Lake spray aerosol emissions alter nitrogen partitioning in the Great Lakes region

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November 21, 2022

Abstract

We develop a new, wind-driven lake spray aerosol (LSA) emissions parameterization that resolves both particle size and chemical composition, and investigate the impact of these emissions on regional chemistry in the Great Lakes region. We conduct WRF-Chem simulations for November 2015, a time period with high LSA emissions. LSA particles emitted from the surface of the Great Lakes increase particulate NO\$-{3}^{-}\$ by 46\% over the Great Lakes and by 16\% over land, primarily due to heterogeneous reactions between CaCO\$-{3}\$ and HNO\$-{3}\$. Cations emitted from lake spray affect the thermodynamic equilibrium, reducing particulate NH\$_{4}^{+}\$ by 42\% over the Great Lakes and by 6\% over the surrounding land. This also influences gas-phase species in the region, decreasing nitric acid by up to 71\% over lakes. Overall, these simulations suggest that understanding LSA and its impact on other air pollutants is important for determining health and climate effects in the Great Lakes region.

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¹⁰ Key Points:

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11	•	Parameterized wind-dependent lake spray aerosol emission fluxes based on lab-
12		oratory observations
13	•	Heterogeneous reactions of $CaCO_3$ with HNO_3 increase nitrate aerosol
14	•	Lake spray emissions of Ca ²⁺ ions alters the thermodynamic equilibrium, lead-

ing to an increase in particulate nitrate and a reduction in particulate ammonium

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16 Abstract

We develop a new, wind-driven lake spray aerosol (LSA) emissions parameteriza-17 tion that resolves both particle size and chemical composition, and investigate the im-18 pact of these emissions on regional chemistry in the Great Lakes region. We conduct WRF-19 Chem simulations for November 2015, a time period with high LSA emissions. LSA par-20 ticles emitted from the surface of the Great Lakes increase particulate NO_3^- by 46% over 21 the Great Lakes and by 16% over land, primarily due to heterogeneous reactions between 22 $CaCO_3$ and HNO_3 . Cations emitted from lake spray affect the thermodynamic equilib-23 rium, reducing particulate NH_4^+ by 42% over the Great Lakes and by 6% over the surrounding land. This also influences gas-phase species in the region, decreasing nitric acid 25 by up to 71% over lakes. Overall, these simulations suggest that understanding LSA and 26 its impact on other air pollutants is important for determining health and climate ef-27 fects in the Great Lakes region. 28

²⁹ 1 Introduction

Sea spray aerosol (SSA) and lake spray aerosol (LSA) are predominantly formed 30 by the action of the wind on the surface of the ocean and fresh water, respectively. Wind 31 stress drives the formation and breaking of waves at the surface, entraining air beneath 32 the water's surface and forming bubbles that burst at the surface. Atmospheric aerosols 33 produced by bubble bursting are one of the greatest global sources of atmospheric par-34 ticulate matter (Andreae & Rosenfeld, 2008; Lewis & Schwartz, 2004). While SSA has 35 been extensively studied, few studies have examined the production of aerosols from large 36 bodies of freshwater. To date, only a few ambient measurements (Slade et al., 2010: Ax-37 son et al., 2016; May et al., 2018; Olson et al., 2020) and one modeling study (Chung 38 et al., 2011) have examined the aerosol generation of fresh water, such as the Lauren-39 tian Great Lakes. Recent studies have observed the presence of lake spray in clouds (Olson 40 et al., 2019), as well as observed the size distributions and chemical composition of LSA 41 both in the field and the laboratory (Axson et al., 2016; May et al., 2016). Here, we uti-42 lize these new measurements in a regional chemistry-meteorology model to investigate 43 the impact of LSA emissions on regional atmospheric chemistry. 44

