



Occurrence of THM and NDMA precursors in a watershed: Effect of seasons and anthropogenic pollution

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ABSTRACT

In pristine watersheds, natural organic matter is the main source of disinfection by-product (DBP) precursors. However, the presence of point or non-point pollution sources in watersheds may lead to increased levels of DBP precursors which in turn form DBPs in the drinking water treatment plant upon chlorination or chloramination. In this study, water samples were collected from a lake used to obtain drinking water for Istanbul as well as its tributaries to investigate the presence of the precursors of two disinfection by-products, trihalomethanes (THM) and N-nitrosodimethylamine (NDMA). In addition, the effect of seasons and the possible relationships between these precursors and water quality parameters were evaluated. The concentrations of THM and NDMA precursors measured as total THM formation potential (TTHMFP) and NDMA formation potential (NDMAFP) ranged between 126 and 1523 $\mu\text{g/L}$ THM and <2 and 1648 ng/L NDMA, respectively. Such wide ranges imply that some of the tributaries are affected by anthropogenic pollution sources, which is also supported by high DOC, Cl^- and NH_3 concentrations. No significant correlation was found between the water quality parameters and DBP formation potential, except for a weak correlation between NDMAFP and DOC concentrations. The effect of the sampling location was more pronounced than the seasonal variation due to anthropogenic pollution in some tributaries and no significant correlation was obtained between the seasons and water quality parameters.

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1. Introduction

Disinfection by-products (DBPs) are chemicals that are formed during disinfection of drinking water to remove pathogens and they include both halogenated and non-halogenated compounds depending on the disinfectant used and the precursors present. Trihalomethanes (THM) are the best known halogenated disinfection by-products and their concentrations have been detected above the maximum allowable concentration in various drinking water samples [1,2]. Natural organic matter (NOM) is the primary source of THM precursors but the presence of wastewater-derived organic matter contributes to the formation of THM, as well [3]. A suggested method for decreasing THM concentration is to use an alternative disinfectant such as chloramines. However, chloramination may lead to the formation of another type of DBP,

N-nitrosodimethylamine (NDMA) [4–6]. Dissolved organic nitrogen (DON) is the primary precursor of NDMA [7–11]. Similar to its role as a THM precursor, NOM is assumed to play an important role as an NDMA precursor as well [12,13]. Not only the amount of organic matter, but also the characteristics of the NOM depending on the drinking water source affect the formation of NDMA. For example, the concentration of NDMA formed at water treatment plants treating groundwater is reported to be smaller (<10 ng/L) than the NDMA concentration formed at plants treating surface water [14]. This finding suggests the presence of higher NDMA precursor concentration in surface waters. In addition, when surface water is used as the source of drinking water, coagulation process using polymers which have been shown to contain NDMA precursors (e.g., cationic polymers, [15]) may induce higher NDMA concentrations at water treatment plant effluent. Moreover, contamination of surface waters by treated or raw wastewater will increase the concentration of nitrogenous organic matter [16,17], which may act as NDMA precursors, thus increasing the concentration of NDMA upon chlorination/chloramination at the water treatment plant.

Although the presence of THM and its precursors in drinking water sources have been studied extensively [18], there is little information on the presence of NDMA and its precursors in sources

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that are used for the abstraction of drinking water. Also, there is a lack of information on the occurrence of THM and NDMA precursors simultaneously in a watershed as well as information on the effect of seasons on the DBP precursor concentrations. To investigate the presence and possible sources of THM and NDMA precursors in a drinking water watershed, samples were collected both from a lake used as a drinking water source of Istanbul and its tributaries. Moreover, the effect of seasons on DBP precursors was investigated by obtaining samples throughout the year in each season. Several water quality parameters including anions, dissolved organic carbon (DOC), DON and Specific Ultraviolet Absorption (SUVA) were measured to characterize the water bodies and investigate the presence of a correlation between DBP formation potential (DBPFP) and the water quality parameters.

2. Materials and methods

2.1. Chemicals

All chemicals used in the experiments were of analytical grade and were purchased from either Sigma–Aldrich or Merck except for d_6 -NDMA, which was purchased from C/D/N Isotopes, Inc. All glassware used in the experiments was rinsed with deionized water and baked at 550 °C for 4 h prior to use.

2.2. Sampling and analysis

Buyukcekmece Watershed (Istanbul, Turkey) includes Buyukcekmece Lake and its five tributaries (Ahlat, Beylikcayi, Hamza, Karasu and Tahtakopru). The climate of the watershed area is moderate with average temperatures for winter and summer 4° and 27°, however, the temperature can drop below zero in winter. The average annual rainfall is approximately 500 mm with the majority of rainfall occurring during fall and winter. In addition to the lake which covers approximately 5% of the total area, the watershed consists of mainly residential and agricultural areas (23 and 67% of the total area, respectively) whereas forests and

industrial areas account for approximately 2 and 3% of the total area, respectively [19].

