

Pristine and Aged Microplastics Can Nucleate Ice Through Immersion Freezing

Heidi L. Busse¹, Devaka Dharmapriya Ariyasena¹, Jessica Orris¹, Miriam Arak Freedman^{1,2}

¹ Department of Chemistry, The Pennsylvania State University, University Park, PA 16802,
United States

² Department of Meteorology and Atmospheric Science, The Pennsylvania State University,
University Park, PA 16802, United States

KEYWORDS: Microplastics, ice nucleation, ozone, photooxidation, sulfuric acid, ammonium sulfate, immersion freezing, atmosphere

ABSTRACT: Microplastics (MP) are ubiquitous in the environment; their atmospheric relevance is increasingly recognized. Because of their atmospheric concentrations, a question exists as to whether MP can act as ice nucleating particles in the atmosphere. This study investigates the immersion freezing activity of lab-prepared MP of four different compositions—low density polyethylene (LDPE), polypropylene (PP), poly(vinyl chloride) (PVC), and polyethylene terephthalate (PET)—using droplet freezing assays. The MP are also exposed to ultraviolet light, ozone, sulfuric acid, and ammonium sulfate to mimic environmental aging of the plastics to elucidate the role that these processes play in the ice nucleating activity of MP. Results show that

1 all studied MP act as immersion nuclei and aging processes can modify this ice nucleating activity,
2 leading, primarily, to decreases in ice nucleating activity for LDPE, PP, and PET. The ice
3 nucleating activity of PVC generally increased following aging which we attribute to a cleaning
4 of chemical defects present on the surface of the stock material. Chemical changes were monitored
5 with infrared spectroscopy (ATR-FTIR) and the growth of a peak at 1650-1800 cm^{-1} was
6 associated with a decrease in ice nucleating activity while loss of an existing peak in that region
7 was associated with an increase in ice nucleating activity. The studied MP have ice nucleating
8 activities sufficient to be a non-negligible source of ice nucleating particles in the atmosphere if
9 present in sufficiently high concentrations.

10 ENVIRONMENTAL IMPACT STATEMENT:

11 Minimal research exists on the role that microplastics can play as ice nucleating particles. This
12 study reports that microplastics can act as ice nucleating particles and that environmental aging
13 can significantly change their ice nucleating activity.

14 INTRODUCTION:

15 Microplastics (MP), defined as plastic particulates less than 5 mm in size, are a rapidly growing
16 branch of research in plastic pollution as their ubiquity in marine, freshwater, soil, and, most
17 recently, atmospheric environments are recognized. MP have been discovered in some of the most
18 pristine environments on Earth including the Antarctic deep seas,¹ the bottom of the Mariana
19 Trench,² the top of Mt. Everest,³ and fresh Antarctic snow.⁴ MP are also shown to have effects on
20 human health.⁵⁻⁷

21 Within MP, there is a subset of particles smaller than 100 μm that are atmospherically
22 relevant.^{6,8-10} MP are aerosolized and entrained in the atmosphere through a broad range of

1 mechanisms. Continental atmospheric MP have been attributed to roadway activity in the western
2 United States¹¹ and bubble bursting has been shown as an effective method of MP aerosolization
3 in sea spray aerosols.¹² Recent studies have estimated that the rate of deposition of atmospheric
4 microplastics could lie above $10 \text{ mg}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$.¹¹ Temporal studies have been conducted looking
5 at ombrotrophic peat and lake cores in remote regions and have shown a >35-fold increase in
6 atmospherically deposited MP entrained in the peat from the 1960s to the 2010s.⁶

7 With the increasing prevalence of MP in the environment and, therefore, the atmosphere,
8 concerns turn to the radiative forcing impacts that MP could have in the atmosphere. Current
9 estimates of the aerosol radiation interactions (ARI) of MP fragments are $-0.016 \pm 0.089 \text{ W}\cdot\text{m}^{-2}$
10 without secondary atmospheric feedback.¹³ In addition to the ARI of MP, studies have begun to
11 investigate the potential of MP to modify cloud properties and contribute aerosol cloud interactions
12 (ACI) to the overall radiative budget. Initial hypotheses posited that MP would not act as cloud
13 condensation nuclei (CCN) due to their hydrophobicity.¹³ However, recent studies show that
14 atmospheric aging and weathering processes can reduce MP hydrophobicity, increase their
15 hygroscopicity, and make them potential candidates to act as CCN.¹⁴⁻¹⁶ Additionally, MP coming
16 from marine and continental environments can have organic or biological coatings or have
17 associated ions which can further increase their likelihood of acting as CCN.¹⁷

18 MP also have the potential to contribute to ACI by acting as ice nucleating particles (INP). Ice
19 nucleation in the atmosphere occurs either homogeneously or heterogeneously. Homogeneous
20 freezing occurs without the aid of an INP and only occurs at or below around -38°C .¹⁸⁻²¹
21 Heterogeneous ice nucleation occurs via INP which provide nucleation sites for an ice nucleus to
22 form, reducing the energy barrier to the formation of a solid phase and, thereby, allowing for
23 freezing to occur at warmer temperatures. Heterogeneous ice nucleation can occur through

1 multiple mechanisms (e.g. immersion, condensation, contact, and deposition/pore condensation
2 freezing).¹⁸ Immersion freezing is of particular importance in the formation of mixed-phase
3 clouds.²² In this mode of heterogeneous nucleation, the INP is immersed in a liquid water droplet,
4 either through deliquescence or coalescence with a liquid droplet, prior to the freezing event.²³

5 MP can display many of the surface features that are integral for the promotion of ice nucleation
6 including surface fractures, pores, the presence of surface hydroxyl and carbonyl functional
7 groups, and large surface areas.¹⁴ Additionally, a previous study by Ganguly and Ariya looked at
8 the heterogeneous ice nucleation of microplastics.²⁴ This study used nanoplastic hydrosols
9 (plastics dissolved in THF and then dispersed in water) to study immersion mode freezing of
10 nanoplastics. The data show that heterogeneous nucleation occurs, as the T_{50} of solutions with
11 HDPE hydrosols, LDPE hydrosols, and PP hydrosols were $-17.3 \pm 0.5^\circ\text{C}$, $-15.1 \pm 0.4^\circ\text{C}$, and -17.4
12 $\pm 0.0^\circ\text{C}$, respectively, compared to $-21.0 \pm 0.4^\circ\text{C}$ for background freezing in this study. Although
13 this study looked at nanoplastics in a model form that would not occur within the environment, it
14 does mark micro- and nanoplastics as possible INP and indicates the need for experimental studies
15 of the ice nucleation of MP in an environmentally relevant form.

16 Here, we aim to address this pertinent gap in the literature and investigate the ice nucleation of
17 MP in forms which are more directly motivated by MP found in the environment. Four common
18 atmospheric MP were selected for study—low density polyethylene (LDPE), polypropylene (PP),
19 poly(vinyl chloride) (PVC), and polyethylene terephthalate (PET).^{9,10,25–27} Additionally, four
20 methods of aging were selected to mimic aging/weathering that MP might experience in the
21 environment—oxidation via ozone, photooxidation with UV light, exposure to sulfuric acid, and
22 exposure to ammonium sulfate (AS). With these systems, we investigate the ice nucleating activity
23 of MP and the impact of environmental aging and weathering on their ice nucleating activity.

1 MATERIALS AND METHODS:

2 **Preparation of Microplastics.** The plastics studied here—polypropylene (isotactic, average M_w
3 $\sim 12,000$, average $M_n \sim 5,000$, Sigma Aldrich), polyethylene (low density, Sigma Aldrich),
4 poly(vinyl chloride) ($M_w \sim 48,000$, Sigma Aldrich), and polyethylene terephthalate (granular, 30%
5 glass fiber, Sigma Aldrich)—were selected on the basis of the frequency of their appearance in
6 studies of atmospheric microplastics.^{9,10,25–27} To prepare the MP, the commercially available
7 plastic pellets or coarse powders (starting material form is shown in Figure S1) were milled using
8 a cryomill (Retsch) to achieve a fine powder. The newly milled MP were sorted into rough size
9 classes (i.e., 25–53 μm , 53–75 μm , 75–106 μm , >106 μm) with a series of mesh sieves.
10 Additionally, a combined size class of MP was made by sieving only through the 106 μm mesh
11 sieve. This size class was used for all aging treatments. Average particle sizes for the <106 μm
12 size class for each plastic are shown in Table 1 and size distributions can be seen in Figure S2.