These prior observational studies have shown that LSA has different physicochem-45 ical properties due to major differences in water salinity and ion concentrations between 46 freshwater and seawater. Freshwater salt concentrations are 250 times lower than salt-47 water and have a different composition, with $[Ca^{2+}] > [Mg^{2+}] > [Na^+] > [K^+]$ common 48 for fresh water as compared to $[Na^+] > [Mg^2+] > [K^+] \sim [Ca^{2+}]$ for seawater. For fresh-49 water, total organic carbon (TOC) concentrations are of the same order of magnitude 50 as inorganic ion concentrations, while TOC is 10^2 to 10^4 times lower than inorganic ions 51 in seawater (Repeta et al., 2002). LSA composition is coupled to the freshwater com-52 position and distinct from SSA (Borduas-Dedekind et al., 2019; Axson et al., 2016), there-53 fore it is expected that Great Lakes LSA has different heterogeneous reactivity and abil-54 ity to act as cloud condensation nuclei (CCN) and ice nucleating particles (INPs) com-55 pared to SSA (Guo et al., 2018; Tang et al., 2015; Moffett, 2016; Baustian et al., 2012). 56 LSA particles collected from Lake Michigan are composed primarily of calcium carbon-57 ate, with lower concentrations of other inorganic ions, organic species, and biological ma-58 terial (Axson et al., 2016). In addition to differences in chemical composition, labora-59 tory observations of Lake Michigan freshwater shows ultrafine and accumulation modes 60 for LSA (with mode diameters of $46 \pm 6 nm$ and $180 \pm 20 nm$ respectively) (May et al., 61 2016). Axon et al., (2016) also show that laboratory number size distributions of LSA 62 have ultrafine and accumulation modes at 53 ± 1 and 276 ± 8 nm, respectively, for wa-63 ter samples collected from two different Great Lakes locations. 64

Because most of the anthropogenic aerosols in the region are acidic (Craig et al., 2018; Pye et al., 2020), the addition of new, positive cations to the region from LSA has the potential to alter the aerosol thermodynamic equilibrium. Dominantly, new cations

will reduce the importance of ammonia as a neutralizing agent (Guo et al., 2018) and

⁶⁹ changes to the aerosol pH will also influence the partitioning of nitrate (Vasilakos et al.,

⁷⁰ 2018; Murphy et al., 2017; Aan de Brugh et al., 2012). In addition to changes in the ther-

⁷¹ modynamic equilibrium, calcium carbonate can react irreversibly via heterogeneous re-

actions with nitric acid (HNO₃) and sulfuric acid (H₂SO₄):

$$CaCO_3(s) + 2HNO_3(g) \to Ca(NO_3)_2(s) + H_2O(g) \uparrow + CO_2(g) \uparrow$$
(1)

$$CaCO_3(s) + H_2SO_4(g) \to CaSO_4(s) + H_2O(g) \uparrow + CO_2(g) \uparrow$$
(2)

In equation 1, calcium carbonate reacts with nitric acid and produces calcium nitrate, carbon dioxide and water, thereby converting gas—phase HNO₃ into particulate NO_3^- . In equation 2, particulate SO_4^{2-} is formed. Over the lower Great Lakes region, HNO₃ concentrations are greater than H_2SO_4 by one to two orders of magnitude, therefore we expect that Equation 1 will dominate in the region. This is supported by May et al. (2018), which found that LSA transported 30 km inland over Michigan was mostly converted to $Ca(NO_3)_2$ from $CaCO_3$.

SSA and LSA are generally modeled as a function of wind speed (de Leeuw et al., 80 2011). Observations of wind speed and vertical aerosol profiles indicate that these par-81 ticles are produced from wave-breaking when the wind speeds are high enough to pro-82 duce whitecaps (greater than 4 and $3.5 m s^{-1}$ over ocean and the Great Lakes, respec-83 tively (Lewis & Schwartz, 2004; Slade et al., 2010). The annual mean wind speeds over 84 the Great Lakes are greater than $6.6 m s^{-1}$ (except for Lake Ontario), indicating the fre-85 quent presence of wind speeds able to produce LSA (Doubrawa et al., 2015). Addition-86 ally, freshwater whitecap lifetime is shorter than saltwater (Monahan and Zietlow, 1969) 87 and we expect that the production of LSA will be lower than those of SSA under sim-88 ilar meteorological conditions. 89

Here, we conduct WRF-Chem model simulations over the Great Lakes region in
 November 2015 to study the impacts of LSA particles on regional gas-phase chemistry.
 Simulations indicate that LSA could change the thermodynamic equilibrium that par titions gases into and out of the aerosol phase, thereby leading to increases in particu late nitrate and reductions in ammonium both over lakes and more broadly in the Great
 Lakes region.

