

Removal characteristics of geosmin by advanced water treatment processes: a case study around the Han River, Republic of Korea

J.W. Seo^{a,*}, Y.S. Kim^b, K.B. Kim^a, M.C. Kim^c, S.H. Park^d, J.Y. Koo^a

^aDepartment of Environmental Engineering, University of Seoul, Seoul, Korea, Tel. +82 2 6490 5460; emails: enendr31@uos.ac.kr (J.W. Seo), kumbo88@hanmail.net (K.B. Kim), jykoo@uos.ac.kr (J.Y. Koo)

^bK-water, Gwangju-Jeonnam District Office, Gwangju, Korea, Tel. +82 62 370 1317; email: cochonys@kwater.or.kr

^cKorea Environmental Industry & Technology Institute, Seoul, Korea, Tel. +82 2 2284 1339; email: dq3d007@nate.com

^dKorea Institute of Civil Engineering and Building Technology, Korea, Tel. +82 31 910 0550; email: karasin811@kist.re.kr

Received 16 January 2017; Accepted 20 March 2019

ABSTRACT

Water treatment plants (WTPs) that intake raw water from the Paldang Dam of the Han River have generally adopted ozone + granular activated carbon (GAC) processes for the effective removal of taste and odor substances. In recent years, the concentration and duration of the substances causing taste and odor in Paldang Lake have gradually increased. Therefore, it is necessary to review the appropriateness of the advanced water treatment processes introduced in the WTPs located in the Han River. This study attempted to compare and review two processes for geosmin removal, one using a pre-ozone GAC filter-adsorber (pre-ozone + F/A) at the B WTP and the other using a post-ozone GAC adsorber (post-ozone + GAC) at the G WTP. The results of the investigation for geosmin and 2-MIB concentrations upstream of the Paldang Dam over the past 5 years showed that 2-MIB exceeded the standard concentration for less than 5 d per year and geosmin was the main cause of taste and odor. At the B WTP in the winter of 2011, the total geosmin concentration in the treated water exceeded 20 ng/L twice. Additionally, the average total geosmin concentration of the treated water after the application of the F/A was 7.81 ng/L. On the other hand, in the case of the G WTP, the total geosmin concentration after post-ozone and GAC treatment was 0.45 ng/L. In the summer of 2012, the fraction of particulate geosmin (66.9%–82.3%) was higher than that of dissolved geosmin (17.7%–33.1%) in the raw water of the two WTPs. During this period, the average removal rates of total geosmin in the final treated water of the G WTP were 0.7% higher than that of the B WTP. Therefore, ozone injection into filtered water after removing particulate geosmin and organic substances through the standard treatment process (coagulation, sedimentation, and filtration) is thought to be effective for removal to lower the concentration of dissolved organic matter and dissolved geosmin. In conclusion, the treatment efficiency was confirmed to vary according to the stage at which the process was used, even when the same ozone + activated carbon adsorption process was used. In addition, the 'post-ozone + GAC' method is considered advantageous when introducing advanced WTPs in the Han River.

Keywords: Advanced water treatment process; Granular activated carbon; Geosmin; Ozone treatment; Taste and odor

1. Introduction

With recent climate change, the occurrence of algae growth in rivers and lakes has been increasing, and taste

and odor problems due to algae have increased in the water supply at water treatment plants (WTPs) from Paldang Lake in the Han River system, Republic of Korea.

Taste- and odor-causing substances in surface water mainly result from the metabolism and biodegradation of certain types of cyanobacteria that normally bloom in

* Corresponding author.

the presence of nutrients at warmer temperatures [1]. The main problems with the presence of taste- and odor-causing substances are their extremely low odor threshold concentrations and their resistance to removal in conventional water treatment processing [2]. The presence of natural organic matter (NOM) in all water sources poses an additional challenge in water processing [3]. Adsorption by activated carbon and oxidation by ozone have been successfully employed by WTPs to remove taste- and odor-causing substances. Many studies have shown that 2-methylisoborneol (2-MIB) and geosmin, the two primary taste- and odor-causing substances, are extremely resistant to removal via coagulation, sedimentation, and filtration [4]. Bruce et al. [2] found that alum coagulation could not be optimized for 2-MIB and geosmin removal. Numerous studies have shown that adsorption by granular or powdered activated carbon (GAC or PAC, respectively) is one of the best available methods for removing organic contaminants and MIB/geosmin from water [4]. Many studies have investigated the adsorption capacity of GAC and PAC for removing MIB and geosmin [3,5,6–8]. PAC is the most commonly used method as it is relatively inexpensive and can be applied only when required. However, the presence of NOM and oxidants such as chlorine or chloramines can significantly reduce the effective adsorption capacity of PAC [9]. Oxidants such as ozone, hydrogen peroxide, and UV have been used to remove the MIB and geosmin in many studies [2,10,11]. Oxidation processes with chlorine and chlorine dioxide were shown to effectively remove some types of taste and odor but did not effectively remove 2-MIB or geosmin [11,12]. In a pilot plant study, the removal efficiencies with Cl_2 and ClO_2 were very low, and only O_3 removed any appreciable amount of MIB and geosmin (85% for 3.8 mg/L dosage at a contact time (CT) of 6.4 min) [4,7]. Ozonation is less commonly used but can be an effective method for removing 2-MIB and geosmin. When used to disinfect surface water, O_3 acts as a strong oxidant, removes tastes and odors, enhances coagulation, and provides other benefits. In addition, O_3 at a sufficiently high dose destroys 2-MIB and geosmin [13,14].

Accordingly, many WTPs in Korea include PAC, or sometimes GAC, to remove NOM and taste- and odor-causing substances [15]. One of the advantages of PAC is its low capital cost, but its applicability is limited to low concentrations of organic material because of the inherently short CT. GAC adsorption can be applied in one of two ways: the first is to build a GAC adsorber after the sand filter; the second is to retrofit a sand filter to a GAC filter-adsorber (F/A) [16].

Most WTPs in the Republic of Korea using conventional water treatment processes depend on PAC addition to cope with the occurrence of taste and odor. However, recently, the frequency of taste and odor and the concentrations of substances causing them in the Paldang Lake water source have rapidly changed; in the summer of 2012, geosmin was detected at concentrations up to 1,125 ng/L. Such changes have, in turn, caused difficulties with early responsiveness and ensuring a proper PAC supply, as well as causing higher costs and limiting treatment efficiency. Therefore, the introduction of an advanced water treatment facility and urgent countermeasures is now necessary. However, advanced water treatment processes have mostly been

researched at the laboratory or pilot scale in the Republic of Korea, involving forced injection or relatively low concentrations of taste- and odor-causing substances, while research involving actual treatment processes has been relatively rare. For this reason, methodological aspects, such as of the effect of changes in the concentration of taste- and odor-causing substances in raw water on removal efficiency, and the removal characteristics of the water treatment processes, is recommended to determine the suitability of current methods. Accordingly, in this research, we comparatively analyze two ozone and GAC processes, that is, “pre-ozone + F/A” and “post-ozone + GAC”, which have been introduced into the WTPs of the Han River water supply system, in order to assess treatment stability and efficiency. This research aims to determine whether the two processes can cope with the recent increase in taste- and odor-causing substances.

2. Methods

Advanced water treatments, such as GAC, PAC, ozonation, and membrane filtration, have been applied with variable success, because their effectiveness depends on factors such as the age of filter beds, type of carbon used, level of source-water dissolved organic material, and proportion of dissolved and particulate (cell-bound) geosmin or 2-MIB [17,18]. The objective of our laboratory experiment was therefore to evaluate the removal efficiencies of conventional treatment processes and PAC adsorption with various proportions of dissolved and particulate geosmin. In a pilot test, the effect of the ozone treatment on the removal efficiency of post-processing was evaluated.

Since each process in the WTP is connected, any previous process may affect the removal efficiency of subsequent processing. Ozone treatment can be used to change the proportion of dissolved and particulate geosmin; here, the effectiveness of these two processes with different treatment locations and GAC types were compared in two actual WTPs, namely B WTP and G WTP. Specifically, the removal efficiency of each process was evaluated.

2.1. Occurrence of taste- and odor-causing substances

The occurrence of taste- and odor-causing substances in the Paldang water source, which supplies raw water to the metropolitan multiregional WTPs and 13 local WTPs, was investigated by analyzing geosmin and 2-MIB at three locations (metropolitan multiregional Paldang 1, 2, and 3 water intake stations) over the period from January 2009 to December 2013. Fig. 1 shows locations of three water intake stations in Paldang Lake. Samples were generally collected and analyzed once per week. However, when the concentration of taste- and odor-causing substances exceeded 20 ng/L (the maximum concentration recommended by the Ministry of Environment for drinking water), analysis was carried out daily until the concentration decreased below 10 ng/L.

To analyze taste- and odor-causing substances, samples were collected in glass containers at a suction well in an intake facility. The glass containers and their polypropylene caps as well as syringes and vials were washed with nitric acid and distilled water. The samples were filled in glass bottles so as not to generate air bubbles. Using a glass syringe, the samples were then transferred into a glass vial to make



Fig. 1. Taste- and odor-causing substance sampling points in the study area.

standard solutions within 1 h of collection. The volume of sample filtered to analyze dissolved geosmin was 100 mL.

Previous research showed that the concentrations of taste- and odor-causing substances in water varies according to the growth phase of algae, as the ratio of intracellular to secreted taste- and odor-causing substances varies according to the degree of exocytosis during algal growth [19]. Most of the MIB and geosmin is released during the death and biodegradation of algal cells [4]. It is essential to recognize that geosmin and 2-MIB occur in surface waters as both dissolved and cell-bound fractions and that differentiating these two fractions is crucial to effective water treatment [20]. In order to investigate the effect of the ratio of these fractions on water treatment, the Paldang water source was examined using the procedure shown in Fig. 2 over a period of 41 d from July 13 to August 23, 2012.

2.2. Method for analyzing taste- and odor-causing substances

The taste- and odor-causing substances analyzed in this research were geosmin and 2-MIB, and the SPME/GC-MSMS method was optimized for analysis. SPME analytical conditions are presented in Table 1. The stock standard solution (Supelco, USA) contained 100 µg/mL of 2-MIB and geosmin in methanol. HPLC-grade methanol (Merck, Germany) was used to dilute the standard stock solution. A standard solution was prepared via the primary dilution of the standard stock solution until the concentration of the target substances to be analyzed reached 0.1 µg/mL. To enhance the concentration/extraction efficiency of SPME by the salting-out effect, pre-treatment involved the saturation of the sample with NaCl (Junsei Chemical Co., Japan).

NaCl was baked for more than 4 h at 550°C in an electric furnace before use to minimize contamination by impurities and organic substances. The SPME fiber used was 2 cm–50/30 µm (DVB/CAR/PDMS) (Supelco, USA), which was conditioned for 1 h at 270°C before use.

CombIPAL (CTC, Switzerland), 450GC (Bruker, USA), and 320MS (Bruker, USA) instruments were used as the SPME auto-sampler, GC, and MS/MS, respectively. Pre-treatment was carried out by mixing 10 mL of sample and 3 g of NaCl in a 20 mL vial, followed by heating of the mixture at 65°C for 3 min and then exposure of the SPME

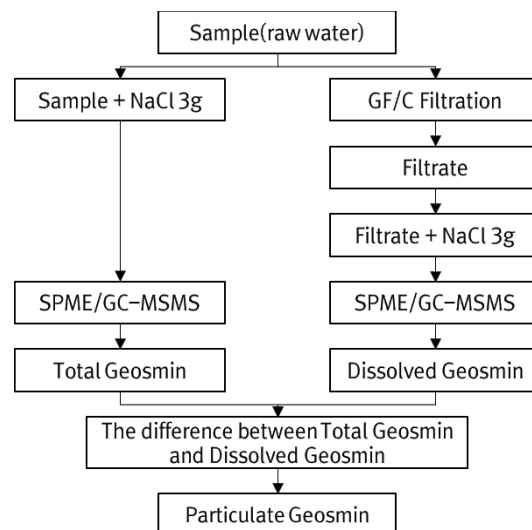


Fig. 2. Process for analyzing the dissolved and particulate geosmin fraction.

Table 1
Experimental pre-treatment conditions of SPME

Parameter	Value
Pre-incubation time, min:s	03:00
Pre-incubation agitator speed, rpm	500
Vial fiber exposure time, min	22
Extraction time, min:s	20:00
Injection fiber exposure time, min	22
SPME fiber	2 cm–50/30 µm DVB/Carboxen/PDMS (divinylbenzene/Carboxen/polydimethylsiloxane)
Incubation temperature, °C	65
Injection needle penetration, mm	30
Vial needle penetration, mm	10
Desorption time, min:s	04:00
GC runtime, min:s	01:00
Bake-out fiber, min:s	05:00

fiber to the headspace of the vial for 20 min for absorption. Desorption was carried out in the GC injector for 4 min prior to GC-MSMS analysis.

GC-MS/MS analytical conditions are presented in Table 2. In the 2-MIB analysis using MS/MS, when the first selected ion (Q_1) was set to 95, the second selected ion (Q_3) overlapped with other ions, resulting in low sensitivity. In order to select non-overlapping ions, the less common ion 107 was selected.

Table 2
Experimental conditions of GC-MSMS

Instrument	Conditions	
Injector	Temperature: 250°C; injection mode: splitless	
Column	VF-5MS (30 mL × 0.25 mm ID × 0.25 μm DF)	
Carrier gas	He constant flow of 1 mL/min	
Oven	35°C (5-min hold), 8°C/min to 180°C, 180°C (hold 2 min)	
MS/MS	Geosmin selected ion: Q ₁ 112 Q ₃ 83, 97	Manifold temperature: 40°C
	2-MIB selected ion: Q ₁ 107 Q ₃ 79, 91	Transfer line temperature: 250°C
	Source temperature: 200°C	Ionization: EI mode

2.3. Quality assurance/quality control (QA/QC)

Quality assurance/quality control (QA/QC) was performed to ensure the reliability of the analyses by plotting a calibration curve and checking the measurement results of standards for each analysis. QA/QC was carried out following the procedures of two standard methods detailed by the Korean Ministry of Environment: “Standard method for drinking water quality” and “Public notification on operation of water quality monitoring items” [19,21]. The calibration curve was created and verified once a day, while other QA/QC measures were performed twice a year. When calibration curves were prepared, the quantification range was 0.001 to 0.02 μg/L, and the curve sampling was repeated seven times. However, if the measured value was out of this range, the sample was diluted and analyzed again. To set the method detection limit (MDL) and the minimum quantitation limit, the standard deviation was first calculated by analyzing samples with analytes added to distilled water. The standard deviation was found to be 2 ng/L, based on seven analyses. MDL was then defined as the standard deviation multiplied by 3.14 (98% reliability), and MOL was obtained by multiplying the standard deviation by 10. The calibration curve was derived using five concentrations within the range of quantification. To meet our QA/QC standards, we ensured that the determination coefficient of the calibration curve was higher than 0.98 and that the relative standard deviation of the response factor was within 25%. When the relative standard deviation of the determination coefficient and the response factor were out of the allowable range, the calibration curve was derived again. Precision and accuracy were measured in accordance with the ES 05001.a QA/QC standard in the “Standard method for drinking water quality” guidelines published by the Korean Ministry of Environment [21]. The QA/QC demonstrated that the accuracy, precision, and reproducibility of the analysis were acceptable.

2.4. Coagulation/sedimentation/filtration and powdered activated carbon treatment (laboratory test)

A laboratory test was conducted in 2012 when high concentrations of taste- and odor-causing substances occurred in the Paldang water source. The target substance of this jar test was geosmin, and the concentrations of dissolved and particulate geosmin were analyzed. Jar tests were employed to examine geosmin removal rates by

coagulation/sedimentation/filtration and PAC during the standard water treatment process like Fig. 3, and the results are summarized in Table 3. The water used for the jar test was the raw water from the second Paldang water intake station. After collection of samples into glass containers, the samples were transferred into square, 2 L acrylic testing jars (Phipps & Bird, USA). The jar test was conducted once per set of experimental conditions. PAC containing less than 20% moisture and the coagulant PACS used in the jar test were same as those used by the B WTP.

Jar test conditions involved rapid mixing for 1 min at 300 rpm, slow stirring (60 → 40 → 20 rpm) for 10 min at each rpm, settling for 20 min, and filtration with filters (GF/C). The settled water used for analysis was collected from the water sampling port of the jar after 20 min settling time, while filtrate from GF/C was used as filtered water for analysis.

2.5. Pre-ozone treatment (pilot test)

To assess the removal efficiency of the pre-ozone treatment and its effect on the presence of taste- and odor-causing substances, an investigation was conducted in the summer of 2012, when such substances were present in high concentrations. In Fig. 4, a pilot ozone processing plant was installed at Paldang 2 water intake station. Samples of raw water were collected at the Paldang 2 water intake station for analysis, and the removal rate of geosmin was examined via the addition of ozone at concentrations of 1–3 ppm. The average ozone injection concentration was 1.9 mg/L, and the average CT was 10.2 min in pre-ozone processing.

2.6. Advanced water treatment (analysis of actual process)

The advanced water treatment process was analyzed to assess both the removal efficiency of high concentrations of taste- and odor-causing substances in the water

Table 3
Characteristics of PAC from the jar test

Parameter	Standard	Result
Loss on drying, %	50 below	16.9
Iodine value, mg/g	950 over	1,069
Methylene blue decolorization, mL/g	150 over	220
Phenol value	25 below	20

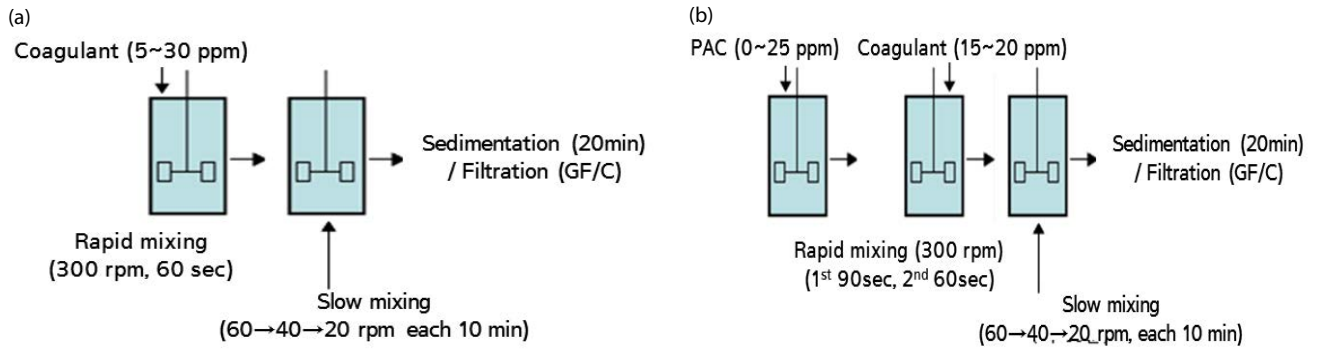


Fig. 3. Experimental conditions of the jar test for examination of geosmin removal rates by coagulation/sedimentation/filtration process (a) without PAC and (b) with PAC.



Fig. 4. Pilot plant for the ozone process.

source and the removal characteristics of individual unit processes. The target processes selected for analysis were the pre-ozone + F/A and post-ozone + GAC processes used by multiregional B WTP (Fig. 5) and G WTP (Fig. 6), which had introduced advanced water treatment facilities. These WTPs are described in Table 4.

2.7. Deduction of optimal operation methods according to geosmin concentrations

Based on the results from the experiments described above, optimal operating conditions for the geosmin concentrations in raw water were deduced for the two advanced water treatment processes. Then, based on the deduced conditions, the economic efficiencies of the two processes were comparatively examined in terms of both construction

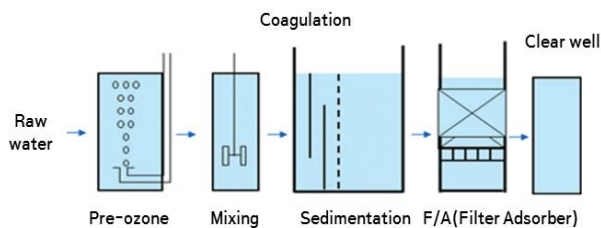


Fig. 5. Water treatment process at B WTP.

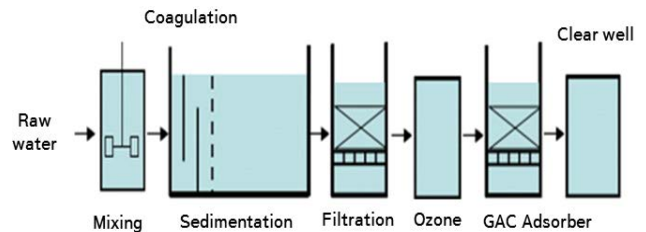


Fig. 6. Water treatment process at G WTP.

and operating costs in an effort to determine an optimal water treatment method for high concentrations of taste- and odor-causing substances in the water source.