Table 1. Feret diameters for each pristine
plastic, <106 μm size class

Plastic	Average Feret diameter (μm)
LDPE	29.0 \pm 16.9
PP	18.8 \pm 18.7
PVC	45.1 \pm 28.6
PET	44.2 \pm 23.9

13 **Purification of PET Microplastics.** PET was unable to be obtained commercially in a high
14 purity form without the inclusion of glass fibers for reinforcement. The sample used contained
15 30% glass fibers. After milling the plastic and size selecting <106 μm particles, the plastic and
16 glass fibers had been almost entirely disassociated from each other (see Figure S3). This was not
17 the case for PET MP >106 μm , as the glass fibers were still embedded in the PET. To remove the
18 glass fibers from the sample, a density separation was performed. The powder was added to a vial

1 of chloroform and sonicated for 20 minutes. The vial was then left to settle for a period of at least
2 48 hours after which the chloroform containing the suspended PET particles was decanted. This
3 process was repeated two more times to ensure complete removal of the glass fibers. The
4 chloroform was then evaporated off to leave the purified PET MP. Complete removal of the glass
5 fibers was confirmed via optical microscopy.

6 **Aging/Weathering of Microplastics.** Treatment of the MP included photooxidation, oxidation
7 via ozone, exposure to aqueous sulfuric acid, and exposure to aqueous AS. These treatments were
8 performed on the milled microplastics <106 μm .

9 Treatment with ultraviolet (UV) light was completed with a broad spectrum metal halide lamp
10 (ZooMed Power Sun H.I.D. Metal Halide UVB Lamp) chosen for its demonstrated similarity to
11 the solar spectrum in previous studies.¹⁵ A fused quartz lid was used to prevent the accumulation
12 of debris/dust on the plastics during the extended exposure time while not limiting the incident UV
13 light. UV exposure was converted to equivalent days with an average annual sunshine hour value
14 of 2614 h for Harrisburg, PA.²⁸ The determined equivalent days of environmental aging is
15 summarized in Table 2.

16 Treatment with ozone was completed by flowing ozone from an ozone generator (Poseidon 200,
17 Ozotech) through a glass chamber containing the MP. MP were spread in a thin layer on a glass
18 slide prior to being put in the chamber and the chamber sealed. The ozone concentration was
19 measured using an ozone analyzer (Ozone Analyzer, Model 430, Teledyne) downstream from the
20 reaction chamber. Ozone exposure in equivalent days (see Table 2) was determined by fitting the
21 downstream ozone concentrations over the exposure period to a logarithmic function and
22 integrating this function over the time of the exposure to give a result in $\text{ppm}\cdot\text{h}$. This result was

1 converted to equivalent days using a surface ozone concentration of 0.030 ppm, an intermediate
 2 value for the surface ozone concentration in the U.S.²⁹

3 Treatment with sulfuric acid and AS were completed by first making a sulfuric acid solution of
 4 pH 2 (0.01 N H₂SO₄, 0.005 M H₂SO₄) and then matching the concentration of the AS to give
 5 equivalent [SO₄²⁻] (i.e., 0.005 M (NH₄)₂SO₄). All solutions were prepared using the same UHPLC
 6 water used in the ice nucleation experiments (described below). MP were then added to the
 7 solutions and allowed to sit at room temperature for 72 hours with periodic stirring. Following the
 8 aging period, the MP were filtered from the sulfuric acid or AS solution and rinsed with UHPLC
 9 water to remove any residual sulfuric acid or AS from the MP.

Table 2. Conversion of simulated aging methods to estimated equivalent days of environmental aging for UV and ozone treatment of each plastic type

Aging method	Atmospheric condition used for conversion	Ref.	Aging conditions/durations	Environmental equivalent (days)	Plastic(s) aged
Ultraviolet (UV1)	Daylight hours per year in Harrisburg, PA: 2614 h	[28]	67 days/1608 h	225	PP
			68 days/1632 h	228	LDPE
			70 days/1680 h	235	PET
			77 days/1848 h	258	PVC
Ultraviolet (UV2)	Daylight hours per year in Harrisburg, PA: 2614 h	[28]	111 days/2664 h	372	PVC
			177 days/4248 h	593	LDPE, PP, PET
Ozone (O ₃)	Representative surface ozone concentration for the U.S.: 0.030 ppm	[29]	71.5 ppm·h	99	LDPE, PP, PVC
			55.6 ppm·h	77	PET

10 **Ice Nucleation Experiments.** Ice nucleation studies were completed using an immersion
 11 freezing chamber previously described by Alstadt *et al.*³⁰ Suspensions of ~0.1 wt % of LDPE or
 12 PP and ~1 wt % of PVC or PET in ultrapure water (UHPLC, Fisher Scientific) were prepared for
 13 ice nucleation assays. Due to the hydrophobic nature of the MP, homogeneous suspensions of the

1 MP were difficult to achieve as the MP tended to aggregate on the water surface. To control for
2 potential inconsistencies in the transfer of MP during pipetting due to this surface layer of MP, all
3 solutions were prepared in 20 mL disposable scintillation vials with a volume of 3 mL.
4 Additionally, LDPE and PP suspensions were prepared at lower concentrations to prevent the
5 clogging of the micropipette tips while the less hydrophobic and more dense PVC and PET were
6 able to be prepared at higher concentrations.

7 The MP suspension was pipetted onto siliconized slides (Hampton Research) in 2.0 μL droplets
8 and the slide was placed onto the cooling plate of the environmental chamber. The chamber was
9 cooled via liquid nitrogen flowed through the copper cooling block which contained the cooling
10 plate. Cooling was maintained at a rate of $-3^\circ\text{C}/\text{min}$ by controlling the flow rate of the nitrogen
11 through the system. Additionally, a low flow rate of dry nitrogen gas flowed through the headspace
12 of the chamber to prevent the accumulation of frost on the cooling block. This purge flow was
13 sufficiently low to cause negligible evaporation of the droplets over the ~ 10 minute timescale of
14 an experiment.

15 LabView was used to image the droplets every 0.5°C or 0.1°C and record the temperature
16 associated with each picture. The obtained images were further processed using ImageJ to
17 determine the contrast of each droplet over the entire image series. A sudden drop in the contrast
18 of a droplet indicated that freezing has occurred as the droplet goes from a reflective liquid droplet
19 to an opaque solid droplet. MATLAB was used to further analyze the obtained contrast data and
20 determine the cumulative frozen fraction, $F(T)$, for each experiment using

21
$$F(T) = \frac{n(T)}{N}$$

1 where $n(T)$ is the total number of drops frozen on the slide at a given temperature and N is the total
2 number of drops on the slide.^{31,32} Experiments for each sample were repeated until at least 100
3 drops total were analyzed. The frozen fraction curve was determined for each run of ~30 drops
4 and averaged across all trials run for each sample. The cumulative density of active nucleation
5 sites per mL of suspension, $K(T)$, was determined using

$$6 \quad K(T) = \frac{-\ln(1 - F(T))}{V}$$

7 where V is the volume of each droplet (i.e. 0.002 mL). The background freezing of the system was
8 determined by running the purified water used in all following experiments and determining the
9 associated $K(T)$ and producing an exponential fit of the $K(T)$ data. This $K_{background, fit}(T)$ was used
10 to correct the experimental $K(T)$ by

$$11 \quad K_{sample}(T) = K(T) - K_{background, fit}(T)$$

12 where $K_{sample}(T)$ is the cumulative density of active nucleation sites associated only with the MP.
13 The cumulative density of active nucleation sites was then further normalized to the mass of MP
14 by

$$15 \quad n_m(T) = \frac{K_{sample}(T)}{C}$$

16 where $n_m(T)$ is the number of active nucleation sites per gram of MP and C is the concentration of
17 the suspension in g/mL.

18 **Characterization of MP.** MP size distributions were characterized via optical microscopy with
19 analysis in ImageJ, representative images used for size analysis can be seen in Figure S4. The
20 average Feret diameters of each of the combined size classes of each plastic are shown in Table 1.
21 Sizes of the MP in the separated size classes were confirmed via optical microscopy but size

1 distribution analysis was not performed on these samples. Chemical characterization of MP was
2 performed with attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy
3 (Nicolet 6700 with Smart iTX, Thermo Scientific).

4 RESULTS AND DISCUSSION:

5 **Impact of Microplastic Size on Ice Nucleation.** Figure 1 shows the relationship between
6 particle size and ice active site density, n_m , for PVC, LDPE, and PP. The density of active sites for
7 PP, LDPE, or PVC is not correlated with changing particle size. Large errors in the n_m at warm
8 temperatures for most MP are due to the early freezing of a few droplets out of the many analyzed.
9 Additionally, discontinuities in some n_m curves are indicative of where the ice nucleation of the
10 MP was similar to that of background freezing (e.g. PP 75-106 μm as seen in Figure 1). The

- 1 lack of a size effect on ice nucleation for the investigated size ranges supported the aging studies
- 2 below being completed using the combined size class of particles $<106 \mu\text{m}$.