⁹⁶ 2 Model description

We employ version 3.9.1 of the mesoscale Weather Research and Forecasting model 97 with online Chemistry (WRF-Chem; Grell et al. (2005)) that simulates trace gases and 98 aerosols simultaneously with meteorology. The physics parameterizations used in the sim-99 ulations include the Morrison double-moment microphysics scheme (Morrison et al., 2009), 100 the Rapid Radiative Transfer Model for general circulation models (RRTMG) model short-101 wave and longwave radiation schemes (Iacono et al., 2008), the Grell 3D ensemble (G3D) 102 scheme for cumulus clouds (Grell & Dvnyi, 2002), and the Yonsei University (YSU) plan-103 etary boundary layer (PBL) scheme (Hong et al., 2006) coupled to the revised MM5 surface-layer 104 scheme, and the Noah land-surface model (Chen & Dudhia, 2001). 105

For chemistry, we utilize the MOZART (Model for OZone And Related chemical Tracers) mechanism for gas-phase chemistry (Emmons et al., 2010), coupled with the MOSAIC (Model for Simulating Aerosol Interactions and Chemistry) aerosol scheme (Zaveri et al., 2008) to simulate the major aerosol components (nitrate, ammonium, sulfate, black carbon (BC), primary OM, water and other inorganic matter). MOSAIC is a sectional

aerosol module that simulates particles with dry diameters between 39 nm and 10 μ m, 111 with the size range divided into either four or eight size bins. Here, we use a four bin rep-112 resentation with dry diameters ranging from 0.039-0.156 (Bin 1), 0.156-0.625 (Bin 2), 113 0.625-2.5 (Bin 3) and 2.5-10.0 (Bin 4) μ m. Thermodynamic equilibrium is simulated 114 in MOSAIC for solid—phase particles with a set of fixed gas-particle equilibrium rela-115 tionships, where calcium salts form first, followed by sodium and then ammonium salts. 116 Therefore, the addition of Ca^{2+} ions from LSA emissions have the potential to influence 117 the partitioning of ammonium ions. For a given cation, salts containing sulfate form first, 118 followed by nitrate, chloride and then carbonate (Zaveri et al., 2005). These four anions 119 are primary LSA emissions as well, therefore further influencing the salt formation. For 120 mixed-phased and liquid-phase particles, the thermodynamic equilibrium is sensitive 121 to changes in variables like relative humidity, pH, and particle composition. 122

In addition, there are 18 irreversible heterogeneous reactions included in the MO-SAIC scheme (Zaveri et al., 2008). Most relevant for this study, particles composed of CaCO₃, the primary inorganic component of LSA, undergo reactions with H_2SO_4 , HNO_3 , HCl, and CH_3SO_3H and produce the salts $Ca(NO_3)_2$ (equation 1), $CaSO_4$ (equation 2) and $CaCl_2$.

The model simulations were run for one month in November 2015. In November, 128 the surface winds reach a seasonal maximum over the lake surface, leading to the most 129 intense lake surface emissions. The first five days were used for model spin-up and are 130 excluded from the analysis. The model is configured with 35 vertical levels and a model 131 top at 50 hPa. The model center is placed at 45° N, 84° W, with 96 by 115 grid points 132 at 12 km horizontal resolution, covering the Great Lakes area (Figure 1c). Meteorolog-133 ical boundary conditions are from the North American Mesoscale Forecast System (NAM), 134 with a horizontal 12 km resolution, 40 vertical levels at 6-hour intervals. Baseline an-135 thropogenic emissions are provided by U.S. EPA NEI14 (National Emissions Inventory, 136 base year 2014) version 2. NEI emissions include 19 gases including SO_2 , NO, NH₃ and 137 VOCs, and aerosol emissions composed of SO_4^{2-} , NO_3^{-} , elemental carbon (EC), organic 138 aerosols, and total $PM_{2.5}$ and PM_{10} . The Model of Emissions of Gases and Aerosols from 139 Nature (MEGAN v. 2.0.4) provides biogenic emissions (Guenther et al., 2006), with bio-140 genic secondary organic aerosol formation from monoterpenes. Chemical initial and bound-141 ary conditions are derived from CAM-Chem (Lamarque et al., 2012). 142

We conduct and analyze two simulations hereinafter referred to as "NEI" and "NEI+Lake".
In the NEI simulation, only the U.S. EPA NEI14 emissions are included and there are
no LSA emissions from the Great Lakes. The NEI+Lake simulation considers both EPA
NEI14 and Great Lakes LSA emissions.

¹⁴⁷ 3 Lake spray aerosol (LSA) emissions parameterization

A previous LSA emission parameterization (Chung et al., 2011) was developed for 148 ultrafine particles (diameter of 10 nm) based on a wind-dependent function, originally 149 derived from marine aerosol emissions estimates at 22 m wind-speed height (Geever et 150 al. 2005) and one set of Great Lakes field observations (Slade et al., 2010). Chung et al. 151 (2011) assumed that the number of droplets emitted should be similar between fresh-152 water and marine surfaces, and the droplet number production does not depend on the 153 lake surface water composition. However, recent work by May et al. (2016) indicated a 154 bi-modal size distribution and lower number emission flux for LSA based on laboratory 155 experiments (Figure 1b). 156

Here, we update the wind-dependent function used in Chung et al. (2011) by scaling to the laboratory observations of May et al. (2016) for Lake Michigan freshwater and
synthetic seawater. The particle number flux parameterization for a marine environment
(Geever et al., 2005) is:

$$log(F_{10nm}) = 0.099U_{22} - 0.73 \tag{3}$$

where U_{22} is the horizontal wind speed at $22 \ m$ (in ms^{-1}) and F_{10nm} is the particle source flux (in $10^6 m^{-2} s^{-1}$) for particles with diameters larger than 10 nm. Wind speeds at 22 m are calculated using modeled surface-level wind speeds and Monin-Obukhov similarity theory with the same stability functions as those used in WRF's 10-m wind field calculations.

We integrate the observed aerosol number size distributions for synthetic seawater (SSA) and Lake Michigan freshwater from May et al. (2016) to be represented by the four size bins of the MOSAIC scheme:

$$log(F_{LSA,39-156nm}) = log(F_{10nm}.\frac{N_{LSA,[39-156nm]}}{N_{SSA,[>10nm]}})$$
(4)

where $F_{LSA,39-156nm}$ is the particle source flux of lake Michigan freshwater between 39 and 156 nm (MOSAIC Bin 1), N_{LSA}, 39–156 nm is the integrated lake Michigan freshwater size distribution between 39 and 156 nm and N_{SSA} is the integrated synthetic seawater size distribution for particles with diameters larger than 10 nm. We scale the other three bins in the model in the same manner.

The mass emission fluxes are calculated from number emission fluxes and an assumed dry particle density of 1.5 g cm^{-3} (May et al., 2018) and mean dry diameter for each bin. We calculate the mean dry diameter based on mass mean for each bin.

Emitted LSA particles are assumed to have the composition of lake surface water 177 from Slade et al. (2010). We also add a CO_3 mass fraction to the LSA composition based 178 on the balance between cations and anions and the 1:1 molar ratio between calcium and 179 carbonate. The mass fractions of emitted LSA particles are 23%, 11%, 14%, 0.2%, 7%, 35%, and 9% for Ca^{2+} , Na^+ , SO_4^{2+} , NO_3^- , Cl^- , CO_3^{2-} , and TOC, respectively (Figure 1a). In WRF-Chem, we classify measured Mg²⁺ as Na⁺, because Mg²⁺ is not explicitly mod-180 181 182 eled in MOSAIC, is usually present in much smaller amounts compared to other cations 183 in aerosol particles, and their sulfate, nitrate, and chloride salts have a similar solubil-184 ity in water. 185

186 4 Results

In November 2015, simulated winds were generally southerly to southwesterly over 187 most of the Great Lakes region (Figure 1c). Wind speeds were greater than 8 ms^{-1} , lead-188 ing to LSA emissions rates on the order of $10^6 m^{-2} s^{-1}$, with the areas of greatest par-189 ticle emissions over Lake Michigan and Lake Erie (Figure 1d). LSA are transported by 190 the wind to the northeast allowing LSA to influence the atmospheric chemistry also over 191 the land surrounding the Great Lakes. Emitted LSA particles are composed of Ca^{2+} , CO_3^{2-} , Na^+ , CI^- , SO_4^{2-} , NO_3^- , and TOC, with CaCO₃ accounting for 58% of the emitted mass (Figure 1a). Components that also have anthropogenic contributions (e.g., NO_3^- , CO_3^{2-}). 192 193 194 SO_4^{2-} , and TOC) comprise less than 24% of the mass fraction. Because the dominant com-195 ponents of LSA emissions are inorganic species, and specifically include cations, they can 196 alter the thermodynamic balance of aerosols in the region. Specifically, here we exam-197 ine the impact of LSA emissions on the fate of nitrogen via changes in particulate ni-198 trate and ammonium. 199

Overall, the amount of nitrate aerosol in the NEI+Lake simulation (Figure S1) is greater than the NEI simulation (Figure 2a-d), with the increase dominated by the larger size bins (Figures 2c and d) and slight reductions over land in the smaller size bins (Figures 2a and b). The changes in nitrate could be explained by three potential factors: (1)

an increase in primary LSA emissions, (2) changes in the thermodynamic equilibrium 204 of the particles that could promote or reduce nitrate formation, and (3) heterogeneous 205 chemical reactions that form particulate nitrate (e.g. Equations 1 and 2). The addition 206 of primary LSA emissions has only a minor contribution to the increase in particulate 207 nitrate, because primary nitrate emissions comprise only 0.2% of the total emitted LSA 208 mass. For the thermodynamic changes, the primary LSA emissions of Ca^{2+} can neutral-209 ize anions over NH_4^+ (Zaveri et al., 2005), increasing aerosol pH (Figure 2i-l) and the ni-210 trate partitioning from the gas to the particle phase (Vasilakos et al., 2018; Aan de Brugh 211 et al., 2012). A sensitivity simulation shows that about 65% of this increase in nitrate 212 aerosol for the two larger size bins (Figure 2c and d) over the lake regions is due to the 213 heterogeneous reaction of $CaCO_3$ with HNO_3 (equation 1). This is most pronounced in 214 Bin 3, while the increase in Bin 4 is driven by both thermodynamic changes and hetero-215 geneous reaction of $CaCO_3$ with HNO_3 . Gas-phase HNO_3 decreases accompany the in-216 creases in over-lake nitrate aerosol in NEI+Lake compared to NEI (Figure 3b), illustrat-217 ing the transition of nitrogen from the gas to the particle phase due to both heteroge-218 neous reactions and thermodynamic changes. 219

For the two smaller size bins where most of the anthropogenically-derived aerosol is present, thermodynamic changes increase nitrate over lakes, yet nitrate aerosol decreases over land (Figure 2a and b) and over the southern portion of Lake Michigan where the regional anthropogenically-driven NOx concentrations are higher (Figure 2b).

The aerosol pH for the smaller size bins ranges from about 2.5-4 over land in the 224 NEI simulation, and pH increases slightly (0.5 pH units) over land when LSA is added 225 (Figure 2i and j). This increase in pH does not increase the partitioning to nitrate, and 226 suggests that the aerosol may already be sufficiently less acidic than other regions in the 227 US where an increase in pH would enable more nitrate partitioning (e.g., Vasilakos et 228 al. (2018)). This slight decrease in nitrate over land may be due to changes in thermo-229 dynamic equilibrium related to the overall ion balance, where additional sulfate from LSA 230 emissions increases in the region and replaces nitrate in the smaller bins. Overall, total 231 particulate mass is reduced slightly in the smallest two size bins over land in the NEI+Lake 232 simulation (Figure 4b), which supports the nitrate reductions over land. 233

Particulate NH₄⁺ is not a primary LSA emission, yet substantial changes are ob-234 served in the first three aerosol bins (Figure 2e-h). For the conditions of the Great Lakes 235 region, the thermodynamic model preferentially forms Ca^{2+} and Na^{+} over NH_{4}^{+} salts 236 (Zaveri et al., 2005) and LSA provides a new source of cations to the atmosphere dom-237 inantly via Ca^{2+} emissions (and to a lesser extent, Na⁺), reducing partitioning of NH_3 238 from the gas to the particle phase. Generally, NH_4^+ decreases over the Great Lakes in 239 the two smallest size bins (Bins 1 and 2; Figure 2e and f), except for some regions of Lakes 240 Michigan and Superior in the first bin (Figure 2e). Because the highest ammonium con-241 centrations are in the second bin both over lakes and surrounding land (Figure 4a and 242 b), ammonium concentrations are reduced on average 49% over the lakes, but decreases 243 are observed in the fine mode broadly across the entire region. As a result, NH_3 concen-244 trations increase in the NEI+Lake simulations over the entire domain, but particularly 245 over water (Figure 3a). For the larger two bins (Figure 2g and h), the equilibrium varies 246 over land and lake. Lake concentrations of Bin 3 NH_4^+ aerosol decrease as in the smaller 247 bins, yet increase over land where aerosol concentrations are higher and sufficient an-248 ions exist. In regions adjacent to LSA sources, the increased aerosol pH leads to more 249 nitrate in the aerosol phase, which then promotes the formation of NH_4^+ over land. This 250 effect is most notable in Bin 3 which is responsible for the largest mass concentrations 251 of LSA emissions, and less so in the largest size bin(Bin 4) where changes are negligi-252 ble. Overall, the reduced formation of particulate NH_4^+ leads to a concomitant increase 253 in the gas-phase NH_3 (Figure 3a). 254