Samples were collected from the lake and its tributaries (Fig. 1) at different time intervals (12/2009, 3/2010, 4/2010, 7/2010 and 10/2010). Buyukcekmece Lake has an average area and depth of 27.5 km² and 6.3 m, respectively. Grab samples were collected in 12-L Teflon-lined polypropylene containers (Nalgene) to prevent any contamination with NDMA precursors. Samples were brought to the laboratory of Istanbul Technical University and filtered through 0.2- μ m cartridge filters (AS75 PolyCap, Millipore Corp.) upon arrival to the laboratory on the same day. The filter-sterilized samples were stored in 4 °C for less than a week, until the analyses were conducted. Measurements of DBPFP in filtrates from 0.2- μ m cartridge filters indicated that these filters are not sources of DBP precursors (results not shown).

To characterize water quality, pH was measured with a Thermo Scientific ORION 4 Star Series pH-meter. DON and ammonia concentrations were measured using the macro Kjeldahl (4500-N_{org} B) and the phenate colorimetric method (4500-NH₃ F), respectively [20]. Nitrate and nitrite concentrations were measured with an ion chromatograph (Dionex, ICS 1500, AS14A column, 8 mM Na₂CO₃/1 mM NaHCO₃ mixture with a flowrate of 1 mL/min). Dissolved organic carbon (DOC) was measured using high temperature combustion method (3510B) [20] with a TOC analyzer (Shimadzu TOC-5000A). UV₂₅₄ measurements were conducted with a Perkin-Elmer Lambda-14 UV-Vis spectrophotometer.

THM analysis was performed with an Agilent 6890N Gas Chromatograph equipped with a micro Electron Capture Detector (GC- μ ECD) according to EPA Method 551.1 of liquid–liquid extraction (LLE) with pentane [21]. The THM precursors were measured by the THM formation potential (THMFP) test (5710B) in which the concentrations of THMs that form during chlorination in 7 days are measured [20].

NDMA concentrations were measured using a Thermo Electron Cooperation TSQ Quantum Access triple quadruple mass spectrometer coupled with Accela Ultra Performance Liquid Chromatograph (UPLC) with a Thermo Hypersil Gold column (100 mm \times 2.1 mm,

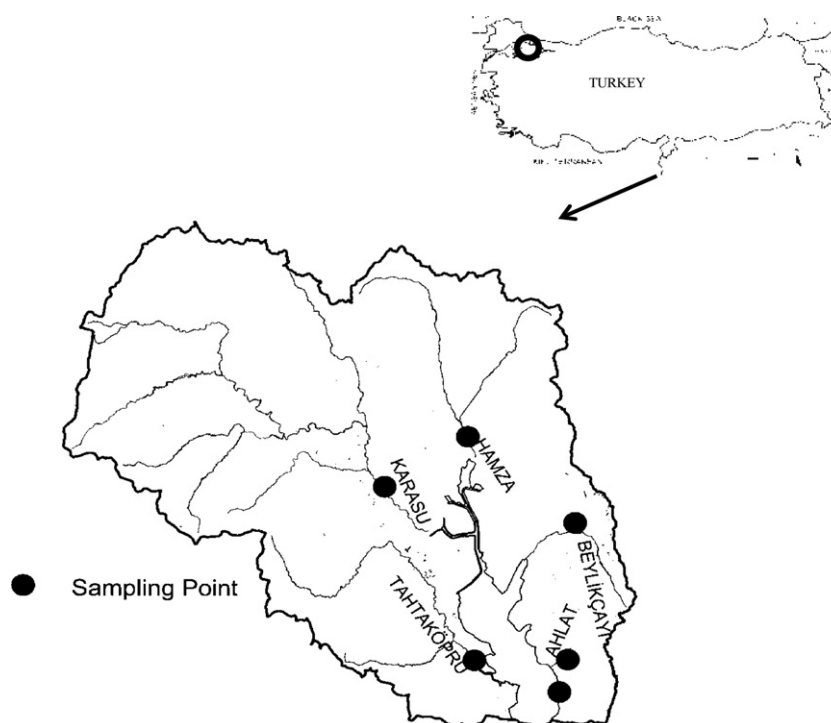


Fig. 1. Sampling points in Buyukcekmece watershed. The unlabeled dots indicate industries within the watershed.

1.9 μm) [22]. Briefly, 1 L of sample was spiked with $\text{d}_6\text{-NDMA}$ and was extracted through 1 g pre-packed activated spherical carbon SPE cartridges (Bakerbond Activated Spherical Carbon SPE Cartridges, Netherland). NDMA and $\text{d}_6\text{-NDMA}$ were eluted using separate additions of 2×2 mL of acetonitrile and acetone. Final volume of the sample was made up from approximately 0.75 mL to 1 mL with DI water after evaporation under N_2 gas (TurboVap II, Caliper Life Sciences). Acetonitrile, water and 1% formic acid were used as mobile phase with a gradient program at 200 $\mu\text{L}/\text{min}$ flowrate. NDMA and $\text{d}_6\text{-NDMA}$ measurements were performed by using electrospray ionization positive mode and single reaction monitoring (SRM) mode. SRM transitions for quantification were $75.4 \rightarrow 43.7$ and $81.4 \rightarrow 46.7$ for NDMA and $\text{d}_6\text{-NDMA}$, respectively, and the transitions for confirmation were $75.4 \rightarrow 58.5$ and $81.4 \rightarrow 64.4$ for NDMA and $\text{d}_6\text{-NDMA}$, respectively. Ionizations were established with protonation of molecules. The concentrations of NDMA precursors were obtained by the NDMA formation potential (NDMAFP) test which consists of the measurement of the NDMA concentrations that form during chloramination in 10 days [7].

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

For water quality parameters, duplicate samples were analyzed and the values reported represent the average concentrations \pm standard deviation. The detection limit for TTHM was 3 $\mu\text{g}/\text{L}$. Strict QA/QC was implemented to ensure the identification and accurate quantification of NDMA. The performance of the NDMA measurement method was tested by analyzing NDMA and $\text{d}_6\text{-NDMA}$ spiked surface water samples. Recoveries of the spiked samples were $115 \pm 2.8\%$ (average \pm standard deviation). The method detection limit was 2 ng/L for NDMA.

3. Results and discussion

Concentrations of water quality parameters for samples collected during five trips from the lake and its 5 tributaries are provided in Supplementary Information except for THMFPP and NDMAFP which are provided in Fig. 2. The results are assessed for the tributaries and the lake in Sections 3.1 and 3.2, respectively.

3.1. Water quality parameters in tributaries

The repeatability in water quality measurements is always within 5% except ammonia for which it was <20%. The concentrations of TKN and DON ranged between 0.1 and 15.4 mg N/L and between below detection limit and 4.7 mg N/L, respectively. The highest concentrations for TKN and DON were observed in July, 2010 in Beylikcayi and in March, 2010 in Ahlat samples, respectively. The wide range of concentrations could be attributed to anthropogenic pollution in the tributaries rather than the effect of seasonal variation.

No seasonal trend was observed for the anions except for chloride. In summer samples, there was a two fold increase in chloride concentrations in all river samples. The highest median concentration for chloride and sulfate was observed in Ahlat samples which were approximately 5 and 10 times higher than the concentrations obtained in the lake sample. The median nitrate concentration was also highest in Ahlat sample. Nitrate concentrations varied widely from <0.2 to 5.9 mg $\text{NO}_3\text{-N}/\text{L}$ depending on the location and time of sampling.

Similar to anions, the change in the THMFPP and NDMAFP concentrations did not show a seasonal trend, either. In the 29 samples collected, the NDMAFP concentrations ranged from <2 to 1648 ng NDMA/L with one sample below the detection limit (<2 ng/L), 22 samples below 20 ng/L and three samples between 20 and 50 ng/L.

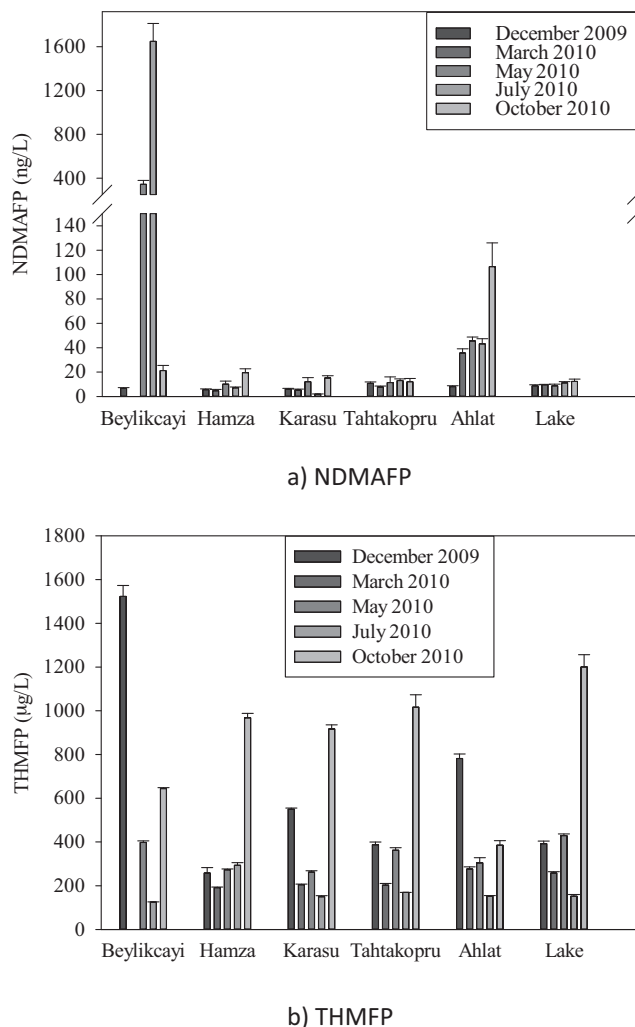


Fig. 2. The seasonal change of the precursors of THM and NDMA (measured as THMFPP and NDMAFP) in samples collected from the tributaries and the lake.

Three samples had concentrations above 100 ng/L which are similar to NDMAFP in wastewater treatment plant effluents [23–26] rather than in surface water. The concentrations of NDMA in all samples were below detection limit.

For NDMAFP concentrations, the effect of sample location was more pronounced than any seasonal effect. The limited literature on the effect of seasonal variation on NDMA formation is non-conclusive. There are studies where no statistically significant difference was observed among samples [27], studies where winter samples had higher NDMA concentration than summer samples [28] as well as studies with fall samples having approximately 50% less NDMA concentrations than summer samples [29].

Even if there was a seasonal trend in NDMAFP, the influence of possible anthropogenic sources to tributaries might have hindered the observation of the trend. NDMAFP can be used to evaluate wastewater impact on drinking water sources [30] and wastewater discharge to the river with a low flowrate may lead to an effluent-dominated stream where the constituents of the wastewater discharge have a serious impact on the water quality parameters of the river [31]. Therefore, the exceptionally high NDMAFP concentrations (106, 344 and 1648 ng/L) obtained in this study could be explained by wastewater discharges to Beylikcayi and Ahlat tributaries. In fact, the sample with the highest NDMAFP concentration has also the highest TKN and DOC concentrations among all samples (Beylikcayi summer sample: 15.4 mg TKN/L and 16.4 mg DOC/L).

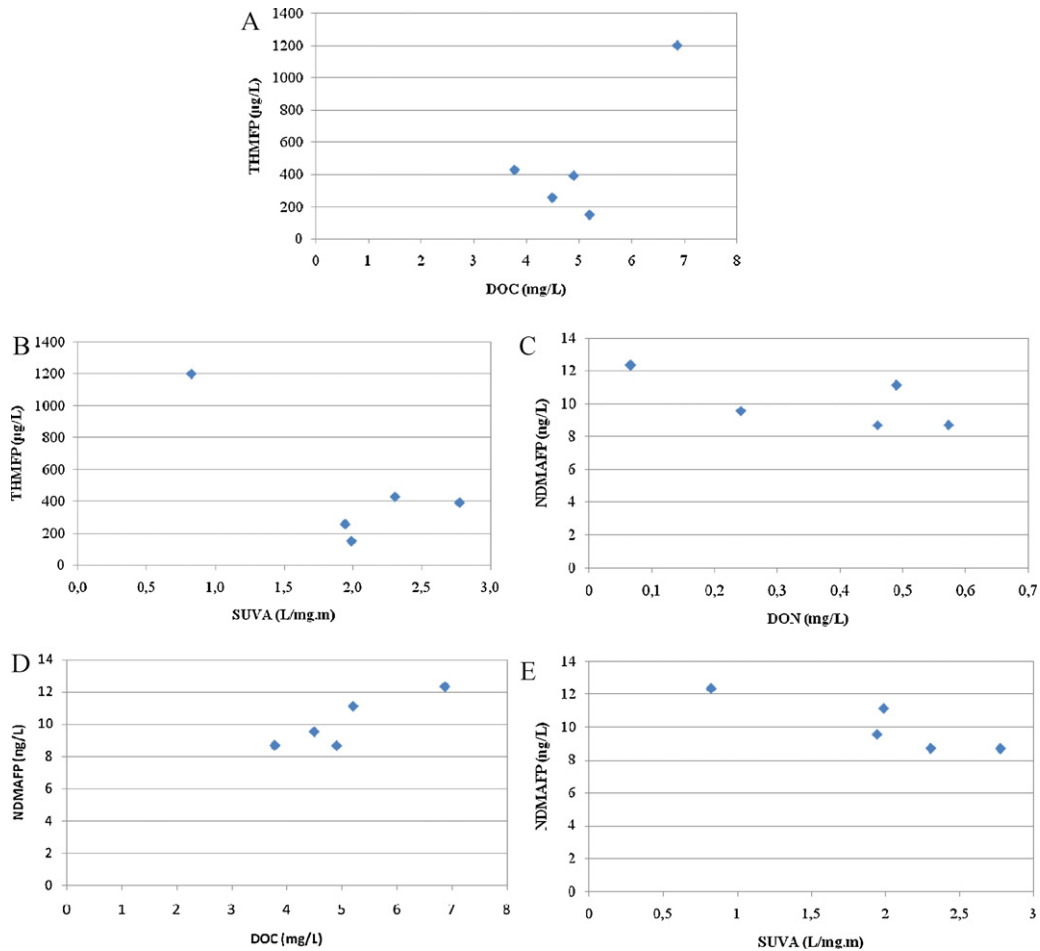


Fig. 3. The relationships between (a) THMFP and DOC, (b) THMFP and DON, (c) NDMAFP and DOC, (d) NDMAFP and DON, (e) NDMAFP and SUVA for lake samples.