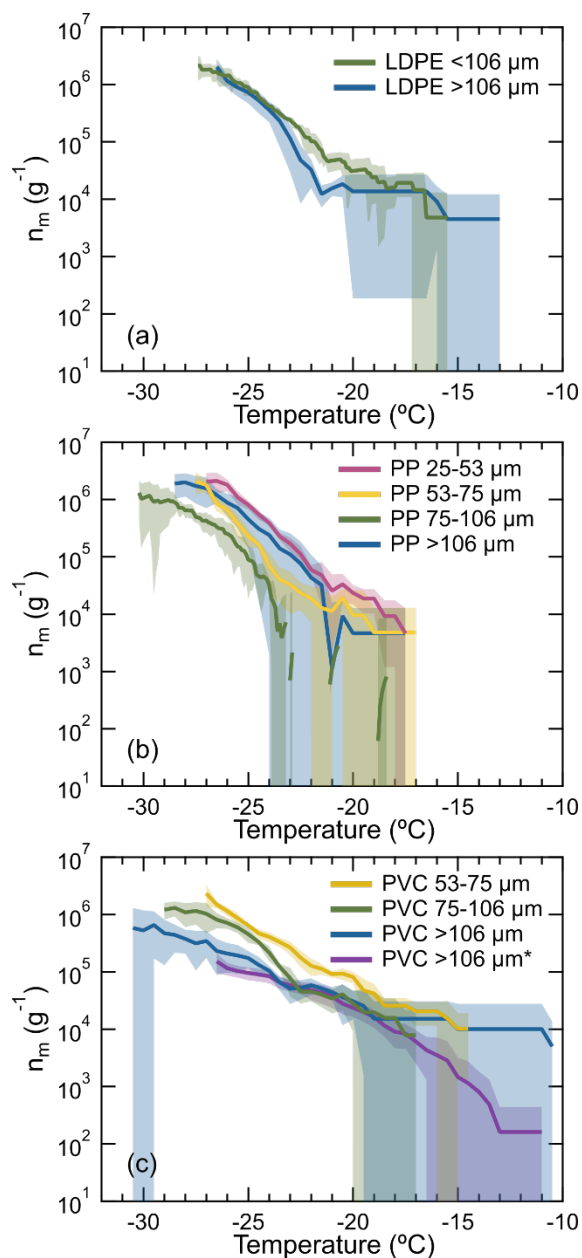


Figure 1. Surface active sites per unit mass, n_m , of a) LDPE, b) PP, and c) PVC MP for all available size classes. Omitted size classes are due to insufficient MP for data to be obtained. Shaded regions indicate uncertainty of ± 1 standard deviation in n_m across trials. PVC marked with * indicates a sample prepared at 1 wt %, all other samples were prepared at 0.1 wt %.

1 **Aging Impacts on LDPE.** Frozen fraction, surface active site density, and FTIR spectra for
 2 pristine and aged LDPE are shown in Figure 2. From these results, we can see that the ice
 3 nucleating activity of LDPE is unaffected by aging with sulfuric acid, ozone, or UV(68 days). A
 4 reduction in ice nucleating activity was observed for the longer period of UV aging with a shift in
 5 the median freezing temperature for a 0.1 wt % suspension from -23.7 ± 0.2 °C for pristine LDPE

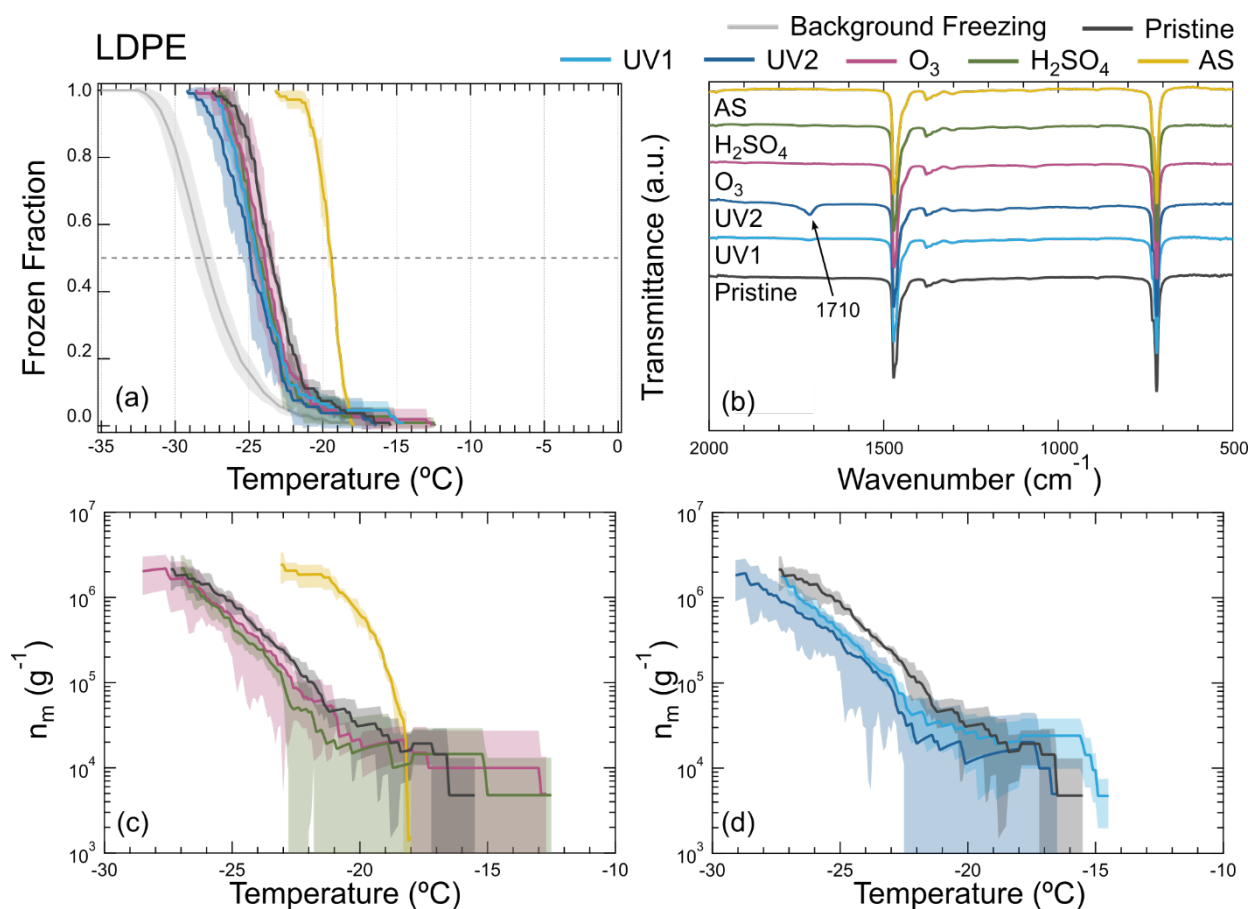


Figure 2. a) Frozen fraction, b) FTIR, and c,d) n_m for pristine (black), 68 days (light blue) and 177 days (dark blue) UV-aged, ozone-aged (pink), sulfuric acid-aged (green), and ammonium sulfate-aged (yellow) LDPE. Background freezing (gray) is also shown on (a). Shaded regions indicate uncertainty of ± 1 standard deviation from the trials run for each sample. Note that only 2000-500 cm^{-1} are shown in (b) for clarity and no changes were observed above 2000 cm^{-1} .

1 to -24.8 ± 0.8 °C for UV2 LDPE (see Figure 2a). This reduction is also apparent in the decrease of
2 n_m for UV2 LDPE as shown in Figure 2d. Most notably, LDPE shows a significant increase in ice
3 nucleating activity following exposure to AS. This is the largest change observed of all plastics
4 and treatments as the median freezing temperature for a 0.1 wt % suspension increased to –
5 19.5 ± 0.1 °C. Spectral changes were only seen after 177 days of UV aging with the growth of a
6 peak at 1710 cm^{-1} . This peak is likely due to a carbonyl and indicates that oxidation occurred
7 following extended exposure to UV light.^{33,34} There are no spectral changes for AS-exposed LDPE
8 and it is uncertain what causes the large increase in ice nucleating activity.