We also investigate the southern lake Michigan and neighboring land area aerosol ion compositions to better understand the NO_3^- and NH_4^+ differences in the two simu-

lations (Figure 4a and b; regions denoted in Figure 1c). Ion fractions and compositions 257 are similar in the first bin over both lake and land, and the amount of LSA ions (in par-258 ticular Ca^{2+} , CO_3^{2-} , Na^+ , and Cl^-) is negligible, thus the difference between the two 259 simulations for NO_3^- and NH_4^+ is small over the lakes (Figure 2a and e). In the second 260 bin, primary LSA emissions add new cations (e.g., Ca²⁺ and Na⁺,) over the lake region, 261 leading to a slight increase in the overall aerosol mass (9%). Because the addition of cations 262 alters the thermodynamic equilibrium, NO_3^- and NH_4^+ ion fractions decrease over south-263 ern lake Michigan in NEI+Lake as compared to the NEI simulation, which is similar to 264 the broad regional changes observed (Figure 2b and f). In bins 3 and 4 (the larger size 265 bins), ion fractions from LSA dominate with an increase in mass by a factor of 12 and 266 3 over southern lake Michigan. However, in addition to the primary LSA emissions in-267 creasing in bins 3 and 4, the thermodynamic equilibrium changes as well. NO_3^- increases 268 due to primary emissions, the heterogeneous reactions that form particulate NO_3^- , and 269 an increase in aerosol pH which favors nitrate in the aerosol phase. In contrast, the NH_4^2 270 fraction for both bin 3 and 4 in the NEI+Lake simulation decreases compared to the NEI, 271 suggesting that the LSA cations reduce the ability of NH_3 to partition to the aerosol phase. 272 The analysis of the ion fractions in the aerosol close to the surface of Lake Michigan and 273 the surrounding land shows that indeed the positive NH_4^+ ions are replaced by positive 274 Ca^{2+} and Na^{+} ions in NEI+Lake compared to NEI (in particular in the larger bins). Fur-275 thermore the increase in positive ions $(Ca^{2+} \text{ and } Na^{+})$ leads also to an increase in NO_3^{-} 276 and SO_4^{2-} anions (Figure S2). 277

Additional LSA and concomitant aerosol thermodynamics alter the regional gas-phase 278 concentrations of nitrogen species as well. Ammonia concentrations increase across the 279 domain up to 150 ppt over lake regions (Figure 3a). HNO_3 is consumed in the hetero-280 geneous reaction with $CaCO_3$ (equation 1) when there are LSA emissions and the amount 281 of HNO_3 decreases compared to the simulation without lake emissions (Figure 3b). Changes 282 in NOx are more heterogeneous than NH_3 or HNO_3 , with small increases of up to 100 283 ppt near urban regions as nitrate partitioning decreases over the land area in the smaller 284 size bins (Figures 2a and b). 285

286 5 Conclusions

We conduct simulations with WRF-Chem for November 2015, a time period with 287 high winds and LSA emissions, to investigate the impacts of lake surface aerosol emis-288 sions on regional aerosol changes over the Great Lakes region. Model simulations that 289 include anthropogenic emissions only (NEI) and anthropogenic plus LSA emissions (NEI+Lake) 290 are evaluated to understand the role LSA plays in regional atmospheric chemistry. We 291 modify the wind-driven emission parameterizations of Chung et al. (2011) to include lab-292 oratory observations of LSA size and composition (May et al., 2016). We simulate lake 293 surface emission rates on the order of $10^6 m^{-2} s^{-1}$ (Figure 1c). 294

