Environ. Sci. Technol. 2009, 43, 5236–5241

Identification of Antiyellowing Agents as Precursors of *N*-Nitrosodimethylamine Production on Ozonation from Sewage Treatment Plant Influent

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Received January 22, 2009. Revised manuscript received May 19, 2009. Accepted May 26, 2009.

In Japan, *N*-nitrosodimethylamine (NDMA) formation associated with ozonation at a relatively high concentration has been reported only at a small number of water treatment plants (WTPs) in the western part of Japan for which the source water is the Yodo River. In the present study, the formation of relatively high concentrations of NDMA was found upon ozonation of water samples taken from sewage treatment plants (STPs) located upstream of the water intake points of the WTPs in the Yodo River basin. NDMA concentrations before and after ozonation were 16–290 and 14–280 ng/L, respectively. At least some of the STPs investigated receive industrial effluents. At one STP in this area, an extremely high concentration of NDMA (10 000 ng/L) was found in one influent water sample after ozonation. To identify potential NDMA precursors upon ozonation in the influent at this STP, the concentrated extracts of the influent were fractionated by high-performance liquid chromatography (HPLC). Ultraperformance liquid chromatography coupled with tandem mass spectrometry (UPLC/MS/MS) identified 4,4′-hexamethylenebis(1,1-dimethylsemicarbazide) (HDMS) and 1,1,1′,1′-tetramethyl-4,4′-(methylene-di-*p*-phenylene)disemicarbazide (TMDS) as precursors of NDMA on ozonation of the influent. Both HDMS and TMDS are used as antiyellowing agents in polyurethane fibers and as light stabilizers in polyamide resins. Their contributions to NDMA production on ozonation of water samples at STPs were up to 17%. The remaining unidentified NDMA precursors may be hydrophilic compounds that were not trapped by the cartridges used for extraction of the water samples. HDMS and TMDS were frequently present in surface waters and STP effluents in the Yodo River basin and were also detected in surface waters from several other areas in Japan.

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Introduction

N-Nitrosodimethylamine (NDMA) has been given a classification of B2 according to the Integrated Risk Information System (IRIS) of the United States Environmental Protection Agency (U.S. EPA) (*1*) and 2A according to the International Agency for Research on Cancer (IARC), both of which indicate that it is a probable human carcinogen (*2*). NDMA has recently been shown to be a disinfection byproduct of chloramination or chlorination in the presence of ammonia (*3*–*9*). In 2003, the Ministry of the Environment (MOE) in Ontario, Canada, established a provisional maximum allowable NDMA concentration of 9 ng/L (*10*), and in 2006, the Office of Environmental Health Hazard Assessment (OEHHA) established a public health goal (PHG) of 3 ng/L NDMA in California (*11*).

More recently, several researchers have reported that NDMA is formed by ozonation. Dimethylamine (DMA) (*12*), tolylfluanid, its decomposition byproducts (e.g., dimethylsulfamide (DMS)), daminozide, and its decomposition byproduct 1,1-dimethylhydrazine (UDMH) (*13*) have been shown to be precursors of NDMA upon ozonation. In addition, some dyes and related compounds were shown to produce NDMA during ozonation (*14*). The molar conversion yields of tolylfluanid, daminozide, and their decomposition products to NDMA by ozonation range from 9 to 80% (*13*). On the basis of the previous report (*13*), DMS was considered the main NDMA precursor upon ozonation only in watersheds where tolylfluanid was used. On the other hand, the molar conversion yields of DMA and these reported dyes and related compounds (e.g., methylene blue and *N,N*-dimethyl-*p*-phenylenediamine) to NDMA were on the order of 10^{-2}%, and therefore, their contributions to NDMA precursors in environmental waters were considered to be very low. In addition, it was reported that NDMA was formed by ozonation of two of seven surface waters in different areas of Canada and the U.S.A. (*15*). In Japan, NDMA formation associated with ozonation at a relatively high concentration was reported only at a small number of water treatment plants (WTPs) in the western part of Japan for which the source water is the Yodo River (*16*, *17*). However, the precursors of NDMA upon ozonation of the river water have not yet been identified.

The occurrence of NDMA in sewage treatment plants (STPs), the effluents of which flow into the river waters of the upper Yodo River basin, was investigated in the present study. The precursors of NDMA upon ozonation in the sewage influent were also identified, and their occurrence was investigated in several other areas in Japan.

Materials and Methods

Reagents and Solutions. All solutions were prepared from ultrapure water obtained using a Gradient A10 water purification system (Millipore, Bedford, MA), except for the eluent for ultraperformance liquid chromatography coupled with tandem mass spectrometry (UPLC/MS/MS) for which distilled water (liquid chromatography coupled with MS grade) purchased from Kanto Chemical (Tokyo, Japan) was used. NDMA was purchased from Supelco (Bellefonte, PA). NDMA-d_6 was purchased from C/D/N Isotopes (Pointe-Claire, Canada). 4,4′-Hexamethylenebis(1,1-dimethylsemicarbazide) (HDMS, >98.0%) and 1,1,1′,1′-tetramethyl-4,4′-(methylene-di-*p*-phenylene)disemicarbazide (TMDS, >95.0%) were purchased from Tokyo Chemical Industry (Tokyo, Japan). All other reagents used were of analytical grade and obtained from commercial suppliers.

10.1021/es900227g CCC: $40.75
Published on Web 06/10/2009

TABLE 1. NDMA Concentrations before and after Ozonation of Water Samples from Rivers and STP Effluents[a]

sampling point	NDMA concentration (ng/L) before ozonation	NDMA concentration (ng/L) after ozonation[b]
Y1	1.8	16
K1	1.2	2.4
K2	11	36
STP1	290	280
STP2-1	16	14
STP2-2	54	190
STP3	20	37
STP4	24	30

[a] Each point was sampled once. [b] Ozonation conditions: ozone concentration in gas phase, 5 mg/L; ozone gas flow rate, 0.5 L/min; reaction time, 2.5 min; temperature, 20 °C.

TABLE 2. NDMA Concentrations before and after Ozonation of Water Samples at STP1[a]

sampling point	NDMA concentration (ng/L) before ozonation	NDMA concentration (ng/L) after ozonation[b]
influent 1	42	100
primary sedimentation 1 effluent	71	460
secondary sedimentation 1 effluent[c]	83	470
influent 2	710	10000
primary sedimentation 2 effluent	130	1800
secondary sedimentation 2 effluent[c]	130	450
effluent[d]	450	

[a] Each point was sampled once. [b] Ozonation conditions: ozone concentration in gas phase, 5 mg/L; ozone gas flow rate, 0.5 L/min; reaction time, 20 min; temperature, 20 °C. [c] After biological treatment. [d] After ozonation.

Sampling. Samples of river waters and effluents (i.e., STP effluents and industrial discharges that flow directly into the public water bodies) were collected. Influent and process waters at some STPs were also collected. Most of these water samples were those in the Yodo River basin. The details of the sampling are described in the Supporting Information including Figures S1 and S2.

Extraction and Fractionation of Water Samples. Influent 2 of STP1 collected in March 2008 was concentrated using Sep-Pak Vac PS-2 cartridges (500 mg; Waters, Milford, MA) by vacuum suction. Concentration was performed twice, and the first and second extracts were designated concentrated extracts I and II, respectively. The detailed concentration and extraction procedures are described in the Supporting Information.

Ozonation, Chlorination, and Chloramination. Semi-batch style ozonation was performed to investigate NDMA formation from the water samples. Batch style experiments were performed to investigate molar conversion yields of HDMS and TMDS to NDMA by ozonation. In addition, chlorination and chloramination of HDMS and TMDS were performed. The details of the experimental procedures are described in the Supporting Information.

Analysis. NDMA concentrations were determined by UPLC/MS/MS operated in the electrospray ionization (ESI) positive-ion mode (*17*). Separation was performed with an ACQUITY UPLC system (Waters) and detection was performed with an ACQUITY TQD tandem mass spectrometer (Waters). The isotope-labeled surrogate NDMA-d_6 was used as an internal standard. The procedures of NDMA analysis are described in the Supporting Information. The limit of detection (LOD) for NDMA differed among the samples because the concentrated sample volumes were different; i.e., the LOD was 1.0 ng/L for river water and STP effluent samples and 5.0 ng/L for other samples. Repeatability of NDMA concentration was confirmed for only a few cases (Table S6 in the Supporting Information), so the error ranges are not shown in the figures and tables. The data shown in the present study are limited for repeatability and reliability.

The fractions of the concentrated extracts of influent 2 at STP1 were analyzed by UPLC/MS/MS. The analytical conditions are described in the Supporting Information. HDMS and TMDS concentrations were determined directly by UPLC/MS/MS without concentration. The analytical conditions are described in the Supporting Information. The LOD was 2.0 ng/L for both HDMS and TMDS. Analytical methods of other parameters are described in the Supporting Information.

Results and Discussion

NDMA and Its Precursors on Ozonation in River and STPs. Table 1 shows the NDMA concentrations before and after ozonation of the samples of river water and STP effluent. For ozonation experiments, quenching of oxidants was not conducted when sampling. Therefore, the results shown in Table 1 may have been affected to some degree by oxidants during sample storage. For example, if residual chloramine was present in the samples, NDMA concentration before ozonation may be overestimated due to NDMA formation by the reaction of chloramine and NDMA precursors in the samples. The effluents of STP1 and STP2 flow into the Katsura River and those of STP3 and STP4 flow into the Uji River. The discharge points of STP1 and STP2 are located between the two sampling points of the Katsura River (K1 and K2) (Figure S1 in the Supporting Information).

NDMA concentrations in the STP effluents were 16–290 and 14–280 ng/L before and after ozonation, respectively. At some STPs, NDMA concentration increased after ozonation indicating that some effluents at STPs contained precursors of NDMA upon ozonation, particularly that at STP2-2. In the case of river water samples, from an upstream point of the Katsura River (K1) to its downstream point (K2), both NDMA concentrations before and after ozonation increased markedly (i.e., before ozonation from 1.2 to 11 ng/L; after ozonation from 2.4 to 36 ng/L). Therefore, the effluents at STP1, STP2-1, and STP2-2 were considered to affect the increases in concentrations of NDMA and NDMA precursors in the river. At the STP1, the NDMA concentration in the effluent sample (290 ng/L) was highest and approximately the same as that of NDMA after ozonation (280 ng/L).

Next, a study was conducted at STP1 where the highest NDMA concentration in the effluent samples was observed. Table 2 shows the NDMA concentrations before and after ozonation of the influent, process water, and effluent samples from STP1. Influents 1 and 2 were filtered with 10 μm polypropylene (PPL) filters (Whatman, Florham Park, NJ), so the NDMA precursors may have been underestimated due to their adsorption on PPL. The NDMA concentrations both before and after ozonation of influents 1 and 2 were high, particularly in influent 2 with concentrations of 710 and 10 000 ng/L before and after ozonation, respectively. Influent 2 contained high levels of industrial effluents compared to influent 1 and was a purple-red solution. Therefore, the high concentrations of NDMA and NDMA precursors in influent 2 were considered to be due to the industrial effluents as in the previous report (*18*). In the sewage treatment process, NDMA concentration increased after ozonation. Thus, the highest NDMA concentration in the STP1 effluent in Table 1 was considered to be due to NDMA formation by ozonation. From the NDMA concentration after ozonation in the water samples and their flow rates, the loads of NDMA after ozonation were calculated to be 5.4 g/day for influent 1, 54 g/day for influent 2, and 26 g/day for the effluent. The water

samples of STP1 were grab samples, so the daily fluctuations were not considered. However, the values of the NDMA loads after ozonation suggested that the NDMA precursors upon ozonation were present in the influents at STP1, and the amounts of NDMA precursors in influent 2 were much larger than those in influent 1.

Identification of NDMA Precursors. To identify the NDMA precursors in influent 2 of STP1, sampling was conducted again in March 2008. Similar to influent 2 collected in December 2007, the sample collected in March 2008 was a colored solution, except it was dark green. The influent 2 sample was concentrated, fractionated, and ozonated.