In addition, the chloride concentration, another possible indicator of wastewater discharge and the DON concentrations were rather high in the same sample (113 mg Cl⁻/L and 2.3 mg N/L). Similarly, at Ahlat, another location where wastewater discharge is suspected the median NDMAFP was approximately 40 ng/L and the median DOC concentration was as high as the median of Beylikcayi sample (e.g., 6.7 mg/L).

The total THMFP concentration measured as duplicates during five sampling trips at five tributaries ranged between 126 and 1523 µg/L with five of the samples having a concentration of 900 µg/L or higher. The highest concentration of TTHMFP at all sampling locations was obtained either in the October or in the December sample suggesting a seasonal trend. A study conducted in Buyukcekmece Lake also obtained similar results where the highest TTHMFP concentrations were observed in winter samples [1]. However, other studies carried out in water sources in Turkey have claimed that fall or summer samples had the highest TTHMFP concentration [32,33]. The concentrations of THMs in all samples were below detection limit.

To sum up, for all of the water quality parameters including the precursors of DBP, the highest concentrations were observed either in Beylikcayi or in Ahlat samples suggesting the importance of sampling location within the watershed. The impact of sampling location being more important than the sampling time could be explained by the presence of a pollution source such as domestic and/or industrial wastewater discharge or diffuse pollution. Although Buyukcekmece Watershed is used as a drinking water

watershed, about 260 industrial facilities (mainly food, petroleum and coal-based [34] exist within the watershed and more than 120 of them are located in the vicinity of Beylikcayi and Ahlat tributaries. Moreover, after 1995, the residential and agricultural land use expanded in the eastern and southern parts of the watershed [19,34], where these tributaries are located. The presence of industries as well as agricultural areas could lead to point and non-point pollution in the watershed. Moreover, caffeine concentrations, which can be used as an indicator of contamination with untreated wastewater [30], ranged between 21 and 20,000 ng/L in Buyukcekmece Watershed samples [35]. Caffeine concentrations were high in all samples collected from Ahlat, implying a domestic wastewater discharge to the tributary throughout the year. A domestic wastewater discharge could also explain the substantially high NDMAFP, TKN, DOC and DON concentrations in these samples. Similarly, the highest concentration of THMFP was observed at Beylikcayi sample collected in December and this sample has the second highest caffeine concentration (5525 ng/L), suggesting a domestic wastewater discharge. The highest NDMAFP concentration (1650 ng/L) was detected in Beylikcayi sample collected in July, but the low caffeine concentration in this sample (e.g., 48 ng/L) excludes the possibility of a domestic wastewater discharge. Nevertheless, as the concentrations of several water quality parameters including TKN, NH₃, and TOC were the highest in July in Beylikcayi sample (Fig. 2), it is believed that an industrial wastewater discharge could be the reason of the unusually high concentration of NDMA precursors. Also, since agricultural runoff could include

NDMA precursors such as the herbicide diuron [8], diffuse pollution from agricultural land may contribute to the NDMA precursors in Beylikcayi sample.

3.2. Water quality parameters and their relationship with DBPFP in Buyukcekmece Lake

In recent years, the studies on the formation of DBPs have focused on finding surrogate parameters for DBPFP and on establishing relationships between DBPs and other more easily measurable water quality parameters [36]. TOC/DOC, UVA₂₅₄ and SUVA are widely used for the characterization of DOM [37]. Moreover, SUVA has been suggested as a surrogate parameter for DBPs since chlorine and other oxidants tend to react with the aromatic functional group [38]. Recently, relationships between NDMAFP and water quality parameters such as DON have been studied [39,40].

To investigate the presence of possible relationships between DBP precursors and a number of water quality parameters, the relationships between TTHMFP and DOC, TTHMFP and SUVA, NDMAFP and DOC, NDMAFP and DON, and NDMAFP and SUVA were assessed in lake water samples (Fig. 3a–e). The use of lake water eliminated the possible effect of anthropogenic sources which may influence not only the concentration of DOC but also the types of DBP precursors in the samples.

A correlation between the DOC concentration and the NDMAFP was observed in this study. A weak but significant correlation between DOC and NDMA has also been stated for both surface and groundwater samples [41] in the literature.

Although a previous study suggested an inverse proportional relationship between NDMAFP and SUVA [42], no relationship between NDMAFP and SUVA was found in this study. Also, there are studies in the literature where no relationship between NDMAFP and SUVA has been reported in surface or groundwater samples [41].

