

1 Historical Trends of Biogenic SOA Tracers in an Ice Core from 2 Kamchatka Peninsula

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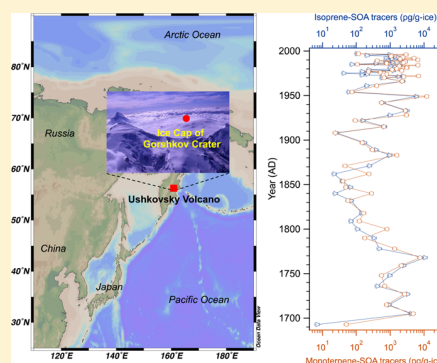
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9 **S** Supporting Information

10 **ABSTRACT:** Biogenic secondary organic aerosol (SOA) is ubiquitous in the
11 Earth's atmosphere, influencing climate and air quality. However, the historical
12 trend of biogenic SOA is not well known. Here, we report for the first time the
13 major isoprene- and monoterpene-derived SOA tracers preserved in an ice core
14 from the Kamchatka Peninsula. Significant variations are recorded during the past
15 300 years with lower concentrations in the early-to-middle 19th century and
16 higher concentrations in the preindustrial period and the present day. We
17 discovered that isoprene SOA tracers were more abundant in the preindustrial
18 period than the present day, while monoterpene SOA tracers stay almost
19 unchanged. The causes of the observed variability are complex, depending on
20 atmospheric circulation, changes in emissions, and other factors such as
21 tropospheric oxidative capacity. Our data presents an unprecedented opportunity
22 to shed light on the formation, evolution, and fate of atmospheric aerosols and
23 to constrain the uncertainties associated with modeling their atmospheric
24 concentrations.



25 ■ INTRODUCTION

26 Palaeoclimate archives containing annual layers (e.g., ice cores,
27 tree rings, speleothems, and coral reefs) have played a central
28 role in reconstructing decadal-scale climatic oscillation of the
29 past.¹ This insight has proved an invaluable tool to constrain
30 climate model projections of future climate change by
31 validating model hindcasts. Similarly, analysis of particles
32 preserved in ice cores provides an unprecedented opportunity
33 to elucidate the distribution, concentration, size distribution,
34 and even chemical composition of atmospheric aerosols in the
35 past. Such data would allow us to deduce the influence of
36 aerosol radiative forcing on past climate change. Previously,
37 aerosol particles preserved in high altitudinal or high latitudinal
38 ice cores have been examined for inorganic species (e.g.,
39 sulfate), black carbon, and organic species such as polycyclic
40 aromatic hydrocarbons, carboxylic acids, biomass burning
41 tracers, and humic-like substances.^{2–7} To date, little was
42 known about the historical trends of secondary organic aerosols
43 at a molecular level.^{3,8} Here, we present the findings of the
44 analysis of ice cores for evidence of organic compounds formed
45 from biogenic trace gases.

46 Terrestrial vegetation emits large quantities ($\sim 1 \text{ Pg C y}^{-1}$) of
47 biogenic volatile organic compounds (BVOCs), including
48 reactive species such as isoprene and monoterpenes, to the
49 atmosphere.⁹ The role of their atmospheric reactions in

governing the production and loss of tropospheric ozone is 50
well studied and relatively well understood, but BVOC 51
oxidation has also been shown to lead to aerosol 52
formation.^{10–12} Organic particles formed by the photooxidation 53
of BVOCs are considered “secondary” organic aerosols (SOA) 54
and are believed to be more abundant than directly emitted 55
“primary” organic aerosols (POA) in the Earth’s atmos- 56
phere.^{11,13–16} It is believed that SOA could be a significant 57
source of new nanoscale particles, especially in pristine remote 58
regions,^{17,18} that can grow into the accumulation mode and act 59
as CCN, influencing local climate and radiative forcing. 60
However, the uncertainties are substantial. Estimates of 61
biogenic SOA production range from 9–910 Tg C y^{-1} with a 62
best estimate of 60–240 Tg C y^{-1} .^{11,19–21} The radiative forcing 63
effect of SOA has been estimated as -0.03 W m^{-2} (-0.27 to 64
 $+0.20 \text{ W m}^{-2}$),^{22,23} but this is highly dependent on assumptions 65
of the total atmospheric burden of SOA. 66

