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Letter

Contribution of Dimethylamine to *N*-Nitrosodimethylamine Formation at Reverse Osmosis Water Reclamation Facilities

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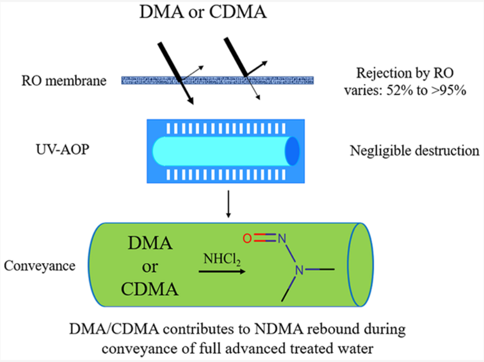
ABSTRACT: *N*-Nitrosodimethylamine (NDMA) is a disinfection byproduct formed from reactions between dichloramine and nitrogenous precursors. At water reuse facilities with reverse osmosis (RO) and ultraviolet-advanced oxidation processes (UV-AOP), NDMA is typically reduced to less than 2 ng/L. However, in some cases, NDMA "rebounds" to low ng/L concentrations during conveyance. The precursors evading RO and UV-AOP are currently unknown. Dimethylamine (DMA) does not substantially contribute to the NDMA precursor pool in treated wastewater or surface water, but DMA occurrence in reuse facilities has not been evaluated. We measured DMA and its chlorinated analogue (CDMA) in four full-scale water reclamation facilities utilizing RO and UV-AOP and one at pilot scale. The median sum of DMA and CDMA in the UV-AOP product and finished waters was 0.4 μg/L across six sampling events. At one reclamation facility sampled three times over one year, finished water DMA/CDMA ranged from 0.4 to 1.4 μg/L. DMA/CDMA accounted for 5%−43% of the total NDMA precursor pool of the UV-AOP product water at one facility and up to approximately 40 ng/L of NDMA formation. These findings enable treatment strategies which will result in reduced NDMA formation, thereby strengthening the future of potable reuse.



DMA/CDMA contributes to NDMA rebound during conveyance of full advanced treated water

KEYWORDS: *NDMA, precursor, disinfection byproduct, wastewater reclamation, potable reuse*

1. INTRODUCTION

Drought has rapidly decreased the availability of conventional water sources driving the urgent need for planned potable water reuse. Full advanced treatment (FAT) is utilized at wastewater reclamation facilities to produce potable water for reuse. FAT consists of secondary or tertiary wastewater treatment followed by microfiltration (MF) or ultrafiltration (UF), reverse osmosis (RO), and an advanced oxidation process (AOP). The most commonly utilized AOP is the ultraviolet-advanced oxidation process (UV-AOP) with hydrogen peroxide (UV/H_2O_2) or chlorine (UV/HOCl). *N*-Nitrosodimethylamine (NDMA) currently stands as a barrier to many potable reuse projects because the concentrations at which it tends to occur in the treated water for reuse are similar or greater to regulatory values (e.g., 10 ng/L California Notification Level).[1−3] It is a carcinogenic disinfection byproduct[1] formed by reactions between dichloramine and nitrogenous precursors.[4−6] Chloramines, including dichloramine, are formed upstream of membrane processes via addition of chlorine for biofouling control, which reacts with residual ammonia to form chloramines. Massachusetts, Canada, Australia, and the World Health Organization have established guidelines for NDMA in drinking water.[7−10] California has a public health goal of 3 ng/L for NDMA[11] and has currently set the drinking water notification level (NL) to 10 ng/L.[12] Exceeding this NL in potable waters triggers increased monitoring and corrective actions.[3]

NDMA is poorly removed by RO with reported rejections between 14% and 78%.[13−15] However, it is effectively destroyed by ultraviolet (UV) light during UV-AOP.[16] Although NDMA concentrations are reduced to below the detection limit (<2 ng/L) by UV-AOP, NDMA can "rebound" to low ng/L concentrations (~2 to 10 ng/L) during conveyance.[17,18] Past studies have shown that NDMA formation is promoted as a result of the reduction in pH (~5.5) that occurs across RO treatment.[4,19] Consequently, an approach to rapidly shift to a more basic pH after RO has been proposed to reduce the formation of NDMA,[19] but a follow-up study found that increasing the pH to ~8.5 via the addition of lime decreased the NDMA destruction from 90% to 64% by UV/H_2O_2 due to the lower NDMA quantum yield at higher pH.[20] Another approach is to mitigate NDMA formation in the finished water by removing or destroying the precursors prior

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to distribution. However, the identities of precursors are not yet known.