No correlation between DON concentration and NDMAFP was observed in this study, although DON pool should include the nitrogenous NDMA precursors such as dimethylamine (DMA), diuron, ranitidine, benzyldimethyltetradecylamine and 3-(*N,N*-dimethyloctyl-ammonia) propanesulfonate [8,10,11,43–45]. The lack of such a correlation could be due to two factors. The first factor is the analytical problems associated with the measurement of DON [9,46] in which DON is determined by subtraction of the sum of the inorganic nitrogen species from total dissolved nitrogen. It might be possible to overcome this problem by using a pretreatment method such as ultrafiltration or dialysis [46,47] to remove the inorganic nitrogen species prior to DON analysis. The second factor could be the low concentration of NDMA precursors which in turn might have no significant effect on the DON concentration. For example, the presence of 25 nM DMA or ranitidine will result in significant NDMAFP concentrations (14 and 300 ng/L NDMAFP, respectively) upon chloramination [44,48], whereas their concentrations as mg N/L would be too low to detect as DON (3.5×10^{-4} and 1.4×10^{-3} mg N/L for DMA and ranitidine, respectively).

Although no relationship was observed between TTHMFP vs. DOC and TTHMFP vs. SUVA in this study, several results indicating such relationships have been published for a variety of waterbodies [49,50]. Nevertheless, there are also several studies which fail to find a correlation between TTHMFP vs. DOC and TTHMFP vs. SUVA [51,52]. Particularly, in waters with low SUVA values (<2.0 L/mg/m) the TTHMFP cannot be correlated with SUVA [53]. Therefore, the lack of a relationship between SUVA and TTHMFP in this study is attributed to the low SUVA values (median: 1.7 L/mg/m) in our samples.

4. Conclusions

The seasonal occurrence of two disinfection by-product precursors was studied in a drinking water watershed. In the samples collected from Buyukcekmece Lake and its tributaries, the concentration of TTHMFP and NDMAFP ranged between 126 and 1523 µg THM/L and <2 and 1648 ng NDMA/L, respectively. The concentrations of water quality parameters in lake samples did not change considerably among samples collected over a year, probably due to dilution within the lake. On the other hand, the samples collected from the tributaries had a wide concentration range depending on the sampling point and time. For example, in Beylikcayi samples, there was an order of magnitude difference between the highest and lowest concentrations of both TTHMFP and NDMAFP. This wide range of concentrations is probably due to point or diffuse anthropogenic pollution sources such as discharge of domestic or industrial wastewater and agricultural runoff.

No significant correlation was found between the DBPFP and water quality parameters except for a weak correlation between NDMAFP and DOC. Although the NDMA precursors are included in the DON pool, it is possible that the low concentrations of NDMA precursors and the analytical problems related to the DON measurement did not enable the relationship to be observed even if one existed. The use of pretreatment methods such as ultrafiltration or dialysis could be useful for obtaining a relationship between DON and NDMAFP. The lack of a relationship between DPBs and water quality parameters suggests that more information is needed on the formation of DBPs to establish models. Fractionation techniques such as molecular weight fractionation and division into hydrophilic/hydrophobic fractions may further be used to understand the relationship between DBPFPs and water quality parameters as well as the fate of DBP precursors in natural and treatment systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2012.04.012>.

References

- [1] N. Ates, S. Kaplan, E. Sahinkaya, M. Kitis, F. Dilek, U. Yetis, Occurrence of disinfection by-products in low DOC surface waters in Turkey, *J. Hazard. Mater.* 142 (2007) 526–534.
- [2] R.J. Summerhayes, G.G. Morgan, D. Lincoln, H.P. Edwards, A. Earnest, M.B. Rahman, P. Byleveld, C.T. Cowie, J.R. Beard, Spatio-temporal variation in trihalomethanes in New South Wales, *Water Res.* 45 (2011) 5715–5726.
- [3] H.P. Chu, J.H.C. Wong, X.Y. Li, Trihalomethane formation potentials of organic pollutants in wastewater discharge, *Water Sci. Technol.* 46 (2002) 401–406.
- [4] W. Mitch, J. Sharp, R. Trussell, R. Valentine, L. Alvarez-Cohen, D. Sedlak, N-nitrosodimethylamine (NDMA) as a drinking water contaminant: a review, *Environ. Eng. Sci.* 20 (2003) 389–404.
- [5] J.H. Choi, R.L. Valentine, Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product, *Water Res.* 36 (2002) 817–824.
- [6] J. Nawrocki, P. Andrzejewski, Nitrosamines and water, *J. Hazard. Mater.* 189 (2011) 1–18.
- [7] W. Mitch, A. Gerecke, D. Sedlak, A N-nitrosodimethylamine (NDMA) precursor analysis for chlorination of water and wastewater, *Water Res.* 37 (2003) 3733–3741.

