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The Role of Oxalic Acid in New Particle Formation from Methanesulfonic Acid, Methylamine, and Water

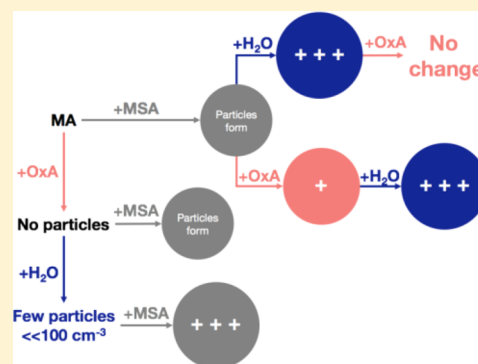
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S Supporting Information

ABSTRACT: Atmospheric particles are notorious for their effects on human health and visibility and are known to influence climate. Though sulfuric acid and ammonia/amines are recognized as main contributors to new particle formation (NPF), models and observations have indicated that other species may be involved. It has been shown that nucleation from methanesulfonic acid (MSA) and amines, which is enhanced with added water, can also contribute to NPF. While organics are ubiquitous in air and likely to be involved in NPF by stabilizing small clusters for further growth, their effects on the MSA–amine system are not known. This work investigates the effect of oxalic acid (OxA) on NPF from the reaction of MSA and methylamine (MA) at 1 atm and 294 K in the presence and absence of water vapor using an aerosol flow reactor. OxA and MA do not efficiently form particles even in the presence of water, but NPF is enhanced when adding MSA to OxA–MA with and without water. The addition of OxA to MSA–MA mixtures yields a modest NPF enhancement, whereas the addition of OxA to MSA–MA–H₂O has no effect. Possible reasons for these effects are discussed.



INTRODUCTION

The effects of atmospheric particles are wide reaching: they impact health,¹ obstruct visibility,^{2,3} and influence climate.^{4,5} Understanding how particles form and grow in air is an important pursuit to develop strategies that mitigate their overall impact. Sulfuric acid, which is formed from the atmospheric oxidation of SO₂ (a byproduct of combustion of sulfur-containing fossil fuels),⁴ has long been identified as a large contributor to new particle formation (NPF).^{6,7} However, atmospheric observations of NPF cannot fully be explained by the nucleation of H₂SO₄ and H₂O alone.^{8,9} Ammonia and amines have been shown to enhance NPF;^{10–20} nonetheless, nucleation of H₂SO₄ and H₂O with ammonia or amines often does not reproduce NPF measurements.¹¹ Such discrepancies between NPF models and observations suggest that other species are involved.^{21–23}

Organics have been measured in particles all over the world²⁴ and are predicted to participate in NPF, but their exact influence on NPF and growth is not well understood. Organic salts formed from the reaction of organic acids with amines have also been proposed to contribute to nucleation and particle growth.^{25,26} Organics may be involved in initial nucleation of sulfuric acid^{21–23} or on their own.^{27–31} They may also play a role on a molecular level in stabilizing small clusters, leading to growth to detectable sizes,^{20–23,27,32–37} although Wang et al.³⁸ showed that H₂SO₄–H₂O nanoparticles did not grow when exposed to representative gas-phase organics. Such results imply that multiple factors lead to

growth by organics and that only some heterogeneous reactions may be important for growth.³⁹

Another potentially significant source of particles in the atmosphere in some locations is reactions of methanesulfonic acid (CH₃SO₃H, MSA). MSA has been measured in particles, for example, above and near marine areas,^{40–47} but also inland.⁴⁸ While MSA may currently be a minor source of particles, the relative importance of MSA in the future is likely to increase as the use of sulfur-containing fossil fuels decreases.⁴⁹ However, even now, some field measurements have reported a strong correlation during the summer between the methanesulfonate ion and particle number concentrations⁵⁰ and between particle growth and MSA concentrations.⁵¹

MSA is formed from the oxidation of organosulfur compounds such as dimethyl sulfide, whose main source is from the ocean but can also be emitted from vegetation, tropical forests, agricultural operations, and even humans.^{52–55} The gas-phase concentration of MSA can range from 10–100% of that of sulfuric acid, ~10⁵ to 10⁷ molecules cm⁻³.^{56–61} Although MSA does not form particles with water under atmospheric conditions,^{62–65} it does so with ammonia and amines, which is enhanced by the presence of water.^{49,66–68} Ammonia and amines are ubiquitous in the atmosphere as they are emitted by sources ranging from animal husbandry to