Dimethylamine (DMA) is one of the most studied model NDMA precursors despite prior studies demonstrating that DMA is not a predominant precursor in secondary municipal wastewater[21] or surface water.[22] However, DMA is present in wastewater at up to μg/L concentrations,[21,23] and if only 0.6 μg/L of DMA was to pass the RO membranes and UV-AOP, the resulting NDMA formation could be as high as 10 ng/L of NDMA assuming a 1% molar yield.[5,24−26] Such formation is meaningful in terms of potable reuse because 10 ng/L of NDMA is near or above many regulatory guidelines. While DMA rejection by pristine RO membranes has varied at bench scale from 88% to >98%,[27−29] DMA rejection by in-service, full-scale RO membranes that have been subject to repeated chemical cleanings has not been reported, but it has been reported that NDMA precursor rejection by RO membranes worsens over time.[17] Chlorinated dimethylamine (CDMA), another NDMA precursor with a somewhat lower yield,[28] forms rapidly from reactions between HOCl or monochloramine (NH_2Cl) and DMA.[26,30,31] CDMA is neutral and thus likely to pass RO membranes.[28]

DMA and CDMA are relatively small molecules present in wastewater that serve as potable reuse influents.[24,32,33] Additionally, CDMA is likely recalcitrant to reactions with hydroxyl radicals during UV-AOP (although no published rate constants are available). For these reasons, we hypothesized that DMA/CDMA may pass through RO membranes and endure UV-AOP unaffected, at concentrations great enough to substantially contribute to the NDMA precursor pool in finished FAT water. To investigate the importance of DMA/CDMA as NDMA precursors at potable reuse facilities, an optimized solid-phase extraction (SPE) gas chromatography-tandem mass spectrometry (GC-MS/MS) method with reduced organic solvent usage for measuring DMA/CDMA was developed to improve upon literature methods reported 20 years ago.[33,34] Using this method, DMA and CDMA were quantified at four full-scale treatment plants. The yields of NDMA from DMA or CDMA were determined through standard addition experiments. Pilot-scale UV-AOP experiments were performed to validate full-scale results.

2. MATERIALS AND METHODS

2.1. Chemicals and Materials. Details of chemicals and solvents are described in the Supporting Information (Text S1). SPE cartridges including EPA 521 activated carbon (2 g/6 mL) and Sep-Pak C_{18} (1 g/6 mL) were utilized for NDMA and DMA analyses, respectively. Further details are provided in Text S1.

2.2. Sample Collection. Samples were collected from four potable reuse facilities in California: Orange County Water District (OCWD) Advanced Water Purification Facility (AWPF) and three other water reclamation facilities utilizing RO and UV-AOP. At the AWPF, samples of the RO feed (ROF), RO permeate (ROP), UV-AOP feed (UVF), UV-AOP product (UVP), and the finished product water (FPW) were collected on three occasions over an approximately one-year period (January 2020, September 2020, and February 2021). The rationale for the sampling plan is provided in Text S2. OCWD AWPF sampling sites are shown in Figure S1. ROF, UVF, and UVP samples from the other three RO-based water reclamation facilities were collected in December 2020, January 2021, and February 2021. Total residual chlorine was measured and immediately quenched with 100 mg/L of sodium sulfite. Samples were shipped overnight on ice to the University of Nevada, Reno (UNR), and stored at 4 °C prior to analysis.

The pilot-scale experiments were conducted at OCWD in April and October 2021. In April, RO permeate from the AWPF was fed to a pilot-scale low-pressure UV reactor with H_2O_2 or HOCl as an oxidant, and in October, a second pilot-scale experiment utilized 20 μg/L of NDMA spiked to deionized (DI) water as the feed solution with H_2O_2 as the oxidant. Pilot UVF and UVP were collected and shipped on ice to UNR for analysis. Further details about the pilot UV-AOP reactor are provided in Text S2.