Figure S4a in the Supporting Information shows the NDMA concentrations after ozonation of the diluted pooled fractions of the concentrated extract I. NDMA was detected at levels close to or greater than its LOD, 5.0 ng/L, after ozonation of the two diluted pooled fractions (i.e., the diluted pooled fractions of 10.5−15.5 and 15.5−20.5 min) although NDMA was below the LOD after ozonation of several other diluted pooled fractions. Figure S4b in the Supporting Information shows the NDMA concentrations after ozonation of the diluted fractions of 10.5−20.5 min. NDMA was detected close to or greater than its LOD after ozonation of three diluted fractions (i.e., the diluted fractions of 13.5−14.5, 14.5−15.5, and 15.5−16.5 min). NDMA was not detected in these three diluted fractions before ozonation. As in the case of the diluted pooled fractions, NDMA was also below the LOD after ozonation of several other diluted fractions. Several of the fractions eluted before 11.5 min were solutions of various colors, such as yellow, green, and blue. Therefore, the dyes themselves may not be the main NDMA precursors upon ozonation in influent 2 although the influent was a colored solution.

Influent 2 at STP1 was again concentrated, and the concentrated extract (i.e., concentrated extract II) was fractionated. The three fractions of 13.5−14.5, 14.5−15.5, and 15.5−16.5 min were then concentrated to 1 mL of methanol solution. Figure 1a shows the total ion chromatogram of the concentrated fraction of 13.5−14.5 min by UPLC/MS (scan mode, m/z range 50−600). Many peaks were observed in the concentrated fraction of 13.5−14.5 min. In general, m/z observed by MS operated in the ESI mode is around the molecular weight (MW) of the chemical of interest. It is also known that NDMA precursors have the *N,N*-dimethylamino structural element upon ozonation (*12*−*14*). Using the m/z of the peaks and database of the chemical information (i.e., MW and structure), a search was performed for potential NDMA precursors. Among the peaks in Figure 1a, peak A (retention time, 4.9 min) had major ions at m/z 289 and 203. Figure 1b,c shows the total ion chromatogram of the concentrated fraction of 13.5−14.5 min and the product ion spectrum of peak A by UPLC/MS/MS (product ion scan mode of m/z 289, m/z range 40−400), respectively. The major fragment ions of peak A at m/z 289 were m/z 61 and 100. Peak A was identified as HDMS (MW, 288.39) on the basis of its retention time, mass spectrum, and product ion spectrum; Figure 1d shows the product ion spectrum of HDMS reagent (product ion scan mode of m/z 289, m/z range 40−400).

Figure 2a also shows the total ion chromatogram of the concentrated fraction of 15.5−16.5 min by UPLC/MS (scan mode, m/z range 50−600). As in the case of the concentrated fraction of 13.5−14.5 min, many peaks were observed in the concentrated fraction of 15.5−16.5 min. Similarly, as in the case of the concentrated fraction of 13.5−14.5 min, a search was performed for potential NDMA precursors. Peak B (retention time, 6.1 min) had a major ion at m/z 371. Figure 2b,c shows the total ion chromatogram and the product ion spectrum of peak B of the concentrated fraction of 15.5−16.5 min by UPLC/MS/MS (product ion scan mode of m/z 371, m/z range 40−400), respectively. The major fragment ions of peak B at m/z 371 were m/z 106 and 199. Peak B was identified as TMDS (MW, 370.45) on the basis of its retention time, mass spectrum, and product ion spectrum; Figure 2d shows the product ion spectrum of TMDS reagent (product ion scan mode of m/z 371, m/z range 40−400). The retention time and MRM transitions of m/z 289−61 and 289−100 for the concentrated fraction of 14.5−15.5 min confirmed the presence of HDMS. Both HDMS and TMDS have the 1,1-dimethylsemicarbazide structural element containing the 1,1-dimethylamino structural element and are used as antiyellowing agents in polyurethane fibers and as light stabilizers for polyamide resins (*19*). The levels of HDMS and TMDS production in 2006 in Japan were 100 and 150 tons, respectively (*19*).

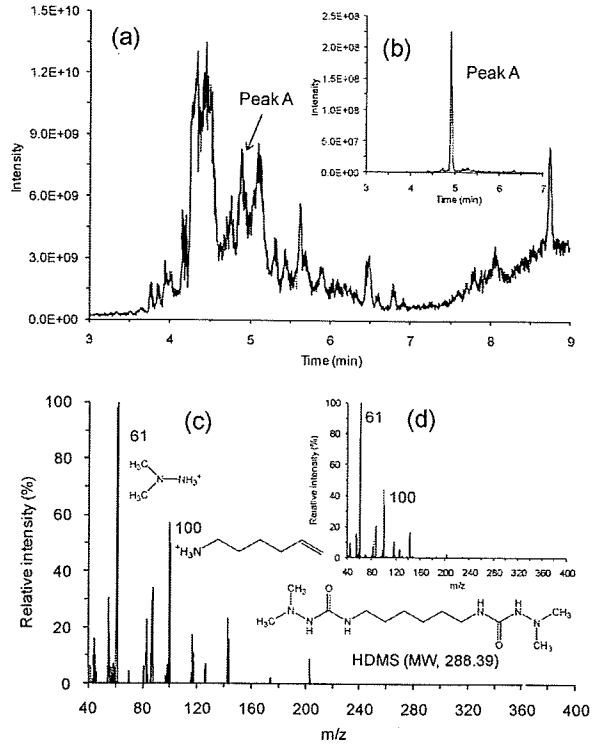

FIGURE 1. Total ion chromatograms of concentrated fraction of 13.5−14.5 min (a) by UPLC/MS (scan mode, m/z range 50−600) and (b) by UPLC/MS/MS (product ion scan mode of m/z 289, m/z range 40−400). Product ion spectra of (c) peak A and (d) HDMS reagent (product ion scan mode of m/z 289, m/z range 40−400).

The molar conversion yields of HDMS and TMDS to NDMA upon ozonation were 10 and 27%, respectively (Figure S5 in the Supporting Information). These molar conversion yields were unaffected by the presence of 5 mM *tert*-butyl alcohol (TBA), a known hydroxyl radical scavenger (data not shown). Thus, it was considered that both HDMS and TMDS were the NDMA precursors by the molecular ozone process. This agreed with the identification of HDMS and TMDS as potential NDMA precursors upon ozonation in the diluted pooled fractions and the diluted fractions containing methanol at high concentrations. Using the concentrations of HDMS, TMDS, and NDMA and the molar conversion yields of HDMS and TMDS to NDMA by ozonation, the contribution of HDMS to NDMA formation in the diluted pooled fractions of 10.5−15.5 min was calculated to be 58% and that of TMDS to NDMA formation in the diluted pooled fractions of 15.5−20.5 min was calculated to be 99%. That is, the sum of the contributions of HDMS and TMDS to NDMA formation in the diluted pooled fractions of 10.5−15.5 and 15.5−20.5 min was calculated to be 86%. Thus, HDMS and TMDS were found to be the main precursors of NDMA upon ozonation

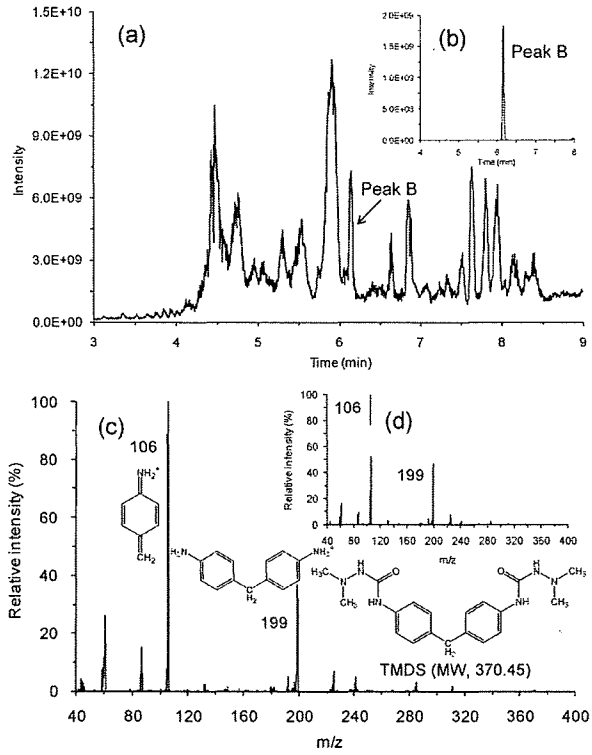

FIGURE 2. Total ion chromatograms of concentrated 15.5–16.5 min fraction (a) by UPLC/MS (scan mode, *m/z* range 50–600) and (b) by UPLC/MS/MS (product ion scan mode of *m/z* 371, *m/z* range 40–400). Product ion spectra of (c) peak B and (d) TMDS reagent (product ion scan mode of *m/z* 371, *m/z* range 40–400).

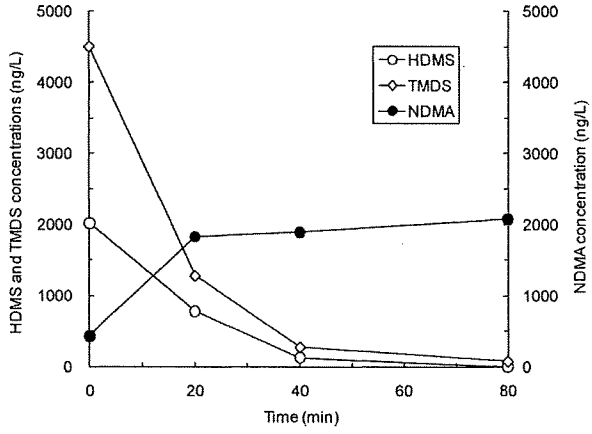

FIGURE 3. Profiles of HDMS, TMDS, and NDMA concentrations during ozonation of influent 2 at STP1. Ozonation conditions: ozone concentration in gas phase, 5.0 mg/L; ozone gas flow rate, 0.5 L/min; pH 8 (5 mM phosphate buffer); temperature, 20 °C.

in the portions of influent 2 of STP1 trapped by PS-2 cartridges although other precursors were also present.

Figure 3 shows the profiles of NDMA, HDMS, and TMDS concentrations during ozonation of influent 2 collected in March 2008. The ozone concentration in the gas phase was 5.0 mg/L, the flow rate was 0.5 L/min, the reaction time was 20–80 min, temperature was 20 °C, and pH was 8 (5 mM phosphate buffer). Before ozonation, the concentrations of NDMA, HDMS, and TMDS were 430, 2000, and 4500 ng/L, respectively. After ozonation, the concentrations of HDMS and TMDS decreased, while that of NDMA increased. The contribution of the sum of HDMS and TMDS to NDMA formation potential in influent 2 by ozonation was calculated to be 17%. Note that it was difficult to generalize the value of the contribution for influent 2 because the daily fluctuation and seasonal variation were not investigated in the present study. The results indicated that these compounds were the main precursors of NDMA upon ozonation in the portions of influent 2 of STP1 trapped by PS-2 cartridges as described above, but unidentified NDMA precursors still remained in the influent. The majority of the unidentified NDMA precursors may be hydrophilic compounds that were not trapped by PS-2 cartridges.

Schmidt and Brauch (*13*) reported that DMS was an NDMA precursor in water sources in Germany. Tolylfluanid, a precursor compound of DMS, is not a registered agricultural chemical in Japan, and so DMS was not considered to be a precursor of NDMA in influent 2. In the same study, Schmidt and Brauch also reported that daminozide and UDMH were precursors of NDMA upon ozonation with high molar conversion yields of 55 and 80%, respectively (*13*). Daminozide is a plant growth generator. Of course, the daily fluctuations and seasonal variations were not considered in the present study, as described in the Supporting Information. However, after attempting to very roughly estimate the loads of the NDMA precursors upon ozonation using the results shown in Table 1 and in the following section along with the flow rates of the water samples, it was suggested that the NDMA precursors in the Yodo River basin mainly originated from point sources (i.e., the STP effluents) (data not shown). Thus, the contribution of daminozide to NDMA precursors in the basin was considered to be low. In addition, UDMH is unstable in water; thus, UDMH may not be present in the water samples. In a previous study in which NDMA concentrations were investigated at six WTPs in Japan (*17*), a relatively large increase in NDMA concentration after ozonation was observed only at WTPs in the Yodo River basin. Therefore, it was presumed that the unidentified NDMA precursors in influent 2 may be compounds used in specific industries. Moreover, both HDMS and TMDS have the 1,1-dimethylsemicarbazide structural element. It was also suggested that such compounds with the 1,1-dimethylsemicarbazide structural element, including intermediates of HDMS and TMDS, may be the unidentified NDMA precursors although we could not obtain information regarding these compounds in the present study.

Concentrations of NDMA Precursors Identified during the Sewage Treatment Process. Table S7 in the Supporting Information shows the concentrations of NDMA, HDMS, and TMDS in the sewage treatment process at STP5. NDMA, HDMS, and TMDS concentrations in the primary sedimentation effluent were 13, 1000, and 170 ng/L, respectively. The HDMS concentration did not change, while the TMDS concentration was reduced by about 50% in the biological treatment process at STP5. There were no changes in HDMS or TMDS concentration with chlorination at STP5. On the other hand, NDMA concentration showed no marked changes with biological treatment but increased after chlorination at STP5. Ammonia concentration in secondary sedimentation effluent (2.8 mg/L as N) was reduced after chlorination (0.65 mg/L as N). The reactivities of HDMS and TMDS with chlorine and chloramine were investigated. Both HDMS and TMDS decomposed rapidly with chlorination but showed little decomposition with chloramination (target concentrations, 20–37 μg/L; chlorine dose, 1.2 mg/L; chloramine dose, 1.1 mg/L; pH 7 (5 mM phosphate buffer), temperature, 20 °C) (Figure S6 in the Supporting Information). These results suggested that chlorine added to the secondary sedimentation effluent was transformed into chloramine at STP5. Thus, HDMS and TMDS showed little decomposition, while NDMA concentration increased. Note that HDMS and TMDS concentrations after chlorination at actual STPs seemed to be dependent on the concentrations of other

TABLE 3. HDMS and TMDS Concentrations Surface Waters and Effluents

	HDMS			TMDS		
		concentration (ng/L)			concentration (ng/L)	
sample	detection rate[a]	median	range	detection rate[a]	median	range
Yodo River basin						
surface water	15/22	6.5	<2.0–410	10/22	<2.0	<2.0–30
effluent[b]	8/12	12	<2.0–4200	7/12	4.1	<2.0–86
other regions						
surface water	7/37	<2.0	<2.0–12	16/37	<2.0	<2.0–12

[a] Sample detected/sample analyzed. Sampling was performed once in most cases and twice in a few cases. In cases in which the water samples at the same sampling points were collected on different sampling days, each sample was counted as a different sample. [b] Effluent was both STP effluent and industrial discharge that flows directly into public water bodies.

compounds, such as ammonia, because HDMS and TMDS were reactive with chlorine (Figure S6a in the Supporting Information).

The results shown in Figure S6a in the Supporting Information indicated that NDMA was not formed after chlorination of HDMS or TMDS, suggesting that they were transformed into other compounds. This tendency was the same as that of DMS in chlorination (*13*) although the reaction pathways in chlorination of HDMS and TMDS were unknown. On the other hand, the results shown in Figure S3b in the Supporting Information indicated that NDMA was formed after chloramination of HDMS and TMDS, and thus, both HDMS and TMDS were precursors of NDMA on chloramination although their reactivities with chloramine were weak. This result also agreed with those of previous studies indicating that compounds with *N,N*-dimethylamino structural elements were NDMA precursors upon chloramination (*5, 20*).

Figure S7a,b in the Supporting Information shows the profiles of NDMA, HDMS, and TMDS concentrations during ozonation of the primary and secondary sedimentation effluents at STP5, respectively. The ozone concentration in the gas phase was 5.0 mg/L, ozone gas flow rate was 0.5 L/min, reaction time was 2.5–80 min, and temperature was 20 °C. NDMA concentrations in both sedimentation effluents increased with ozonation indicating the presence of precursors of NDMA upon ozonation in the sample waters at STP5.

Using the concentrations of HDMS, TMDS, and NDMA and the molar conversion yields of HDMS and TMDS to NDMA upon ozonation (Figure S5 in the Supporting Information), the sums of the contributions of HDMS and TMDS to NDMA formation were calculated to be 0.8% for the primary sedimentation effluent and 1.4% for the secondary sedimentation effluent. Thus, as in the case of influent 2 at STP1, HDMS and TMDS were shown to be NDMA precursors in the sample waters at STP5 although their contributions were not high. The reasons for the differences in their contributions to total NDMA precursors between influent 2 at STP1 and water samples at STP5 are unclear. One possible reason was that the types of industry that mainly contributed to the discharge of the NDMA precursors may be different between the two STPs. Further, investigations of the unidentified NDMA precursors upon ozonation in sample waters at STPs are required.

Occurrence of NDMA Precursors Identified in Surface Waters and Effluents. Table 3 shows the occurrence of HDMS and TMDS in surface waters and effluents. In the effluents, HDMS and TMDS were detected in 8 and 7 of the 12 with concentration ranges of <2.0–4200 and <2.0–86 ng/L, respectively. Thus, it was shown that HDMS and TMDS were frequently present in the effluents. HDMS and TMDS were detected in 16 and 10 samples, respectively, from 22 surface waters in the basin, and HDMS concentration was high in some cases (maximum concentration: 410 ng/L). Particularly, HDMS and TMDS were frequently detected in the areas downstream of the effluents. Therefore, it was considered that the effluent was the main source of HDMS and TMDS in the basin. On the other hand, HDMS was detected in 7 of 37 surface water samples from other regions with a concentration range of <2.0 to 12 ng/L. TMDS was detected in 16 samples and ranged in concentration from <2.0 to 12 ng/L. Taken together, these results indicated that HDMS and TMDS were also present in some areas other than the Yodo River basin in Japan.

Acknowledgments

We thank Dr. Shinya Echigo of Kyoto University, Mr. Masanori Miyata and Mr. Masayuki Miwa of Osaka City Waterworks Bureau, Mr. Toshiharu Segawa and Ms. Hiroko Nakagawa of Waterworks Bureau, City of Kyoto, and the staff of the WTPs, STPs, and related organizations for their help in sample collection. The present study was supported in part by research grants from the Ministry of Health, Labour, and Welfare, Japan, and Kurita Water and Environmental Foundation, Japan.

Supporting Information Available

Sampling; extraction and fractionation of water samples; ozonation, chlorination, and chloramination; analytical methods; Figures S1–S7; Tables S1–S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES900227G

Science of the Total Environment 407 (2009) 3540–3545

Contents lists available at ScienceDirect

Science of the Total Environment

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A nationwide survey of NDMA in raw and drinking water in Japan

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ARTICLE INFO

Article history:
Received 3 September 2008
Received in revised form 27 January 2009
Accepted 10 February 2009
Available online 12 March 2009

Keywords:
N-nitrosodimethylamine (NDMA)
Drinking water treatment plants
Sewage treatment plants
Ozonation
Source water

ABSTRACT

A nationwide survey of *N*-nitrosodimethylamine (NDMA) in both raw and finished water samples from drinking water treatment plants (DWTPs) in Japan was conducted. NDMA was analyzed by solid-phase extraction (SPE) followed by ultra performance liquid chromatography (UPLC) coupled with tandem mass spectrometry (MS/MS). NDMA was detected in 15 of 31 raw water samples collected in the summer at concentrations up to 2.6 ng/L, and in 9 of 28 raw water samples collected in winter at concentrations up to 4.3 ng/L. The NDMA concentrations were higher in raw water samples collected from treatment plants with catchment areas that have high population densities. The NDMA concentrations were higher in river water samples collected from the east and west of Japan than in those collected from other areas. NDMA was detected in 10 of 31 finished samples collected in summer at reduced concentrations of up to 2.2 ng/L, while 5 of 28 finished samples collected in winter showed NDMA concentrations up to 10 ng/L. The highest NDMA levels were detected in finished water samples collected from the Yodo River basin DWTP, which uses ozonation. Furthermore, evaluation of the process water produced at six advanced water treatment plants was conducted. Influent from the Yodo River indicated that the NDMA concentration increased during ozonation to as high as 20 ng/L, and then decreased with subsequent biological activated carbon treatment. To our knowledge, this is the first nationwide evaluation of NDMA concentrations in water conducted in Japan to date.

1. Introduction

N-Nitrosodimethylamine (NDMA) is a highly water-soluble nitrosamine that is a member of a family of extremely potent carcinogens known as *N*-nitrosoamines (Mitch et al., 2003). Some nitrosamines, including NDMA, have been classified as probable human carcinogens (B2) by the Integrated Risk Information System (IRIS) of the United States Environmental Protection Agency (US EPA, 2009a) and as 2A, probably carcinogenic, by the World Health Organization's International Agency for Research on Cancer (IARC, 2009). In the past, NDMA was used as an intermediate in the production of rocket fuel, an inhibitor of nitrification in soil, a plasticizer in the manufacture of rubber and polymers, a solvent in the fiber and plastic industry, an antioxidant, a softener of copolymers, and as an additive to lubricants (Najm and Trussell, 2001). Recently, NDMA was found to be a disinfection byproduct following chloramination or chlorination in the presence of ammonia (Mitch et al., 2003). NDMA precursors during chlorination and chloramination include nitrogenous organic compounds such as dimethylamine (DMA) and trimethylamine (TMA) (Lee et al., 2007). The US EPA has estimated that an NDMA concentration of 7 ng/L in drinking water is associated with an excess lifetime cancer risk of 10^{-5} (US EPA, 2009a), and NDMA is included among the 104 contaminants on Contaminant Candidate List 3 (CCL3) (US EPA, 2009b). Although the maximum contaminant level (MCL) for NDMA in drinking water has not been established in the USA, other regulatory agencies have established NDMA guidelines. For example, the office of Environmental Health Hazard Assessment (OEHHA) in California has set a public health goal (PHG) of maintaining NDMA at concentrations $\leq$3 ng/L based on a cancer risk of 10^{-6} (California Department of Public Health, 2009). In addition, although no MCL for NDMA in drinking water has been established to date in Canada, the Ministry of the Environment (MOE) of Ontario has set the provisional maximum allowable concentration of NDMA at 9 ng/L (Ministry of the Environment of Ontario, 2009). Although estimates of the various sources of NDMA exposure indicated that water contributes less than 10% of the overall exposure in Canada and it is less than 1% of the overall human exposure to NDMA estimated in the USA, the relative source contribution (RSC) is usually not utilized in cancer risk calculations, and no official evaluation has been conducted to determine the contributions of each source in these risk assessments (California Department of Public Health, 2009).

NDMA was first detected in drinking water in Ontario, Canada in 1989 (Charrois et al., 2007). In the USA, NDMA was first discovered as a groundwater contaminant at a Northern California aerospace facility in 1998 (Najm and Trussell, 2001). Since then, the occurrence of NDMA in drinking water treatment plants (DWTPs) has been investigated throughout Canada and the USA. A survey of quarterly samples of raw, finished, and distribution system water collected from 21 North American DWTPs indicated the presence of NDMA in concentrations greater than the method detection limit (MDL) of 0.6–1.0 ng/L in only 1 of 81 raw water samples, and that the NDMA concentrations were

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doi:10.1016/j.scitotenv.2009.02.014

<MDL–30 ng/L in 81 finished water samples and <MDL–24 ng/L in 95 distribution system water samples (Barrett et al., 2003). However, a survey of 20 municipal drinking water distribution systems in Alberta, Canada, revealed NDMA concentrations in some systems as high as 100 ng/L. In addition, an extensive survey of 179 DWTPs in Ontario, Canada, indicated that NDMA was present in concentrations as high as 66 ng/L in one distribution system water sample (Charrois et al., 2007).

Some of recent studies have evaluated the formation of NDMA during ozonation. For example, Andrzejewski et al. (2008) reported the formation of NDMA by DMA ozonation (initial DMA concentrations, 30–700 mg/L). In addition, Schmidt and Brauch (2008) reported that the plant growth regulator, daminozide, the fungicide, tolylfluanid, and their decomposition products were NDMA precursors during ozonation. However, there have been few evaluations of NDMA in Japan.

Here, a nationwide study of the occurrence of NDMA in DWTPs, including small facilities, was conducted using ultra performance liquid chromatography (UPLC) coupled with tandem mass spectrometry (MS/MS). NDMA concentrations were also investigated at each treatment process in all six DWTPs included in the study. In addition, the concentrations of nitrogen species (total nitrogen, organic nitrogen, and inorganic nitrogen) and organic substances were also determined. This information was then used to identify the relationships between the concentrations of NDMA and water quality parameters that could be potential indicators and/or precursors of the formation of NDMA.

2. Materials and methods

2.1. Sampling

This nationwide survey of raw water and finished water of DWTPs was conducted in September to October 2007 (summer) and December 2007 to January 2008 (winter). DWTPs were selected such that the major water sources in each of the six areas (Fig. 1) could be evaluated, and they also included three water facilities that employ hypochlorite treatment at a high injection ratio. Raw water and finished water samples were collected from DWTPs and transported immediately to our laboratory in glass containers under cool and dark conditions before analysis within 10 days. The process water samples were collected in September–October 2007 at each unit process in six large advanced water treatment plants selected based on their area. Sodium thiosulfate solution, a quenching agent, was added to process water and finished water samples containing hypochlorite.

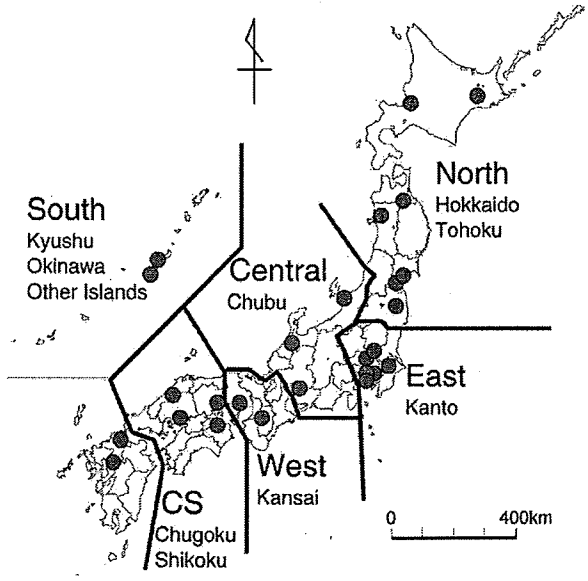

Fig. 1. Sampling areas evaluated in this study.

Table 1
NDMA analysis using UPLC/MS/MS.

UPLC/MS/MS: ACQUITY UPLC/TQD (Waters)
Column: BEH C18 (2.1 × 150 mm, Waters)
Eluent: A: 10 mM Ammonium bicarbonate, B: Acetonitrile
B: 5% (0–3.50 min) → 95% (3.85–6.35 min) → 5% (6.70–8.35 min)
Flow rate: 0.2 mL/min, injection volume: 30 μL, ionization: ESI positive
Capillary voltage: 2.2 kV, source temperature: 140 °C
Desolvation gas flow: 900 L/h, desolvation temperature: 400 °C, cone gas flow: 50 L/h,
MRM:NDMA: 74.9>43.1 (quantitative), collision: 14 eV,
74.9>57.9 (confirmative), collision: 12 eV,
NDMA-d_6: 81.0>46.0, collision: 14 eV

2.2. Reagents

All reagents used in this study were of analytical grade. Ultrapure water prepared with a Gradient A10 water purification system was used (Millipore, Bedford, MA). Furthermore, a stock solution of NDMA (40 mg/L) was prepared by diluting 2000 mg/L certified nitrosamine mix standard solutions that included NDMA in methanol (Supelco, Bellefonte, PA). Working solutions (2.0–1000 μg/L) were prepared by diluting 40 mg/L NDMA methanol solution with dichloromethane (Wako Pure Chemical, Osaka, Japan). Each working solution contained 50 μg/L NDMA-d_6 (C/D/N Isotopes, Pointe-Claire, Canada) as an isotope-labeled surrogate standard.

2.3. Sample preparation

All of the water samples described below were stored in the dark at 4 °C prior to analysis, referring to previous researches (US EPA, 2009c, for example). Sodium bicarbonate (Wako Pure Chemical) was added at a final concentration of 2 g/L to adjust the samples to approximately pH 8. In addition, the samples were spiked with known concentrations of NDMA-d_6. The 500 mL of samples were then filtered through 0.7 μm GF/F filters (Whatman, Florham Park, NJ), after which they were passed through coupled Sep-Pak® Plus AC-2 cartridges (400 mg × 2; Waters, Milford, MA) at flow rates of 3–5 mL/min under vacuum. The Sep-Pak® Plus AC-2 cartridges had been preconditioned with 20 mL of a solution of dichloromethane (Wako Pure Chemical) and diethylether (Kanto Chemical, Tokyo, Japan) (50:50 v/v), followed in sequence by 20 mL of methanol (Wako Pure Chemical) and 20 mL of ultrapure water. After passing through the cartridges, the samples were dried under nitrogen gas and then eluted with 10 mL of a solution of dichloromethane and diethylether (50:50 v/v) at a flow rate ranging from 2 to 3 mL/min. The eluent was then purified by passing through a Sep-Pak® Vac Florisil® cartridge (1 g; Waters) preconditioned with 10 mL of hexane (Wako Pure Chemical) followed by 10 mL of a solution of dichloromethane and diethylether (50:50 v/v). The combination of these two solutions was used because it enabled better separation or recovery than either methanol or dichloromethane alone. The eluate was then concentrated to around 50 μL to minimize the amount of diethylether, after which it was diluted to 200 μL with dichloromethane. Multiple reaction monitoring (MRM) chromatograms of the samples indicated that a cleanup procedure was necessary to obtain the NDMA peak in raw and finished water samples, especially following chlorination.

Table 2
Recovery of NDMA from water samples.

Category	Concentration (ng/L)	Absolute recovery (%) (RSD (%))[a]	Relative recovery (%)[b] (RSD (%))[a]
Ultrapure water	2	55 (16)	95 (17)
River water	10	59 (1.1)	102 (4.6)
Finished water	10	64 (8.4)	103 (3.4)

[a] Relative standard deviation.
[b] Recovery adjusted relative to NDMA-d_6.

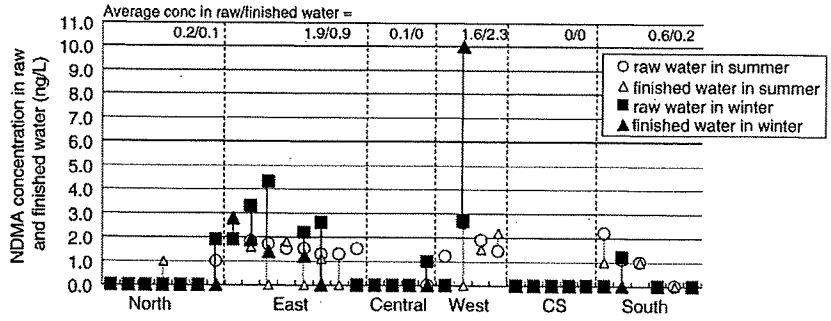

Fig. 2. NDMA in raw and finished water samples evaluated in this study. Average concentration was calculated by arithmetic mean applying zero for ND data.

2.4. Sample analysis

Separation was performed using an ACQUITY UPLC system (Waters) with a BEH C18 column (2.1 mm×150 mm; Waters). The mobile phase was composed of 10 mM ammonium bicarbonate (Fluka, St. Louis, MO) aqueous solution (eluent A) and 100% acetonitrile (eluent B; Wako Pure Chemical). The ratio of eluent B was changed as follows: 5% for 3.5 min, which was then increased to 95% from 3.5 to 3.85 min, and then maintained at 95% for 2.5 min. The flow rate was 0.2 mL/min for all stages and the sample injection volume was 30 μL. Detection was performed using an ACQUITY TQD tandem mass spectrometer (Waters) operated in the electrospray ionization (ESI) positive-ion mode. The MRM transitions were m/z 74.9–43.1 (quantification) and m/z 74.9–57.9 (confirmation) for NDMA and m/z 81.0–46.0 for NDMA-d_6 (Table 1).

2.5. Method detection limit (MDL)

The average absolute recovery rates of NDMA in ultrapure water, river water, and drinking water samples were 55, 59, and 64%, respectively (number of replicates, $n=5, 3, 3$, respectively) (Table 2). The relative recovery obtained using NDMA-d_6 ranged from 95 to 103%. The MDL for NDMA, which was calculated based on 3× the standard deviation of five concentrated ultrapure water samples containing 2 ng/L NDMA, was 1.0 ng/L.

2.6. Basic parameters

The total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were determined using a TOC analyzer (TOC-V CPH; Shimadzu, Kyoto, Japan). Nitrate and nitrite concentrations were determined using an ion chromatograph (DX-500; Dionex, Sunnyvale, CA). Ammonia concentrations were determined spectrophotometrically as a derivative of phenol. Total organic nitrogen (TON) concentrations were determined by subtracting the nitrate, nitrite, and ammonia concentrations from the total nitrogen (TN) concentration, which were determined spectrophotometrically after oxidation by peroxodisulfate (Japan Water Works Association, 2001).

3. Results

3.1. National survey of NDMA in raw water

Fig. 2 shows the regional distribution of NDMA concentrations in raw water samples collected for this study. NDMA was detected in 15 of 31 raw water samples collected in summer, with concentrations ranging from not detected (ND) to 2.6 ng/L. In addition, NDMA was detected in 9 of 28 samples collected in winter, with concentrations ranging from ND to 4.3 ng/L. These concentrations of NDMA are rather low in comparison to previous studies conducted in Canada and the USA (Charrois et al., 2007). Specifically, the maximum concentrations of NDMA in the studies in Canadian and the USA were 8.0 ng/L and 9.4 ng/L, respectively. However, the detection ratio of NDMA was higher in the present study than in the Canadian study, in which NDMA was detected in only 3 of 11 raw water samples.

Samples from the east and west of Japan were found to have higher concentrations of NDMA than those from other areas (Fig. 2). NDMA is often discharged from sewage treatment systems (Krauss and Hollender, 2008)), and can be present in discharge associated with industries, such as rubber manufacturing, leather tanning, pesticide manufacturing, food processing, foundries, and dye manufacturing. In the recent survey of discharge water from sewage treatment plants,

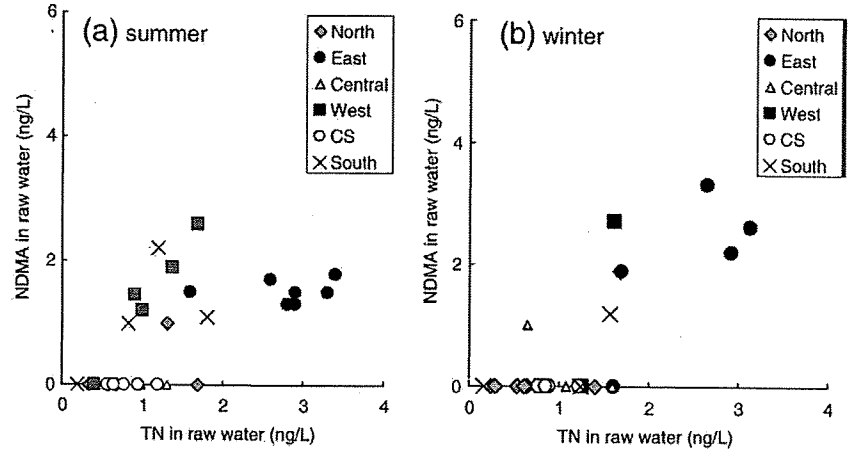

Fig. 3. TN and NDMA in raw water.

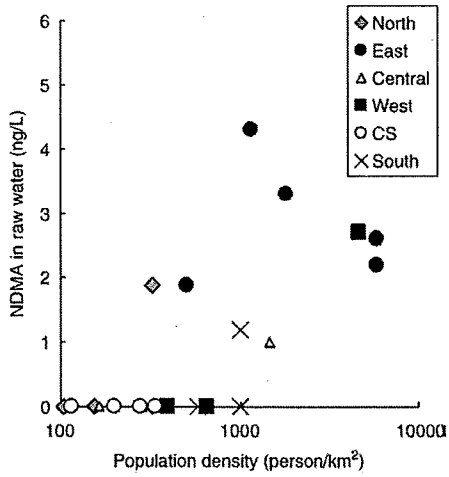

Fig. 4. Population density and NDMA concentration in raw water samples collected in winter.

NDMA was found during ozonation of water samples taken from sewage treatment plants located in the Yodo River Basin, the west area of Japan. The concentrations of NDMA before and after ozonation were 16–290 ng/L and 24–280 ng/L, respectively, and specific compounds related to the textile industry were identified in these discharges (Kosaka et al., submitted for publication). These contaminants may partially account for the NDMA in the west area.

The causes of contamination in the east and other areas are still unclear. However, NDMA levels were higher in waters containing nitrogen species. Although ammonia, nitrite, and nitrate all showed the same tendencies as NDMA concentrations, as shown in Fig. S1, TN seemed to be related to NDMA in raw water samples (Fig. 3). Although only limited data are available at present, this is probably because TN is an indicator of total nitrogen-related contamination, such as discharge from sewage treatment plants or other activities.

. Fig. 4 shows the relationship between the population density of the each river basin and NDMA concentration in raw water samples. There is not a clear correlation between them because this study considered several large areas, where each area or processing plant may have source waters and treatment configurations with very different characteristics. However, NDMA was found in the water from areas in which the catchment population density was over 300 persons/km^2. Seasonal differences between summer and winter samples may exist due to flow rate, environmental fate, and/or NDMA burden. The ratio of NDMA to TN was slightly higher in the east in winter, but was higher in the west in summer. In this study, the relationship between total organic carbon and NDMA was also examined but no obvious correlation was found (data not shown).

3.2. National survey of NDMA in finished water

Fig. 2 shows the regional distribution of NDMA in finished water samples. The concentration of NDMA in the finished water samples ranged from ND to 2.2 ng/L (10/31) in summer and from ND to 10 ng/L (5/28) in winter. The concentrations of NDMA in finished water samples were generally lower than those in raw water samples. In addition, the concentration of NDMA in the finished water samples was higher in the winter than in the summer.

Additional samples containing high concentrations of hypochlorite had NDMA concentrations that were equivalent to or less than the MDL. One DWTP included in this study utilized chloramination during the treatment process; however, no NDMA was detected in samples of finished drinking water collected from this plant.

In comparison to studies performed in Canada and the USA (Charrois et al., 2007), the concentrations of NDMA observed in the finished water samples in the present study were low (max. 65 ng/L in finished water in Canada and 30 ng/L in finished water in the USA). This may have been because chloramination is not generally used in Japanese facilities; to our knowledge, there is only one water treatment plant intentionally employs chloramination to reduce the formation of trihalomethane in Japan. In addition, the level of NDMA is decreased by biological activated carbon treatment (BAC), as described in the following section, even once it has been generated.

On comparison of NDMA concentrations between raw and finished water samples, the sample with the highest concentration of NDMA (10 ng/L) was collected from a DWTP at which the treatment process included ozonation. Fig. 5 shows the relationship between TN in raw water samples and NDMA in finished water samples. The results can be divided into two categories, *i.e.*, east and other areas.

Fig. S2 shows the relationships between ammonia and nitrate in raw water and NDMA in finished water. NDMA tended to be detected more frequently in samples that contained high concentrations of each of ammonia, nitrite, and nitrate. It should be noted that the data from the finished water sample with the highest NDMA concentration from a DWTP in the Yodo River Basin, which employs ozonation, were obviously separated from the other data. Based on these results, the formation and degradation of NDMA in DWTPs appear to be dependent on the watershed in which these facilities are located, as the Yodo River is the largest water source in the western part of Japan with a population of tens of millions utilizing the river water as a

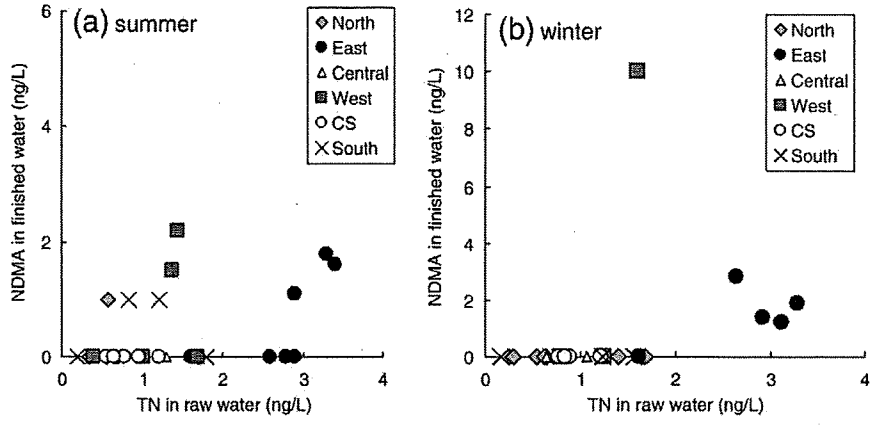

Fig. 5. TN in raw water and NDMA in finished water.

source and many water treatment facilities in this area employ ozonation.

3.3. Survey of NDMA in DWTPs

To clarify the behavior of NDMA during the purification process, NDMA concentrations were examined in each purification process in six major DWTPs (DWTP1-6) (Fig. 6). Each DWTP utilized various treatment processes, including coagulation, flocculation, sedimentation, and sand filtration. However, for convenience, these processes are simply classified here as before ozonation, after ozonation, after biological activated carbon treatment, and finished water. The NDMA concentrations of water samples following each process are shown in Fig. S3, and the concentrations before and after ozonation are summarized in Fig. 6.

The NDMA concentration increased to 7.0 ng/L following chlorination in DWTP2, which was higher than the level observed in raw water (1.5 ng/L). This increase was probably due to the use of a high dose of chlorine (4.5 mg/L) during the first stage of treatment at this facility. Although the ammonia:chlorine molar ratio of 6.8 exceeded the chlorine dose necessary for breakpoint chlorination, TOC was as high as 3.5 mg/L. Therefore, it was considered to consume chlorine so as to be combined, chlorination condition at that time.

At DWTP3 and DWTP6, the NDMA concentration increased to as high as 15 ng/L following ozonation. Both of these treatment plants are located in the Yodo River Basin, and formation of NDMA likely occurred during the ozonation process.

The NDMA concentration decreased markedly (from 20 ng/L to 1.5 ng/L in DWTP3 and from 17 ng/L to 1.3 ng/L in DWTP6) following BAC treatment, regardless of the level formed by ozonation. Although it has been reported that NDMA shows poor absorption onto activated carbon due to its hydrophilic nature (Mitch et al., 2003; World Health Organization, 2008), removal of more than 90% of the NDMA following BAC treatment was observed in the present study. This finding indicates that the NDMA concentration decreased due to biological degradation during BAC treatment, similar to the findings of a previous study (Tateishi et al., 2008). However, the mechanism responsible for this decrease in NDMA concentration was not elucidated in this study. Following BAC treatment, the NDMA concentrations in the finished water samples ranged from <MDL (1.0) to 2.2 ng/L, which was below the concentration of 7 ng/L considered by the US EPA as the level in drinking water associated with an excess cancer risk of 10^{-5} (US EPA, 2009a), but was close to the public health goal of 3 ng/L proposed by California (California Department of Public Health, 2009).

As the behavior of NDMA varied among DWTPs, the relationships between NDMA concentration and other organic or inorganic water quality parameters were analyzed. The results revealed no clear relationships between the increase in NDMA concentration that occurred due to ozonation and the concentrations of organic compounds in the raw water samples (TOC, E260, and TON). In addition, no relationships were observed between the increases in NDMA concentration and pH, nitrate, nitrite, or ammonia concentrations, or the ozone dose (Fig. S4 in Appendix A).

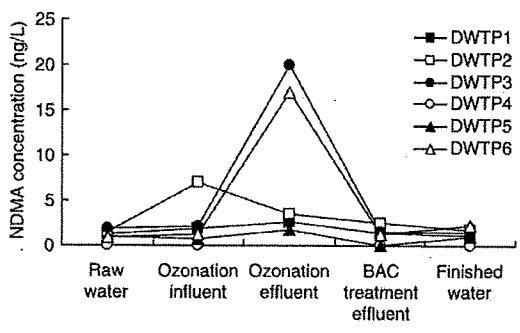

Fig. 6. NDMA concentrations at six treatment plants.

The water source for both DWTPs that showed marked increases in NDMA concentration following ozonation (DWTP3 and DWTP6) was the Yodo River, which is located in western Japan. These findings were in agreement with those of a previous study conducted to evaluate the concentrations of NDMA at DWTPs in the Yodo River Basin (Tateishi et al., 2008) and our previous study suggesting that these increases in NDMA concentration during ozonation at the two DWTPs with the Yodo River as the water source may be due to specific contaminants (Kosaka et al., submitted for publication).

4. Discussion

The present study was performed to determine the NDMA concentrations in water samples from various areas in Japan. Higher NDMA concentrations were found in water containing nitrogen species, which was consistent with the results reported previously (Mitch et al., 2003). The results of this study also indicated that NDMA formation occurs during ozonation in selected DWTPs, which was similar to the findings of other studies indicating that this phenomenon occurs in the presence of *N,N*-dimethylsulfamide (DMS), which is one of the decomposition products of tolylfluanid (Schmidt and Brauch, 2008). Coagulation polymers have also been indicated as precursors of NDMA (Mitch et al., 2003; Charrois and Hrudey, 2007). Although tolylfluanid is not approved for agricultural use and coagulation polymers are prohibited in Japan, the formation of NDMA from specific compounds was observed during ozonation in DWTPs, and further studies are required to determine the concentrations of chemicals that can lead to its formation.

Taken together, the findings of this study indicate that it is necessary to investigate the mechanism by which NDMA is formed during ozonation so that the specific compound(s) responsible for its formation in water in the western part of Japan can be identified. Accordingly, we are currently investigating the relationship between the load of NDMA precursors and its formation during ozonation in upstream sewage treatment plants (STPs) because the effluents from these STPs flow into river water that is subsequently used as the raw water supply for drinking water.

It is important to note that higher NDMA concentrations were detected in prefectures that had higher levels of human activity. Although this study provided only a rough estimate, the level of NDMA in raw water tended to increase in proportion to human activity in the area. Therefore, these activities should be regarded as area-specific and/or non-point sources of NDMA and NDMA precursors.

5. Summary

1. A national survey of *N*-nitrosodimethylamine (NDMA) levels in raw and finished water samples collected from drinking water treatment plants (DWTPs) was conducted using solid-phase extraction (SPE) followed by ultra performance liquid chromatography (UPLC) coupled with tandem mass spectrometry (MS/MS).
2. NDMA was detected in 15 of 31 raw water samples collected in winter at concentrations up to 2.6 ng/L. NDMA was also detected in 9 of 28 samples collected in summer, with a maximum concentration of 4.3 ng/L. NDMA was detected in 8 of 31 finished water samples collected in summer with a maximum concentration of 2.2 ng/L, while in winter, NDMA was detected in 5 of 28 samples with a maximum concentration of 2.8 ng/L, except in one sample with a high concentration of 10 ng/L.
3. The NDMA concentration was greater in raw water samples containing higher levels of nitrogen species. In addition, river water samples collected from the east and west of Japan showed

higher concentrations of NDMA than those collected from other areas.

4. Process water was examined during each of the processes in six advanced water treatment plants. NDMA concentrations were shown to increase during ozonation when water from the Yodo River Basin was utilized as the source water.

Acknowledgments

This study was financially supported in part by a research grant from the Ministry of Health, Labour, and Welfare, Japan. We are grateful to the staff members of the DWTPs and related organizations for their assistance during sampling. In addition, we thank Mr. Hayato Kojima of the Saitama Bureau of Enterprise and Mr. Shinji Okuhama of the Okinawa Bureau of Enterprise for their help in analyzing the DWTP samples.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2009.02.014.

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Notes

Analytical Method for Perchlorate in Water by Liquid Chromatography-Mass Spectrometry Using an Ion Exchange Column

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A practical analytical method was developed for the routine analysis of perchlorate in environmental and drinking-water samples by liquid chromatography-electrospray ionization mass spectrometry (LC/ESI-MS) using an anion exchange column. By using ^{18}O-enriched perchlorate as an internal standard, the limits of quantification of perchlorate determined by tenfold of the signal-to-noise ratio and tenfold of the standard deviation were 0.1 and 0.03 μg L^{-1}, respectively. The perchlorate concentrations in the raw and finished water samples from seven water purification plants were determined by LC/ESI-MS. Perchlorate was detected in 12 out of 13 samples, and the perchlorate concentrations in the samples were from 0.1 to 36.1 μg L^{-1}.

(Received October 28, 2008; Accepted January 8, 2009; Published March 10, 2009)

Introduction

Perchlorate is highly soluble and stable in water.[1] Perchlorate compounds are manufactured as its salts or perchloric acid.[2,3] Perchlorate compounds are widely used in various products: for example, as a primary ingredient of solid rocket propellant, blasting agents, fireworks, and automotive air bag inflators.[1] Since the late 1990s, perchlorate has been detected in surface, ground and drinking-water samples, human and cow's milk samples, and vegetable samples throughout the United States (US).[4-8] Recently, it has been widely detected in river, industrial effluent and drinking-water samples in Japan, as reported by the authors.[9] A potential health effect associated with perchlorate is interference with iodine uptake into the thyroid gland, which may cause a decreased synthesis of thyroid hormones, and may potentially affect metabolism as well as normal growth and development. Consequently, these effects are known to be significant on pregnant women, fetuses, infants, and children.[1,6,10] In 2005, the National Academy of Sciences (NAS) recommended a reference dose (RfD) of 0.7 μg kg^{-1} per day for perchlorate.[11] In 2009, the US Environmental Protection Agency (EPA) released an interim health advisory level (HAL) of 15 μg L^{-1} for perchlorate.[12] Several states also have advisory levels of perchlorate, ranging from 1 to 18 μg L^{-1}.[13] The drinking-water standards of perchlorate were set at 2 μg L^{-1} in Massachusetts and 6 μg L^{-1} in California.[14,15]

Initially, perchlorate at low concentration has been analyzed by ion chromatography coupled with conductivity detection (IC/CD).[16] The minimum reporting limit (MRL) of IC/CD is as high as several μg L^{-1}. To improve the detection specificity and sensitivity, an analysis of perchlorate has been performed by IC or liquid chromatography-electrospray ionization mass spectrometry (IC(LC)/ESI-MS) or tandem mass spectrometry (IC(LC)/ESI-MS/MS).[1,17-22] Note that in this study, the IC/ESI-MS(/MS) system is an ESI-MS(/MS) system connected to a normal IC system with a suppressor, and the LC/ESI-MS(/MS) system is an ESI-MS(/MS) system connected to an LC system, which is very common in many labs. The limits of detection (LODs), limits of quantification (LOQs) or MRL of these methods are generally from the low-ng L^{-1} to sub-μg L^{-1} levels. However, a well-known problem of these methods is ionization suppression by coexisting anions, such as chloride, nitrate and sulfate, which are usually found at mg L^{-1} levels or more in environmental water samples. If the separation of perchlorate from these anions is insufficient, and they severely affect the determination of perchlorate, pretreatment cartridges are used to remove coexisting anions from the sample.[17,18]

To analyze perchlorate by IC(LC)/ESI-MS(/MS) without any pretreatment, the chromatographic separation of perchlorate from the coexisting anions is required to avoid or minimize ionization suppression caused by coelution of the coexisting anions. For example, in the EPA method 332.0,[19] IC-ESI/MS was used for perchlorate analysis, and the LOD was 0.02 μg L^{-1}. It was also reported that the LODs of IC/ESI-MS/MS were from 0.0005 to 0.005 μg L^{-1}.[21] In the case of the LC/ESI-MS(/MS) system, the procedure without pretreatment is shown in EPA method 331.0.[20] The LODs were 0.005 μg/L for LC/ESI-MS/MS and 0.008 μg/L for LC/ESI-MS.[20]

In this study, an analytical method for perchlorate in environmental and drinking-water samples by LC/ESI-MS without the need for pretreatment was investigated. The separation column was an anion exchange column, and the eluent was a volatile and weakly alkaline solution. Recovery studies were performed using spiked matrix samples, which were river and tap-water samples, and ultrapure water samples containing coexisting anions. Furthermore, the perchlorate concentrations in raw and finished water samples from water-purification plants were determined, and the measurement results were compared with those obtained by IC/ESI-MS/MS, a previously developed analytical method.

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Table 1 Perchlorate concentrations in raw and finished water samples from water-purification plants

Plant	Sample type[a]	Perchlorate concentration/μg L^{-1}	
		IC/ESI-MS/MS[b]	LC/ESI-MS[c]
A	Raw/finished water	0.09/0.12	< 0.1/0.1
B	Raw water	39.8	36.1
C	Raw/finished water	10.8/10.3	10.5/10.1
D	Raw/finished water	2.34/1.37	2.3/1.4
E	Raw/finished water	0.48/0.67	0.5/0.6
F	Raw/finished water	4.60/6.03	4.1/6.4
G	Raw/finished water	7.96/7.91	7.5/8.0

a. Raw water at plant B was raw ground water and the other raw waters were raw surface waters.
b. Perchlorate concentrations were determined by IC/ESI-MS/MS (MRL: 0.05 μg/L).
c. Perchlorate concentrations were determined by LC/ESI-MS, the proposed method.

Experimental

Standards and reagents

A 1000 mg L^{-1} standard solution of perchlorate was obtained from GFS Chemicals (Powell, OH). ^{18}O-enriched sodium perchlorate ($NaClO_4$) obtained from Cambridge Isotope Laboratories (Andover, MA) was used for an internal standard (IS) of perchlorate. One thousand milligrams per liter standard solutions of fluoride, chloride, nitrite, nitrate, sulfate and chlorate were obtained from Kanto Chemical (Tokyo, Japan) or Wako Pure Chemical (Osaka, Japan). Ammonium carbonate ($(NH_4)_2CO_3$) and ammonium chloride (NH_4Cl) were obtained from Sigma-Aldrich (St. Louis, MO). Twenty-five percent (v/v) ammonium hydroxide (NH_4OH) aqueous solutions, sodium ascorbate, and acetonitrile (high-performance liquid chromatography grade) were obtained from Wako Pure Chemical (Japan). For preparing the standard and stock solutions and eluents as well as diluting the samples, ultrapure water prepared by a Gradient A10 water purification system (Millipore, Bedford, MA) was used.

Sample collection and preparation

For a recovery study of perchlorate, river and tap-water samples were collected in October 2006. For investigating the presence of perchlorate in water samples from water-purification plants, raw and finished water samples from seven water-purification plants (Plants A - G) were collected in September 2006 (Table 1). The river water of the Tone River Basin, the largest basin in Japan, is widely contaminated by perchlorate, owing to the discharge of industrial effluents containing perchlorate in the upper Tone River Basin.[9] All of the water-purification plants investigated are located in the Tone River Basin, and, except for Plant A, the water intake points of the plants are downstream of the discharging points of industrial effluents containing perchlorate. All of the sample solutions collected were refrigerated at 4°C. River and raw-water samples were filtered with 0.2-μm polytetrafluoroethylene (PTFE) disposable filters (Advantec Toyo, Tokyo, Japan). Residual free chlorine in finished and tap-water samples was quenched using NH_4Cl or sodium ascorbate. ^{18}O-enriched $NaClO_4$ was added to the sample solutions and mixed before analysis (its concentration in sample solution: 1.0 μg L^{-1}).

Sample analysis

The perchlorate concentrations in the sample solutions were analyzed by LC/ESI-MS. The separation was performed using an Agilent 1100 series binary pump (Agilent Technologies, Palo Alto, CA) with anion exchange columns (*i.e.*, IonPac AG21 (2 × 50 mm) as a guard column and IonPac AS21 (2 × 250 mm) as a separation column (Dionex, Sunnyvale, CA)). The IonPac AS21 is suitable for separating highly retainable ions, such as perchlorate. The eluent, which was a mixture of 73 mmol L^{-1} $(NH_4)_2CO_3$ and 20 mmol L^{-1} NH_4OH aqueous solutions and acetonitrile (55/45), was isocratically eluted at 0.2 mL min^{-1}. These ammonium species (*i.e.*, $(NH_4)_2CO_3$ and NH_4OH) are the types of the eluent typically used in LC/MS; the eluent used in this study seemed to be nontoxic and much easier to handle. The injection volume was 100 μL. The detection was performed using an Agilent 1100 VL mass spectrometer (Agilent Technologies) operated in the negative-ion ESI mode. The optimized conditions were as follows: dry gas temperature (nitrogen), 350°C; dry gas flow, 10 L min^{-1}; nebulizer pressure, 20 psi; capillary voltage, 1000 V; fragmentor voltage, 110 V. Perchlorate analysis was performed by selective ion monitoring (SIM) and the monitored ions were *m/z* 99 (quantification), *m/z* 101 (identification) for perchlorate, and *m/z* 107 for ^{18}O-enriched perchlorate. For investigating the presence of perchlorate in water samples from water-purification plants, perchlorate concentrations were also determined by IC/ESI-MS/MS. The analytical conditions for IC/ESI-MS/MS are described elsewhere.[22] In some cases, the retention times of coexisting anions were investigated by LC/ESI-MS/MS or non-suppressed IC/CD under the same LC conditions as those of the LC/ESI-MS system.

Results and Discussion

Limit of quantification of perchlorate

Figure 1 shows SIM chromatograms of 0.1 μg L^{-1} perchlorate and 1 μg L^{-1} ^{18}O-enriched perchlorate in an ultrapure water sample. The separation column used in this study was a type of hydroxide-selective anion column.[23] However, the pH of the eluent in this method was much lower than those of the other methods (EPA method 331.0 and IC/ESI-MS), although the same separation column was used for perchlorate analysis.[20,23] That is, the pH of the mixture of the $(NH_4)_2CO_3$ and NH_4OH aqueous solutions was 9.2, and that of the 200 mmol L^{-1} methylamine aqueous solution, the eluent used in the EPA 331.0, was 12. This was because, in this study, carbonate salt was used as the eluent, and an organic solvent (*i.e.*, acetonitrile) was mixed in it. Also, $(NH_4)_2CO_3$ and NH_4OH aqueous solutions are generally used as the eluents in LC/MS. In the case of EPA 331.0, if the components of the LC system are normally not tolerant to high-pH solutions, the materials have to be replaced with suitable ones.[20] Therefore, it was considered that the effect of the alkaline pH of the eluent used in this study on the components in the LC system was much smaller than that of other alkaline solutions used in the LC system, such as a methylamine aqueous solution.

The LOQ of perchlorate obtained by LC/ESI-MS was determined from the signal-to-noise ratio (*S/N*) and the standard deviation (SD) by repetition analysis. The *S/N*s of the SIM chromatograms of 0.1 μg L^{-1} perchlorate were 10 for *m/z* 99 (quantification) and 4.4 for *m/z* 101 (identification), and that of 1 μg L^{-1} ^{18}O-enriched perchlorate was 125 for *m/z* 107 (Fig. 1). Also, the *S/N* of the peak of 0.05 μg L^{-1} perchlorate was 5.0 for *m/z* 99. Thus, when the LOQ was defined as 10*S/N*s, the LOQ

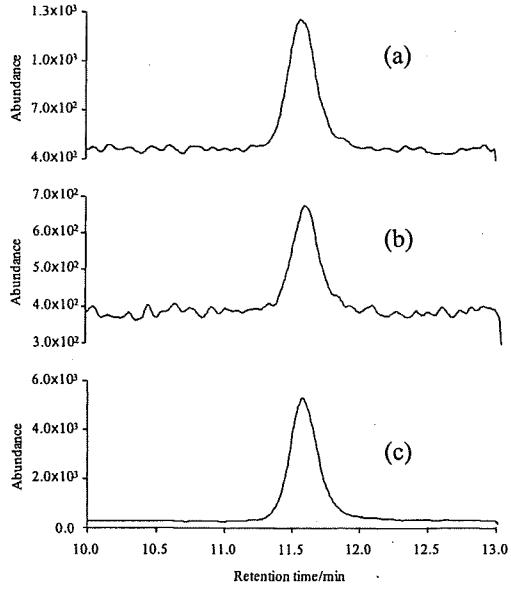

Fig. 1 SIM chromatograms of 0.1 μg L^{-1} perchlorate and 1.0 μg L^{-1} ^{18}O-enriched perchlorate in ultrapure water sample. (a) *m/z* 99, perchlorate (quantification), (b) *m/z* 101, perchlorate (identification), (c) *m/z* 107, ^{18}O-enriched perchlorate.

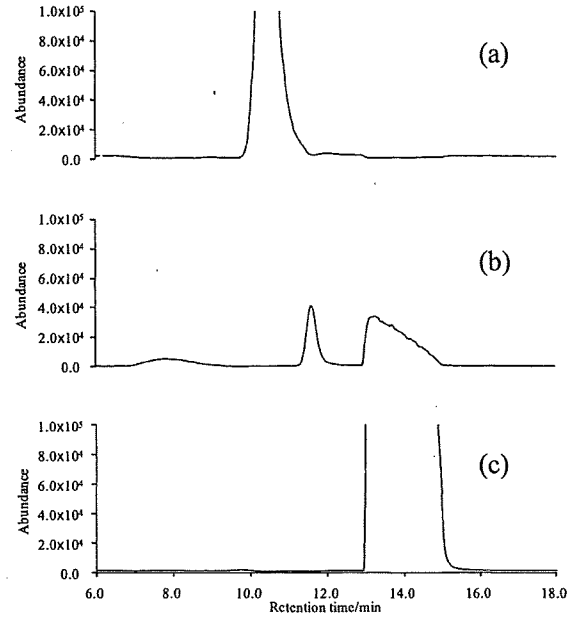

Fig. 2 SIM chromatograms of 1.0 μg L^{-1} perchlorate in an ultrapure water sample containing 100 mg L^{-1} chloride, 10 mg L^{-1} nitrate and 100 mg L^{-1} sulfate. (a) *m/z* 62, nitrate, (b) *m/z* 99, perchlorate, (c) *m/z* 97, sulfate.

of perchlorate was 0.1 μg L^{-1}. Li and George[18] reported that the *S/N*s of the peaks of multiple reaction monitoring (MRM) chromatograms of 0.05 μg L^{-1} perchlorate in deionized water sample determined by LC/ESI-MS/MS are 11 for *m/z* 99 - 83 (quantification) and 1.3 for *m/z* 101 - 85 (identification). Asami *et al.*[22] reported that the *S/N* of the peaks of 0.05 μg L^{-1} perchlorate in an ultrapure water sample by IC/ESI-MS/MS is 280 for *m/z* 99 - 83 (average of 5 replications). Thus, it was considered that the detection sensitivity for perchlorate of the proposed method was lower than that of IC/ESI-MS/MS, but not very different from that of LC/ESI-MS/MS. For an LOQ determination from the SD value by repetition analysis, 0.1 μg L^{-1} perchlorate was selected because this concentration was the LOQ determined from the *S/N*s. When the LOQ was defined as 10SD (n = 5), the LOQ was calculated to be 0.03 μg L^{-1}. In the case of the calibration curve, when the range of the perchlorate concentration was from 0.1 to 10 μg L^{-1} in the ultrapure water sample, its linearity was observed (R^2 = 0.9997). Although the values of LOD, LOQ or MRL are dependent on the studies, the LOQ and MRL used in this study were not very different from those in other studies. Thus, it was considered that the proposed method is sufficient for determining the perchlorate concentration in water samples.

Separation of perchlorate from common anions

Figure 2 shows SIM chromatograms of 1.0 μg L^{-1} perchlorate in an ultrapure water sample containing coexisting anions (100 mg L^{-1} chloride, 10 mg L^{-1} nitrate, and 100 mg L^{-1} sulfate). Because the mass scan range in Fig. 2 was *m/z* 50 - 350, the *m/z* 35 of chloride was beyond the scan range, and the chloride peak was not observed. However, when these anions were analyzed by LC/ESI-MS/MS, the chloride peak was observed at a much earlier retention time than the nitrate peak (data not shown). In the case of nitrate, the tail of the nitrate peak slightly overlapped with the perchlorate peak, but most of the nitrate and perchlorate peaks were separated. The presence of nitrate in the sample seemed to affect the ionization suppression of perchlorate, but the degree was not very large (see next section). Also, the shape of the perchlorate peak was not affected by the presence of nitrate. The sulfate peak was observed later than the perchlorate peak. Sulfate, the most important anion, should be separated from perchlorate, because the minor sulfate isotope (^{34}S) has an *m/z* 99 signal as $H^{34}SO_4^-$, and the *m/z* is the same as that of the quantification for perchlorate. Furthermore, the retention times of nitrite, chlorate and fluoride were also investigated. The LC/ESI-MS/MS system was used for nitrite and chlorate, and a non-suppressed IC/CD system was used for fluoride. The retention time of fluoride was earlier than that of chloride, and those of nitrite and chlorate were earlier than that of nitrate; therefore, all of those peaks did not affect the perchlorate analysis. From these results, it was shown that the combination of the column and the eluent resulted in a rapid and successful isocratic separation of perchlorate from coexisting anions.

In general, IC/ESI-MS(/MS) is superior to separate these anions from perchlorate, because the IC system is designed to separate ions. However, sodium and potassium-based aqueous solutions are usually used as eluents in IC/ESI-MS(/MS); therefore, a suppressor is required to remove these nonvolatile ions. Moreover, an organic solvent, such as acetonitrile, must be mixed as a postcolumn solvent with an additional LC pump to improve the sensitivity.[19,21,22] Therefore, the analytical system using IC/ESI-MS(/MS) is inevitably too complex to control. On the other hand, the LC/ESI-MS(/MS) method is considered to be simpler and less expensive than the IC/ESI-MS(/MS) method. Also, in many cases, MS(/MS) systems are currently connected to the LC systems for the analysis of organic micropollutants. For such laboratories, routine switching from the LC/MS(/MS) system to the IC/MS(/MS) system and *vice versa* can be avoided even if they have only one MS(/MS) system. Considering these aspects, it is considered that the LC/ESI-MS(/MS) method is more applicable if the separation of perchlorate from coexisting anions is achieved like in the case of this study.

Recovery studies

Recovery studies were performed by spiking the matrix samples with 1.0 μg L^{-1} perchlorate. The matrix samples were river and tap water, and ultrapure water containing 100 mg L^{-1} chloride, 20 mg L^{-1} nitrate, and 100 mg L^{-1} sulfate (synthesized water). Residual free chlorine in a tap-water sample was quenched by NH_4Cl or sodium ascorbate. The mean percentage recoveries of perchlorate were 102% for a raw-water sample, 101% for a tap-water sample with NH_4Cl, 98% for a tap-water sample with sodium ascorbate, and 99% for a synthesized water sample. The relative standard deviation (RSD, n = 5) was less than 3% for each case. The direct recoveries of the ^{18}O-enriched perchlorate (*i.e.*, the percentages of perchlorate peak areas in the samples to that in ultrapure water) ranged from 85 to 89% for each sample. Ionization suppressions seemed to occur to some degree, although the determination of perchlorate by the IS method was not affected.

Determination of perchlorate in water samples from water-purification plants by LC/ESI-MS and a comparison of the measurement results with those determined by IC/ESI-MS/MS

The perchlorate concentrations in raw and finished water samples from seven water-purification plants were determined by LC/ESI-MS and IC/ESI-MS/MS (Table 1). The lowest calibration standard, 0.1 μg L^{-1}, was set to be the MRL of perchlorate by LC/ESI-MS. Perchlorate was detected in 12 out of 13 samples by LC/ESI-MS, and the perchlorate concentrations detected were from 0.1 to 36.1 μg L^{-1}. The remaining sample was raw water from Plant A. Compared to the interim HAL for perchlorate (15 μg L^{-1}), the perchlorate concentration in a raw-water sample from Plant B was higher than the interim HAL. Also, the perchlorate concentrations in raw and finished water samples from Plants C and G were higher than 50% of the interim HAL, and those from Plants D and F were higher than 10% of the interim HAL. From these results, it was shown that drinking water from the Tone River Basin is widely contaminated by perchlorate, as reported in a previous study.[9] Thus, it was considered that perchlorate is a type of contaminant that must be paid attention, although Japanese people generally take sufficient iodine from marine foods.[9] When the perchlorate concentrations of the 12 samples determined by LC/ESI-MS and IC/ESI-MS/MS were statistically compared using a paired t-test (level of significance: 0.05), the difference for each sample was not statistically significant.

Conclusions

In this study, an analytical method for perchlorate in a water sample by LC/ESI-MS using an anion exchange column and a volatile and weakly alkaline eluent in an isocratic mode was proposed. Perchlorate was chromatographically separated from coexisting anions, particularly chloride and sulfate, using the proposed analytical method. The perchlorate concentrations in raw and finished water samples from water-purification plants determined by LC/ESI-MS were not statistically different from those determined by IC/ESI-MS/MS, the previously developed analytical method.

Acknowledgements

The authors thank Dr. Sekiguchi (Dionex) for advice concerning the chromatographic conditions, and Ms. Yoshida (National Institute of Public Health) for help with the experiment. This study was financially supported by a research grant from the Ministry of Education, Culture, Sports, Science and Technology, Japan (19560557).

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Bromate, chlorate, chlorite and perchlorate in sodium hypochlorite solution used in water supply

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ABSTRACT

A survey was conducted to reveal the concentrations of bromate, chlorite, chlorate and perchlorate as impurities in sodium hypochlorite solutions and those of chlorate and perchlorate in raw and processed waters including a metropolitan area. High concentrations of bromate (max. 414 mg l^{-1}) and chlorate (max. 260,000 mg l^{-1}) were found in purchased sodium hypochlorite solutions for drinking water disinfection that had been stored for a long time, more than two years at a maximum. In the survey of chlorate and perchlorate in raw and processed waters in the Tone River Basin, the highest concentration of chlorate in raw water was 78 $\mu g\,l^{-1}$ and that of perchlorate was 40 $\mu g\,l^{-1}$. Chlorate and perchlorate concentrations in 32 purchased sodium hypochlorite solutions and six on-site-generated hypochlorite solutions were also analysed. In the purchased sodium hypochlorite solutions, perchlorate concentrations ranged from 0.170 to 33.0 mg l^{-1}. In hypochlorite solutions whose measured FAC (free available chlorine) concentration was lower than the manufacturer-specified FAC concentrations, the chlorate and perchlorate concentrations were higher than those in relatively fresh sodium hypochlorite solutions. In on-site-generated hypochlorite solutions, the maximum concentrations of chlorate and perchlorate were 1,700 mg l^{-1} (140 mg g^{-1} of measured FAC) and 0.660 mg l^{-1} (0.053 mg g^{-1} of measured FAC), respectively.

Key words | bromate, chlorate, chlorite, perchlorate, sodium hypochlorite solution

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INTRODUCTION

Sodium hypochlorite solution is frequently used as a disinfectant and as an oxidizing agent in waterworks. Since the concentration of residual chlorine should be maintained at more than 0.1 mg l^{-1} in distribution systems, sodium hypochlorite solution is commonly used as a residual disinfectant in over 80% of treatment facilities in Japan. It is usually added at the final stage of the treatment process, and sometimes added at the first and/or the middle stage as an oxidizing agent. A 12% (or 6%) stock solution has been widely used in waterworks for the chlorination of water; more recently, on-site generation of hypochlorite has been introduced into 10% of treatment facilities (JWWA 2006).

doi: 10.2166/aqua.2009.014

The duration of storage of stock solutions is sometimes longer, over several months, for example, in small water treatment facilities. In addition, attention should be paid to impurities in hypochlorite solutions, especially in raw waters containing ammonia, which is a chlorine-consuming compound, since the injection ratios of hypochlorite solutions are relatively high in ammonia-contaminated raw water.

For example, in April 2004, bromate concentration in chlorinated drinking water in Hokkaido was found to be 0.168 mg l^{-1}, 16.8 times higher than the concentration limit stipulated by Japanese standards (*Hokkaido News* 2004). Later analysis showed bromate at a concentration of

668 mg l^{-1} in the sodium hypochlorite solution used in the water treatment process, illustrating the fact that sodium hypochlorite solution can be a major source of bromate in chlorinated drinking water.