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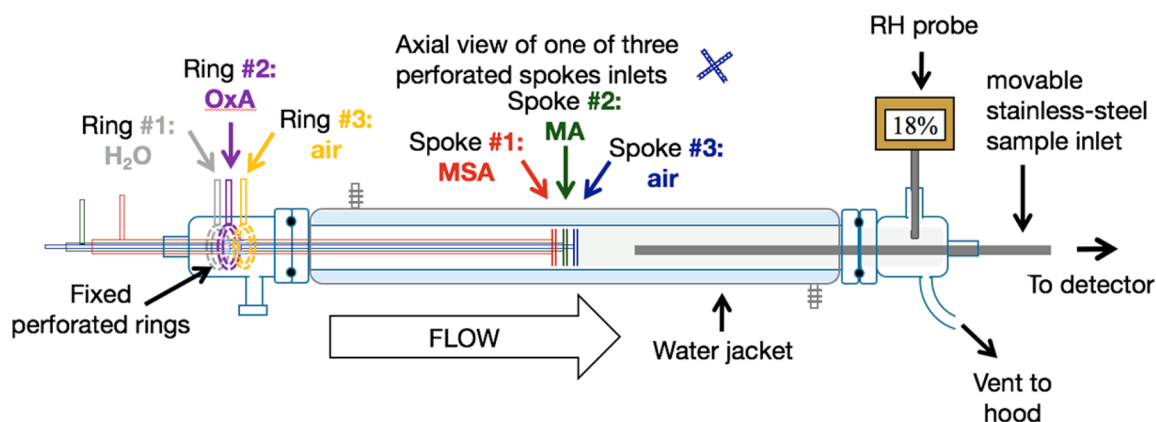


Figure 1. Aerosol flow tube reactor 1.45 m in length with a 7.6 cm inner diameter.

biodegradation of and by marine life.⁶⁹ Though ambient amine concentrations are typically 2–3 orders of magnitude lower than that of ammonia,⁶⁹ they are much more efficient in forming particles,^{13–19} and amines have been shown to displace ammonia in clusters with MSA.⁷⁰ Whether organics play a role in NPF from reactions involving MSA and amines is not yet known.

This work explores the effect of oxalic acid ((COOH)₂, OxA) on particles formed from the reaction of MSA and methylamine (CH₃NH₂, MA) in the absence and presence of water vapor. OxA, the smallest dicarboxylic acid, has been measured in particles collected over both urban and marine areas.^{71,72} OxA has also been measured along with MSA and ammonia and amines in submicrometer atmospheric particles.^{73,74} With its polar nature and potential for hydrogen bonding, combined with an intermediate volatility (IVOC)^{75–78} (VP at 298 K = 1.4×10^{-2} Pa),⁷⁹ OxA may be a good candidate for potentially enhancing NPF.

EXPERIMENTAL SECTION

Experiments were performed in a small volume (~6.6 L) aerosol flow reactor (Figure 1) similar in design to that described elsewhere.⁸⁰ The flow reactor has multiple inlets: three fixed rings upstream and three spokes, movable as a unit, downstream. Details of the flow reactor and determination of residence times are in Section 1 of the Supporting Information. Reactants were added to the flow reactor in a consistent configuration with H₂O through ring #1, OxA through ring #2, MSA through spoke #1, and MA through spoke #2; dry air was added through the remaining inlets so that the total flow was always 17 L per minute (Lpm) in the system. The air used here and throughout the experiment was dry air from a purge air generator (Parker-Balston, 75-62). All experiments were performed at atmospheric pressure and 294 K.

For all experiments except the controls, there was a base case experiment where two or three of the components were present in the flow reactor and measurements were taken. To test the effect of a particular reactant (OxA, MSA, MA or H₂O), it was then added to the base case experiment and subsequent measurements were made. This facilitated elucidation of the effects of having an additional single component present during particle formation compared to a base case because it eliminated the need to achieve identical conditions within the flow reactor from day to day.