2.3. DMA Quantification. DMA was analyzed by a modified SPE method[34] and a published GC-MS/MS method.[33] The modifications to the extraction method were made to reduce solvent use. Multiple variables were optimized, and the optimized method is described in Text S3. Note that because CDMA is reduced to DMA by the quenching agents employed in the present study at full and pilot scales,[28] both DMA and CDMA were captured by the analytical method and are referred to as DMA/CDMA.

GC-MS/MS (Shimadzu TQ8040, Japan) was conducted in electron impact positive ionization mode using a capillary column (DB 1701P, 30 m × 0.25 mm × 0.25 μm). The instrument conditions for DMA analysis are summarized in Table S1. DMA and DMA-d6 were quantified using the 215 m/z parent ion and 215 m/z daughter ion for DMA and the 221 m/z parent ion and 221 m/z daughter ion for DMA-d6, similar to GC-MS/MS of DMA conducted by others.[33] The fragmentation of interfering compounds that make it past the first mass filter was the goal of this type of MS/MS, where in other MS approaches the collision cell is used to fragment the target. The Pearson coefficient for the calibration curve with a range of DMA concentrations from 1−100 μg/L was >0.99 (Figure S3). The calibration range provided is for samples injected into the GC-MS/MS, after 50× concentration by SPE, corresponding to a range of 0.2−2 μg/L in the samples prior to extraction. Method validation was conducted with recoveries of DMA spiked into tap water and Milli-Q water between 92% and 113%, and the method detection limit (MDL) was 0.15 μg/L. Further method validation details are provided in Text S4.

2.4. NDMA Formation Potential and NDMA Analysis. NDMA formation potential (FP) tests were conducted with 500 mL samples in 1-L amber bottles as described elsewhere.[35,36] Briefly, samples were buffered at pH 8.0 with a borate solution and dosed with 18 mg-Cl_2/L of freshly prepared NH_2Cl. NDMA FP tests with 18 mg-Cl_2/L of NH_2Cl were chosen over uniform formation condition (UFC) tests for two reasons: (1) The low concentrations of NDMA formed from UFC tests would result in substantial variability in NDMA measurement, and (2) UFC and FP tests tend to be well correlated.[37] Samples were allowed to react in the dark at room temperature for 72 h. Residual monochloramine was always >4.5 mg-Cl_2/L before quenching with 5 mL of 0.5 M ascorbic acid. The quenching agents used by respective sampling and lab experimental teams were based on their on-site availability and familiarity. 1 mL of 100 μg/L isotopically labeled NDMA was added, and samples were stored in the dark at 4 °C before analysis. NDMA was quantified by a modified U.S. EPA Method 521.[36,38] Further details regarding NDMA analysis are described in Text S5.

3. RESULTS AND DISCUSSION

3.1. Occurrence of DMA/CDMA in Potable Reuse Facilities. DMA/CDMA were measured at four facilities that produce potable water for reuse to understand if DMA/CDMA pass through full-scale RO and UV-AOP treatment processes. Available water quality data are provided in Table S4. DMA/CDMA in the ROF samples ranged from 0.5 to 8.1 μg/L (Figure 1), consistent with previous studies where DMA concentrations in the secondary effluents ranged from <0.9 to 13 μg/L.[21] DMA/CDMA concentrations in the ROP samples were reduced to <0.15 to 0.9 μg/L, corresponding to DMA/CDMA rejections by the RO membranes from 52% to ≥95% (MDL of 0.15 μg/L used to calculate the rejection for ROP where the DMA was below the detection limit). Rejection measured at bench scale by prior research utilizing virgin membranes varied less. For example, two studies reported >98% rejections of DMA,[27,29] while a third study observed 71% and 88% rejections of CDMA and DMA, respectively.[28] The variability in full-scale DMA/CDMA rejections in this study may be attributable to variable RO membrane age and feedwater chemistry. Factors such as plant operational history (e.g., frequency and aggressiveness of membrane cleanings) cause variable RO membrane aging. Increased salt and trace organic compound permeabilities, including unidentified NDMA precursors, have been observed with aging of the membrane from continuous use and repeated chemical cleanings.[17,39] The contribution from CDMA is likely another factor influencing permeability, because CDMA is neutral, compared to DMA, which is ionized at this pH.[28] The dominant factor affecting DMA/CDMA rejections needs further study, likely at bench scale. DMA/CDMA concentrations in UVP samples from the four facilities ranged from <0.15 to 1.0 μg/L. DMA/CDMA concentrations were generally comparable between ROP and UVP (i.e., across UV-AOP) for all treatment plants and all sampling dates suggesting that DMA/CDMA are not well removed or destroyed by UV-AOP (Figure 1).