9 **Aging Impacts on PP.** Frozen fraction, surface active site density, and FTIR spectra for pristine
10 and aged PP are shown in Figure 3. PP experienced significant decreases in ice nucleating activity
11 following aging as can be seen by the complete loss of nucleation events, the onset of freezing is
12 competing with that of background freezing, at temperatures above -22.2 °C and -22.6 °C following
13 aging with sulfuric acid and ozone, respectively. No impact on ice nucleation was seen following
14 treatment with UV for 67 days, however, continued exposure to UV up to a total of 177 days lead
15 to a complete loss of ice nucleation above -18.7 °C and a reduction in n_m for all nucleation below
16 this temperature. Spectral changes were observed for PP following treatment with ozone, UV (both
17 67 days and 177 days), and sulfuric acid. These spectra all saw the growth of broad and ill-defined
18 peaks in the 1650 to 1800 cm^{-1} region indicating the growth of a large variety of carbonyl
19 environments as the plastic oxidized during the exposure to UV, ozone, and sulfuric acid.
20 Additionally, ozone, UV1, and UV2 saw the loss of a peak at 885 cm^{-1} which has been attributed
21 to pendant-type unsaturations ($\text{R}_1\text{R}_2\text{C}=\text{CH}_2$) which are eliminated following UV and ozone
22 aging.³⁵ In contrast to the other similarities between the spectra for UV- and ozone-treated PP, the
23 spectrum following ozone treatment saw the growth of a peak at 1062 cm^{-1} although it is unclear

1 what this peak assignment is. H₂SO₄-aged PP has the appearance of a peak at 725 cm⁻¹ which
 2 corresponds to CH₂ rocking within the sidechains of the LDPE where the sidechain contains four
 3 or more methylene groups.³⁶ The growth of this peak possibly indicates the growth in the length
 4 of the sidechains of LDPE following sulfuric acid aging. Similarly as for LDPE, the growth of peaks

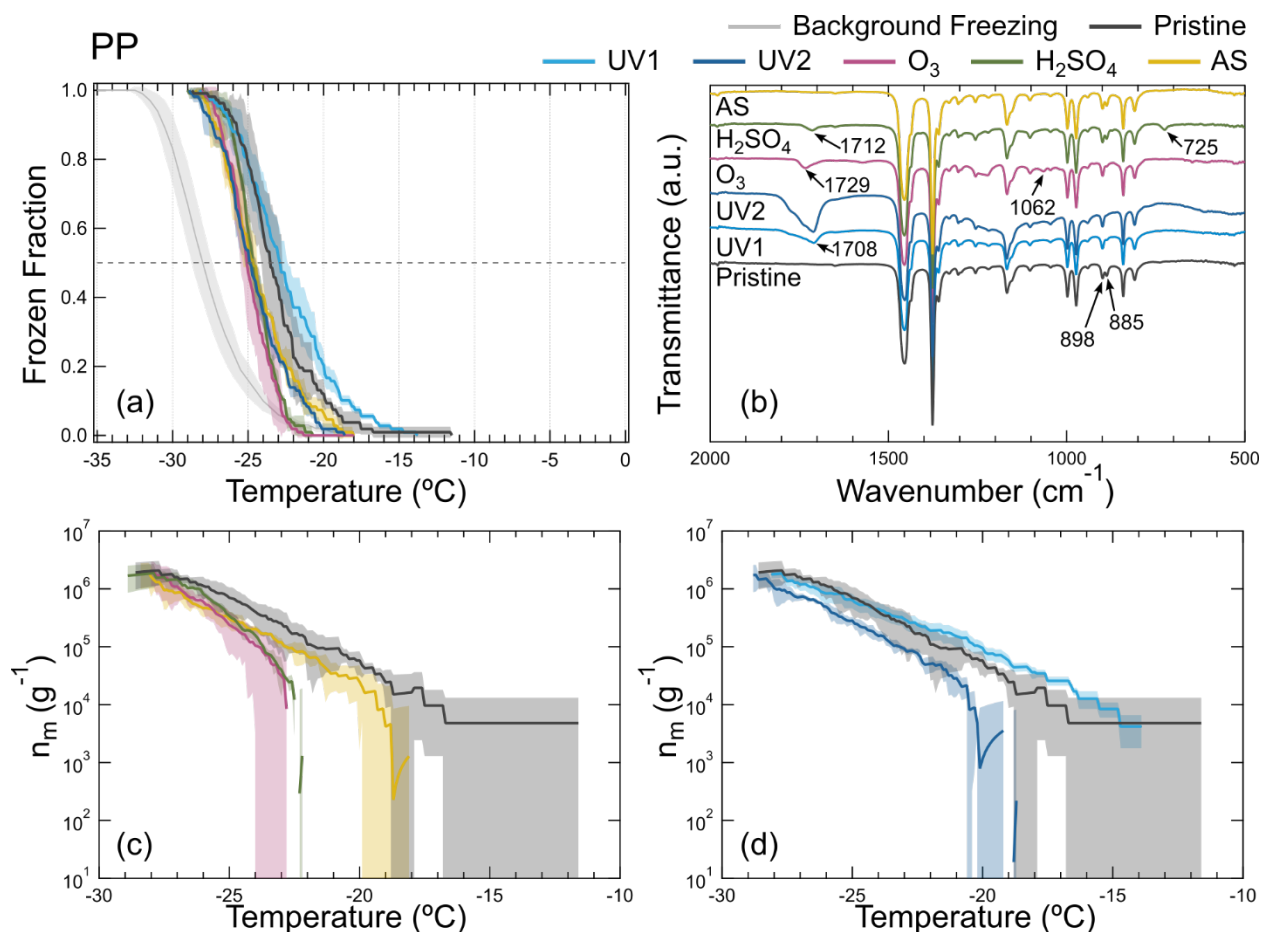


Figure 3. a) Frozen fraction, b) FTIR, and c,d) n_m for pristine (black), 67 days (light blue) and 177 days (dark blue) UV-aged, ozone-aged (pink), sulfuric acid-aged (green), and ammonium sulfate-aged (yellow) PP. Background freezing (gray) is also shown on (a). Shaded regions indicate uncertainty of ± 1 standard deviation from the trials run for each sample. Note that only 2000-500 cm⁻¹ are shown in (b) for clarity and no changes were observed above 2000 cm⁻¹.

1 in the 1650-1850 cm^{-1} region, potentially due to the addition of carbonyl groups following aging,
2 is associated with a decrease in ice nucleating acitivity.

3 **Aging Impacts on PET.** In contrast to LDPE and PP, PET saw large impacts on ice nucleation
4 without any apparent changes to the IR spectra (see Figure 4). Aging with sulfuric acid and UV2