In addition to the primary emissions of LSA that are dominated by calcium car-295 bonate, simulated nitrate aerosol increases, predominantly due to irreversible heteroge-296 neous reactions between CaCO₃ and HNO₃. Changes to thermodynamic equilibrium from 297 additional LSA cations decreases smaller particulate nitrate over land, yet increases larger 298 particulate nitrate over the entire region, leading to an overall decrease in HNO₃ when 299 LSA emissions are included in simulations. Particulate NH_4^+ generally decreases across the Great Lakes because Ca^{2+} and Na^+ from LSA emissions provide additional com-300 301 petitive cations that reduce NH_3 partitioning to the particle phase in the Great Lakes 302 area. In some regions over land where larger nitrate aerosol increases are simulated, NH_4^+ 303 increases slightly but overall the particulate ammonium decreases and gas-phase NH3 304 increases. Overall, the addition of LSA increases particulate matter less than 2.5 ($PM_{2,5}$) 305 and 10 microns in diameter (PM₁₀) by 1.79 (34%) and 2.22 (33%) $\mu g \ m^{-3}$ over lakes, 306 with an increase of PM_{2.5} and PM₁₀ by 0.36 (8%) and 0.42 (7%) $\mu g \ m^{-3}$ over the sur-307 rounding land. Particulate matter greater than 2.5 microns and less than 10 microns in-308

creases by 0.43 (31%) $\mu g m^{-3}$ over lakes and 0.07 (5%) $\mu g m^{-3}$ over the surrounding land. Nitrate can represent a large fraction of aerosol in some urban and agricultural regions and is expected to become likely more important SO₂ and NOx decreases and NH₃ increases(Bian et al., 2017). Because LSA emissions affect the H₂SO₄, HNO₃ and NH₃ concentrations, it is necessary to account for LSA emissions when studying the trend of future aerosol composition, specifically nitrate, in the Great Lakes region.

Although the results here suggest that the impacts of lake emissions on aerosols 315 are confined to the source regions and neighboring areas, their effects on aerosol-cloud 316 317 interactions is unknown. Olson et al. (2019) show that LSA can act as cloud condensation nuclei (CCN) and possibly ice nucleating particles (INPs) over the Great Lakes, 318 which could potentially influence lake-effect cloud formation and properties. This could 319 change cloud microphysical and radiative properties in the Great Lakes region, as well 320 as other areas with large bodies of freshwater. Further modeling work is needed to in-321 vestigate the aerosol-cloud interactions in the Great Lakes area. Additionally, LSA can 322 contain large amounts of organics in the presence of harmful algal blooms, which can be 323 harmful to human health (May et al., 2016, 2018), which are not included in these sim-324 ulations. Based on the work presented here, future work can explore the role of LSA emis-325 sions on coupled cloud chemistry and human health impacts. 326

327 Acknowledgments

Funding for this project was provided by the University of Michigan Cooperative Institute for Great Lakes Research (CIGLR), through the National Oceanic and Atmospheric Administration (NOAA) Cooperative Agreement NA17OAR4320152.

The data model simulations analyzed during the current study are available on: https://doi.org/10.7302/y2q7f47.

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Figure 1. (a) Simulated mass fraction of the emitted LSA components, with the same composition in each of the four MOSAIC aerosol size bins. (b) Aerosol number size distribution for Lake Michigan freshwater from May et al. (2016) (solid line), with equivalent aerosol number concentration for the four MOSAIC bins for the area shown in blue box in (c) from a simulation with LSA emissions only. (c) Simulated 22-m wind speed (ms^{-1}) and direction, and (d) simulated wind-generated aerosol number flux $(10^6m^{-2}s^{-1})$ over the lakes, with wind vector overlay. The values in (b-d) are averaged over November 2015 for the surface model layer. The blue and red rectangles in (c) indicate the area for which the aerosol composition was analyzed.



Figure 2. The difference between NEI+Lake and NEI simulations (NEI+Lake - NEI) of particulate NO₃⁻ (a-d), NH₄⁺ (e-h) concentrations (μ g (kg dry air)⁻¹), and pH (i-l) for the four MOSAIC bins (0.039-0.156 (Bin 1; a,e,i), 0.156-0.625 (Bin 2; b,f,j), 0.625-2.5 (Bin 3; c,g,k) and 2.5-10.0 (Bin 4; d,h,l) μ m). Changes represent the difference in monthly average mixing ratios for the surface model layer in November 2015.



Figure 3. The difference between Lake+NEI and NEI simulations(NEI+Lake - NEI) surface model layer mixing ratios (ppt) for (a) NH₃, (b) HNO₃, and (c) NOx in November 2015.



Figure 4. Simulated NEI+Lake and NEI average November 2015 surface model layer ion composition over the southern part of lake Michigan (a) and neighboring land (b), as the molar concentration of the aerosol particulate mass in dry air multiplied by ion charge is shown.