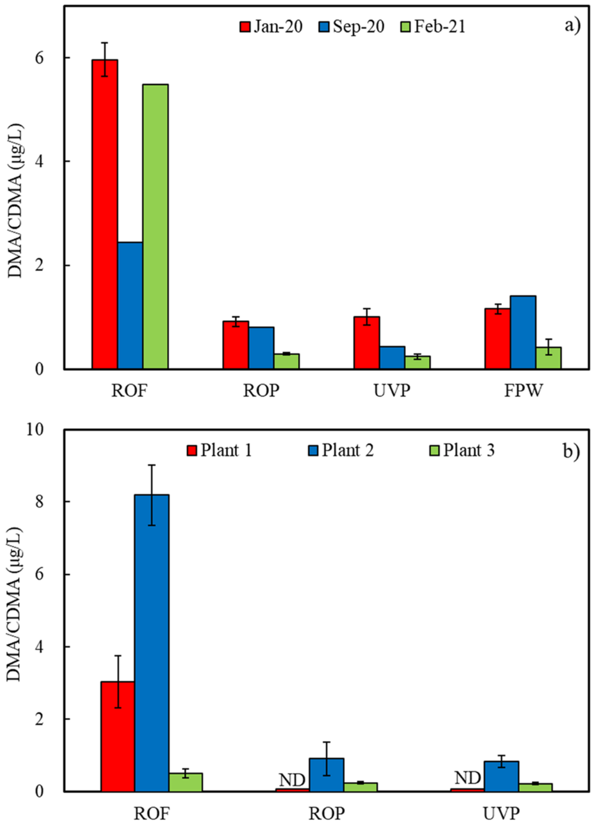

Figure 1. DMA/CDMA concentrations in source waters from (a) the OCWD AWPF on three occasions and (b) three additional RO potable reuse facilities in California. Nondetect DMA/CDMA concentrations (ND) in ROP and UVP at Plant 1 are plotted as one-half the MDL (0.15 μg/L). Error is shown as the range of duplicates except ROP and UVP from OCWD AWPF which are the standard deviation of triplicates. The height of the bar indicates the average concentration. CDMA present is measured as DMA after reduction caused by quenching agents. When replicates were taken (Jan-20 and Feb-21), there was not a statistically significant (t test, $p >$ 0.05) change in DMA/CDMA from UVP to FPW.

At OCWD AWPF, the UVP water is stabilized to minimize corrosion of the cement mortar conveyance pipeline. The pH of UVP is adjusted from 5.5 to 8.5 by partial decarbonation and addition of a saturated lime supernatant,[40] resulting in FPW. FPW samples contained from 0.4 to 1.4 μg/L DMA/CDMA, similar or slightly greater than concentrations in the UVP samples in the three sampling events, although not significantly different (t test, $p > 0.05$). Overall, at the four potable reuse facilities, DMA/CDMA concentrations in the UVP and FPW samples fell within the narrow range from 0.2 to 1.4 μg/L when detected. In some cases, DMA/CDMA were rejected well by RO membranes (≥95%), but in most cases, rejection was poor (52%−89%). UV-AOP had minimal or no additional impact on DMA/CDMA removals.

3.2. Contributions of DMA/CDMA to NDMA Formation. In order to assess the contributions of DMA/CDMA to NDMA formation, we conducted experiments to determine DMA and CDMA yields in forming NDMA. We sampled AWPF UVP an additional time (March 2021) and spiked DMA at varying concentrations to determine NDMA yield from DMA in the UV permeate matrix (i.e., standard addition, Figure S2a). The slope indicates the NDMA mass yield from DMA, equivalent to a molar yield of 1.73%, which is comparable to published yields ranging from 1% to 3%[24−26] and indicates that the low level of background organic matter in UVP water had no effect on NDMA formation. NDMA yield from 1 to 100 μg/L CDMA was investigated in DI water because of the negligible impact from the matrix demonstrated for DMA and because of the large volume of shipped water required to conduct the experiments in UVP. The CDMA to NDMA molar yield was 0.09% (Figure S2b). The molar yield is somewhat greater than a previously published yield (∼0.01%),[28] reflective of the lower oxidant concentration used in a prior study. Finally, because UV treatment of CDMA may alter the NDMA yield,[28,41] the NDMA molar yield was investigated exposing CDMA to 1000 mJ/cm^2 of 254 nm light (experiment details are provided in Text S6), followed by chloramination, and the NDMA molar yield was 0.32% (Figure S3).

The potential contributions to NDMA formations in the UVP and FPW samples were calculated from the measured DMA/CDMA multiplied by the range of NDMA molar yields expected from DMA, CDMA, and UV-irradiated CDMA (Table 1). Because of the limited volume of water sampled, NDMA FP was only directly measured in one UVP sample collected from the AWPF. Measured DMA/CDMA and NDMA FP in this UVP sample were 0.6 μg/L and 36.5 ng/L, respectively. Comparing the expected NDMA FP from these

Table 1. Calculated NDMA FPs in UVP and FPW Samples Based on Varying NDMA Molar Yields from DMA, CDMA, and UV Irradiated CDMA

Sample information			Potential NDMA FP (ng/L) from possible precursors		
Location	Date	Measured DMA/CDMA (μg/L)	DMA[a]	CDMA[b]	UV-irradiated CDMA[c]
UVP at OCWD	Jan-20	1.0	28.4	0.8	3.0
FPW at OCWD	Jan-20	1.2	34.1	1.0	3.6
UVP at OCWD	Sep-20	0.4	11.4	0.3	1.2
FPW at OCWD	Sep-20	1.4	39.8	1.2	4.2
UVP at OCWD	Feb-21	0.2	5.7	0.2	0.6
FPW at OCWD	Feb-21	0.4	11.4	0.3	1.2
UVP at OCWD	Mar-21	0.6	15.9	0.5	1.8
UVP at Plant 1	Jan-21	<0.15	–	–	–
UVP at Plant 2	Feb-21	0.8	22.8	0.7	2.4
UVP at Plant 3	Dec-20	0.2	5.7	0.2	0.6

[a]Assuming only DMA present, 1.73% NDMA molar yield. [b]Assuming only CDMA present, 0.09% NDMA molar yield. [c]Assuming only CDMA present, 0.32% NDMA molar yield.

three precursors and their respective yields to the NDMA FP observed in the sample results in the finding that DMA/CDMA contributed from 5% to 43% of the precursor loading. DMA/CDMA concentrations in UVP or FPW samples at the other four facilities ranged from <0.15 to 1.4 μg/L, corresponding to NDMA FP of up to ~40 ng/L, assuming only DMA was present, substantially greater than NL of 10 ng/L in California, although treatment plants are likely to use a substantially lower dose of oxidant. If only CDMA was present, or only irradiated CDMA, the expected NDMA FP would be 1.2 or 4.2 ng/L, respectively, similar to what is observed at full-scale facilities. DMA/CDMA are therefore important or primary contributors to the precursor pool in finished full advanced treated water.

If NDMA rebound in finished water is observed to be significant at a particular facility,[18] whether resulting from DMA occurrence or a combination of DMA and other NDMA precursors, the resulting NDMA concentration could impede implementation of direct potable reuse depending on state regulatory thresholds or guidance values. Treatment facilities with short residence time environmental buffers or no environmental buffer will particularly benefit from an understanding of DMA/CDMA as precursors. In the case of groundwater augmentation, which is a form of indirect potable reuse practiced by OCWD in the present study in California, NDMA rebound may not be as great of a concern since drinking water regulatory thresholds apply later at the production well (groundwater) where NDMA concentrations may have been reduced due to various factors (e.g., photolysis in recharge ponds,[42] blending, and limited soil aquifer treatment).