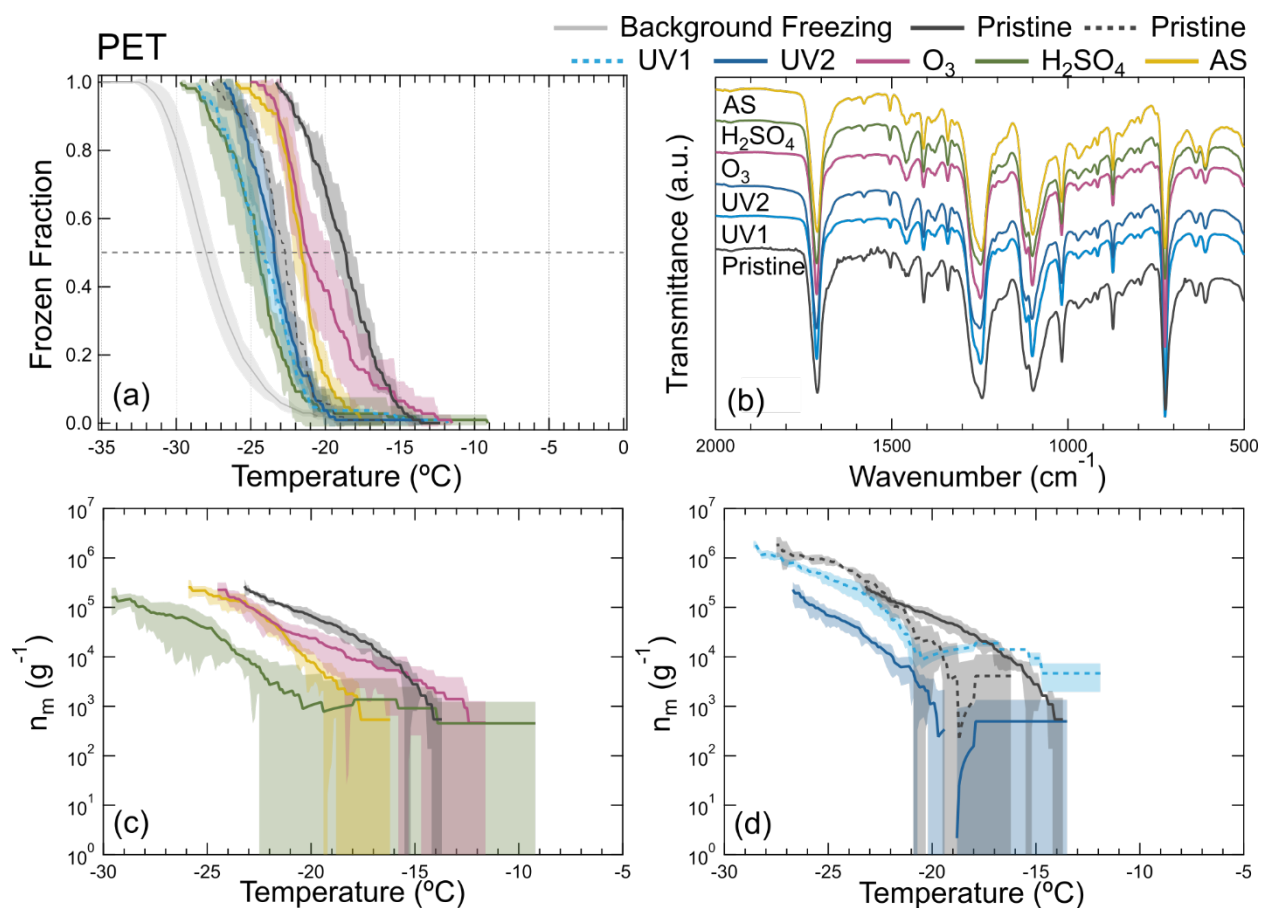


Figure 4. a) Frozen fraction, b) FTIR, and c,d) n_m for pristine (black), 67 days (light blue) and 177 days (dark blue) UV-aged, ozone-aged (pink), sulfuric acid-aged (green), and ammonium sulfate-aged (yellow) PET. Background freezing (gray) is also shown on (a). Shaded regions indicate uncertainty of ± 1 standard deviation from the trials run for each sample. Note that only 2000-500 cm^{-1} are shown in (b) for clarity and no changes were observed above 2000 cm^{-1} . Dashed lines (black and light blue) correspond to samples analyzed at a 0.1 wt % concentration.

1 (177 days) saw the largest decreases in ice nucleation while treatment with ozone, AS, and UV1
2 (70 days) saw a moderate decrease. Treatment with UV exposure for 70 days saw no apparent
3 reduction in ice nucleation.

4 **Aging Impacts on PVC.** Compared to the other plastics, PVC most consistently saw an increase
5 in ice nucleating activity following aging treatments as is shown in Figure 5. UV-, sulfuric acid-,

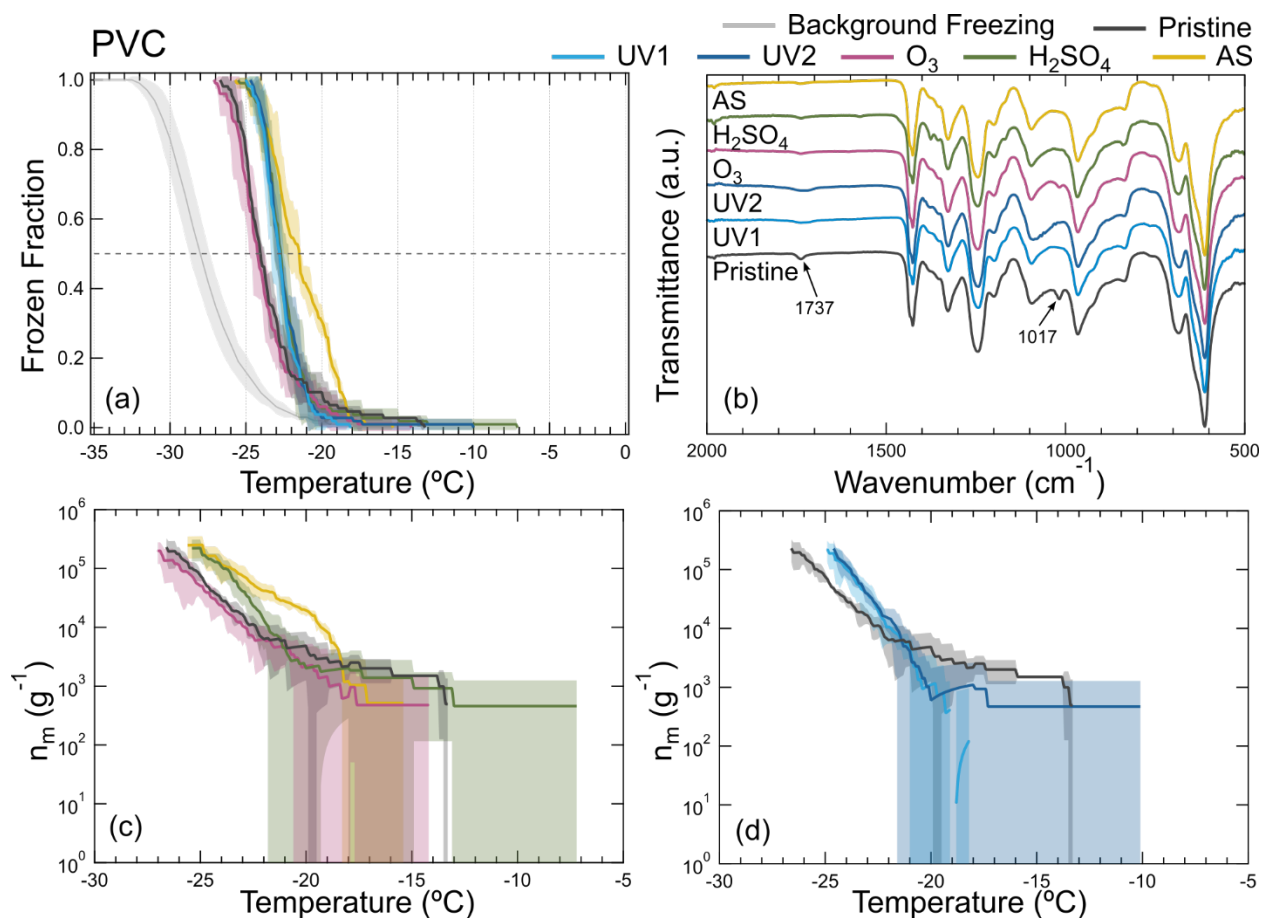


Figure 5. a) Frozen fraction, b) FTIR, and c,d) n_m for pristine (black), 67 days (light blue) and 177 days (dark blue) UV-aged, ozone-aged (pink), sulfuric acid-aged (green), and ammonium sulfate-aged (yellow) PVC. Background freezing (gray) is also shown on (a). Shaded regions indicate uncertainty of ± 1 standard deviation from the trials run for each sample. Note that only 2000-500 cm^{-1} are shown in (b) for clarity and no changes were observed above 2000 cm^{-1} .

1 and AS-treated PVC saw an increase in ice nucleating activity at colder temperatures, although
2 there were no changes in the warmer temperatures where freezing was observed. Treatment
3 following ozone is the only aged sample of PVC that sees no change to ice nucleation. The loss of
4 the 1017 cm^{-1} peak, which can be attributed to C-O, was observed for UV-, sulfuric acid-, and AS-
5 aged PVC, all of which experienced an increase in ice nucleating activity. Ozone-aged PVC did
6 not see a change in ice nucleation and experienced a slight decrease in the intensity of the 1017
7 cm^{-1} peak, but not a total loss. All aged samples saw a decrease in intensity and/or a broadening
8 of the peak at 1737 cm^{-1} which we attribute to a loss of carbonyl groups or a change in their
9 chemical environment. The presence of both the 1017 cm^{-1} and the 1737 cm^{-1} peaks are not
10 expected for pristine PVC and may indicate that the plastic stock material contained contaminants
11 or was surface oxidized prior to the milling into MP. PVC was purchased as a coarse powder rather
12 than as nurdles (raw plastic material sized 5-10 mm) as was the case for all other plastics (see
13 Figure S1) which would allow for a higher prevalence of surface oxidation to appear in the milled
14 MP. The combination of the changes in the two peaks mentioned above may indicate that the aging
15 procedures were cleaning the surface of these possible contaminants or oxidation products and is
16 associated with an increase in ice nucleating activity.

17 **Comparison to Ice Nucleation of Other Systems.** Similarly to Ganguly and Ariya,²⁴ we see
18 positive shifts in the median freezing temperatures of the MP suspensions when compared to the
19 freezing of pure water. Their study overlaps with ours in the study of pristine LDPE and PP where
20 their hydrosols exhibited a difference in median freezing temperatures of $5.9 \pm 0.6^\circ\text{C}$ and $3.6 \pm$
21 0.4°C , respectively, from their background freezing as compared to our observed differences of
22 $4.1 \pm 0.9^\circ\text{C}$ and $4.1 \pm 1.1^\circ\text{C}$, respectively. Additionally, they saw an increase in ice nucleating
23 activity when their HDPE MP hydrosols were exposed to pH 3. The closest sample to HDPE in

1 this study is LDPE which did not experience an increase in ice nucleating activity following
2 treatment with sulfuric acid at a similar pH (i.e. pH 2). However, here, we rinsed the MP of any
3 sulfuric acid prior to ice nucleating experiments where Ganguly et al. ran their experiments at low
4 pH. They also saw a change in hydrosol particle size with lower and higher pH to which they
5 attribute to the increasing ice nucleating activity. However, direct comparisons between the
6 Ganguly and Ariya study and the study here cannot be made as their nanoplastics are significantly
7 smaller than the MP studied here.