Bromate, known as a carcinogenic ozonation by-product, was introduced in the Japanese drinking water quality standard in 2004 and has been regulated to be less than 0.01 mg l^{-1}. Chlorate and chlorite, known by-products of chlorine dioxide disinfection, have also been listed as chemicals to be monitored. The criterion has been set at 0.6 mg l^{-1} for both chlorate and chlorite based on their oxidative property for red blood cells in humans (MHLW 2003). In a national survey of monitored items (MHLW 2005), chlorate concentrations exceeded the criterion in 14 of the 598 monitored finished waters. The principal criterion for including a monitored compound in the list of drinking water standards is the detection of the compound in finished water at a concentration near or above one-tenth of its threshold standard. Accordingly, chlorate was introduced into the drinking water standards in April 2008. Perchlorate has only been recently addressed as a contaminant of concern in drinking water, though it is naturally occurring and was identified in Chilean salt caliche in the early 1900s (Dafert 1908). More recently it has been used as a chemical propellant in rocket fuels and an oxidizing agent in many products. Perchlorate is known to interfere with the iodine uptake of the thyroid gland (Greer *et al.* 2002; National Research Council 2005). In 2005, the United States Environmental Protection Agency (US EPA) established an official reference dose (RfD) of 0.7 μg kg^{-1} day^{-1} of perchlorate and specified its drinking water equivalent level (DWEL) to be 24.5 μg l^{-1} (US EPA 2005), based on a report by the National Academy of Sciences (NAS) (National Research Council 2005).

Chlorate and perchlorate have been detected in Japanese aquatic environments, especially in the Tone River Basin, which is one of the largest water sources for drinking water supply in the Tokyo metropolitan area (Asami *et al.* 2007; Kosaka *et al.* 2007). The maximum concentration of chlorate and perchlorate in river water affected by industrial effluents was measured at 9,000 μg l^{-1} and 15,000 μg l^{-1}, respectively. One of the highest concentrations of perchlorate was attributable to unintentional production of perchlorate in an electrolysis process.

All oxyhalides listed here (i.e. bromate, chlorate, chlorite and perchlorate) are industrial chemicals and are also known to exist in chlorinated drinking waters as impurities from sodium hypochlorite solutions. The concentrations of bromate, chlorate, chlorite and perchlorate in hypochlorite solution have been shown to increase during storage (Gordon *et al.* 1995 for chlorate; Weinberg *et al.* 2003 for bromate). However, the quality of the hypochlorite solution used in water treatment plants and the parameters which may contribute to increased rates of production of undesirable oxyhalide species are not well known. In this study, we investigated the concentrations of bromate, chlorate, chlorite and perchlorate in raw, processed and finished waters and hypochlorite solutions collected from various water treatment plants.

MATERIALS AND METHODS

Bromate, chlorate and chlorite in stored sodium hypochlorite solutions

The primary study was conducted to detect bromate, chlorate and chlorite concentrations in hypochlorite solutions. Thirty-seven samples were collected from hypochlorite solutions used in water supply facilities from 11 prefectures including Kanto (east), Kansai (west), Hokkaido (north) and Okinawa (south) regions in Japan. The water supply facilities include 28 treatment plants and 9 distribution facilities. Out of 37 facilities, 14 stored the sodium hypochlorite solutions in an air-conditioned environment. Samples were collected and stored in cool and dark conditions and analysed within 2 days. Sodium hypochlorite solutions were diluted 10,000 times by pure water (MilliQ Gradient A10 water purification system, Millipore, Bedford, Massachusetts) and the concentration of free available chlorine (FAC) was analysed by the DPD method. Chlorate was analysed using ion chromatography (IC, DX-500, Dionex, Sunnyvale, California), electric conductivity with an Ion Pac AG19/AS19 (4 mm) column and KOH generator. Bromate and chlorite were analysed by the IC-post-column colouring method using the same eluent reacted with 1.2 mM l^{-1} $NaNO_2$ and 1.5 M KBr 1.0 M l^{-1} H_2SO_4 solution, according to the official Japanese notification method (MHLW 2004).

Chlorate and perchlorate in raw, processed and finished waters and hypochlorite solutions

An intensive survey of chlorate and perchlorate concentrations in source and finished waters was conducted in conjunction with the Ministry of Health, Labour and Welfare, Japan. Raw, processed and finished water and hypochlorite solutions were collected from water treatment plants, especially in the Tone River Basin, to quantify the effect of industrial effluents. The Tone River is the largest water source in the Tokyo Metropolitan area and has been previously found to be contaminated by chlorate and perchlorate (Kosaka *et al.* 2007). More than ten other large cities and water supply bodies previously reporting high concentration of disinfection by-products (DBPs) were selected (MHLW 2006). In addition, 32 purchased and six on-site-generated hypochlorite solutions were collected and analysed. Chlorate and perchlorate concentrations were analysed with IC-tandem mass spectrometry (MS/MS) (Dionex ICS-2000 and API 3200QTrap, Applied Biosystems) as described elsewhere in detail (Kosaka *et al.* 2007). ^{18}O-enriched $NaClO_4$ (Cambridge Isotope Laboratories) was used as an internal standard for perchlorate. The minimum reporting limits (MRLs) for perchlorate and chlorate were set to be 0.05 and 0.05 $mg\,l^{-1}$, respectively, except the MRL for chlorate of the sample waters in several water treatment plants was 0.1 $mg\,l^{-1}$.

RESULTS AND DISCUSSION

Bromate, chlorate and chlorite in hypochlorite solutions

In the 37 sodium hypochlorite solutions collected, the concentration of measured free available chlorine (FAC) in the solution ranged from 0.04 to 15%, and the average concentrations of bromate in the solution were 96 $mg\,l^{-1}$ (maximum 414 $mg\,l^{-1}$). When the concentrations were converted into their finished water, bromate concentration was below 0.001 $mg\,l^{-1}$; chlorate and chlorite concentrations were below 0.20 and 0.003 $mg\,l^{-1}$, respectively, assuming the dose of the hypochlorite solution to be 1 $mg\,l^{-1}$. However, in some cases, chlorate concentration in the hypochlorite solution was extremely high when the measured FAC in the solution was much lower than its manufacturer-specified FAC at the time of purchase. The concentration of FAC is a critical factor for controlling residual chlorine, chlorate and bromate, because, if the sodium hypochlorite solutions which contain lower FAC than manufacturer-specified are used for disinfection, bromate and chlorate concentration may increase subsequently because of the increased amount of hypochlorite solution used in order to accomplish residual chlorine concentration.

Bromate concentration varied as shown in Figure 1. One factor is that bromate concentration varied among manufacturers. Though the number of samples was limited in this study, the bromate concentrations in sodium hypochlorite solutions of one manufacturer ranged from 5.4 to 49.5 $mg\,l^{-1}$ ($n = 7$), while those of another manufacturer ranged from 24.5 to 96.5 $mg\,l^{-1}$ ($n = 7$).

The other factor seems to be the timing of the purchase of hypochlorite solutions. It was recently reported that the concentration of bromate is largely dependent upon the salts used to produce hypochlorite solutions and can be controlled by changing the salt to those salts whose concentration of bromide is lower or by refining the salts. It is also reported that the manufacturers have changed the salts to refined types in accordance with the revision of the standard (JWWA 2006). Therefore, the high bromate concentration in older samples may be attributable to the bromide present in salts that were used as a basic ingredient in the production process.

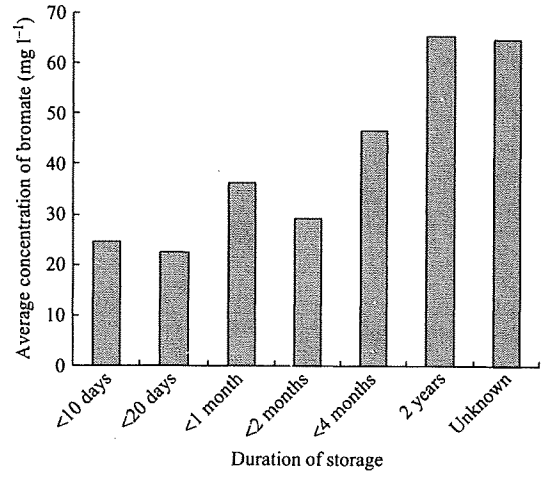

Figure 1 | Concentration of bromate in the hypochlorite solutions in relation to the duration of storage after purchase of each hypochlorite solution.

Weinberg *et al.* (2003) indicated the mechanism of bromate formation in hypochlorite solution as described in Equation (1) below. Since no residual bromide was found in any of the samples, and the reaction has been reported in the literature to occur very rapidly, the majority of bromide in sodium hypochlorite solution was expected to react to produce bromate.

$$Br^- + 3ClO^- \rightarrow BrO_3^- + 3Cl^- \quad (1)$$

Thus the authors consider that the high concentration of bromate might depend mainly on the bromide concentration in salts, while bromate concentration was higher in those sodium hypochlorite solutions that had been stored for more than two years or for an unknown period after the purchase of each hypochlorite solution.

Chlorite concentration was rather low in the hypochlorite samples, with an average of 145 $mg\,l^{-1}$ and a maximum of 397 $mg\,l^{-1}$. Chlorite concentrations in the treated water were below 0.003 $mg\,l^{-1}$ and 0.03 $mg\,l^{-1}$ assuming respective hypochlorite solution doses of 1 $mg\,l^{-1}$ and 10 $mg\,l^{-1}$. So chlorite concentrations were not expected to be very high in hypochlorite solutions and finished water.

The average concentration of chlorate in the hypochlorite solutions was 15,300 $mg\,l^{-1}$ (maximum 260,000 $mg\,l^{-1}$), and was largely different between samples and FAC levels. Chlorate concentrations in finished water were estimated to be 0.20 $mg\,l^{-1}$ and 2.0 $mg\,l^{-1}$ when the dose of the sodium hypochlorite solution was assumed to be 1 $mg\,l^{-1}$ and 10 $mg\,l^{-1}$, respectively. Thus, further study was conducted as described in the next section.

Chlorate and perchlorate in raw, processed and finished water

Chlorate and perchlorate concentrations in raw, processed and finished water in water treatment plants are shown in Table 1. Out of the 368 samples, chlorate was detected in 93.2% of the raw water samples and 100% of the processed and finished water samples. Perchlorate was detected in 98.8% of the raw water samples and 94.9% of the processed and finished water samples. The highest concentration of chlorate in raw water (78 $\mu g\,l^{-1}$) was found in groundwater apparently affected by the chlorate and perchlorate contamination in the Tone River. The concentrations of chlorate and perchlorate, and the ratio of their concentrations, were higher in the samples taken from the Tone River Basin. Perchlorate concentrations in raw, processed and finished waters at the same treatment plant were almost unchanged during the process. Chlorate concentrations were much higher in processed and finished waters, especially in the smaller facilities located in remote areas. The maximum concentration of chlorate in this study was 2.9 $mg\,l^{-1}$ (2,900 $\mu g\,l^{-1}$) due to chlorate in sodium hypochlorite solution used for disinfection.

Figures 2 and 3 show some examples of chlorate and perchlorate concentration through different stages of treatment in water treatment plants using different types of chlorine disinfectant. In Figure 2, the water treatment plant shown on the left-hand side used hypochlorite generated on-site while the plant on the right used manufactured sodium hypochlorite solutions. Chlorate concentrations increased during the treatment process. Both plants showed a large increase in chlorate concentrations. Figure 3 shows

Table 1 | Chlorate and perchlorate concentrations in raw, processed and finished water in water treatment plants

	Chlorate ($\mu g\,l^{-1}$)			Perchlorate ($\mu g\,l^{-1}$)		
	Detection rate	Min*	Max	Detection rate	Min*	Max
Raw water of water treatment plants						
Tone River Basin	116/116	0.06	78	114/116	0.09	40
Other than the Tone River Basin	62/75	0.08	53	55/55	0.06	2 .5
Processed water and finished water from water treatment plants						
Tone River Basin	178/178	0.17	2,900	168/178	0.05	24

*The minimum is data detected above LO Q (limits of quantification).