3. Results and discussion

3.1. Occurrence of taste- and odor-causing substances upstream of Paldang

Fig. 7 shows the occurrence of geosmin (Fig. S1) and Fig. 8 shows the occurrence of 2-MIB (Fig. S2) by year in Paldang Lake. The maximum amount of geosmin increased constantly from 2009 to 2012, except in 2013, while our results indicate that 2-MIB had a greater prevalence in 2012 and 2013 than in the previous 3 years. Geosmin primarily appeared in summer from June to August, except in 2011, when it was exceptionally prevalent in the winter season. In 2013, it occurred in lower concentrations. The Paldang 1, 2, and 3 water intake facilities were located within 1.1 km of each other, so water quality was very similar at each facility.

The number of days that the geosmin concentration exceeded the guideline for drinking water set by the Korean Ministry of Environment (20 ng/L) [19], as well as the concentration itself, increased from 2009 to 2012. There were 45 such days, with an average concentration of 157 ng/L, in 2012. These values were 2–3.8 and 2.6–3 times higher than those of 2009 and 2010 in terms of days and concentration, respectively. Because 2-MIB exceeded the standard concentration for less than 5 d per year, geosmin was regarded as the main taste- and odor-causing substance upstream of Paldang for the past 5 years.

The odor threshold concentration for geosmin and 2-MIB ranges from 4 to 20 ng/L [22–25], though consumers

Table 4
Characteristics of B and G WTPs

	Parameter	B WTP	G WTP
General status	Capacity, m ³ /d	195,000	210,000
	Water source	First intake facility in Padang Lake	First intake facility in Padang Lake
	Distance, km	53	52
	Conveyance duration time, h	Average 16	Average 17
Ozone process	Process	Pre-ozone treatment	Post-ozone treatment
	Ozone contact bed	6 m × 17 m × 6 m × 2	6 m × 18 m × 18.2 m × 2
	Detention time, min	10.2	15.4
	Injection rate, mg/L	0.5–3.0	0.5–2.0
GAC adsorber	Format	Filter/adsorber	GAC
	Filtration type	Constant rate filtration	Constant rate filtration
	Filtration velocity, m/d	150	245
	EBCT, min	14.5	14.1
	GAC	Coal-based	Coal-based
	Filling depth, m	1.4	2.4
	Uniformity coefficient	<1.5	<1.9

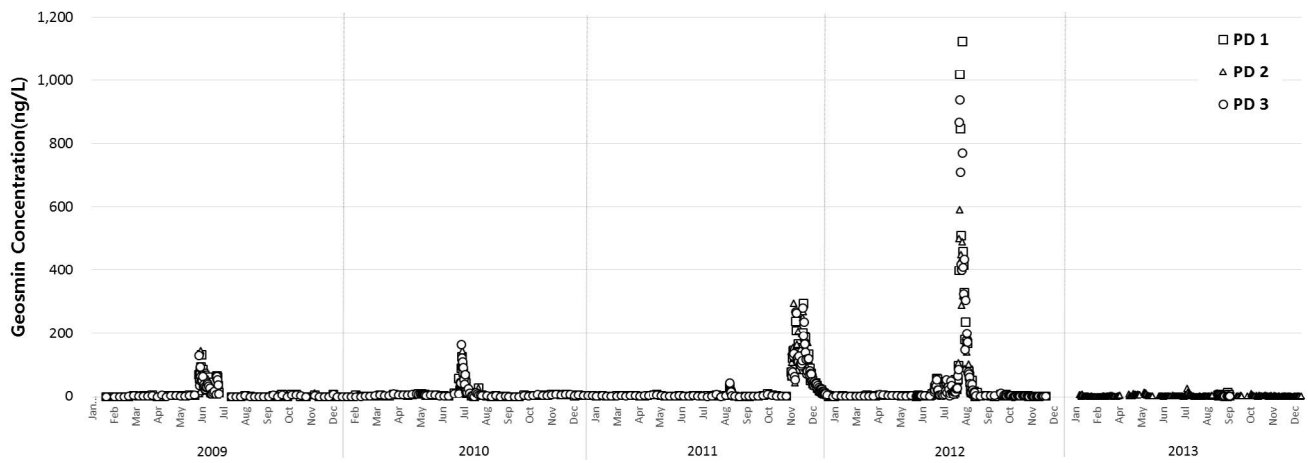


Fig. 7. Occurrence of geosmin by year in Paldang Lake (Fig. S1).

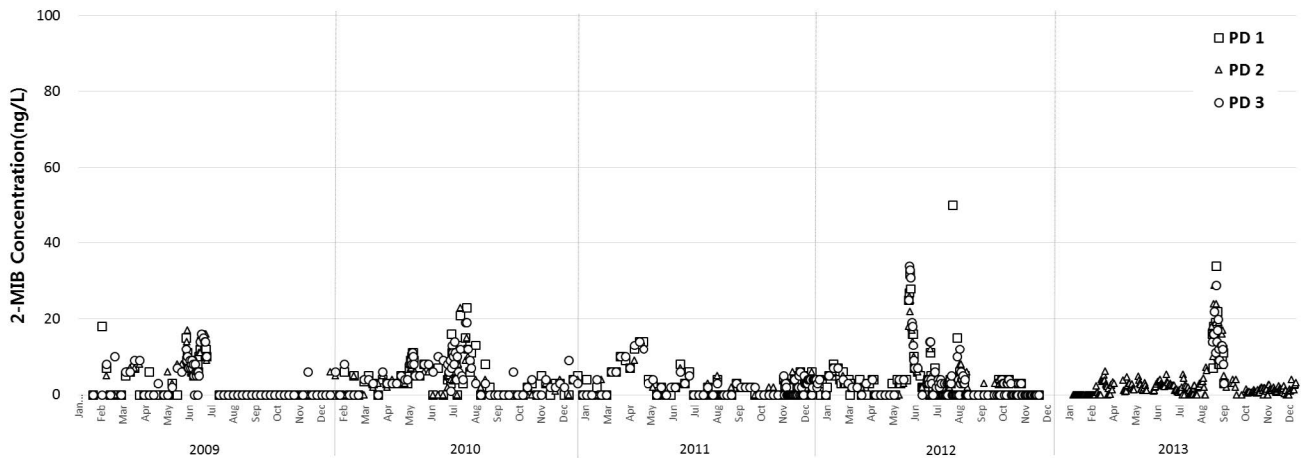


Fig. 8. Occurrence of 2-MIB by year in Paldang Lake (Fig. S2).

can experience an unpleasant odor even when levels are below the threshold. According to the calculated results, geosmin concentration exceeded 10 ng/L for 65 d in 2012, and 2-MIB exceeded this level for 3–14 d per year. Therefore, the total number of days in which workers should enhance water treatment will gradually increase when taste- and odor-causing substance regulations are reinforced.

3.2. Dissolved and particulate fraction of geosmin upstream of Paldang

To investigate the influence of the water treatment process on the proportion of dissolved and particulate geosmin, research was conducted over 40 d (July 14 to August 24, 2012). Fig. 9 shows fraction of dissolved and particulate geosmin in raw water (Fig. S3). The majority of geosmin (68%–72% on average) was found to have particulate (cell-bound) form, with 28%–32% having dissolved form on average. The particulate geosmin fraction was 52%–64% at total geosmin concentrations below 20 ng/L, 72%–75% at concentrations between 20 and 200 ng/L, and 78%–80% at concentrations above 200 ng/L. This analysis shows that the particulate ratio was relatively high when the total geosmin concentrations were higher.

The results of this study, however, are from July to August 2012, when Paldang Lake underwent massive growth of *Anabaena*, a taste- and odor-generating algae. Therefore, when periods of algae appearance and taste- and odor-substance occurrence are not concurrent or when upstream geosmin affects the downstream area, it is possible that the proportions of particulate and dissolved geosmin will differ.

3.3. Coagulation, sedimentation, filtration, and PAC treatment (laboratory test)

To understand the effect of the deduced particulate geosmin fraction on conventional water treatment processes (coagulation, sedimentation, filtration) and their removal efficiency, the jar test was conducted.

The first experiment measured the removal efficiency of coagulation, sedimentation, and filtration in a conventional

water treatment process without the injection of PAC. Water quality in raw water was measured as follows: turbidity 4.5 NTU, pH 8.6, alkalinity 34 mg/L, and total geosmin concentration 352 ng/L.

Fig. 10 shows the total and dissolved geosmin concentrations according to the coagulant concentration injected after the conventional water treatment process. It also shows the total geosmin removal rate in the sedimentation and filtration process.

In Fig. 11, The results of the first jar test showed an average 40.9% removal efficiency of total geosmin with a 15 ppm coagulant injection after sedimentation. Average removal efficiency after filtration was 48.8%, so about half of the total geosmin was removed in the conventional water treatment process without additional PAC. In this case, the dissolved geosmin concentration after filtration was similar, regardless of the coagulant injection (5–30 ppm); therefore, dissolved geosmin may be insufficiently eliminated through conventional water treatment processes. Over-injection of coagulant also failed to increase the removal efficiency of dissolved geosmin concentration.

In the second experiment, the turbidity was relatively high owing to 90 mm of rainfall on a previous day. The water quality of raw water was as follows: turbidity 40.2 NTU, pH 7.3, alkalinity 30.6 mg/L, and total geosmin concentration 59 ng/L (dissolved geosmin: 12 ng/L, 20.3%).

An increased amount of the coagulant (20 ppm) was injected for turbidity elimination, and the total geosmin removal efficiency reached 86% by using the conventional water treatment process without PAC injection. Fig. 12 shows the results of second jar test on conventional water treatment process and PAC injection (low geosmin concentration). The particulate geosmin fraction in raw water was 80%, which was similar to the removal efficiency, showing that most of the particulate geosmin was removed. Because the second experiment had a lower concentration of total geosmin than the first experiment, 100% of geosmin was eliminated with the injection of when more than 15 ppm of PAC was injected.

The results above clearly demonstrated that particulate geosmin was mainly removed by coagulation, sedimentation, and filtration, and the rest of the dissolved geosmin was eliminated by the PAC. Therefore, if a treatment process

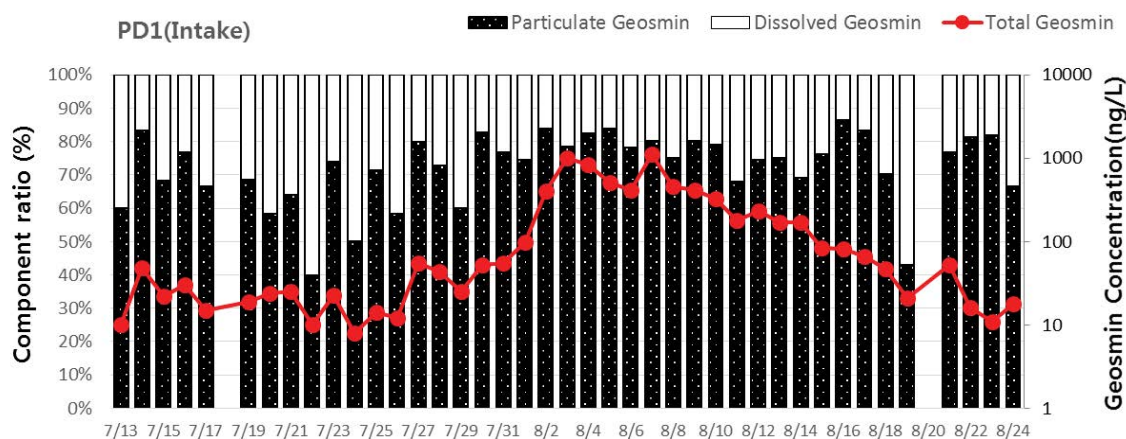


Fig. 9. Fraction of dissolved and particulate geosmin in raw water (Fig. S3).

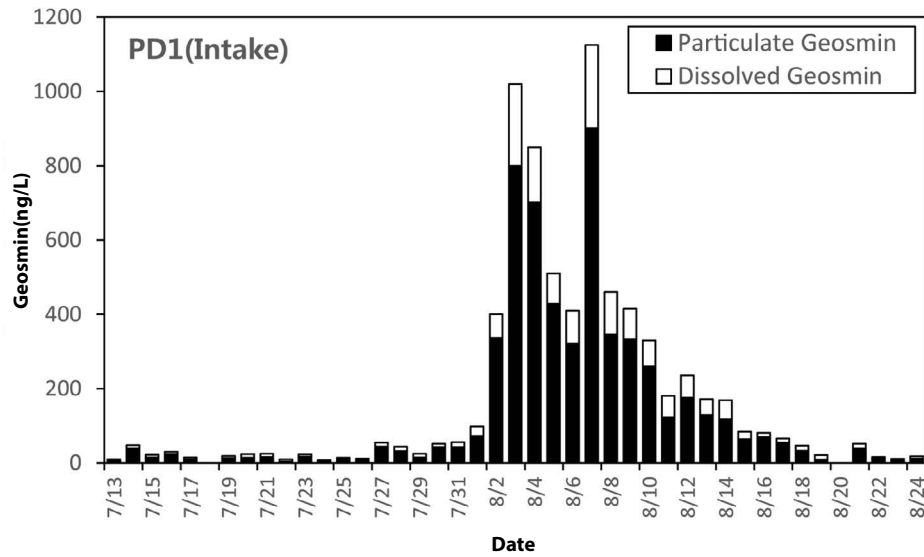


Fig. 10. Concentration of dissolved and particulate geosmin in raw water (Fig. S4).

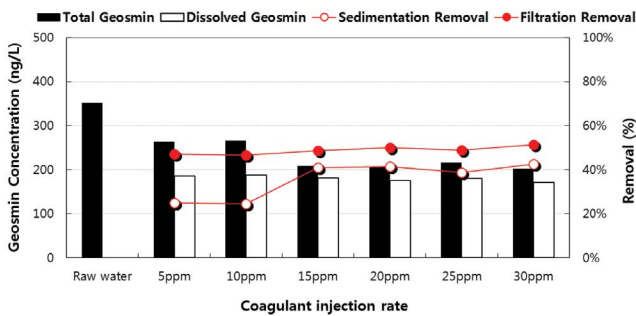


Fig. 11. Results of first jar test on conventional water treatment process (high geosmin concentration).

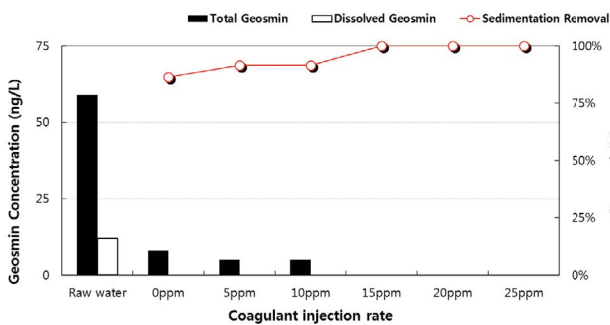


Fig. 12. Results of second jar test on conventional water treatment process and PAC injection (low geosmin concentration).

that destroys the algal cells, such as pre-chlorine treatment, is used before coagulation and sedimentation, the geosmin removal efficiency would decrease and the amount of applied PAC would need to increase. Additionally, if the geosmin concentration in the raw water is lower than 59 ng/L, the conventional water treatment process is enough for total geosmin elimination; however, the conventional

water treatment process is limited when the concentration exceeds 352 ng/L.

3.4. Evaluation of pre-ozone treatment efficiency (pilot test)

In Fig. 13, geosmin removal efficiencies of the pre-ozone treatment at the pilot plant are plotted as a function of the ozone injection concentration.

The geosmin removal efficiency after the pre-ozone injection was 9.5% at 0.5 ppm ozone and 87.0% at 3 ppm, revealing a linear increase in efficiency with the injection amount. The concentration of the dissolved geosmin was almost equal to the total geosmin concentration when the pre-ozone treatment was strengthened to more than 2 ppm ozone, indicating that geosmin was totally converted into the dissolved state. Additionally, when a higher geosmin concentration (over 300 ng/L) occurred, the concentration of total geosmin in the treated water still exceeded 100 ng/L, even after a pre-ozone injection of up to 2 ppm ozone. Because in this case all the geosmin would be dissolved, additional elimination by coagulation and sedimentation was expected to be difficult. Meanwhile, the removal efficiency of total geosmin after pre-ozone treatment with 0.5 and 1 ppm ozone

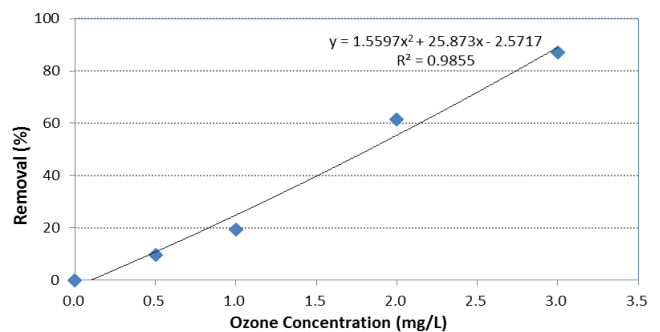


Fig. 13. Variation in total geosmin removal efficiency with the pre-ozone injection rate.

Table 5
Evaluation of removal efficiency by pre-ozone treatment

Ozone injection rate	Raw water geosmin (A) (ng/L)		Treated water geosmin (B) (ng/L)		Removal efficiency (A – B)/A	Average removal efficiency	
	Total	Dissolved	Total	Dissolved			
0.5 ppm	168	140	152	126	9.5%	19.4%	
1 ppm	1st	490	–	426	–	13.1%	
	2nd	414	233	307	203	25.8%	
2 ppm	1st	460	276	136	143	70.4%	61.6%
	2nd	470	–	226	–	51.9%	
	3rd	306	221	115	112	62.4%	
3 ppm	1st	362	–	38	–	89.5%	87.0%
	2nd	270	170	42	50	84.4%	

concentration was lower than that with the conventional water treatment process (50%–60%) but similar to that with pre-ozone injection with an ozone concentration of 2 ppm. These results are summarized in Table 5.

3.5. Evaluation of advanced water treatment process for geosmin removal

Based on the laboratory and pilot test results, control of highly concentrated geosmin seems to be limited with the conventional water treatment process and pre-ozone treatment alone. Therefore, to investigate how to effectively control this taste- and odor-causing substance, we evaluated the advanced water treatment process in two WTPs.

3.5.1. Evaluation of advanced water treatment processes employed in winter 2011

Taste- and odor-causing substances occurred in upstream Paldang between November and December 2011, when the water quality was as follows: turbidity 2.7 NTU (range 1.9–3.4 NTU), temperature 7.1°C (3.1°C–9.9°C), TOC 1.87 mg/L (1.70–2.09 mg/L), geosmin concentration 94 ng/L (31–256 ng/L).

Table 6 shows that at B WTP, which implemented the pre-ozone + F/A treatment, the total geosmin concentration was reduced by 57%, 68% and 71% with 0.5, 1, and 1.5 ppm ozone injections, respectively. Compared with the results from G WTP, which implemented the post-ozone treatment, these results were about 10% lower for the 1.0 and 1.5 ppm ozone injections. This is because even if the geosmin concentration of the filtered water is the same as that of raw water, the TOC of the raw water is higher than that of the filtered water, so the level of impurities in raw water for the ozone

treatment is higher than that in the filtered water. Tables 7 and 8 show the post-treatment water quality at both WTPs. The average TOC concentration in the filtered water at G WTP over the study period was approximately 20% lower than that (1.49 mg/L) in the raw water. Cook et al. [5,17] reported that the presence of NOM significantly reduced adsorption capacity for MIB and geosmin. Newcombe et al. [26,27] found that NOM with a size similar to that of MIB made up the majority of the competition, with smaller NOM particles also competing for the available adsorption sites. In addition, larger NOM compounds reduce the equilibrium adsorption capacity by adsorbing closer to external surfaces and blocking access to pores. For these reasons, dissolved organic substances are considered to decrease the treatment efficiency when eliminating taste- and odor-causing substances. Furthermore, the efficiency of taste- and odor-causing substance removal was relatively low in the raw water with higher DOC concentration.