- [8] W.-H. Chen, T.M. Young, NDMA formation during chlorination and chloramination of aqueous diuron solutions, *Environ. Sci. Technol.* 42 (2008) 1072–1077.
- [9] E. Pehlivanoglu-Mantas, D.L. Sedlak, Measurement of dissolved organic nitrogen forms in wastewater effluents: concentrations, size distribution and NDMA formation potential, *Water Res.* 42 (2008) 3890–3898.
- [10] H. Chang, C. Chen, G. Wang, Identification of potential nitrogenous organic precursors for C-, N-DBPs and characterization of their DBPs formation, *Water Res.* 45 (2011) 3753–3764.
- [11] J. Le Roux, H. Gallard, J.-P. Croue, Chloramination of nitrogenous contaminants (pharmaceuticals and pesticides): NDMA and halogenated DBPs formation, *Water Res.* 45 (2011) 3164–3174.
- [12] A.C. Gerecke, D.L. Sedlak, Precursors of N-nitrosodimethylamine in natural waters, *Environ. Sci. Technol.* 37 (2003) 1331–1336.
- [13] Z. Chen, R.L. Valentine, Formation of N-nitrosodimethylamine (NDMA) from humic substances in natural water, *Environ. Sci. Technol.* 41 (2007) 6059–6065.
- [14] Luo X., Formation studies on N-nitrosodimethylamine (NDMA) in natural waters, University of Missouri-Columbia Ph.D. Thesis, 2006.
- [15] A. Wilczak, A. Assadi-Rad, H.H. Lai, L.L. Hoover, J.F. Smith, R. Berger, F. Rodigari, J.W. Beland, L.J. Lazzelle, E.G. Kinicannon, H. Baker, C.T. Heaney, Formation of NDMA in chloraminated water coagulated with DADMAC cationic polymer, *J. Am. Water Works Assoc.* 95 (2003) 94–106.
- [16] A. Dotson, P. Westerhoff, Occurrence and removal of amino acids during drinking water treatment, *J. Am. Water Works Assoc.* 101 (2009) 101–115.
- [17] E. Pehlivanoglu-Mantas, D.L. Sedlak, The fate of wastewater-derived NDMA precursors in the aquatic environment, *Water Res.* 40 (2006) 1287–1293.
- [18] D. Brown, J. Bridgeman, J.R. West, Predicting chlorine decay and THM formation in water supply systems, *Rev. Environ. Sci. Biotechnol.* 10 (2011) 79–99.
- [19] D. Maktav, F.S. Erbek, Analysis of urban growth using multi-temporal satellite data in Istanbul, Turkey, *Int. J. Remote Sens.* 26 (4) (2005) 797–810.
- [20] APHA, Standard Methods for the Examination of Water and Wastewater, American Water Works Association & Water Environment Federation, APHA-AWWA-WEF, Washington, D.C., USA, 2005.
- [21] USEPA, Method 551, Determination of chlorination disinfection by-products and chlorinated solvents in drinking water by liquid-liquid extraction and gas chromatography with electron-capture detection, Environmental Monitoring Systems Laboratory, Office of Research and Development, US Environmental Protection Agency, Cincinnati, USA, 1990.
- [22] E. Topuz, E. Aydin, E. Pehlivanoglu-Mantas, An LC-MS/MS method for the detection of NDMA at low concentrations in different water matrices, *Water Air Soil Poll* submitted for publication.
- [23] D.L. Sedlak, R.A. Deeb, E.L. Hawley, W.A. Mitch, T.D. Durbin, S. Mowbray, S. Carr, Sources and fate of nitrosodimethylamine and its precursors in municipal wastewater treatment plants, *Water Environ. Res.* 77 (2005) 32–39.
- [24] M. Krauss, P. Longree, E. Van Houtte, J. Cauwenberghs, J. Hollender, Assessing the fate of nitrosamine precursors in wastewater treatment by physicochemical fractionation, *Environ. Sci. Technol.* 44 (2010) 7871–7877.
- [25] M.J. Farre, J. Keller, N. Holling, Y. Poussade, W. Gernjak, Occurrence of N-nitrosodimethylamine precursors in wastewater treatment plant effluent and their fate during ultrafiltration-reverse osmosis membrane treatment, *Water Sci. Technol.* 63 (2011) 605–612.
- [26] S. Yoon, N. Nakada, H. Tanaka, Occurrence and removal of NDMA and NDMA formation potential in wastewater treatment plants, *J. Hazard. Mater.* 190 (2011) 897–902.
- [27] R.L. Valentine, J. Choi, Z. Chen, S.E. Barrett, H. Cordelia, C. Guo, Y. Wehner, M. Fitzsimmons, S. Andrews, S.A. Werker, A.G. Brubacher, K. Kohut, Factors Affecting the Formation of NDMA in Water and Occurrence, American Water Works Research Foundation, Denver, CO, 2006.
- [28] M. Asami, M. Oya, K. Kosaka, A nationwide survey of NDMA in raw and drinking water in Japan, *Sci. Total Environ.* 407 (2009) 3540–3545.
- [29] J.W.A. Charrois, M.W. Arend, K.L. Froese, S.E. Hrudey, Detecting N-nitrosamines in drinking water at nanogram per liter levels using ammonia positive chemical ionization, *Environ. Sci. Technol.* 38 (2004) 4835–4841.