3.3. Pilot-Scale Destruction of DMA/CDMA and NDMA. HOCl addition prior to UV-AOP (rather than H_2O_2) was investigated because it is being considered as an alternative by many utilities due to its perceived potential to destroy trace organic contaminants better than advanced oxidation with H_2O_2. ROP from the OCWD AWPF was fed to the pilot UV-AOP reactor (Figure S6) at a dose of 2.6 mg/L of H_2O_2 or 2 mg-Cl_2/L of HOCl, and UVF and UVP samples were grabbed. The water quality data are provided in Table S5. A control experiment was conducted without dosing an oxidant into the ROP feed that contained 2.0−2.3 mg-Cl_2/L of total chlorine (chloramines). DMA/CDMA concentrations in the ROP ranged from 0.7 to 1.0 μg/L, comparable with that of ROP measured on the three occasions at the AWPF. DMA/CDMA concentrations decreased from 0.7−1.0 to 0.5 μg/L independent of the applied oxidant (H_2O_2 or HOCl). In the presence of UV light with no added oxidant (and residual chloramines), the concentrations of DMA/CDMA increased from 0.7 to 1.0 μg/L, suggesting that some precursors, including NDMA,[32,43] may be decomposed to DMA/CDMA by UV photolysis. Therefore, HOCl did not perform substantially better as an oxidant for UV-AOP (similar reduction in DMA/CDMA when either H_2O_2 or HOCl was the oxidant) and is not a viable alternative to reduce NDMA formation from DMA/CDMA based on results from this limited study.

To understand the mass balance of DMA in the system, including its potential to form as a photolytic decomposition product during UV-AOP, DI water free of measurable NDMA was spiked with 20 μg/L of NDMA and then treated by UV/H_2O_2 or only UV at pilot scale (Figure S7). Although the photolysis of NDMA to DMA is well known,[32,43] there has not yet been any experimentation to demonstrate that it is a negligible precursor during conveyance of FAT-treated waters (i.e., "reformation" of NDMA from its photolytic decomposition product). For control samples (DI water), no DMA was detected with or without oxidant addition. We refer here to DMA as measured by the analytical method, which captures both DMA and CDMA as DMA, because there is no chlorine present in the system, and thus, DMA will not be oxidized to CDMA. With UV only and DI water spiked with NDMA, DMA concentrations increased from below the MDL to 0.2 μg/L, indicating some DMA is produced from NDMA photolysis. With H_2O_2 addition, 1.0 μg/L of DMA was formed across the UV-AOP system, equivalent to a DMA molar yield of 14%. NDMA concentrations in ROP from the OCWD AWPF have been reported between 9 and 30 ng/L,[20] suggesting that only 0.8−2.5 ng/L of DMA would be produced from NDMA photolysis. Thus, since DMA/CDMA present in the ROP are not well destroyed by UV-AOP, and because NDMA is not present at concentrations high enough in ROP to account for the DMA/CDMA detected in the UVP, the primary source of DMA/CDMA within the water reclamation facility that results in the formation of NDMA downstream of the treatment process is likely to be the wastewater effluent rather than in-system production via photolysis (i.e., "reformation").

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4. IMPLICATIONS

DMA/CDMA present in the treated wastewater influent are likely to contribute significantly to the total NDMA precursor pool and are at least partially or primarily responsible for observed NDMA "rebound" downstream of full advanced treatment potable reuse facilities in the presence of residual chloramines in the finished product water. Such NDMA rebound could hinder implementation or approval of direct potable reuse of full advanced treated water in regions where NDMA regulatory limits or response levels are set low. Potable reuse is increasingly being adopted in the U.S. and throughout the world to improve drought resilience and to adapt to climate change. To this end, reliable treatment strategies outside of RO membranes and UV-AOPs are needed to effectively remove (i.e., sorption) or degrade DMA to mitigate NDMA formation during conveyance and strengthen the future of potable reuse. Expanded sampling campaigns that are outside the scope of this research will help to understand the contributions of DMA/CDMA to individual treatment plants' NDMA precursor pools, the temporal variabilities of DMA/CDMA, and the potential to be rejected by in use RO membranes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.2c00852.

Details about the chemicals and materials, sample collection, quantification methods of DMA/CDMA and NDMA, and batch-scale UV experiments (PDF)

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Notes

The authors declare no competing financial interest.

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