8 Additionally, a study by Teska *et al.* looked at the ice nucleating activity of fibers from worn
9 clothing textiles and found that polyester (PET) fibers had an increase in median freezing
10 temperature, ΔT_{50} , of 5.0°C compared with background freezing.³⁷ However, this high freezing
11 activity was attributed to non-bacterial biological ice nucleating particles, as freezing dropped to
12 around background freezing temperatures following H₂O₂ digestion, which deactivates any
13 biological ice nucleating particles. This result stands in comparison to our pristine PET fragments
14 which had a ΔT_{50} of $8.8 \pm 1.1^\circ\text{C}$ and $5.0 \pm 1.1^\circ\text{C}$ compared with background freezing at 1 wt %
15 and 0.1 wt % concentrations compared with background freezing, respectively.

16 The role of atmospheric oxidation and aging on the ice nucleating activity of INPs has been
17 studied in many systems and is well established to play a large role in the activity of these INPs.
18 Studies on kaolinite, montmorillonite, and Arizona test dust, well studied mineral dust INPs, have
19 found that acid-treatment by nitric acid and/or sulfuric acid impairs the ice nucleating activity of
20 the mineral dusts.^{38–40} Oxidative aging by UV and ozone has also been found reduce the
21 concentration of INPs in experimentally generated sea spray aerosols.⁴¹

22 **Limitations of Study.** Unfortunately, the challenges in producing a homogeneous suspension
23 of the MP limits the comparisons that can be made between plastics and conclusions can only

1 confidently be stated comparing aging processes within a MP composition. Although no major
2 differences in size were observed for the studied size classes, the impact of size may be larger for
3 smaller and more atmospherically relevant sizes of MP.

4 One of the largest limitations of this study is the lack of surface area data for the MP samples.
5 Gas adsorption methods and BET analysis were unable to give reliable surface area data for the
6 studied MP. Additional methods attempted included nano-computed tomography (nanoCT) and
7 stereoscopic scanning electron microscopy (stereoSEM). The MP, however, were not resolvable
8 through nanoCT due to their highly uniform nature and stereoSEM proved time consuming and
9 high-resolution reconstructions were difficult and limited to the fact that a single particle
10 constitutes each individual dataset. Surface area data may be able to provide better insight into the
11 possible mechanism by which ice nucleation is impacted following aging as many of these aging
12 techniques have been shown to have significant impacts on the surface roughness of plastic
13 samples.

14 **Atmospheric Implications.** Overall, all MP samples studied show some degree of ice
15 nucleating activity. Aging of these plastics with UV, ozone, sulfuric acid, and AS showed mixed
16 effects on ice nucleating activity, with increases observed for some plastics and decreases observed
17 for others. Ozone-aging resulted in the fewest changes to ice nucleation, only causing decreases in
18 ice nucleating activity for PP and PET. This result is unsurprising as unsaturation in the PP MP
19 would likely only occur terminally, leaving few sites where ozone could react, and PET has been
20 shown to have only limited, surface-based chain scission when exposed to ozone without UV.⁴²
21 Sulfuric acid and AS lead to the greatest changes in ice nucleating activity, leading to changes for
22 all MP and highlighting the potential for atmospheric aging greatly impacting the ice nucleation
23 of MP. UV also led to changes in ice nucleation for all MP, but only on the longer timescale.

1 However, MP emitted into the environment would likely experience even longer exposure to UV
2 prior to reaching an atmospherically relevant size.

3 On a broad scale, the aging of three of the four plastics studied (i.e., LDPE, PP, and PET)
4 generally lead to either no change or a decrease in ice nucleating activity when compared to the
5 pristine MP. PVC was the primary exception to this observation, aging resulted in no change or an
6 increase in ice nucleating activity, which we attribute to the presence of contaminants or prior
7 surface oxidation within the pristine plastic stock. This attribution is supported by the unexpected
8 C=O and C-O peaks presented within the FTIR spectrum of the pristine plastic and the loss of
9 those peaks with subsequent aging (see Figure 5). The other exception is AS-aged LDPE which
10 has ice nucleating activity greater than that of pristine LDPE. No chemical changes following
11 aging are observed through FTIR and we are unsure of what causes this large increase in ice
12 nucleating activity.

13 Importantly, MP have viability to be a perturbing force in atmospheric ice nucleation, with some
14 samples studied here having very similar ice nucleating activity to mineral dust (i.e. kaolinite).
15 Mineral dust aerosol particles nucleate ice in the temperature range of -12 to -33°C and make up
16 50% of the contributions to ice formation in the atmosphere, making them a relevant INP to which
17 to compare.⁴³ Here, we used kaolinite as a proxy for mineral dust aerosol. Comparisons between
18 the active site densities of pristine MP, aged-MP with an increase in ice nucleating activity
19 following aging, and kaolinite are shown in Figure 6. AS-aged LDPE, the sample with the highest
20 ice nucleating activity, showed freezing temperatures and active site densities equivalent that of
21 kaolinite at some temperatures.

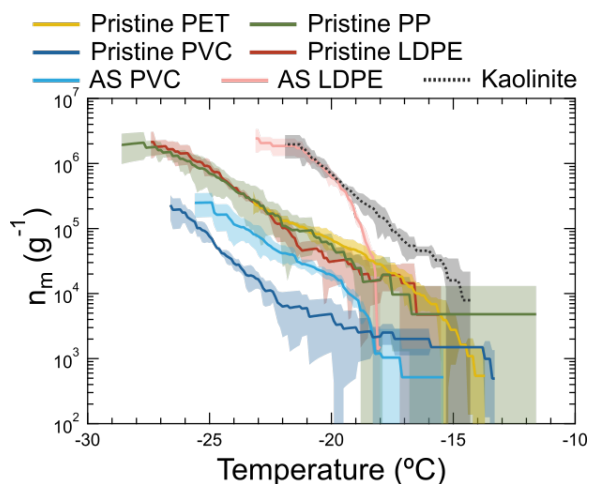


Figure 6. Comparison of the active site densities of pristine PET (yellow), PP (green), PVC (blue), and LDPE (red) and select aged MP, AS-aged PVC (light blue) and AS-aged LDPE (pink), to that of kaolinite (black dashed)

1 Mineral dust aerosol has large temporal and spatial variability which can make it difficult to
 2 make a direct comparison to MP, especially considering the limited reported data on the
 3 concentration of atmospheric MP. However, one location where comparable concentrations of MP
 4 and mineral dust aerosol particles are reported is over the Southern Ocean where concentrations
 5 of MP fragments are $7 \text{ ng} \cdot \text{m}^{-3}$ and $65 \text{ ng} \cdot \text{m}^{-3}$ for MP fibers.⁴⁴ These concentrations are comparable
 6 to that of mineral dust at $0.1 \text{ } \mu\text{g} \cdot \text{m}^{-3}$ in the same region.⁴⁵ Additionally, the concentration of MP in
 7 the atmosphere will increase in the future as environmentally entrained plastics continue to break
 8 down to sizes with sufficient atmospheric lifetimes. Overall, the role of MP as INP needs to be
 9 further studied to explore more diverse compositions and morphologies (i.e. films and fibers) of
 10 MP as well as impacts of common chemical additives to plastics such as plasticizers and colorants.

11 AUTHOR INFORMATION:

12 **Corresponding Author**

1 Miriam Arak Freedman – Department of Chemistry, The Pennsylvania State University,
2 University Park, PA 16802, United States; orcid.org/0000-0003-4374-6518; Phone: 814-867-
3 4267; Email: maf43@psu.edu

4 **Authors**

5 Heidi L. Busse – Department of Chemistry, The Pennsylvania State University, University Park,
6 PA 16802, United States; orcid.org/0000-0002-3879-6185

7 Devaka Dharmapriya Ariyasena – Department of Chemistry, The Pennsylvania State University,
8 University Park, PA 16802, United States; ORCID: orcid.org/0009-0008-7227-6811

9 Jessica Orris – Department of Chemistry, The Pennsylvania State University, University Park, PA
10 16802, United States; orcid.org/0009-0001-8818-0784

11 **Notes**

12 The authors declare no competing financial interest.

13 **ACKNOWLEDGEMENTS:**

14 This research was supported by the National Science Foundation (CHE-2304879). The authors
15 would like to acknowledge the Materials Characterization Lab at the Pennsylvania State University
16 for use of instruments (SEM, Cryomill), the Center for Quantitative Imaging at the Pennsylvania
17 State University for microCT consultation and data, and T. Zimudzi for helpful conversations
18 regarding interpretation of FTIR data. H. L. B. is grateful for support from a National Science
19 Foundation Graduate Research Fellowship under Grant No. DGE-1255832.