Gas-phase MSA was produced by flowing air over the pure liquid held in a trap (Fluka, 99.0%). Air was flowed over pure

MA in permeation tubes (VICI Metronics, 72 ng/mL or 1003 ng/mL) that were kept in a water bath at 294 K to generate gas-phase MA. Generation of gas-phase OxA was achieved by flowing air over the solid (Aldrich, 98%) held in a round-bottom flask and heated to 303 K using a water bath. Humid conditions were reached by flowing air through a bubbler filled with Nanopure water (Nanopure, 18.2 MΩ cm). Relative humidity (RH) was measured by an RH probe (Vaisala, Type HMP 234) positioned in the downstream end-cap. Reactant concentrations were altered by adjusting the air flow over the liquid or solid using mass flow controllers (Alicat).

Two methods were used to quantify MSA. For both methods, gas-phase MSA was collected for 10 min onto a 0.45 μm Durapore filter (Millex-HV) placed prior to the entrance of the reactor. With the first method, the filter was extracted with 10 mL of Nanopure water and then analyzed by ultra performance liquid chromatography tandem mass spectrometry (Waters, Acquity). For the second method, the filter was extracted with 10 mL of water (J.T. Baker, LC-MS grade), diluted by half with methanol (J.T. Baker, LC-MS grade), and then analyzed by electrospray ionization mass spectrometry in negative mode (Waters, Xevo TQ-S). Gas-phase MA was quantified by collection on a weak cation exchange resin (as described elsewhere)⁸¹ placed prior to its point of entry into the flow reactor, extracted with 10 mL of oxalic acid (Fluka, 0.1 M), and then analyzed by ion chromatography (IC; Metrohm, 850 or Dionex, ICS-1100). Neither NH₃ nor additional amines were detected with MA by IC. Concentrations of MSA and MA in the flow reactor were calculated using their concentrations out of the trap or permeation tube, respectively, and the total gas flow in the system. The OxA concentration in the flow reactor was calculated from its vapor pressure⁷⁹ at 303 K and the total gas flow. The presence of OxA in the system was confirmed using atmospheric pressure chemical ionization tandem mass spectrometry (Waters, Xevo TQ-S). However, it was not possible to make quantitative measurements of OxA in the system due to sampling losses. These may be larger in the presence of water vapor because of the time to reach the MSA-MA points of addition (water vapor is not expected to have a significant effect on MSA and MA loss because of their rapid mixing and reaction). The calculated concentrations reported represent upper limits because of potential losses in the tubing and inlets.

In most cases, number concentrations were measured directly with an ultrafine condensation particle counter

(CPC; TSI, 3776), where reactant concentrations were adjusted to keep the total number of particles $\leq 3 \times 10^5 \text{ cm}^{-3}$ (the instrument maximum). In some cases, particle size distributions were also measured with a scanning mobility particle sizer (TSI, classifier 3080, nano differential mobility analyzer 3085, and CPC 3776). The TSI instruments detect particles as small as 2.5 nm according to the manufacturer, although detection efficiency of CPCs has been shown to vary with particle composition.⁸² A particle size magnifier (PSM; AirModus, A10) with stated cutoff diameter of $\sim 1.4 \text{ nm}$ for ammonium sulfate particles was used to obtain additional number concentrations of smaller particles. Figures S2 and S3 show typical particle sizes were larger than 2.5 nm, consistent with the PSM and CPC yielding comparable results.

The aerosol flow reactor was cleaned periodically with Nanopure water and isopropyl alcohol and then dried overnight with air. As described elsewhere, the system was then conditioned with MSA for at least two days (unless the effect of MSA was investigated) to passivate the tubing, inlets, and walls of the system.⁶⁶ Upon addition of amine, the system was allowed to condition until particle concentrations were steady. Measurements were made at alternating reaction times (i.e., in the following order: 12.4, 7.6, 3.8 s, 0.8, 1.3, 5.1, 10.1 s) to avoid sampling bias with time.