In G WTP, as shown in Fig. 14, the geosmin concentrations of the raw and filtered water were similar, indicating that

Table 6
Geosmin removal efficiency by ozone treatment in winter 2011

Ozone injection rate, ppm	Average removal efficiency at B WTP (pre-ozone treatment), %	Average removal efficiency at G WTP (post-ozone treatment), %
0.5	57	59
1	68	78
1.5	71	84
2	–	100

Table 7
Average water quality parameters after treatment process in winter 2011 (B WTP)

Turbidity (NTU)			Temperature (°C)	pH			UV254			TOC (mg/L)		
Raw water	Sedimentation	F/A-treated		Raw water	Sedimentation	F/A-treated	Raw water	Sedimentation	F/A-treated	Raw water	Sedimentation	F/A-treated
3.40	0.609	0.056	9.2	7.5	7.4	7.3	0.058	0.022	0.014	1.872	1.492	1.217

Table 8
Average water quality parameters after treatment process in winter 2011 (G WTP)

Turbidity (NTU)				Temperature (°C)	pH			TOC (mg/L)	
Raw water	Sedimentation	Filtered water	Ozone-GAC-treated water		Raw water	Sedimentation	Ozone-GAC Treated water	Raw water	Ozone-GAC-treated water
3.414	0.744	0.068	0.063	7.785	7.585	7.448	7.312	1.900	1.080

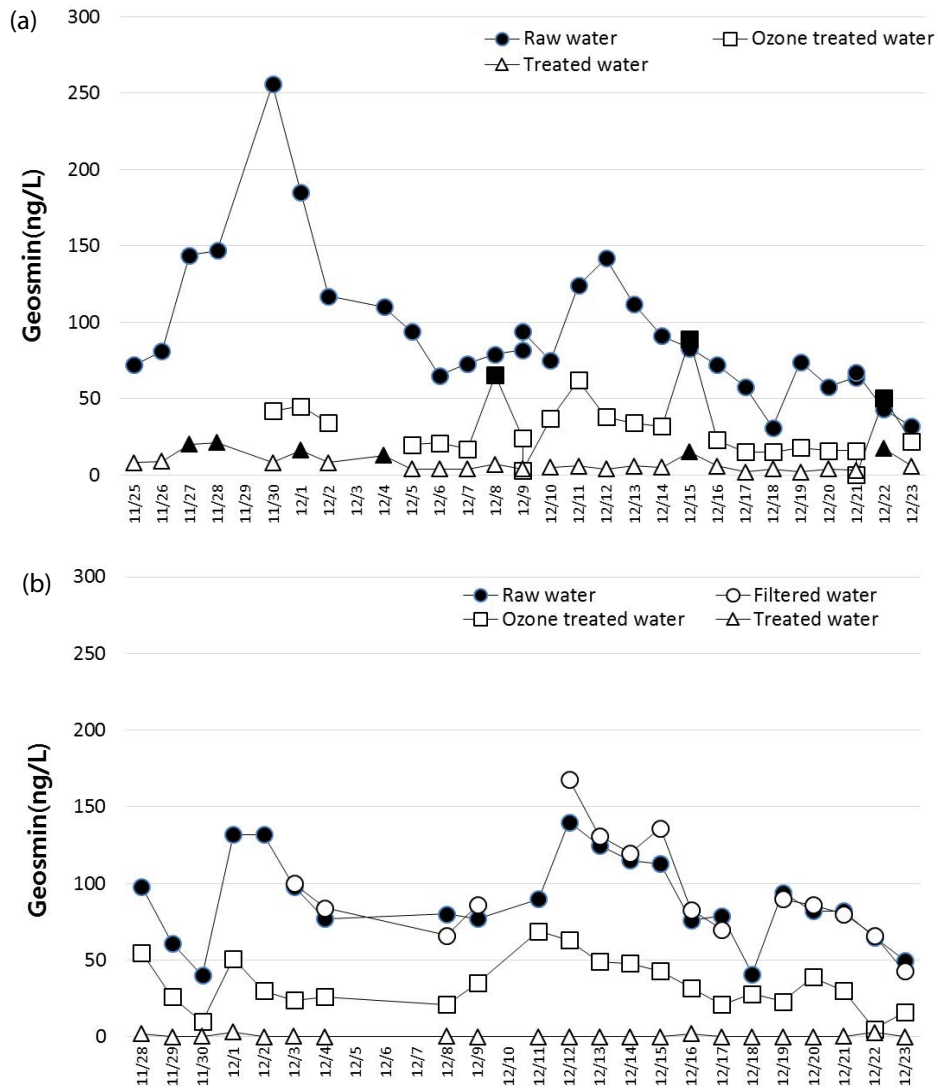


Fig. 14. Geosmin concentration of each process in winter 2011 (a) B WTP and (b) G WTP.

coagulation and sedimentation did not eliminate geosmin. During the taste- and odor-causing substance occurrence period in 2011, the average concentration of cyanobacteria in Paldang source water was low at 52 cells/mL.

Fig. 15 shows the GAC treatment efficiency in winter 2011. In B WTP in this period, total geosmin concentration in the treated water exceeded 20 ng/L twice. Additionally, the average total geosmin concentration of treated water after the F/A was 8 ng/L, which increased the difficulty

of eliminating the odor-causing substance. It is believed that geosmin could not be completely removed owing to the lower level of biological activation in this period, with water temperatures below 10°C. Therefore, the total geosmin concentration should be lowered as much as possible using the ozone treatment, with the water then input to the activated carbon adsorption process.

On the other hand, in G WTP, the total geosmin concentration did not exceed 3 ng/L owing to the secured

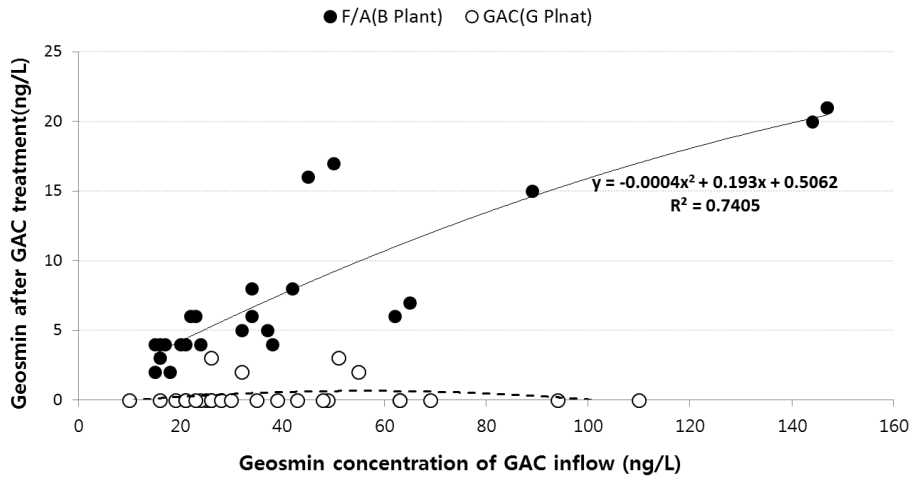


Fig. 15. GAC treatment efficiency in B and G WTPs.

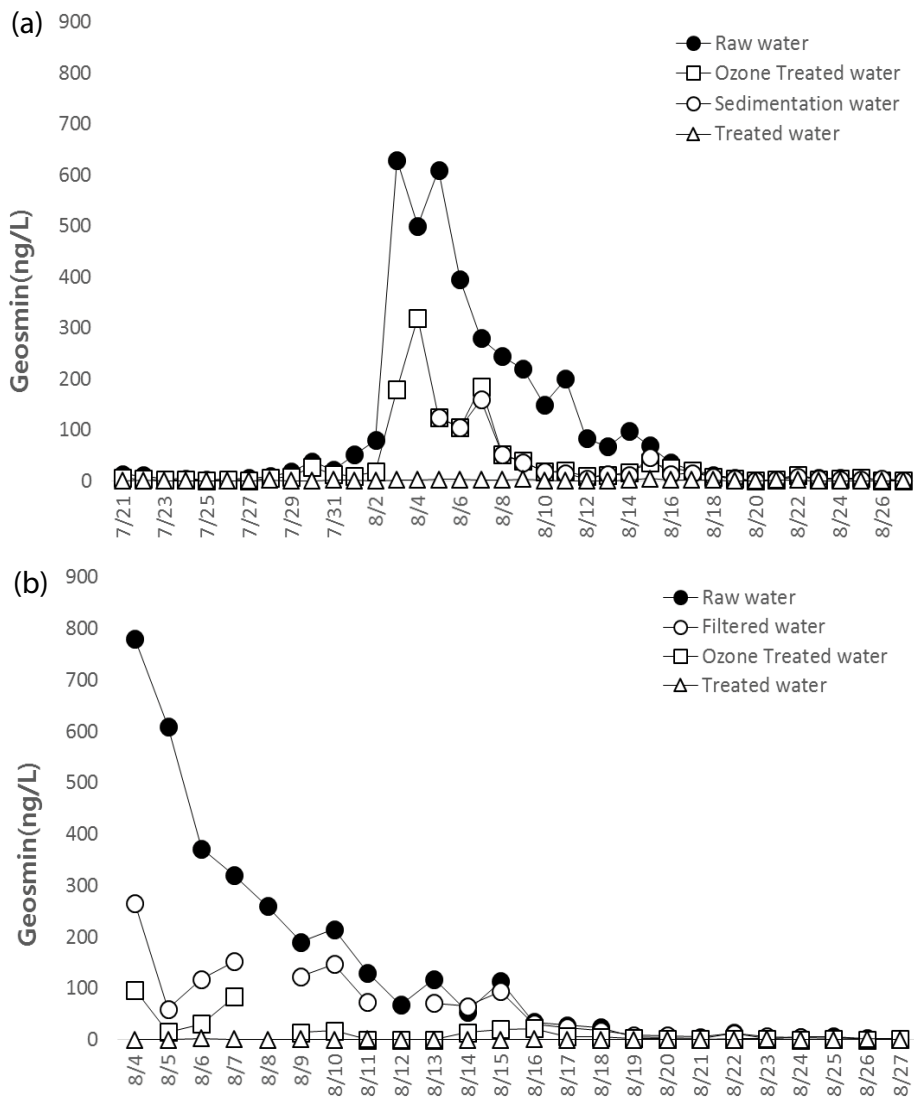


Fig. 16. Geosmin concentration of each process in summer 2012 (a) B WTP and (b) G WTP.

treatment of GAC water, even though the adsorption capacity had been significantly decreased, as in B WTP, with 90–100 mL/g of methylene blue bleaching and 879–961 mg/g iodine concentration. While the empty bed contact time (EBCT) of facilities B (14.5 min) and G (14.1 min) was almost equal, B had a height of 1.4 m with a filtration speed of 150 m/d. Meanwhile, G had a height of 2.4 m with a 245 m/d filtration speed. G WTP, therefore, had an advantage over B WTP in eliminating taste- and odor-causing substances.

The F/A process limits GAC height in a structural way because it is introduced via improving the existing filtration site. The filtration speed must also be limited for the purpose of turbidity elimination. Additionally, because F/A is required to have frequent backwash and common filtration to achieve both adsorption and turbidity removal simultaneously, the effect of the backwash frequency on the biological decomposition of microorganisms should be considered. The difference in geosmin removal efficiency between both activated carbon adsorption processes in winter can be reviewed, but a more detailed removal mechanism would require additional study.

3.5.2. Evaluation of current advanced water treatment processes in summer 2012

Fig. 16 and Tables 9 and 10 show the geosmin concentration according to treatment process in B and G WTPs when geosmin concentrations were high in upstream Paldang in July–August 2012, when the average raw water quality was as follows: turbidity 10.8 NTU (range 2.1–43.2 NTU), temperature 26.1°C (22.1°C–30.0°C), TOC 2.36 mg/L (1.78–2.83 mg/L), total geosmin 188 ng/L (ND–1,125 ng/L). Tables 11 and 12 show the water quality parameters during the experimental periods.

In B WTP, regardless of the raw water geosmin concentration, for all periods within the odor occurrence, total geosmin concentration was less than 5 ng/L in treated water. G WTP also achieved less than 2 ng/L of total geosmin concentration for the whole period. Because microorganism activity increased from the winter season, with an average water temperature of 26.1°C, the biological elimination process was more active inside the activated carbon process.

Table 9

Evaluation of removal efficiency by treatment processes in summer 2012 (B WTP)

Date	Geosmin concentration (ng/L) total geosmin (dissolved geosmin)				Ozone injection rate (ppm)	Removal efficiency (%) raw water (in process)		
	Raw water	Ozone-treated water	Sedimentation effluent	F/A-treated water		Ozone treatment	Coagulation/ sedimentation effluent	F/A treatment
Average	325 (76)	108 (94)		2	1.9	70	77 (9)	99.2 (95.8)
8/4	500 (108)	320 (208)	–	2	2	36	–	100
8/5	610 (116)	125 (128)	–	3	2	80	–	100
8/6	395 (86)	105 (94)	–	3	2	73	–	99
8/7	280 (92)	185 (178)	160	2	2	34	43 (14)	99 (99)
8/8	245 (81)	52 (63)	52	2	1.5	79	79 (0)	99 (96)
8/9	220 (45)	39 (37)	37	4	2	82	83 (5)	98 (89)
8/10	150 (44)	18 (21)	19	1	2	88	87 (0)	99 (95)
8/11	200 (39)	20 (21)	15	ND	1.8	90	93 (25)	100 (100)

Table 10

Evaluation of removal efficiency by treatment processes in summer 2012 (G WTP)

Date	Geosmin concentration (ng/L) total geosmin (dissolved geosmin)				Ozone injection rate (ppm)	Removal efficiency (%) raw water (in process)		
	Raw water	Filtered water	Ozone-treated water	GAC-treated water		Sedimentation/ filtration effluent	Ozone treatment	GAC treatment
Average	360 (54)			ND	0.7	55.4	91 (76)	99.9 (98.9)
8/4	780	265	97	ND	1	66	88 (63)	100 (100)
8/5	610	60	15	ND	0.5	90	98 (75)	100 (100)
8/6	372 (66)	118	31	2	0.7	68	92 (74)	99 (94)
8/7	320 (57)	152	84	ND	0.7	53	74 (45)	100 (100)
8/8	260 (77)	–	–	ND	0.7	–	–	100
8/9	190 (35)	123	14	ND	0.7	35	93 (89)	100 (100)
8/10	215 (51)	147	18	ND	0.7	32	92 (88)	100 (100)
8/11	130 (38)	73	ND	ND	0.7	44	100 (100)	100

Table 11
Water quality parameters by treatment process in summer 2012 (B WTP)

Date	Turbidity (NTU)			Temperature (°C)	pH			UV254		
	Raw water	Sedimentation water	F/A-treated water		Raw water	Sedimentation water	F/A-treated water	Raw water	Sedimentation water	F/A-treated water
Average	2.25	0.310	0.076	27.8	8.1	7.4	7.1	0.050	0.017	0.010
8/6	2.67	0.337	0.082	27.7	8.2	7.4	7.1	0.061	0.019	0.010
8/7	2.44	0.400	0.077	27.9	8.4	7.5	7.1	0.050	0.022	0.012
8/8	2.00	0.344	0.069	28.7	8.1	7.3	7.2	0.049	0.016	0.010
8/9	2.19	0.185	0.081	27.7	8.0	7.3	7.2	0.046	0.012	0.009
8/10	1.93	0.286	0.074	27.2	7.7	7.4	7.2	0.041	0.016	0.010

Table 12
Water quality parameters by treatment process in summer 2012 (G WTP)

Date	Turbidity (NTU)				Temperature (°C)	pH		
	Raw water	Sedimentation effluent	Filtered water	Ozone- + GAC-treated water		Raw water	Sedimentation effluent	Ozone- + GAC-treated water
Average	3.665	0.659	0.073	0.071	28.5	7.99	7.25	6.93
8/4	4.081	0.739	0.111	0.073	27.9	8.30	7.28	6.94
8/5	3.906	0.667	0.082	0.073	28.2	8.40	7.42	6.93
8/6	3.237	0.641	0.065	0.070	28.4	8.13	7.29	6.92
8/7	3.188	0.641	0.070	0.073	27.3	8.14	7.23	6.89
8/8	3.246	0.661	0.081	0.069	29.5	7.96	7.21	6.92
8/9	2.969	0.652	0.064	0.068	29.1	7.84	7.20	6.94
8/10	3.817	0.650	0.056	0.078	28.7	7.61	7.19	6.95
8/11	4.878	0.620	0.056	0.066	28.7	7.52	7.16	6.94

The left side of Fig. 16 reveals that the total geosmin concentration of pre-ozone-treated water in B WTP for about 10 d in early August was almost equal to that in the sedimentation water. This was because the elimination process did not occur with coagulation and sedimentation after the ozone treatment, as particulate geosmin (cell-bound) was converted into a dissolved state after the pre-ozone treatment, as shown in the pilot test.

The proportion of dissolved geosmin in the ozone-treated water in B WTP reached 90%–100%, except on August 4. Geosmin was mostly dissolved, so little was removed, as evidenced by the nearly equal geosmin concentrations in the ozone-treated and sedimentation water. Additionally, the concentration of dissolved geosmin in the ozone-treated water increased from that in the raw water from August 4 through 7. This may indicate that the portion eliminated by coagulation and sedimentation was reduced by the ozone treatment.

Both B and G WTPs had an ozone + activated carbon adsorption process. At G WTP, however, because the total geosmin concentration was reduced by 50% via coagulation, sedimentation, and filtration before the ozone treatment, the ozone treatment was 6% more effective, despite only a half or quarter of the amount of ozone injection compared with the other facility.

In both facilities, the removal efficiency right before treatment by the activated carbon adsorption process, that is, the final process, affected the total load of that site. In the period with a high geosmin concentration, B WTP had an average removal efficiency of 77% right before F/A, while G WTP had an average removal efficiency of 91% right before treatment with the GAC adsorber, that is, a difference of 14%. In other words, the pre-ozone + F/A treatment produced a total load to the activated carbon adsorption process that was 2.6 times that of the post-ozone + GAC treatment.

4. Conclusions

Two actual WTPs have successfully employed adsorption by activated carbon and oxidation by ozone to remove taste- and odor-causing substances. Based on the results of existing studies, the ozone + GAC process is usually selected. However, geosmin occurrences coming from algae in Paldang Lake have recently become more frequent. However, the effectiveness of advanced water treatment systems in removing taste- and odor-causing substances under the current conditions has not been adequately studied. Thus, the adequacy of the currently employed processes must be reexamined, such as the impact of changes in the concentration of taste- and odor-causing substances in feed

water on the efficiency of removal in the water treatment process. Two ozone + activated carbon adsorption processes (pre-ozone + F/A and post-ozone + GAC) have already been introduced into WTPs on the Han River. In this study, these water treatment processes were investigated during a period of high geosmin concentration, and their geosmin removal efficiency were evaluated. When the concentration of particulate geosmin in the summer season was high, almost all geosmin was transformed into a dissolved state after pre-ozone treatment, and it was difficult to further remove geosmin in subsequent coagulation and sedimentation steps. It has been reported that when algal cells are lysed due to ozone treatment, DOC and extracellular organic matter may increase, which may inhibit coagulation and increase taste- and odor-causing substances and disinfection byproducts [28]. On the other hand, in the case of post-ozone treatment, when the ratio of particulate geosmin is high, it is possible to remove 50%–60% of geosmin by coagulation, sedimentation, and filtration. In addition, the post-ozone treatment process decreased the geosmin concentration to half that in the previous step, with this form of removal more efficient than the pre-ozone treatment process. While the coagulation and sedimentation removal methods are of limited efficiency in winter due to the low proportion of geosmin in particulate form, ozone injection into the filtered water showed a better removal efficiency due to low background concentration of dissolved organic matter. The results thus confirmed that treatment stability and efficiency, and thus the occurrence of taste- and odor-causing substances, can differ according to the stage in which the process is used, even when the same ozone + activated carbon adsorption process is used.

Acknowledgment

This study was supported by the Korean Ministry of Environment as a “Global Top Project” (2016002120006).