20 **REFERENCES:**

21 (1) Cunningham, E. M.; Rico Seijo, N.; Altieri, K. E.; Audh, R. R.; Burger, J. M.;
22 Bornman, T. G.; Fawcett, S.; Gwinnett, C. M. B.; Osborne, A. O.; Woodall,

- 1 L. C. The Transport and Fate of Microplastic Fibres in the Antarctic: The Role
2 of Multiple Global Processes. *Front Mar Sci* **2022**, *9*.
3 <https://doi.org/10.3389/fmars.2022.1056081>.
- 4 (2) Chiba, S.; Saito, H.; Fletcher, R.; Yogi, T.; Kayo, M.; Miyagi, S.; Ogido, M.;
5 Fujikura, K. Human Footprint in the Abyss: 30 Year Records of Deep-Sea
6 Plastic Debris. *Mar Policy* **2018**, *96*, 204–212.
7 <https://doi.org/10.1016/j.marpol.2018.03.022>.
- 8 (3) Napper, I. E.; Davies, B. F. R.; Clifford, H.; Elvin, S.; Koldewey, H. J.;
9 Mayewski, P. A.; Miner, K. R.; Potocki, M.; Elmore, A. C.; Gajurel, A. P.;
10 Thompson, R. C. Reaching New Heights in Plastic Pollution—Preliminary
11 Findings of Microplastics on Mount Everest. *One Earth* **2020**, *3* (5), 621–630.
12 <https://doi.org/10.1016/j.oneear.2020.10.020>.
- 13 (4) Aves, A. R.; Revell, L. E.; Gaw, S.; Ruffell, H.; Schuddeboom, A.;
14 Wotherspoon, N. E.; Larue, M.; McDonald, A. J. First Evidence of
15 Microplastics in Antarctic Snow. *Cryosphere* **2022**, *16* (6), 2127–2145.
16 <https://doi.org/10.5194/tc-16-2127-2022>.
- 17 (5) Sankar Sana, S.; Kumar Dogiparthi, L.; Gangadhar, L.; Chakravorty, A.;
18 Abhishek, N. Effects of Microplastics and Nanoplastics on Marine
19 Environment and Human Health. *Environmental Science and Pollution*
20 *Research* **2020**, *27*, 44743–44756. [https://doi.org/10.1007/s11356-020-](https://doi.org/10.1007/s11356-020-10573-x)
21 [10573-x](https://doi.org/10.1007/s11356-020-10573-x).
- 22 (6) Allen, D.; Allen, S.; Le Roux, G.; Simonneau, A.; Galop, D.; Phoenix, V. R.
23 Temporal Archive of Atmospheric Microplastic Deposition Presented in
24 Ombrotrophic Peat. *Environ Sci Technol Lett* **2021**, *8* (11), 954–960.
25 <https://doi.org/10.1021/acs.estlett.1c00697>.
- 26 (7) Leslie, H. A.; van Velzen, M. J. M.; Brandsma, S. H.; Vethaak, A. D.; Garcia-
27 Vallejo, J. J.; Lamoree, M. H. Discovery and Quantification of Plastic Particle
28 Pollution in Human Blood. *Environ Int* **2022**, *163*.
29 <https://doi.org/10.1016/j.envint.2022.107199>.
- 30 (8) Zhang, Y.; Kang, S.; Allen, S.; Allen, D.; Gao, T.; Sillanpää, M. Atmospheric
31 Microplastics: A Review on Current Status and Perspectives. *Earth-Science*
32 *Reviews*. Elsevier B.V. April 1, 2020.
33 <https://doi.org/10.1016/j.earscirev.2020.103118>.
- 34 (9) Allen, S.; Allen, D.; Phoenix, V. R.; Le Roux, G.; Durántez Jiménez, P.;
35 Simonneau, A.; Binet, S.; Galop, D. Atmospheric Transport and Deposition of
36 Microplastics in a Remote Mountain Catchment. *Nat Geosci* **2019**, *12* (5),
37 339–344. <https://doi.org/10.1038/s41561-019-0335-5>.
- 38 (10) Huang, Y.; He, T.; Yan, M.; Yang, L.; Gong, H.; Wang, W.; Qing, X.; Wang,
39 J. Atmospheric Transport and Deposition of Microplastics in a Subtropical

- 1 Urban Environment. *J Hazard Mater* **2021**, *416*, 126168.
2 <https://doi.org/10.1016/j.jhazmat.2021.126168>.
- 3 (11) Brahney, J.; Mahowald, N.; Prank, M.; Cornwell, G.; Klimont, Z.; Matsui, H.;
4 Prather, K. A. Constraining the Atmospheric Limb of the Plastic Cycle.
5 *Proceedings of the National Academy of Sciences* **2021**, *118* (16),
6 e2020719118. <https://doi.org/10.1073/pnas.2020719118>.
- 7 (12) Harb, C.; Pokhrel, N.; Foroutan, H. Quantification of the Emission of
8 Atmospheric Microplastics and Nanoplastics via Sea Spray. *Environ Sci*
9 *Technol Lett* **2023**. <https://doi.org/10.1021/acs.estlett.3c00164>.
- 10 (13) Revell, L. E.; Kuma, P.; Le Ru, E. C.; Somerville, W. R. C.; Gaw, S. Direct
11 Radiative Effects of Airborne Microplastics. *Nature* **2021**, *598*:7881
12 (7881), 462–467. <https://doi.org/10.1038/s41586-021-03864-x>.
- 13 (14) Aeschlimann, M.; Li, G.; Kanji, Z. A.; Mitrano, D. M. Potential Impacts of
14 Atmospheric Microplastics and Nanoplastics on Cloud Formation Processes.
15 *Nature Geoscience* **2022**, *15*:12 (12), 967–975.
16 <https://doi.org/10.1038/S41561-022-01051-9>.
- 17 (15) Bain, A.; Preston, T. C. Hygroscopicity of Microplastic and Mixed
18 Microplastic Aqueous Ammonium Sulfate Systems. *Environ Sci Technol*
19 **2021**, *55*, 11775–11783. <https://doi.org/10.1021/acs.est.1c04272>.
- 20 (16) Wang, Y.; Okochi, H.; Tani, Y.; Hayami, H.; Minami, Y.; Katsumi, N.;
21 Takeuchi, M.; Sorimachi, A.; Fujii, Y.; Kajino, M.; Adachi, K.; Ishihara, Y.;
22 Iwamoto, Y.; Niida, Y. Airborne Hydrophilic Microplastics in Cloud Water at
23 High Altitudes and Their Role in Cloud Formation. *Environ Chem Lett* **2023**,
24 *21* (6), 3055–3062. <https://doi.org/10.1007/s10311-023-01626-x>.
- 25 (17) Sun, H.; Jiao, R.; Wang, D. The Difference of Aggregation Mechanism
26 between Microplastics and Nanoplastics: Role of Brownian Motion and
27 Structural Layer Force. *Environmental Pollution* **2021**, *268*.
28 <https://doi.org/10.1016/j.envpol.2020.115942>.
- 29 (18) Hoose, C.; Möhler, O. Heterogeneous Ice Nucleation on Atmospheric
30 Aerosols: A Review of Results from Laboratory Experiments. *Atmos Chem*
31 *Phys* **2012**, *12* (20), 9817–9854. <https://doi.org/10.5194/acp-12-9817-2012>.
- 32 (19) Kanji, Z. A.; Ladino, L. A.; Wex, H.; Boose, Y.; Burkert-Kohn, M.; Cziczo,
33 D. J.; Krämer, M. Overview of Ice Nucleating Particles. *Meteorological*
34 *Monographs* **2017**, *58* (1), 1.1-1.33. [https://doi.org/10.1175/amsmonographs-](https://doi.org/10.1175/amsmonographs-d-16-0006.1)
35 [d-16-0006.1](https://doi.org/10.1175/amsmonographs-d-16-0006.1).
- 36 (20) Vali, G.; Demott, P. J.; Möhler, O.; Whale, T. F. Technical Note: A Proposal
37 for Ice Nucleation Terminology. *Atmos. Chem. Phys* **2015**, *15*, 10263–10270.
38 <https://doi.org/10.5194/acp-15-10263-2015>.