RESULTS AND DISCUSSION

Experiments were designed to determine the effect of each reactant on NPF in a multicomponent system consisting of

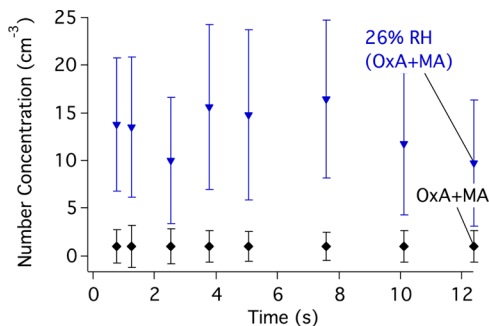


Figure 2. Number concentrations from the reaction of OxA (17 ppb) + MA (890 ppt) with and without water vapor (26% RH) measured with the CPC; errors are $\pm 2\sigma$.

OxA, MSA, MA, and H_2O . Particles were measured as a function of reaction time for different combinations of the reactants in the presence or absence of water vapor. Tables S1–S4 summarize the experiments that were carried out. In the figures, the base case experiment is shown in parentheses, and the added component, whose effect on the base system was being probed, is shown outside the parentheses. For example, in Figure 2, the data labeled 26% RH (OxA + MA) show the effect of adding water to the base case, which contained only OxA and MA.

Figure 2 shows particle concentrations from OxA (17 ppb; $4 \times 10^{11} \text{ cm}^{-3}$) and MA (0.9 ppb; $2 \times 10^{10} \text{ cm}^{-3}$) in the absence and presence of water. At 0.9 ppb MA, the number of particles formed is only a few per cm^3 without water vapor. With added water vapor corresponding to 26% RH ($1.6 \times 10^{17} \text{ cm}^{-3}$), the particle number concentration increases by about an order of magnitude but is still only tens of particles cm^{-3} . At MA concentrations greater than $\sim 9 \text{ ppb}$ with a consistent 17 ppb of

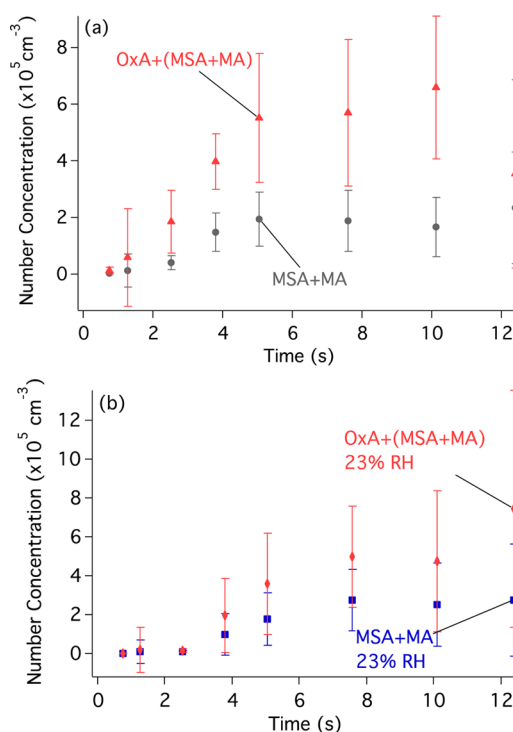


Figure 3. Number concentrations from the reaction of (a) MSA (5 ppb) + MA (159 ppt) with and without OxA (17 ppb) measured with the PSM and (b) MSA (380 ppt) + MA (780 ppt) with and without OxA (17 ppb) in the presence of water vapor (23% RH) measured with the PSM; errors are $\pm 2\sigma$. Note that number concentrations for OxA + (MSA + MA) with and without water vapor may be slightly underestimated due to higher coincidence in particle counting from the CPC above $3 \times 10^5 \text{ cm}^{-3}$.

OxA (Figure S4), the particle concentrations increase slightly to larger values with added water vapor, but the error bars are large, potentially due to the need for more conditioning with each increase in MA. If OxA and MA are representative of dicarboxylic acids and amines in air, then these reactions do not seem likely to contribute significantly to NPF on their own at ambient RH with low concentrations of MA ($< 9 \text{ ppb}$).

It has been shown that the reaction of MSA with MA forms particles efficiently⁶⁷ and that the presence of water vapor greatly enhances both the number concentration (Figure S5) and diameter. However, there are numerous organics in air, including dicarboxylic acids, which may contribute to stabilizing and growing small acid–amine clusters that lead to new particles more efficiently than the acid–amine combination alone.^{20–23,27,32–37} To probe this, particles formed from MSA–MA–OxA were compared to those from MSA–MA (base case) in the presence and absence of water vapor (Table S1, experiments 3a, 3b, 8a, and 8b). Figure 3a shows a modest enhancement of new particle formation (< 1 order of magnitude) when only 17 ppb OxA is added to MSA and MA without water vapor. On the other hand, there is no significant change when OxA is added in the presence of water vapor (Figure 3b). Note, however, that the concentrations of water vapor used in these experiments (20–40% RH) are much larger than the concentrations of OxA that can be added to the system, so a quantitative per-molecule comparison cannot be made between the roles of H_2O and OxA. OxA concentrations are limited by volatility, and reliably delivering water at ppb levels in this system is not feasible.

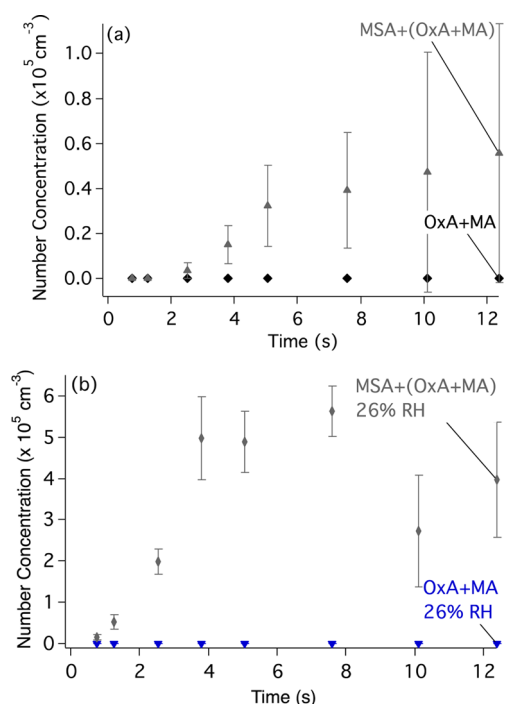


Figure 4. Number concentrations from the reaction of (a) OxA (17 ppb) + MA (890 ppt) with and without MSA (9 ppb) measured with the CPC and (b) OxA (17 ppb) + MA (890 ppt) with and without MSA (620 ppt) in the presence of water (26% RH) measured with the CPC; errors are $\pm 2\sigma$. Note that in panel b, number concentrations for MSA + (OxA + MA) 26% RH may be underestimated due to higher coincidence in particle counting from the CPC above $3 \times 10^5 \text{ cm}^{-3}$.

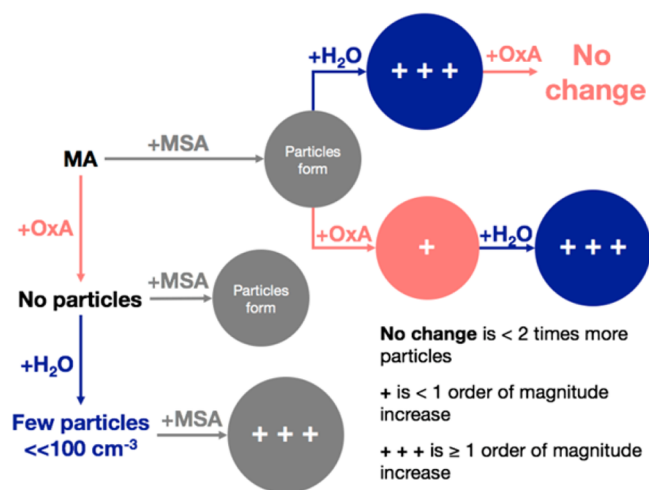


Figure 5. Summary of the overall results from experiments. Note this schematic is intended to show the net results of the presence of single components, not the experimental protocols.

The data show that the MSA–amine reaction is the most important combination in this multicomponent system, with both water vapor and OxA acting to increase NPF from this acid–amine combination. Further confirmation of the critical role of MSA in NPF is seen in Figure 4 (Table S2, experiments 17a, 17b, 19a, and 19b) in which MSA was added to the OxA–MA system in the absence and presence of water vapor. In both cases, there is little NPF until MSA is added (MA concentrations were ≤ 9 ppb to minimize NPF from OxA–MA alone). These experiments were performed on a freshly cleaned

flow reactor prior to exposure to MSA to examine the effect of the sulfur-based acid on NPF. Some uptake of MSA on the unconditioned reactor walls may occur in competition with particle formation; note, however, that the configuration of the spokes through which MSA and MA are added (Figure S1) is such that they are rapidly mixed across the cross-sectional area of the flow reactor.

