した場合と除去しない場合について臭気強度を測定したところ、両者に大きな差異がみられること、高度浄水処理水においても残留塩素が関与した臭気が存在する実態の一部を把握した。

キーワード：臭気強度、三点比較法、残留塩素、トリクロラミン、ジェオスミン
分類項目：水質試験その他（120210）、消毒一般（050701）、高度処理一般（050801）

1. 緒言

国民の飲用水としての水道水の使用が減少し、いわゆる水道水離れが進み、ボトルウォーターの消費量が増大している。水道水源の汚濁等により、水道水の異臭味被害が発生し、平成2年度には、全国の異臭味被害人口は2千万人を超えた[1]。その後、水道事業体において高度浄水施設の導入が進むなどし、現在では、異臭味被害人口は2～3百万人程度に減少している[1]。しかし、伊藤ら[2]の研究によると、高度浄水処理を導入したところでも、カルキ臭などの異臭味に不満をもつ需要者が依然として多く、水道水の満足度を向上させるには、異臭味の解消を図るとともに、需要者に適切に情報提供を行う必要があることを指摘している。したがって、水道水の異臭味が改善されたことを客観的に示し、需要者とコミュニケーションを図り、満足度を向上させることが重要であり、水道水の異臭味のより精度の高い判断指標が求められている。

水道水の臭気の測定は、厚生労働省告示では、単純に、検査対象の水道水を入れたフラスコのヘッドスペースの臭気を鼻で嗅ぎ、異常でないかを判定することとされている[3]。また、上水試験方法では、無臭の対照水と比較して、検水が無臭となるまで無臭味水で希釈した倍数（臭気強度）を測定する方法が示されている[4]。一方、悪臭防止法では、事業場の排水の臭気測定法として、排水が含まれる試料水が入った1個のフラスコ及び無臭の対照水が入った2個のフラスコを用意し、パネルがフラスコのヘッドスペースの臭気を嗅ぎ、試料水が入ったフラスコをあてるという三点比較式フラスコ法が採用されている[5]。試料水の希釈倍数を大きくし、パネルが試料水の入ったフラスコをあてることができなくなるまで試験を行い、閾値に相当する希釈倍数を求めるものである。

本研究は、水道水の臭気の測定を定量的、客観

的に実施するため、臭気強度（TON）の測定に、偶然の正解の影響を排除することができるようにした三点比較法を適用することを目的としている。はじめに測定値に関する確率論的考察を行った上で、人工付臭水を用いた実験を行った。ついで、実際の水道水の臭気の測定等を行い、その実用性について検討したものである。

2. 偶然の正解の影響に関する確率論的考察

三点比較法の場合、パネルが実際には臭いの違いを認識していないにも関わらず、偶然に試料水が入ったフラスコを的中させる可能性が存在する。三点比較法を用いた測定の信頼性を損ねている最も大きな要因と考えられる。このため、偶然の正解が起こる確率と影響の大きさを確率論的に考察し、その影響を小さくする方法を検討した。

各パネルの測定結果が本来の結果からずれてしまう確率f（x）は幾何分布を示す。一般に、幾何分布は最初に成功（または失敗）をするまでに行われるベルヌイ試行数に関する確率分布である。

$f(x)=p\cdot q^{x-1}$……式-1

x：当該パネルが無臭フラスコを選定するまでのフラスコ選定操作（4.3参照）の数

p：当該パネルが偶然に無臭フラスコを選定する確率

q：当該パネルが偶然に付臭フラスコを選定する確率

また、複数のパネルを用いて測定する場合、その測定値が本来の結果からずれてしまう確率は負の二項分布（パスカル分布）を示す。一般に、負の二項分布は、幾何分布の一般形で、k回成功（または失敗）するまでに行われるベルヌイ試行数に関する確率分布である。

$f(x)={}_{k+x-1}C_x p^k q^x$……式-2

x：パネルが偶然に付臭フラスコを選定した数の合計数

k：パネルの人数

p：当該パネルが偶然に無臭フラスコを選定する確率

q：当該パネルが偶然に付臭フラスコを選定する確率

負の二項分布の平均E（x）及び標準偏差S（x）は次のとおりである。

$$E(x)=k\cdot\frac{q}{p}\quad\cdots\cdots\text{式-3}$$

$$S(x)=\frac{\sqrt{k\cdot q}}{p}\quad\cdots\cdots\text{式-4}$$

複数のパネルで三点比較法により測定した場合、1人のパネルの1回の偶然の正解によるパネル全体の平均値（臭気強度（TON））への影響は、パネルの人数で除した値となるので、臭気強度（TON）の測定値の本来の結果からのずれの平均及び標準偏差は次のとおりとなる。