References

- [1] S.B. Watson, J. Ridal, G.L. Boyer, Taste and odour and cyanobacterial toxins: impairment, prediction, and management in the Great Lakes, *Can. J. Fish. Aquat. Sci.*, 65 (2008) 1779–1796.
- [2] D. Bruce, P. Westerhoff, A. Brawley-Chesworth, Removal of 2-methylisoborneol and geosmin in surface water treatment plants in Arizona, *J. Water Supply Res. Technol. AQUA.*, 51 (2002) 183–198.
- [3] M. Pirbazari, V. Ravindran, B.N. Badriyha, S. Craig, M.J. McGuire, GAC adsorber design protocol for the removal of off-flavors, *Water Res.*, 27 (1993) 1153–1166.
- [4] R. Srinivasan, G.A. Sorial, Treatment of taste and odor causing compounds 2-methyl isoborneol and geosmin in drinking water: a critical review, *J. Environ. Sci.*, 23 (2011) 1–13.
- [5] D. Cook, G. Newcombe, P. Sztajn bok, The application of powdered activated carbon for MIB and geosmin removal: predicting PAC doses in four raw waters, *Water Res.*, 35 (2001) 1325–1333.
- [6] C. Ng, J.N. Losso, W.E. Marshall, R.M. Rao, Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin–water system, *Bioresour. Technol.*, 85 (2002) 131–135.
- [7] S.W. Jung, K.H. Baek, M.J. Yu, Treatment of taste and odor material by oxidation and adsorption, *Water Sci. Technol.*, 49 (2004) 289–295.
- [8] L. Ho, G. Newcombe, Effect of NOM, turbidity and floc size on the PAC adsorption of MIB during alum coagulation, *Water Res.*, 39 (2005) 3668–3674.
- [9] T.E.T. Gillogly, V.L. Snoeyink, J.C. Vogel, C.M. Wilson, E.P. Royal, Determining GAC bed life, *J. Am. Water Works Assn.*, 91 (1999) 98–110.
- [10] D.W. Ferguson, M.J. McGuire, B. Koch, R.L. Wolfe, E. Aieta, Comparing peroxide and ozone for controlling taste and odor compound, disinfection by-products, and microorganisms, *J. Am. Water Works Assn.*, 82 (1990) 181–191.
- [11] W.H. Glaze, J.J. Zarnoch, E.C. Ruth, W. Chauncey, R. Schep, Evaluating oxidants for the removal of model taste and odor compounds from a municipal water supply, *J. Am. Water Works Assn.*, 82 (1990) 79–84.
- [12] S. Lalezary, M. Pirbazari, M.J. McGuire, Oxidation of five earthy-musty taste and odor compounds, *J. Am. Water Works Assn.*, 78 (1986) 62–69.
- [13] B.V. Lundgren, A. Grimvall, R. Savenhed, Formation and removal of off-flavor compounds during ozonation and filtration through biologically active sand filters, *Water Sci. Technol.*, 20 (1988) 245–253.
- [14] B. Koch, J.T. Gramith, M.S. Dale, D.W. Ferguson, Control of 2-methylisoborneol and geosmin by ozone and peroxide: a pilot study, *Water Sci. Technol.*, 25 (1992) 291–298.
- [15] J. Kim, B. Kang, DBPs removal in GAC filter-adsorber, *Water Res.*, 42 (2008) 145–152.
- [16] I.N. Najm, V.L. Snoeyink, B.W. Lykins, J.Q. Adams, Using powdered activated carbon: a critical review, *J. Am. Water Works Assn.*, 83 (1991) 65–76.
- [17] D. Cook, G. Newcombe, Can we predict the removal of MIB and geosmin with PAC by using water quality parameters?, *Water Sci. Technol. Water Supply*, 4 (2004) 221–226.
- [18] H.W. Hung, T.F. Lin, Predicting the adsorption capacity and isotherm curvature of organic compounds onto activated carbons in natural waters, *Environ. Technol.*, 27 (2006) 255–267.
- [19] Ministry of Environment, Republic of Korea, Public Notification on Operation of Water Quality Monitoring Items, 2016.
- [20] F. Jüttner, S.B. Watson, Biochemical and ecological control of geosmin and 2-methylisoborneol in source waters, *Appl. Environ. Microbiol.*, 73 (2007) 4395–4406.
- [21] Ministry of Environment, Republic of Korea, Standard Method for Drinking Water Quality, 2017.
- [22] P.-E. Persson, Sensory properties and analysis of two muddy odour compounds, geosmin and 2-methylisoborneol, in water and fish, *Water Res.*, 14 (1980) 1113–1118.
- [23] D.M.C. Rashash, A.M. Dietrich, R.C. Hoehn, FPA of selected odorous compounds, *J. Am. Water Works Assn.*, 89 (1997) 131–141.
- [24] A. Rescorla, M.J. Semmens, R.M. Hozalski, Effect of NOM and lime softening on Geosmin removal by PAC, *J. Am. Water Works Assn.*, 109 (2017) E85.
- [25] W.F. Young, H. Horth, R. Crane, T. Ogden, M. Arnott, Taste and odour threshold concentrations of potential potable water contaminants, *Water Res.*, 30 (1996) 331–340.
- [26] G. Newcombe, J. Morrison, C. Hepplewhite, Simultaneous adsorption of MIB and NOM onto activated carbon: I. Characterisation of the system and NOM adsorption, *Carbon*, 40 (2002) 2135–2146.
- [27] G. Newcombe, J. Morrison, C. Hepplewhite, D.R.U. Knappe, Simultaneous adsorption of MIB and NOM onto activated carbon: II. Competitive effects, *Carbon*, 40 (2002) 2147–2156.
- [28] J.D. Plummer, J.K. Edzwald, Effects of chlorine and ozone on algal cell properties and removal of algae by coagulation, *J. Water Supply Res. Technol. AQUA.*, 51 (2002) 307–318.

Supplementary Information

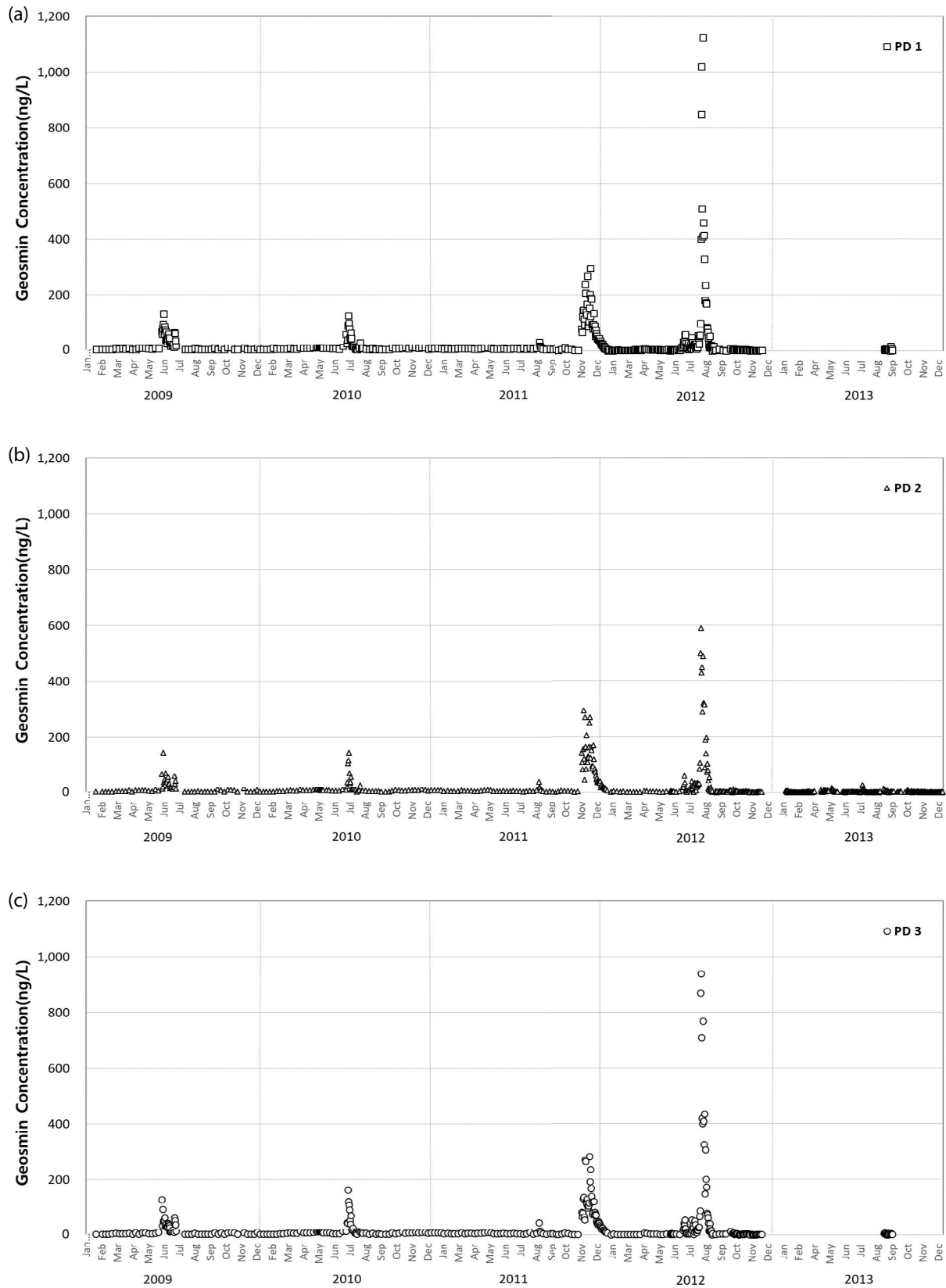


Fig. S1. Occurrence of geosmin by year in Paldang Lake (a) PD 1, (b) PD 2, and (c) PD 3 water intake facility.

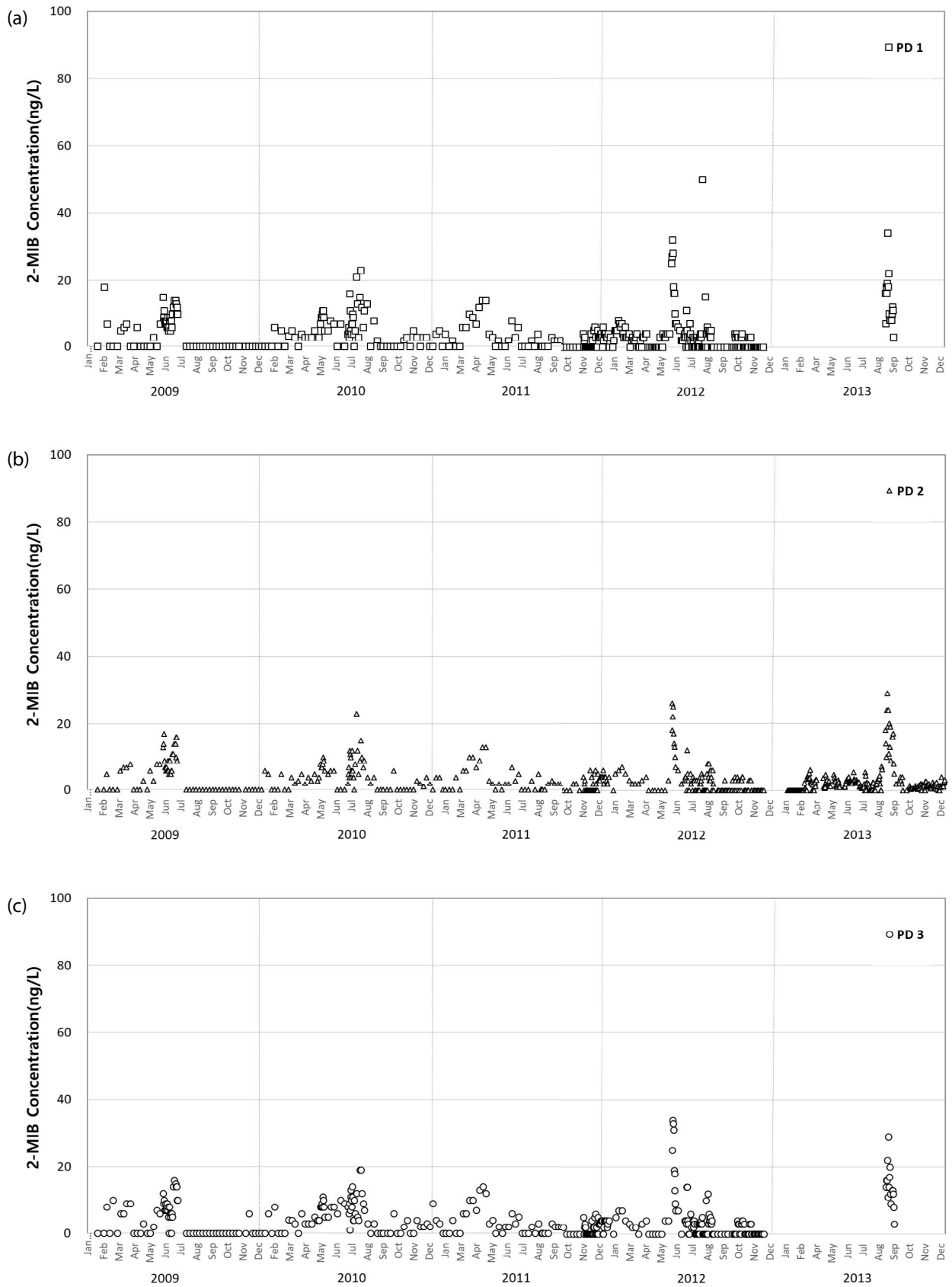


Fig. S2. Occurrence of 2-MIB by year in Paldang Lake (a) PD 1, (b) PD 2, and (c) PD 3 water intake facility.

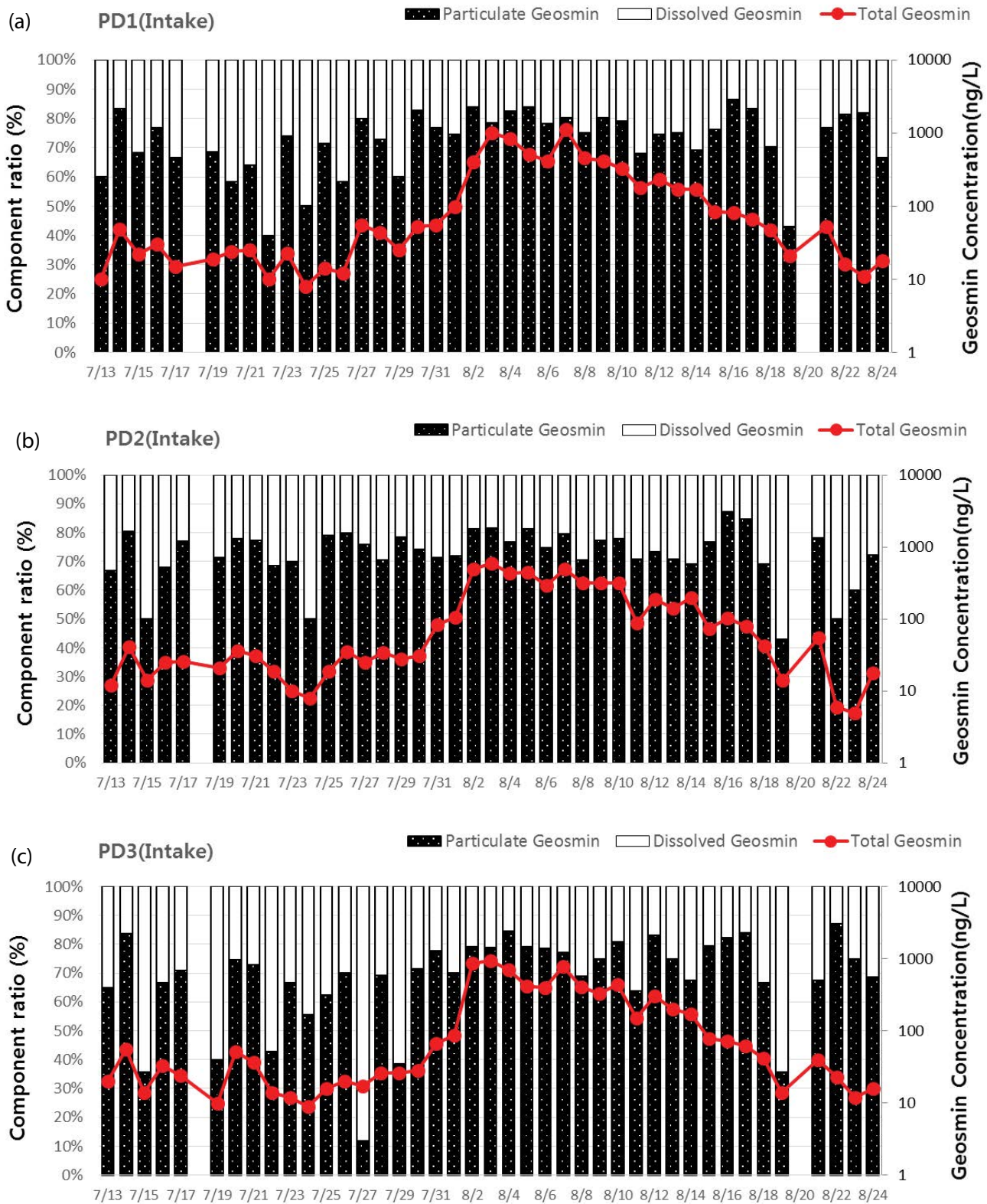


Fig. S3. Fraction of dissolved and particulate geosmin in raw water (a) PD 1, (b) PD 2, and (c) PD 3 water intake facility.

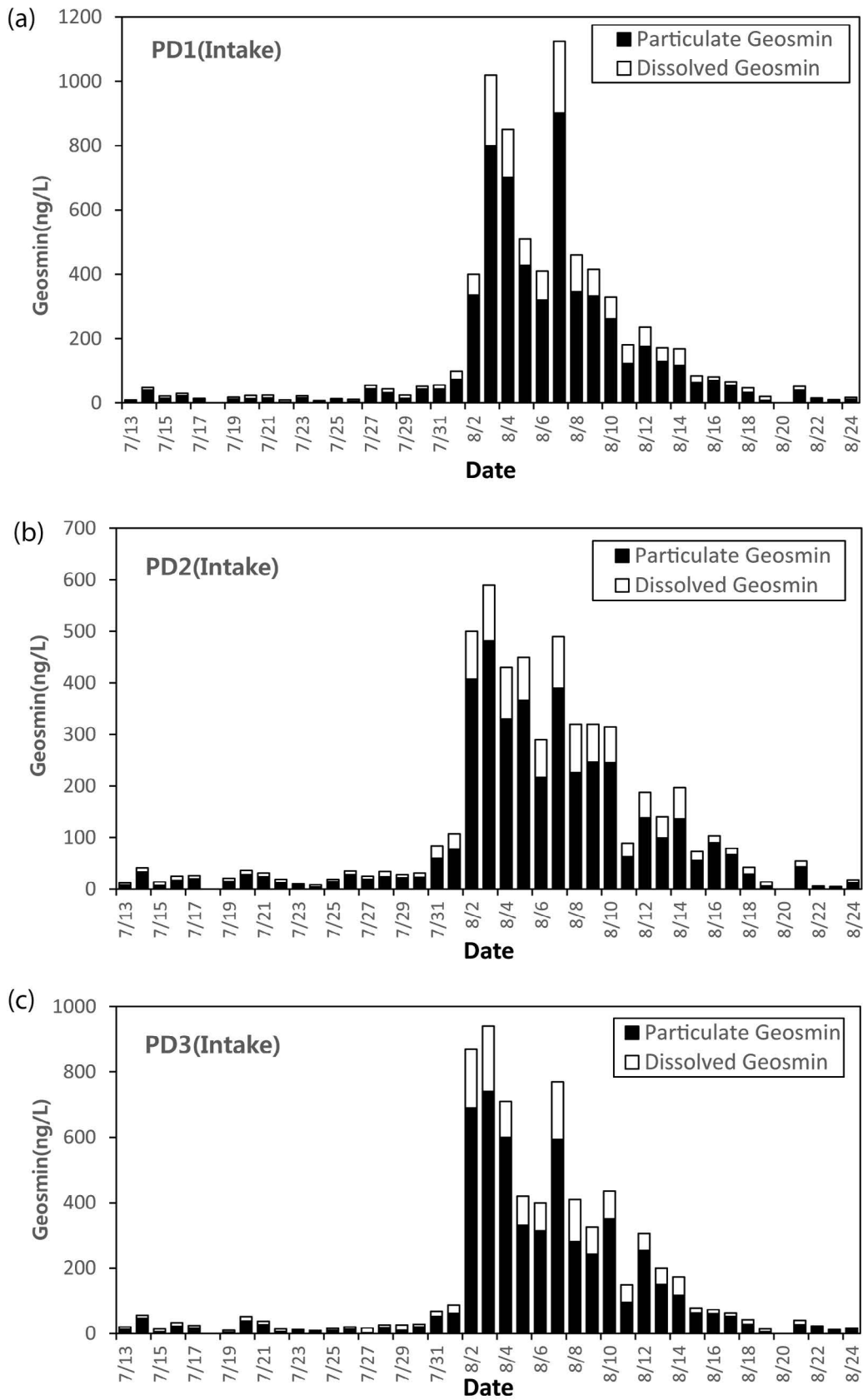


Fig. S4. Concentration of dissolved and particulate geosmin in raw water (a) PD 1, (b) PD 2, and (c) PD 3 water intake facility.