- [30] Y.C. Guo, S.W. Krasner, Occurrence of primidone, carbamazepine, caffeine, and precursors for N-nitrosodimethylamine in drinking water sources impacted by wastewater, *J. Am. Water Resour. Assoc.* 45 (2009) 58–67.
- [31] B. Chen, S. Nam, P. Westerhoff, S. Krasner, G. Amy, Fate of effluent organic matter and DBP precursors in an effluent-dominated river: a case study of wastewater impact on downstream water quality, *Water Res.* 43 (2009) 1755–1765.
- [32] B. Tokmak, G. Capar, F.B. Dilek, U. Yetis, Trihalomethanes and associated potential cancer risks in the water supply in Ankara, Turkey, *Environ. Res.* 96 (2004) 345–352.
- [33] V. Uyak, K. Ozdemir, I. Toroz, Seasonal variations of disinfection by-product precursors profile and their removal through surface water treatment plants, *Sci. Total Environ.* 390 (2008) 417–424.
- [34] IPESR, Istanbul province environmental status report, Istanbul, 2007.
- [35] E. Aydin, I. Talinli, Analysis of highly used pharmaceuticals and hormones in surface water with ultra performance liquid chromatography-tandem mass spectrometry, *J. Hydrol.* unpublished results.
- [36] S. Chowdhury, P. Champagne, P. McLellan, Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review, *Sci. Total Environ.* 407 (2009) 4189–4206.
- [37] J.K. Edzwald, W.C. Becker, K.L. Wattier, Surrogate parameters for monitoring organic-matter and THM precursors, *J. Am. Water Resour. Assoc.* 77 (1985) 122–132.
- [38] P. Westerhoff, P. Chao, H. Mash, Reactivity of natural organic matter with aqueous chlorine and bromine, *Water Res.* 38 (2004) 1502–1513.
- [39] B.Y. Chen, P. Westerhoff, Predicting disinfection by-product formation potential in water, *Water Res.* 44 (2010) 3755–3762.
- [40] B. Xu, T. Ye, D.P. Li, C.Y. Hu, Y.L. Lin, S.J. Xia, F.X. Tian, N.Y. Gao, Measurement of dissolved organic nitrogen in a drinking water treatment plant: size fraction, fate, and relation to water quality parameters, *Sci. Total Environ.* 409 (2011) 1116–1122.
- [41] N. Van Huy, M. Murakami, H. Sakai, K. Oguma, K. Kosaka, M. Asami, S. Takizawa, Occurrence and formation potential of N-nitrosodimethylamine in ground water and river water in Tokyo, *Water Res.* 45 (2011) 3369–3377.
- [42] Z. Chen, R. Valentine, Modeling the formation of N-nitrosodimethylamine (NDMA) from the reaction of natural organic matter (NOM) with monochloramine, *Environ. Sci. Technol.* 40 (2006) 7290–7297.
- [43] W.A. Mitch, D.L. Sedlak, Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination, *Environ. Sci. Technol.* 36 (2002) 588–595.
- [44] R. Shen, S.A. Andrew, Demonstration of 20 pharmaceuticals and personal care products (PPCPs) as nitrosamine precursors during chloramine disinfection, *Water Res.* 45 (2011) 944–952.
- [45] J. Kim, T. Clevenger, Prediction of N-nitrosodimethylamine (NDMA) formation as a disinfection by-product, *J. Hazard. Mater.* 145 (2007) 270–276.
- [46] W. Lee, P. Westerhoff, Dissolved organic nitrogen measurement using dialysis pretreatment, *Environ. Sci. Technol.* 39 (2005) 879–884.
- [47] B. Xu, D. Li, W. Li, S. Xia, Y. Lin, C. Hu, C. Zhang, N. Gao, Measurements of dissolved organic nitrogen (DON) in water samples with nanofiltration pretreatment, *Water Res.* 44 (2010) 5376–5384.
- [48] F. Sacher, C. Schmidt, C. Lee, U. von Gunten, Strategies for Minimizing Nitrosamine Formation During Disinfection, American Water Works Association, 2008.
- [49] A.T. Chow, S. Gao, R.A. Dahlgren, Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: a review, *J. Water Supply Res. Technol.* 54 (2005) 475–507.
- [50] S. Platikanov, X. Puig, J. Martin, R. Tauler, Cemometric modeling and prediction of trihalomethane formation in Barcelona's water works plant, *Water Res.* 41 (2007) 3394–3406.
- [51] T.F. Marhaba, A. Mangmeechai, C. Chaiwatpongskorn, P. Pavasant, Trihalomethanes formation potential of shrimp farm effluents, *J. Hazard. Mater.* 136 (2006) 151–163.
- [52] N. Ates, U. Yetis, M. Kitis, Effects of bromide ion and natural organic matter fractions on the formation and speciation of chlorination by-products, *J. Environ. Eng.-ASCE* 133 (2007) 947–954.
- [53] M. Kitis, N. Yigita, B. Harmana, H. Muhammetoglu, A. Muhammetoglu, I. Karadirek, I. Demirel, T. Ozdenc, I. Palancic, Occurrence of trihalomethanes in chlorinated groundwaters with very low natural organic matter and bromide concentrations, *Environ. Forensics* 11 (2010) 264–274.