$$\text{平均}：\frac{q}{p}$$

$$\text{標準偏差}：\frac{\sqrt{\frac{q}{k}}}{p}$$

通常の三点比較法の場合、p＝2／3、q＝1／3となるため、測定の際の次の希釈倍数との距離を1とした場合、平均は1／2（＝0.5）にまで達する。測定値の信頼性を高めるためには、偶然に正解する確率を無視できる程度に減ずる必要がある。このため、同じ希釈倍数で2回測定を実施し、2回とも的中してはじめて正解とみなす（p＝8／9、q＝1／9）と、偶然の正解による測定値のずれの平均は1／8（＝0.125）となる。3回では1／26（＝0.038）となる。なお、偶然の正解による測定値のずれの平均は、パネルの人数（k）と関係がない。

同一希釈倍数における測定の数、パネルの数の違いによる測定値のずれの平均及び標準偏差を表-1に示した。標準偏差は、1回の的中を正解とみなす場合と比べて、2回または3回の的中を正解とみなす場合の方が大幅に小さくなることがわかる。平均に標準偏差を加えた数値を0.5未満とすること、すなわち、四捨五入すると本来の測定値となることを目標とすると、1回の的中を正解とみなす方法では、平均が0.5であるのでその目標を達成することはできず、2回の的中を正解とみなしパネルの人数を2人以上とすることが必要である。

3. 嗅覚の個人差に関する考察

パネルの嗅覚を用いた臭気の測定の信頼性に疑

表-1　三点比較法の偶然の正解による臭気強度（TON）の測定値の影響

正解の方法 / パネル人数	同一希釈倍数で1回の的中を正解とみなす			同一希釈倍数で2回の的中を正解とみなす			同一希釈倍数で3回の的中を正解とみなす		
	平均	標準偏差	平均＋標準偏差	平均	標準偏差	平均＋標準偏差	平均	標準偏差	平均＋標準偏差
1人	0.500	0.866	1.366	0.125	0.375	0.500	0.038	0.200	0.238
2人		0.612	1.112		0.265	0.390		0.141	0.180
3人		0.500	1.000		0.217	0.342		0.115	0.154
4人		0.433	0.933		0.188	0.313		0.100	0.138
5人		0.387	0.887		0.168	0.293		0.089	0.128
6人		0.354	0.854		0.153	0.278		0.082	0.120
7人		0.327	0.827		0.142	0.267		0.076	0.114
8人		0.306	0.806		0.133	0.258		0.071	0.109
9人		0.289	0.789		0.125	0.250		0.067	0.105
10人		0.274	0.774		0.119	0.244		0.063	0.102

問がもたれる大きな要因の一つに、パネルの嗅覚の個人差が大きく、パネルにより測定値が大きく変動する可能性があることがあげられる。このため、嗅覚の個人差の程度を確認し、臭気の測定における対処方法について考察した。

これまでの研究によると、嗅覚の個人差は相当大きいことが判明している。豊田ら[6]が嗅覚測定用基準臭を作成する過程で、18歳から25歳の嗅覚正常者を対象として10種類の基準臭について637人から多いものでは1,030人の嗅力が調査された。鼻鏡検査により病的所見がなく、また自覚的にも嗅覚障害を有しないと判定された日本人男女が被検者とされた。各基準臭は、それぞれ10倍希釈系列で用意されたものである。各基準臭について薄い方から順に上昇系列で、ある希釈倍数で初めて臭いを感じたときに、その希釈倍数が閾値とされた。その結果、何らかの臭いが感じられた検知閾値については、10種類の基準臭の5パーセンタイル値と95パーセンタイル値の差は、基準臭の希釈倍数で平均$10^{3.6}$（範囲$10^{3.2}$～$10^{4.4}$）であり、当該臭気が感じられた認知閾値については、基準臭の希釈倍数で平均$10^{3.1}$（範囲$10^{2.2}$～$10^{3.7}$）と、1,000倍を超える大きなものであった。また、嗅覚の正常者と障害者では、基準臭に関して大きな差異がみられた。

なお、悪臭防止法にもとづく基準臭による嗅覚障害者を除く方法では、基準臭は嗅覚正常者の平均値に近い濃度に設定されており、この方法を用いると嗅覚の個人差の影響を大幅に除くことができる。

嗅覚の個人差による測定値の差異を小さくする方法としては、パネルの人数を多くし、平均値を算出することが有効であるが、このような嗅覚の大きな差異がある中で、迅速な測定が求められる水道水の臭気の測定において、大人数のパネルを確保して臭気の測定を行うことは現実的でない。したがって、嗅覚の個人差の大きさを克服する方法としては、①悪臭防止法にもとづく測定のように、一定の基準臭を用いて、嗅覚障害者など嗅覚が他の者と大きく異なる者を除いた上で、実際の検体の測定を行うこと、②パネルを特定の者に限定するとともに、パネルを可能な限り多くし、平均値を算出すること、③上水試験方法において定められているように、一定の基準臭を用いて補正を行うことが有効と考えられた。