Multiple factors determine whether clusters will grow to detectable sizes in this system. As discussed in conjunction with the previous studies of NPF from the reactions of MSA with amines,^{66–68} the presence of hydrogen bonding sites in the small clusters may play a role through providing a mechanism for attracting and holding additional acid, base, and water molecules. The fact that MSA ($pK_a -1.9$)⁸³ is so much more efficient than OxA ($pK_{a1} 1.2$, $pK_{a2} 3.6$)^{84,85} at forming particles with MA suggests that the strength of the acid–base interaction, i.e., the extent of proton transfer, may also be important. For example, Barsanti et al.²⁵ showed that the magnitude of the difference in pK_a , ΔpK_a , between an acid and base, influenced organic salt formation from an amine and acetic acid or pinic acid in an aqueous system. The ΔpK_a between MA ($pK_a 10.6$)⁸⁶ and OxA is 9.4, whereas the ΔpK_a between MA and MSA is 12.5. While proton transfer is expected between an acid and a base to form an ion pair, water is often required, even for strong acids. Tao et al.^{87,88} showed that proton transfer to form an ion pair from one molecule of NH₃ with one molecule of H₂SO₄ occurred only if at least one water molecule was present, and for MSA, two water molecules were needed. Similar results were found with MSA and pyridine, where proton transfer was observed only when one or two water molecules were present.⁸⁹ Xu et al.²⁶ showed that proton transfer from succinic acid to dimethylamine occurred with more than three water molecules and that interactions between the acid and amine were strengthened by further hydration. Chen et al.⁹⁰ showed H₂O also promoted proton transfer in the 1:1 OxA–dimethylamine system. This is consistent with the lack of formation of particles from OxA and MA under dry conditions and increased NPF in the presence of water (Figure 2). Proton transfer to form an ion pair is also consistent with enhanced formation of particles in the MSA–amine system in the presence of water, as experimentally observed in earlier studies.^{66–68} The fact that only 17 ppb OxA increases particle formation in the dry MSA–MA case (Figure 3a) suggests that OxA plays a role similar to that of water, providing sites for additional attachment of MSA and amines to grow the cluster and possibly enhancing proton transfer between MSA and MA as well.

The addition of water to the OxA–MSA–MA system greatly enhances NPF (Figure S6), attributable to either or both of the following mechanisms: (1) increasing opportunities for hydrogen bonding or (2) promoting proton transfer. It is possible that both effects contribute to the increase in NPF due to H₂O. Therefore, if water already promotes proton transfer between MSA and MA, then adding the much smaller amount of OxA (17 ppb) to the system at 23% RH (Figure 3b) would not be expected to have significant impact. Such results highlight the complexity of particle formation in the atmosphere.

Our studies show that OxA modestly enhances NPF from the MSA–MA system but has no effect on MSA–MA–H₂O (Figure 5) because water at atmospherically relevant concentrations overwhelms the contribution of much smaller concentrations of organics. OxA, however, is only one of many organics found in air; other species individually or in

concert might have a greater enhancement effect on NPF. Understanding how acids, bases, and water interact in the atmosphere on a molecular level is clearly important for the ability to accurately forecast NPF at the regional and global scale.

■ ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05056.

Details of the flow reactor (Figure S1) and supplemental results; size distributions of $\text{OxA} + [(\text{MSA} + \text{MA}) + \text{H}_2\text{O}]$ (Figures S2–S3); number concentration from $\text{OxA} + \text{MA}$ as a function of MA concentration with and without added H_2O (Figure S4); number concentration from $\text{H}_2\text{O} + (\text{MSA} + \text{MA})$ (Figure S5); number concentration from $\text{H}_2\text{O} + (\text{OxA} + \text{MSA} + \text{MA})$ (Figure S6); and summary of conditions, configurations, and results (Tables S1–S4) (PDF)

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Notes

The authors declare no competing financial interest.

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