- 1 (21) Koop, T.; Luo, B.; Tsias, A.; Peter, T. Water Activity as the Determinant for
2 Homogeneous Ice Nucleation in Aqueous Solutions. *Nature* **2000**, *406*, 611–
3 614. <https://doi.org/10.1038/35020537>.
- 4 (22) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air*
5 *Pollution to Climate Change*, Third Edit.; John Wiley & Sons, Ltd, 2016.
- 6 (23) Pruppacher, H. R.; Klett, J. D. *Microphysics of Clouds and Precipitation*,
7 Second.; Mysak, L. A., Hamilton, K., Eds.; Springer, 2010.
8 <https://doi.org/10.1007/978-0-306-48100-0>.
- 9 (24) Ganguly, M.; Ariya, P. A. Ice Nucleation of Model Nanoplastics and
10 Microplastics: A Novel Synthetic Protocol and the Influence of Particle
11 Capping at Diverse Atmospheric Environments. *ACS Earth Space Chem* **2019**,
12 *3* (9), 1729–1739. <https://doi.org/10.1021/acsearthspacechem.9b00132>.
- 13 (25) Sridharan, S.; Kumar, M.; Singh, L.; Bolan, N. S.; Saha, M. Microplastics as
14 an Emerging Source of Particulate Air Pollution: A Critical Review. *J Hazard*
15 *Mater* **2021**, *418*, 126245. <https://doi.org/10.1016/j.jhazmat.2021.126245>.
- 16 (26) Chen, Y.; Jing, S.; Wang, Y.; Song, Z.; Xie, L.; Shang, X.; Fu, H.; Yang, X.;
17 Wang, H.; Wu, M.; Chen, Y.; Li, Q.; Zhang, Y.; Wang, W.; Zhang, L.; Wang,
18 R.; Fang, M.; Zhang, Y.; Li, W.; Zhao, D.; Li, C.; Rudich, Y.; Wang, L.;
19 Zhang, R.; Liu, W.; Wanger, T. C.; Yu, S.; Chen, J. Quantification and
20 Characterization of Fine Plastic Particles as Considerable Components in
21 Atmospheric Fine Particles. *Environ Sci Technol* **2024**.
22 <https://doi.org/10.1021/ACS.EST.3C06832>.
- 23 (27) Dris, R.; Gasperi, J.; Rocher, V.; Saad, M.; Renault, N.; Tassin, B.; Dris, R.;
24 Gasperi, J.; Rocher, V.; Saad, M.; Renault, N.; Tassin, B. Microplastic
25 Contamination in an Urban Area: A Case Study in Greater Paris. *Environ*
26 *Chem* **2015**, *12* (5), 592–599. <https://doi.org/10.1071/en14167>.
- 27 (28) National Oceanic and Atmospheric Administration. RANKING OF CITIES
28 BASED ON % ANNUAL POSSIBLE SUNSHINE IN DESCENDING
29 ORDER FROM MOST TO LEAST AVERAGE POSSIBLE SUNSHINE.
30 *Comparative Climatic Data*. March 30, 2024.
- 31 (29) Jaffe, D. A.; Cooper, O. R.; Fiore, A. M.; Henderson, B. H.; Tonnesen, G. S.;
32 Russell, A. G.; Henze, D. K.; Langford, A. O.; Lin, M.; Moore, T. Scientific
33 Assessment of Background Ozone over the U.S.: Implications for Air Quality
34 Management. *Elementa*. University of California Press 2018.
35 <https://doi.org/10.1525/elementa.309>.
- 36 (30) Alstadt, V. J.; Dawson, J. N.; Losey, D. J.; Sihvonen, S. K.; Freedman, M. A.
37 Heterogeneous Freezing of Carbon Nanotubes: A Model System for Pore
38 Condensation and Freezing in the Atmosphere. *Journal of Physical Chemistry*
39 *A* **2017**, *121* (42), 8166–8175. <https://doi.org/10.1021/acs.jpca.7b06359>.

- 1 (31) O’Sullivan, D.; Murray, B. J.; Ross, J. F.; Whale, T. F.; Price, H. C.; Atkinson,
2 J. D.; Umo, N. S.; Webb, M. E. The Relevance of Nanoscale Biological
3 Fragments for Ice Nucleation in Clouds. *Sci Rep* **2015**, *5*.
4 <https://doi.org/10.1038/srep08082>.
- 5 (32) Vali, G. Quantitative Evaluation of Experimental Results on the
6 Heterogeneous Freezing Nucleation of Supercooled Liquids. *J Atmos Sci*
7 **1971**, *28*, 402–409. [https://doi.org/10.1175/1520-](https://doi.org/10.1175/1520-0469(1971)028<0402:qeoera>2.0.co;2)
8 [0469\(1971\)028<0402:qeoera>2.0.co;2](https://doi.org/10.1175/1520-0469(1971)028<0402:qeoera>2.0.co;2).
- 9 (33) Coates, J. Interpretation of Infrared Spectra, A Practical Approach. In
10 *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; John Wiley & Sons
11 Ltd: Chincester, England, 2000; pp 10815–10837.
- 12 (34) Krimm, S.; Liang, C. Y.; Sutherland, G. B. B. M. Infrared Spectra of High
13 Polymers. II. Polyethylene. *J Chem Phys* **1956**, *25* (3), 549–562.
14 <https://doi.org/10.1063/1.1742963>.
- 15 (35) Luongo, J. P. Infrared Study of Polypropylene. *J Appl Polym Sci* **1960**, *111*
16 (9), 302–309. <https://doi.org/10.1002/app.1960.070030907>.
- 17 (36) Smith, B. C. The Infrared Spectra of Polymers II: Polyethylene. *Spectroscopy*
18 **2021**, *36* (9), 24–29. <https://doi.org/10.56530/spectroscopy.xp7081p7>.
- 19 (37) Teska, C. J.; Dieser, M.; Foreman, C. M. Clothing Textiles as Carriers of
20 Biological Ice Nucleation Active Particles. *Environ Sci Technol* **2023**.
21 <https://doi.org/10.1021/acs.est.3c09600>.
- 22 (38) Sihvonen, S. K.; Schill, G. P.; Lykтей, N. A.; Veghte, D. P.; Tolbert, M. A.;
23 Freedman, M. A. Chemical and Physical Transformations of Aluminosilicate
24 Clay Minerals Due to Acid Treatment and Consequences for Heterogeneous
25 Ice Nucleation. *Journal of Physical Chemistry A* **2014**, *118* (38), 8787–8796.
26 <https://doi.org/10.1021/jp504846g>.
- 27 (39) Sullivan, R. C.; Miñambres, L.; Demott, P. J.; Prenni, A. J.; Carrico, C. M.;
28 Levin, E. J. T.; Kreidenweis, S. M. Chemical Processing Does Not Always
29 Impair Heterogeneous Ice Nucleation of Mineral Dust Particles. *Geophys Res*
30 *Lett* **2010**, *37* (24), 1–5. <https://doi.org/10.1029/2010GL045540>.
- 31 (40) Freedman, M. A. Potential Sites for Ice Nucleation on Aluminosilicate Clay
32 Minerals and Related Materials. *Journal of Physical Chemistry Letters*.
33 American Chemical Society October 1, 2015, pp 3850–3858.
34 <https://doi.org/10.1021/acs.jpcllett.5b01326>.
- 35 (41) DeMott, P. J.; Hill, T. C. J.; Moore, K. A.; Perkins, R. J.; Mael, L. E.; Busse,
36 H. L.; Lee, H.; Kaluarachchi, C. P.; Mayer, K. J.; Sauer, J. S.; Mitts, B. A.;
37 Tivanski, A. V.; Grassian, V. H.; Cappa, C. D.; Bertram, T. H.; Prather, K. A.
38 Atmospheric Oxidation Impact on Sea Spray Produced Ice Nucleating

1 Particles. *Environmental Science: Atmospheres* **2023**, 3 (10), 1513–1532.
2 <https://doi.org/10.1039/d3ea00060e>.

3 (42) Walzak, M. J.; Flynn, S.; Foerch, R.; Hill, J. M.; Karbaszewski, E.; Lin, A.;
4 Strobel, M. UV and Ozone Treatment of Polypropylene and Poly(Ethylene
5 Terephthalate). *J Adhes Sci Technol* **1995**, 9 (9), 1229–1248.
6 <https://doi.org/10.1163/156856195X01012>.

7 (43) Murray, B. J.; O’Sullivan, D.; Atkinson, J. D.; Webb, M. E. Ice Nucleation by
8 Particles Immersed in Supercooled Cloud Droplets. *Chem Soc Rev* **2012**, 41
9 (19), 6519–6554. <https://doi.org/10.1039/c2cs35200a>.

10 (44) Chen, Q.; Shi, G.; Revell, L. E.; Zhang, J.; Zuo, C.; Wang, D.; Le Ru, E. C.;
11 Wu, G.; Mitrano, D. M. Long-Range Atmospheric Transport of Microplastics
12 across the Southern Hemisphere. *Nat Commun* **2023**, 14 (1).
13 <https://doi.org/10.1038/s41467-023-43695-0>.

14 (45) Li, F.; Ginoux, P.; Ramaswamy, V. Distribution, Transport, and Deposition of
15 Mineral Dust in the Southern Ocean and Antarctica: Contribution of Major
16 Sources. *Journal of Geophysical Research Atmospheres* **2008**, 113 (10).
17 <https://doi.org/10.1029/2007JD009190>.

18

19 For Tables of Contents Only:

