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Removal Characteristics of *N*-Nitrosamines and Their Precursors by Pilot-Scale Integrated Membrane Systems for Water Reuse

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Abstract

This study investigated the removal characteristics of *N*-nitrosamines and their precursors at three pilot-scale water reclamation plants. These plants applies different integrated membrane systems: (1) microfiltration (MF) / nanofiltration (NF) / RO; (2) sand filtration/three-step RO; and (3) ultrafiltration (UF) / NF and UF / RO. Variable removal of *N*-nitrosodimethylamine (NDMA) by the RO membrane processes could be attributable to membrane fouling and feed water temperature. The effect of membrane fouling on *N*-nitrosamines removal was extensively evaluated at one of the plants by conducting one month of operation and chemical cleaning of the RO membrane element. Membrane fouling enhanced *N*-nitrosamines removal by the pilot-scale RO membrane process. This finding contributes to better understanding of variable removal of NDMA by RO membrane processes. This study also investigated the removal characteristics of *N*-nitrosamines precursors. The NF and RO membrane processes greatly reduced NDMA formation potential (FP), but the UF process had little effect. The contributions of MF, NF, and RO membrane processes for reducing FPs of NDMA, *N*-nitrosopyrrolidine (NPYR) and *N*-nitrosodiethylamine (NDEA) were different, suggesting different size distributions of their precursors.

Key words: *N*-nitrosamines; formation potential; membrane treatment; reverse osmosis; membrane fouling; pilot-scale

1. Introduction

In response to increasing indirect and direct potable reuse of reclaimed water, the monitoring and control of micropollutant concentrations are increasingly important. In many potable reuse schemes, reverse osmosis (RO) membrane processes are key components due to their high removal performance for inorganic salts and trace organic chemicals [1–3]. However, residual trace organic chemicals in RO permeate have been reported [4–6]. Among the chemicals, *N*-nitrosamines in RO permeate are of key concern for potable reuse, and further research and monitoring of them are recommended [4,7,8]. These *N*-nitrosamines include *N*-nitrosodimethylamine (NDMA), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosodiethylamine (NDEA), *N*-nitrosopiperidine (NPIP), *N*-nitrosomorpholine (NMOR), *N*-nitrosodipropylamine (NDPA), and *N*-nitrosodi-n-butylamine (NDBA). Most of these *N*-nitrosamines are probable carcinogens [9], and their frequent occurrence in raw and secondary-treated wastewater [10–12] and reclaimed water [7,13–17] has been reported. For the augmentation of drinking water sources, the California Department of Public Health sets a drinking water notification level of 10 ng/L for NDMA and NDEA [18], and the Australian Guidelines for Water Recycling sets guideline values for NDMA (10 ng/L), NDEA (10 ng/L), and NMOR (1 ng/L) [19].

N-nitrosamines, in particular NDMA, have become a major driver for the design and operation of potable reuse treatment trains. Due to the low and variable removal of NDMA by RO membranes, additional processes such as advanced oxidation process (AOP) are installed to remove NDMA from RO permeate, which results in a high energy cost. The removal characteristics of *N*-nitrosamines by RO membranes have been extensively investigated at laboratory-scale [20–23]. Since *N*-nitrosamines are hydrophilic and non-ionized at the typical environmental pH range of 6–8, their removal by RO membranes is governed mainly by steric hindrance. A laboratory-scale study showed increased removal of *N*-nitrosamines in order of increasing molecular weight [21]. The previous study also found a significant decrease in the removal of *N*-nitrosamines with increasing feed water temperature, and a discernible decrease in NDMA removal with decreasing feed water pH and with increasing feed water ionic strength. An increase in the removal of *N*-nitrosamines with increasing permeate flux has also been observed [21]. In addition, RO membrane characteristics influence the removal of *N*-nitrosamines [22]. Furthermore, membrane fouling can enhance NDMA removal by RO membranes as a result of enhanced size exclusion [23].

These laboratory-scale studies clearly show the removal characteristics of *N*-nitrosamines by RO membranes. However, pilot-scale data to assess the effects of realistic operating conditions on *N*-nitrosamines removal are scarce. In addition, the previous pilot-scale studies have focused extensively on NDMA and evaluation for other *N*-nitrosamines are still limited. Fujioka et al. assessed the removal of eight *N*-nitrosamines in three full-scale RO plants and reported that discrepancies in *N*-nitrosamine removal data between laboratory- and full-scale studies were occurred probably due to differences in water recovery and operating conditions such as temperature, membrane fouling, and hydraulic conditions [14]. However, no pilot-scale study has investigated the effect of membrane fouling on the removal of *N*-nitrosamines by RO membrane processes. Pilot- and full-scale investigations to reaffirm findings from laboratory-scale studies are necessary.

N-nitrosamines have also attracted attention as disinfection by-products (DBPs), which are formed during the disinfection of biologically treated wastewater with chlorine or chloramines

[24–26] as well as alternative disinfectants such as chlorine dioxide (ClO_2) and ozone (O_3) [27]. NDMA can be formed from compounds which can release a secondary amine, including pharmaceuticals [28], pesticides [29], cationic polymers and ion exchange resins [30], and quaternary amines used in toiletries [31]. Although some precursors convert to NDMA with molar yields of 90% [28], specific precursors responsible for significant NDMA formation have not yet been identified. In water reclamation processes using RO membrane process, disinfectants are often added upstream of the RO membrane process to inhibit biological fouling, and to the final water before distribution. The addition of these disinfectants leads to the formation of *N*-nitrosamines during membrane processes [32–34] and distribution [33]. To control *N*-nitrosamine concentrations in reclaimed water, it is therefore important to understand the fate of their precursors during membrane treatment processes.

The fate of NDMA precursors in integrated membrane processes has been studied mainly at microfiltration (MF)–RO treatment plants [16,34,35] and ultrafiltration (UF)-RO treatment plants [32,35], but not in other membrane processes such as nanofiltration (NF). In addition, previous studies have focused on NDMA precursors and the fate of other *N*-nitrosamines precursors is still limited. Mamo et al. assessed the fate of NDMA precursors in pilot-scale membrane bioreactor (MBR)–NF processes and found that the rate of reduction of NDMA formation potential (FP) by NF process was high (>90%) [17]. Miyashita et al. investigated the removal of *N*-nitrosamine precursors (i.e. dimethylamine, methylethylamine, diethylamine, and dipropylamine) in bench-scale NF treatment and reported >98% removal of all four precursors [36]. However, evaluation of the removal efficiency of specific precursors by membrane processes is insufficient to evaluate the efficiency of removal of *N*-nitrosamine precursors, because not all precursors have been identified.

This study aimed (1) to investigate the occurrence and fate of eight *N*-nitrosamines and their FPs in three pilot-scale membrane processes using MF, UF, NF and RO membrane processes, (2) to explore realistic operating conditions that contribute to the variability of the removal of *N*-nitrosamines by pilot-scale RO membrane processes; and (3) to extensively assess the effect of membrane fouling on the removal of *N*-nitrosamines by a pilot-scale RO membrane process by performing chemical cleaning of the RO membrane element.

2. Materials and methods

2.1 Site description

Samples were collected at three pilot-scale water reclamation plants (A, B, C) receiving secondary effluent derived from municipal wastewater treatment plants. Plant A applies MF-NF-RO membrane system following an anaerobic–oxic activated sludge process (Fig. 1, Table 1). Plant B uses sand filtration (SF) and three-step RO membrane system following a conventional activated sludge process (Fig. 1, Table 1). Plant C applies UF and two parallel NF and RO membrane system following a conventional activated sludge process (Fig. 1, Table 1). To mitigate biofouling of membranes, sodium hypochlorite was continuously added to the MF feed water at plant A and to the SF feed water at plant B. Polyaluminum chloride (PACl) was added as a coagulant prior to the MF and SF processes. To mitigate biofouling at plant C, 2,2-dibromo-3-nitrilopropionamide was periodically added prior the NF and RO membrane processes.

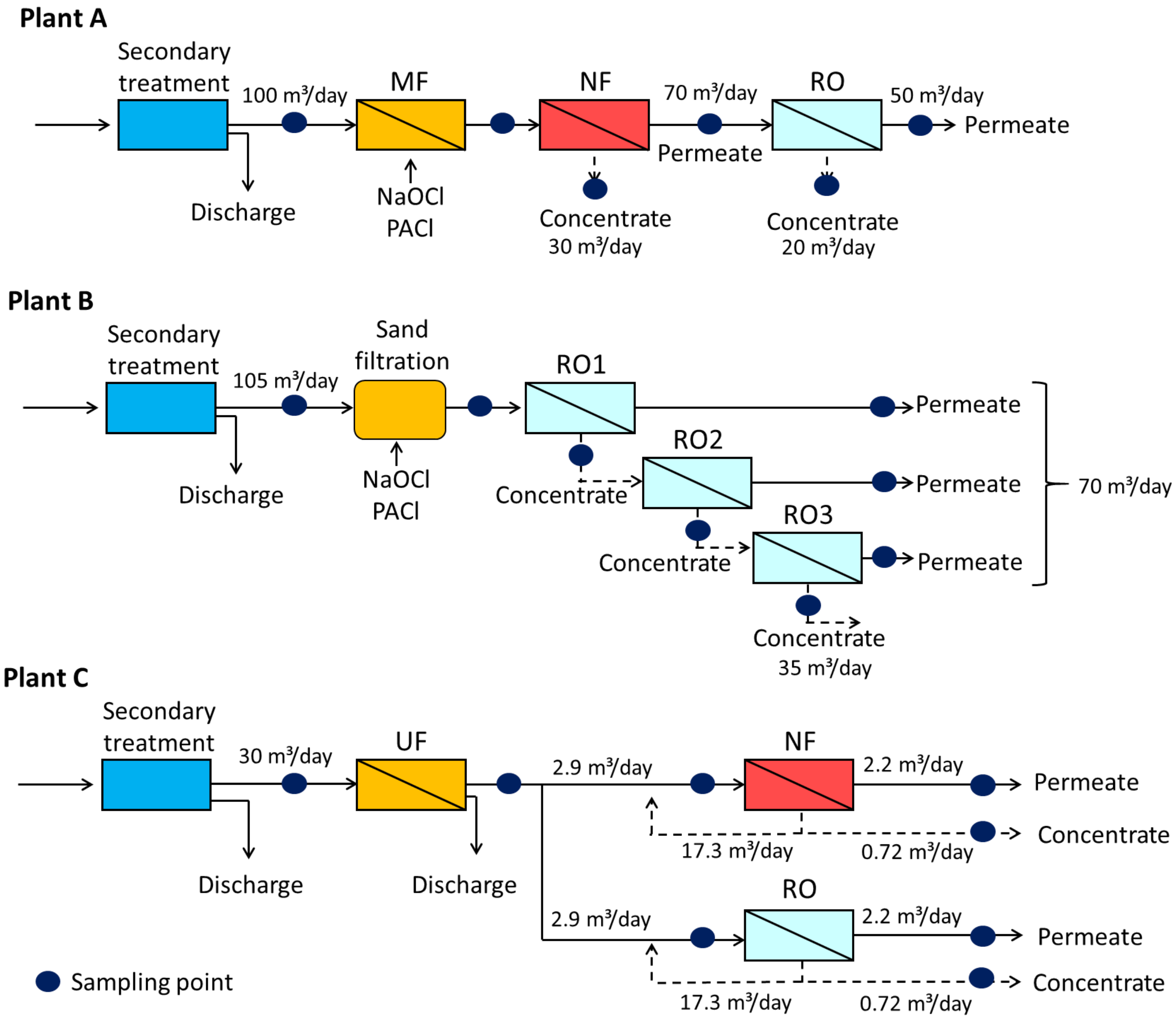

Figure 1. Process flows and sampling points in the water reclamation plants.

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Table 1. Characteristics of membranes used at plants A, B, and C.

Plant	Membrane	Membrane material	Type	Pore size [a] (μm)	NaCl rejection [a]	Recovery rate (%)
A	MF	Ceramic	Cylindrical	0.1	N.A.	100
	NF	Poly-vinyl alcohol polyamide	Spiral	N.A.	92%	65
	RO	Poly-vinyl alcohol polyamide	Spiral	N.A.	99.5%	80
B	RO	Aromatic composite polyamide	Spiral	N.A.	99.7%	67
C	UF	Poly-vinylidene fluoride	Hollow fiber	0.01	N.A.	100
	NF	Piperazine polyamide	Spiral	N.A.	60%	75
	RO	Aromatic composite polyamide	Spiral	N.A.	99.7%	75

N.A.: not available.

[a] Pore size and NaCl rejection values as specified by the manufacturers.

2.2 Sampling protocol

Grab samples were taken across the water reclamation treatment trains (Fig. 1). All samples were collected in amber glass bottles and stored in darkness at 4 °C until analysis. Chlorine concentrations were measured with hypochlorite test kits (Hach, CO, USA) at plants A and B, where sodium hypochlorite was added across the treatment trains (Fig. 1). To quench residual chlorine and stop the formation of *N*-nitrosamines, sodium thiosulfate was added to all samples except secondary effluent to give a final concentration of 10 mg/L.

Water temperature, pH, and conductivity were measured on site with a multi-function water quality meter (U-52G, Horiba, Kyoto, Japan). Operating pressure and flows were monitored within the plants. Sampling campaigns were conducted at plant A from January 2013 to August 2014 (n = 3), at plant B from December 2012 to December 2014 (n = 3), and at plant C from June 2013 to January 2014 (n = 5).

2.3 Chemical cleaning of RO membrane element

To assess the effect of RO membrane fouling on removal of *N*-nitrosamines, RO feed and permeate samples at plant C were collected at different stages of membrane fouling development. Samplings were conducted once a week from November to December 2015. After 1 month of operation, the RO membrane element was chemically cleaned as follows: (1) circulate cleaning solutions (below) in the RO system for 1 h; (2) soak the element in cleaning solution for 1 h; and (3) flush sufficient RO permeate to displace remaining cleaning solution. The chemical cleaning was performed using 0.03% sodium dodecyl sulfate (pH 11), 2% citric acid (pH 2), and sodium hydroxide (pH 11). To evaluate the effect of chemical cleaning on membrane fouling and removal of *N*-nitrosamines, RO feed and permeate samples were collected after the cleaning.

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2.4 Analytical techniques

N-nitrosamines

Eight *N*-nitrosamines –NDMA, NMEA, NPYR, NDEA, NPIP, NMOR, NDPA, and NDBA– were targeted in this study. These *N*-nitrosamines have molecular weights in the range of 74 to 158 g/mol (Table 2). An analytical method previously developed for the determination of *N*-nitrosamines in wastewater was employed [25]. This method uses solid-phase extraction, gas chromatography and analysis by tandem mass spectrometry. Eight deuterated *N*-nitrosamines –NDMA-d_6, NMEA-d_3, NPYR-d_8, NDEA-d_{10}, NPIP-d_{10}, NMOR-d_8, NDPA-d_{14}, and NDBA-d_{18}– were used as surrogate. These deuterated chemicals were obtained from CDN Isotopes (Pointe-Claire, Quebec, Canada) and a stock solution was prepared in pure methanol at 1 mg/L of each deuterated *N*-nitrosamines. After spiking surrogate solution into each sample, *N*-nitrosamines were extracted with Sep-Pak NH-2 and AC-2 cartridges (Waters, MA, USA) at a flow rate of 10 mL/min. After the AC-2 cartridges were dried, the analytes were eluted from the cartridges with 2 mL dichloromethane (Wako Pure Chemical Industries, Tokyo, Japan) and concentrated under a nitrogen gas stream. After adding dichloromethane solution and deuterated toluene (toluene-d8) stock solution (Supelco, Bellefonte, PA, USA), used as an injection internal standard, into the eluents, *N*-nitrosamine concentrations were quantified using Varian 450 Series gas chromatograph coupled with a Varian 300 series tandem mass spectrometer. The limits of detection and quantification of *N*-nitrosamines are shown in Table S1 (Supplementary Materials).

Table 2. Physicochemical properties of eight *N*-nitrosamines.

Compound	NDMA	NMEA	NPYR	NDEA	NPIP	NMOR	NDPA	NDBA
Molecular weight (g/mol) [a]	74.08	88.11	100.12	102.14	114.15	116.12	130.19	158.25
pK_a [a]	3.22	3.42	3.30	3.32	3.30	3.14	3.30	3.30
$LogK_{ow}$ [a]	0.08	0.41	0.39	0.75	0.81	-0.32	1.05	2.56

[a] Calculated in MarvinSketch software (ChemAxon, Budapest, Hungary).

Formation potentials

N-nitrosamines precursors were evaluated as formation potentials as described [24] with minor modifications [11]. In brief, 20 mM chloramine stock solution (~1400 mg Cl_2/L) was prepared before each experiment because of its tendency to auto-decompose at high concentrations. First, the sample pH was adjusted to 7 with 10 mM phosphate buffer. Next, chloramination was performed in a 1-L amber glass bottle by adding 20 mM chloramine stock solution (100 mL) to samples (900 mL). The samples were then stirred for 10 days at room temperature on a shaker (NR-80, Taitec, Saitama, Japan). FP was defined as the increment of *N*-nitrosamine

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concentration during 10 days.

2.5 Calculations

N-nitrosamine removal rate (R_{N}) and FP reduction rate (R_{FP}) in each process was calculated using the following equations:

$$R_{\mathrm{N}}\ [\%] = \left(1 - \frac{C_{\mathrm{p}}}{C_{\mathrm{f}}}\right) \times 100 \tag{1}$$

$$R_{\mathrm{FP}}\ [\%] = \left(1 - \frac{FP_{\mathrm{p}}}{FP_{\mathrm{f}}}\right) \times 100 \tag{2}$$

where C_{p} and C_{f} are *N*-nitrosamine concentrations in the permeate and feed, respectively; and FP_{p} and FP_{f} are formation potentials in the permeate and feed, respectively.

3. Results and discussion

3.1 Occurrence of *N*-nitrosamines

NDMA and NMOR were prevalent *N*-nitrosamines, as reported in other studies [7,13,14]. NDMA was detected in all secondary effluent samples at 9 to 41 ng/L at plant A, 11 to 20 ng/L at plant B, and 8 to 70 ng/L at plant C (Fig. 2). NMOR was present in some secondary effluent samples at 50 to 358 ng/L at plant A, N.D. (not detected) to 8 ng/L at plant B, and N.D. to 4 ng/L at plant C (Fig. 2). Along with NDMA and NMOR, NDBA was detected in secondary effluent at plant B in the second sampling campaign at 11 ng/L. NMEA, NPYR, NDEA, NPIP, and NDPA were not detected at any sampling campaigns.

NDMA was detected in all RO permeate samples at 12 to 22 ng/L at plant A, 2 to 8 ng/L at plant B, and 5 to 10 ng/L at plant C (Fig. 2). Due to the low NDMA removal by the RO membrane process, NDMA concentrations in RO permeate were slightly higher than the guideline value of 10 ng/L [19] at plant A, but were lower than the guideline value at plants B and C. NMOR was also detected in RO permeate samples at all three plants at up to 71 ng/L. RO permeate samples at plant A had high concentrations of NMOR (7–71 ng/L), which was much higher than the guideline value of 1 ng/L established for potable reuse [19]. High NMOR concentrations in RO permeate have been reported in previous studies (5–30 ng/L [10]; 177–475 ng/L [14]). These results indicate that both NMOR and NDMA can pose risks for potable reuse and should be monitored at water reclamation plants.

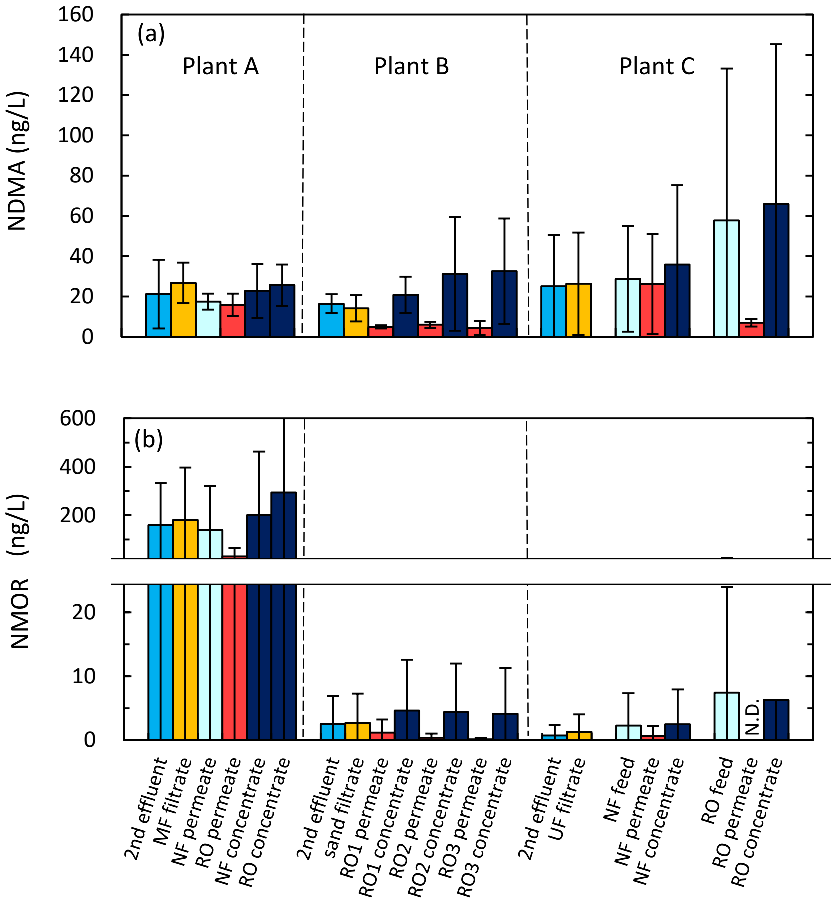

Figure 2. Concentrations of (a) NDMA and (b) NMOR detected across the treatment trains at plants A, B, and C (means ± standard deviation (SD)). N.D.: not detected.

3.2 Occurrence of formation potentials

NDMA FP was detected most frequently at all three plants (Fig. 3). The NDMA FP level in secondary effluent ranged from 67 to 232 ng/L at plant A, 70 to 242 ng/L at plant B, and 236 to 482 ng/L at plant C. These NDMA FP levels were in general lower than values reported from the U.S. (200–2000 ng/L [12]) and Australia (300–1020 ng/L [32]). In addition to NDMA FP, NPYR FP (101 ng/L), NDEA FP (41 ng/L), and NMOR FP (4 ng/L) were detected in secondary effluent at plant A at the second sampling campaign (Fig. 3a).

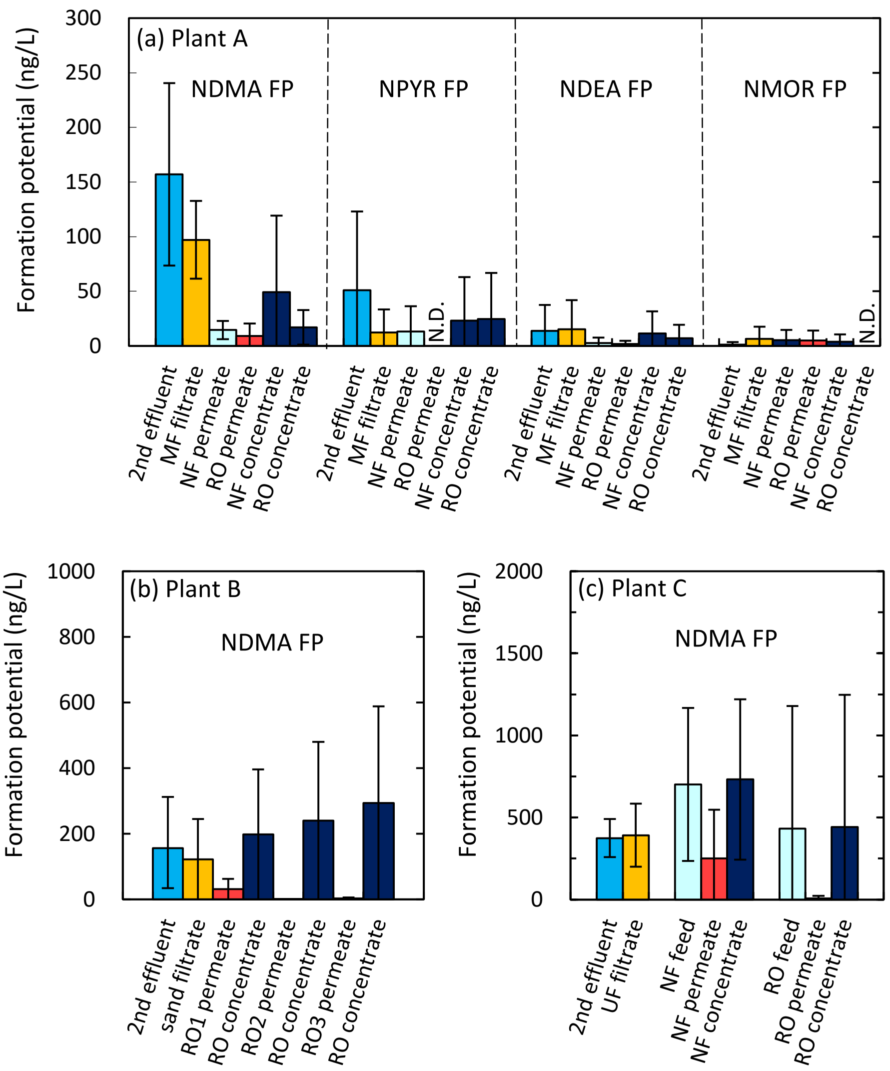

Figure 3. (a) *N*-nitrosamine FPs detected across the treatment trains at plant A, and (b, c) NDMA FPs detected at plants B and C (means ± SD). N.D.: not detected.

The presence of *N*-nitrosamine FPs could lead to the formation of *N*-nitrosamines during the membrane processes due to the reaction between precursors and disinfectant added upstream of the RO membrane processes. Chlorine added upstream of the MF process at plant A and of the SF process at plant B (Fig. 1) was converted to chloramines probably by reaction with ammonium in the secondary effluent. Concentrations of disinfectant detected across the treatment trains are shown in Table S2 (Supplementary Materials).

To evaluate the formation of *N*-nitrosamines during the membrane processes, mass loadings of *N*-nitrosamines across the treatment train at plant A were calculated. There was no increase in NDMA mass loadings during the NF and RO membrane processes (Fig. S1 in the Supplementary Materials). This result indicates that NDMA was not formed during these

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processes despite the presence of NDMA precursors and chloramines. On the other hand, NDMA mass loadings increased during the MF process in the second sampling campaign, indicating NDMA formation (Fig. S1). At the second sampling campaign at plant A, relatively high chloramine concentration (1.2 mg/L) was observed, which could explain the NDMA formation. Since NDMA was not well removed by the RO membrane process, some NDMA formed during the MF process may pass through the RO membrane and increase NDMA concentration in the final product water. The chlorine concentration added needs to be optimized to avoid the formation of excessive NDMA in the treatment process. NDEA, NPYR, and NMOR were not formed across the treatment train despite the presence of FPs.

NDMA FP was also detected in some RO permeate samples at 2 to22 ng/L at plant A, N.D. to 89 ng/L at plant B, and N.D. to 29 ng/L at plant C (Fig. 3). These values are comparable to values reported from the U.S. (12–59 ng/L [12]) and Australia (6 ng/L [32]). Even though NDMA FPs in RO permeate were lower than those in secondary effluent, NDMA precursors remaining in RO permeate might reduce RO permeate quality. For example, a previous study reported an increase in NDMA concentration from 13 ng/L to 24 ng/L during 24 h chloramination of RO permeate [33]. In assessing NDMA risks associated with the use of reclaimed water, not only NDMA but also NDMA FP in RO permeate need to be considered.

3.3 Removal of *N*-nitrosamines

The three integrated membrane systems provided variable removal performance for the detected three *N*-nitrosamines (Fig. 4). Although RO membrane processes removed NMOR and NDBA with high efficiency, their removal of NDMA varied significantly, even at the same plant (Fig. 5).

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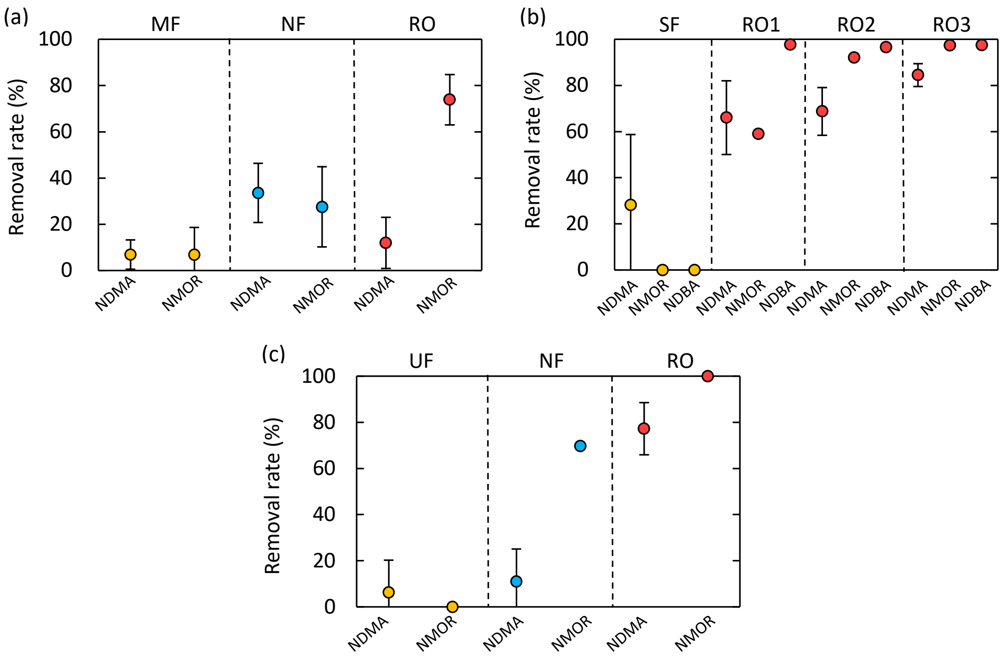

Figure 4. *N*-nitrosamines removal by each membrane process at (a) plant A, (b) plant B, and (c) plant C (means ± SD).

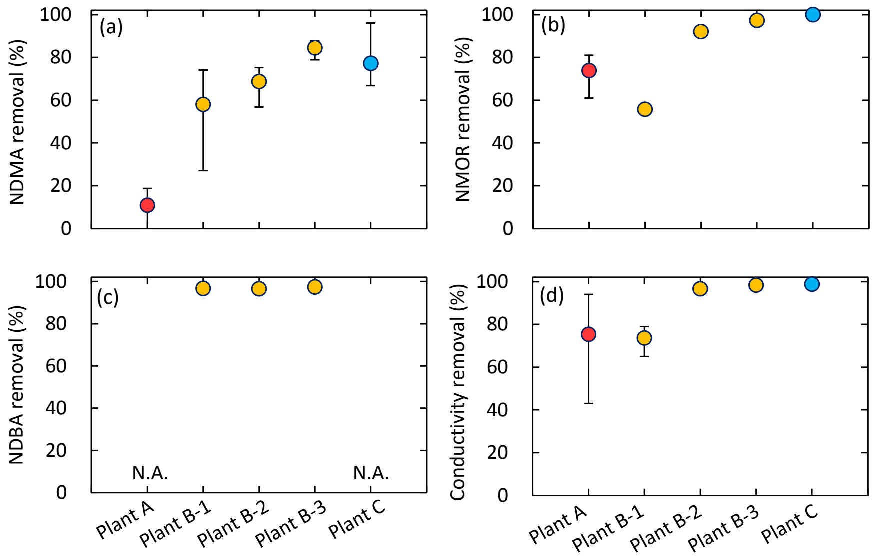

Figure 5. Removal of (a) NDMA, (b) NMOR, (c) NDBA, and (d) conductivity by RO membrane processes at plants A, B, and C (means ± minimum and maximum). N.A.: not available.

Plant A

The MF process exhibited limited removal for NDMA (<8%) and NMOR (<20%) (Fig. 4a). The small NDMA molecule easily passes through the MF process, and the removal level was comparable to a previous report of <10% [37]. The NF process gave low to moderate removal rate for efficiency for NDMA (13–41%) and NMOR (16–47%), respectively (Fig. 4a). The rates of NDMA removal in our study (13–41%) were slightly higher than those reported in previous studies (<10% [22]; <20% [36]). Since enhanced NDMA removal by fouled NF membranes was reported in a previous study [38], the relatively high NDMA removal observed in this study might relate to membrane fouling.

The difference in removal efficiency between NDMA and NMOR was noticeable during the RO membrane process (Fig. 4a). While the removal of NDMA was <19%, that of NMOR was as high as 81%. This result is in accordance with a previous study reporting that the removal of *N*-nitrosamines by RO membranes increased in order of increasing molecular weight [21]. Thus, molecular size can significantly affect removal by RO membrane processes. Surprisingly, the RO membrane process exhibited lower removal rate for NDMA (<19%) than the NF process (19%–41%) at plant A. Since the RO membrane process exhibited low salt rejection (Fig. 5d), the quite low NDMA removal can be attributed to damage of the RO membrane rather than to membrane characteristics or operational conditions. This result suggests that RO membrane damage affects the removal of NDMA.

Plant B

As expected, removal of NDMA, NMOR, and NDBA by sand filtration was limited, indicating that these *N*-nitrosamines were too small to remove by sand filtration (Fig. 4b). Plant B applies a three-step RO membrane process following the sand filtration. The removal of *N*-nitrosamines by the three RO membrane stage ranged from 27 to 88% of NDMA, from 59 to 97% of NMOR, and >97% of NDBA. The rates of removal increased in order of increasing molecular weight, as found at plant A and in other studies [21,36]. The increase in NDMA removal from the first to the third RO stage (Fig. 5a) might be due to membrane fouling. According to laboratory-scale studies, increased NDMA removal is caused by decreasing temperature, increasing permeate flux, and formation of membrane fouling [21,23]. Since the feed water temperature was the same in each RO stage (Fig. S2 in the Supplementary Materials), feed water temperature was not the reason for the increased NDMA removal. Although the permeate flux of each RO stage was not monitored, permeate flux would decrease with advancing stage because each stage received the concentrate of the previous stage, and the increased salt concentration (Fig. S2 in the Supplementary Materials) would result in increased osmotic pressure. A decrease in permeate flux would result in a decrease in NDMA removal [21], but this is the opposite trend observed in our study. Thus, changes in permeate flux through the three-stage RO process is not the main reason for the increased NDMA removal. Instead, RO membrane fouling would be more severe with advancing RO stage because each RO membrane

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stage received concentrate of the previous RO membrane stage. Thus, RO membrane fouling would contribute to the increased NDMA removal. Water reclamation plants often apply multiple-step RO systems to increase recovery rate. Due to the effect of membrane fouling, variable NDMA removal can be provided in multiple-step RO systems.

Plant C

Removal of NDMA and NMOR by the UF process was limited (Fig. 4c). The NF process removed <32% of NDMA and 70% of NMOR. The RO membrane process removed 67% to 96% of NDMA and >99% of NMOR. Since the RO membrane process was operated with stable water recovery (75%) and permeate flux (11 L/m^2/h), the variable NDMA removal by the RO membrane process would be due to differences in RO feed water characteristics or to RO membrane fouling (Fig. S3). NDMA removal had relatively strong correlations with feed water temperature (R^2 = 0.49; Fig 6a) and transmembrane pressure (TMP) (R^2 = 0.33; Fig. 6c). The TMP values were compensated with feed water temperature. An increase in NDMA removal was observed with increasing TMP (Fig 6c), with the only exception in the fifth sampling campaign. This result suggests that membrane fouling is a key factor enhancing NDMA removal by the RO membrane process. In the fifth sampling campaign, high NDMA removal was observed regardless of the relatively low TMP value (Fig 6c). The high NDMA removal might be attributable to feed water temperature. According to previous study [21], decreased feed water temperature resulted in an increase in NDMA removal by RO membranes. Thus, feed water temperature could be the reason for the high NDMA removal.

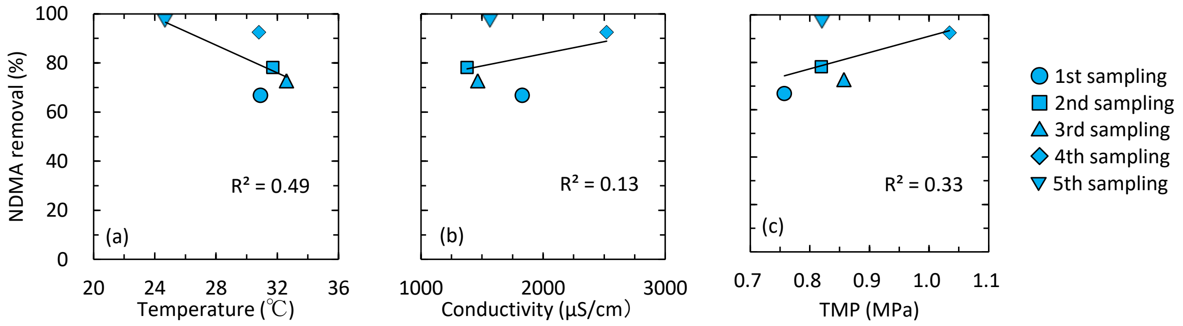

Figure 6. Correlation between NDMA removal and (a) feed water temperature, (b) conductivity, and (c) TMP.

3.4 Impact of RO membrane fouling on *N*-nitrosamines removal

To assess the impact of RO membrane fouling on *N*-nitrosamine removal, samplings were conducted at plant C every week for 1 month. During 1 month of operation, TMP increased

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from 0.60 to 0.79 MPa, indicating the development of RO membrane fouling (Fig. 7a). At the same time, NDMA removal increased from 71 to 99% and NMOR removal increased from 92 to 99% (Fig. 7a). By performing chemical cleaning of the RO membrane, TMP decreased from 0.79 to 0.70 MPa, indicating partial reduction of membrane fouling. At the same time, NDMA removal decreased from 99 to 77% and NMOR removal decreased from 99 to 94%. NDMA removal had a relatively strong correlation with TMP (R^2 = 0.83, n = 5; Fig. 7b). Water temperature and permeate flux, which have been reported to affect NDMA removal by RO membranes, did not fluctuate enough to affect NDMA removal during the sampling campaigns. These results indicate that membrane fouling enhanced the removal of these *N*-nitrosamines. In a laboratory-scale study, membrane fouling increased the removal of micropollutants by RO membrane by enhancing the effect of size exclusion [23]. Our data indicate that RO membrane fouling is one of the most important factors affecting *N*-nitrosamines removal, even at pilot scale.

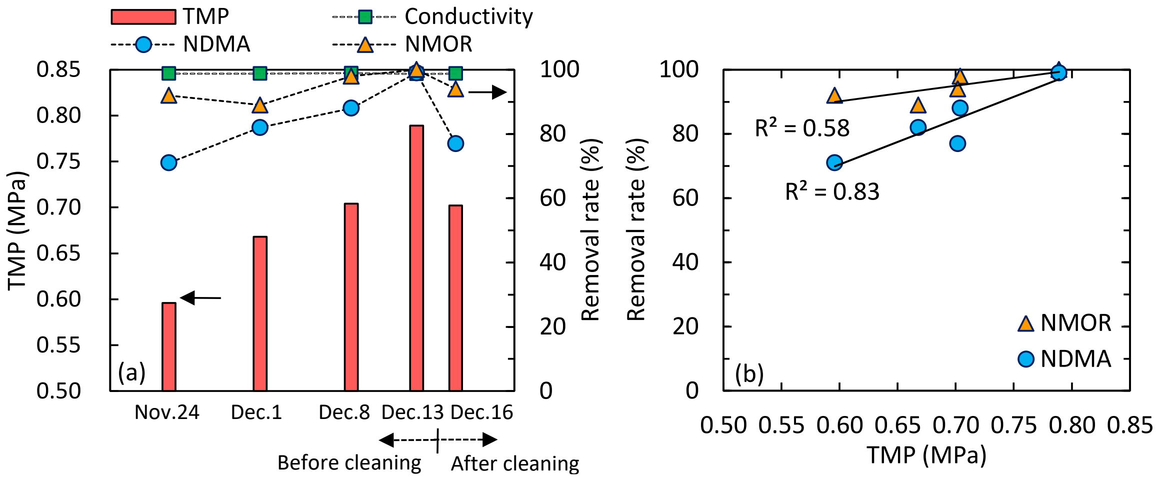

Figure 7. (a) Relations between TMP and removal of NDMA, NMOR, and conductivity before and after chemical cleaning, and (b) correlation between TMP and removal of the two *N*-nitrosamines.

3.5 Rate of reduction of *N*-nitrosamine FPs

The overall reduction rates of NDMA FP achieved more than 75% at the three plants (Fig. 8a). Even though NDMA was not sufficiently removed by the NF and RO membrane processes, precursors of NDMA were well removed by these processes. This result suggests that most precursors were ionized or were large enough to be removed by the NF and RO membrane processes. However, the reduction rates of NDMA FP by the NF processes were lower than values (>98%) reported in a previous study which investigated the removal of four NDMA precursors (dimethylamine, ethylmethylamine, diethylamine, and dipropylamine) using a

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bench-scale NF process [36]. That study attributed the high rates of removal to electrostatic interactions between the negatively charged NF membrane and the positively charged precursors. Therefore, the lower rate of reduction by the NF processes observed in our study suggests that some NDMA precursors are present in their uncharged forms and are thus difficult to remove by NF processes. For example, dimethylsulfamide and dimethylformamide are small uncharged NDMA precursors which can likely pass through NF processes [35]. Further research to identify uncharged NDMA precursors and their efficiencies of removal by water reclamation processes is necessary.

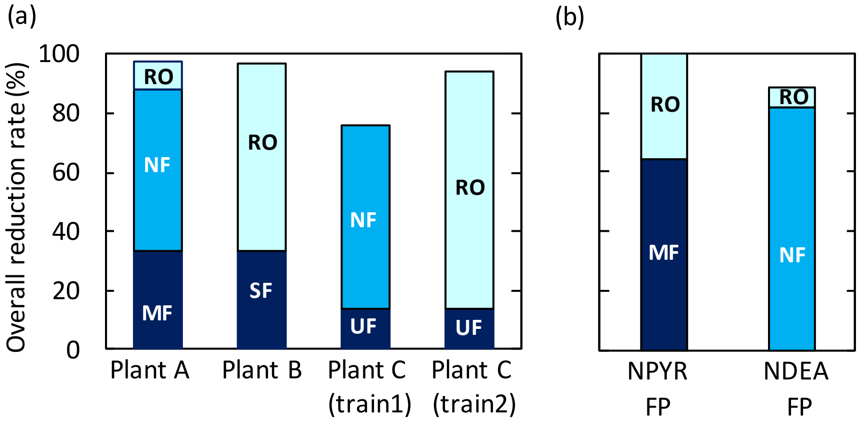

Figure 8. Overall rates of reduction of (a) NDMA FP at plants A, B, and C and of (b) FPs of NPYR and NDEA at plant A.

While NF and RO membrane processes at the three plants removed high proportions of NDMA FP, the MF and SF processes removed widely variable proportions: <59% by MF at plant A and <67% by SF at plant B (Fig. 8a). The relatively high reduction rates by the MF and SF processes could be attributed to the effect of coagulant added upstream, because a previous study reported greater reduction of NDMA FP by coagulation than by MF process [32]. On the other hand, the UF process at plant C removed little NDMA FP (Fig. 8a). These results suggest that NDMA precursors were present mainly as dissolved compounds at plant C, but partially as colloidal or particulate compounds at plants A and B.

FPs of NPYR, NDEA, and NMOR were detected only at plant A. Since NMOR FP was low (Fig. 3a), and it was difficult to clearly evaluate reduction across the treatment train, the efficiency of the integrated membrane processes was evaluated only for FPs of NPYR and NDEA. These FPs were effectively reduced (>89%) by the MF-NF-RO membrane system (Fig. 8b). The membrane processes were effective at removing these *N*-nitrosamine precursors. However, the efficiencies of removal of the *N*-nitrosamine FPs differed among processes,

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indicating different size distributions of these *N*-nitrosamines precursors. For example, the contribution of each membrane process to the overall rates of reduction of NPYR FP were 64% by MF, 1% by NF, and 36% by RO, and those of NDEA FP were negligible by MF, 82% by NF, and 7% by RO (Fig. 8b). Most NPYR precursors were removed by the MF process, and the rest were removed mostly by RO membranes process. This result suggests that most NPYR precursors were present as colloidal or particulate compounds and rest were present as dissolved compounds, which cannot be removed well by the NF process. On the other hand, NDEA precursors were removed not by the MF process, but by the NF and RO membrane processes. This result suggests that NDEA precursors would be predominantly present as dissolved compounds.

4. Conclusions

This study investigated the removal characteristics of *N*-nitrosamines and their precursors at three pilot-scale water reclamation plants that apply integrated membrane systems. NDMA removal by the RO membrane processes varied among the three plants and even at the same plant. The main reasons for the variable NDMA removal observed at a plant could be membrane fouling and feed water temperature. The effect of membrane fouling on *N*-nitrosamines removal by an RO membrane process was extensively evaluated at one of the plant by conducting 1 month of operation and chemical cleaning of the RO membrane element. The extensive evaluation revealed membrane fouling enhanced *N*-nitrosamines removal by the pilot-scale RO membrane process. The finding contributes to better understanding of the variable NDMA removal by RO membrane processes. The three-step RO membrane process at a plant showed increased NDMA removals as progress of the RO stages, which might be attributable to the effect of membrane fouling. Since RO membranes in multi-step RO system would have different membrane fouling or permeate flux conditions, these differences might lead to variable NDMA removals by multi-step RO membrane processes.

This study also investigated the removal characteristics of *N*-nitrosamines precursors at the three plants. NDMA FP was predominant at all three plants. The NF and RO membrane processes greatly reduced NDMA FP. However, remaining NDMA FP in their permeates implies the presence of uncharged precursors that are not easily removed by the membrane processes. FPs of NPYR, NDEA, and NMOR were detected at a plant which used MF-NF-RO treatment system. Each membrane process removed FPs of NPYR and NDEA with different efficiencies, suggesting different size distributions of their precursors. In designing new water

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reclamation plants, it is important to investigate which kinds of *N*-nitrosamines FP are present in the feed water.

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Author contributions

Hiroaki Tanaka conceived and designed the study. Haruka Takeuchi, Naoyuki Yamashita and Norihide Nakada collected samples and analyzed the results. Haruka Takeuchi wrote the first draft of the article. All authors read and approved the final version of the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

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