4.　新しい臭気強度（TON）の測定方法の提案

4.1　基本的考え方

多くの水道事業体において、臭気強度（TON）の測定は上水試験方法に従って実施されている。このため、新しい測定方法は、水道事業体において利用されやすいものとするため、これまでの測

定方法を基礎として、それを改良したものとし、上水試験方法の臭気強度（TON）の測定における本試験で三点比較法を適用したものを提案する。

三点比較法を適用するに当たっては、濃度が高いものから測定を行う下降系列で測定を行う。これは、希釈倍数の高い（濃度が低い）試料から上昇系列で測定すると、最初に偶然の正解が発生し、その次に、より小さな希釈倍数（濃度が高い）試料において不正解が発生するという矛盾した結果を生じさせる可能性があるためである。また、各希釈倍数の試料について、各パネルに2回以上測定をさせることとし、検水が入ったフラスコを全ての回で的中することができた場合にその希釈倍数での正解とみなす。なお、臭気を感知する能力は非常に大きな個人差があり、また、嗅覚に障害がある人は、臭気を嗅ぎ分ける人として適当でない。このため、予めパネルの選定試験を行い、嗅覚が他の者と大きく異なる者はパネルに採用しないこととする。

4.2　パネル

2における考察を踏まえ、パネルは2人以上とし、3における検討結果により、可能な限り多くする。なお、悪臭防止法にもとづく臭気指数等の判定ではパネルは6人以上充てることとされている（平成7年環境庁告示第63号）。悪臭防止法は事業場排水の規制を目的としており嗅覚の個人差による測定値の差異が小さくなることが強く求められるが、水道水の臭気強度（TON）の測定は日常の水道水質管理のために実施されるため、三点比較法による偶然の正解の影響を排除する観点からパネルは2人以上とし、可能な限り多くすることとした。また、パネルは、平成7年環境庁告示第63号に示された、基準臭液を用いたパネルの選定方法により、正常な嗅覚を保持していることを確認する。

4.3　試験操作

予備試験は、現行の上水試験方法のとおりとし、本試験の操作は次のとおりとする。予備試験で求めた最小検水量を表-2の数値に照らして該当する予備試験検水量の縦系列に示す本試験に用いる検水量を求める。3個の三角フラスコのうち1個に検水を注入し、無臭味水で当初希釈倍数になるよう希釈し、検水と無臭味水を足した全量が200mLとなるよう調製し、三角フラスコを密栓する。調製した水の入ったフラスコ（付臭フラスコ）1個と200mLの無臭味水のみを注入し密栓した三角フラスコ（無臭フラスコ）2個を1組としてパネルに渡す。パネルは、三角フラスコをそれぞれ縦に2～3回強く振とうした後、3個の三角フラスコのうちから検水が注入されていると判定するフラスコ1個を選定する（以上の操作を「フラスコ選定操作」という。）。同一希釈倍数で、同じ操作を再度実施する。2回のフラスコ選定操作において、2回とも付臭フラスコを選定した場合は、当該希釈倍数における正解とみなす。希釈倍数を大きくしてフラスコ選定操作を繰り返し、当該パネルが無臭フラスコを選定するか付臭フラスコを選定することが不能となった時点で終了する。なお、高い希釈倍数で偶然と思われるような不自然に正解が出るような場合等必要と考えられる場合は、同一希釈倍数で3回以上フラスコ選定操作を行う。

表-2　臭気強度（TON）測定希釈検水量

予備試験の検水量（mL）	200	40	10	4
本試験に用いる検水量（mL）	200	40	10	4.0
	100	28.5	8.0	2.9
	67	20	6.7	2.0
	50	13.3	5.0	1.3
	40	10	4.0	1.0

4.4　臭気強度（TON）の算出方法

各パネルについて、最後に正解した希釈倍数を各パネルの臭気強度（TON）とする。複数のパネルで測定を実施した場合は、各パネルの臭気強度（TON）を幾何平均した値を臭気強度（TON）とする。

5.　新しい臭気強度（TON）の測定方法の検証

5.1　臭気物質濃度の減衰に関する検討

フラスコ選定操作において、パネルが三角フラスコの蓋を開け、ヘッドスペース中の空気を嗅ぐことにより、試料水中の臭気物質濃度が低減する。同じ三角フラスコの試料を複数回測定に使用できるかどうかは、測定に要する労力、時間等に関係するため実用性に大きな影響を与える。このため、フラスコ選定操作を繰り返すことによる三角フラ