Given the ubiquity and influence of organic particles in the 67
atmosphere, there is an urgent need to better understand and 68
constrain the processes leading to the formation of SOA and to 69

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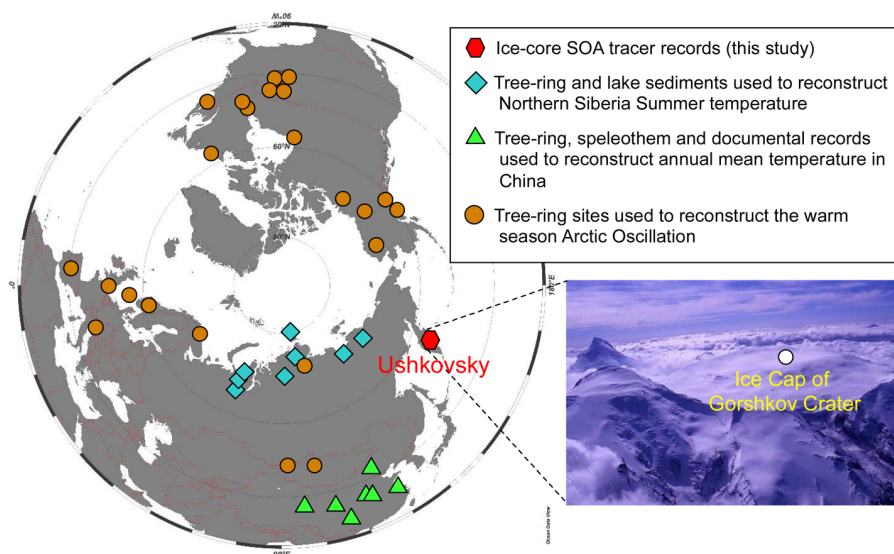


Figure 1. Sampling site of the ice core (211.7 m long) at the ice cap of the Gorshkov crater at the Ushkovsky Volcano ($56^{\circ}04' N$, $160^{\circ}28' E$; 3903 m a.s.l.), Kamchatka Peninsula. In this study, we used ice core sections from depths from 1.32 to 152.5 m (1997–1693). The deeper sections were not used because of the presence of many sand layers; their data are presented in Table S1. The ice core chronology was determined by counting the annual layers of a seasonal oxygen isotopic signal ($\delta^{18}O$) from the surface to a depth of 103.58 m, whereas the chronology for deeper layers was determined using a two-dimensional thermodynamic coupled model.³³ Sites used for reconstruction of the Northern Hemispheric temperatures (Figure 2D,E) are also shown in the map.

70 elucidate the role of aerosols in governing global and regional
 71 climate. Studies of production, transformation, and removal
 72 processes have been extensively conducted for ambient aerosols
 73 and simulated in laboratory conditions.^{24–28} Relationships
 74 between the phases of organic aerosols and their reactivity^{29,30}
 75 have been investigated. Model simulations have been
 76 performed to identify trends in SOA concentrations and
 77 distributions and to quantify modern and past SOA
 78 budgets.^{31,32} However, the uncertainties of such estimates are
 79 substantial, and better constraints are required.

80 Here, we report 300 years of ice core records of biogenic
 81 SOA based on organic marker compounds produced by the
 82 oxidation of isoprene and monoterpenes from the Ushkovsky
 83 ice cap in Northeast Asia (Figure 1). Such data represent a
 84 potential source of direct evidence of biogenic SOA
 85 concentrations and chemical properties that could be used to
 86 evaluate model hindcasts and constrain model projections of
 87 future budgets and radiative forcing of atmospheric aerosols.

88 ■ MATERIALS AND METHODS

89 **Study Area.** The ice core (211.7 m long) was drilled from
 90 the ice cap of the Gorshkov crater at Ushkovsky volcano
 91 ($56^{\circ}04' N$, $160^{\circ}28' E$; 3903 m a.s.l.) in the central part of the
 92 Kamchatka Peninsula, Russia (Figure 1). Detailed ice core
 93 chronology³³ and analytical methodology are provided in the
 94 Supporting Information (SI). Here, 75 sections were cut off
 95 using a band saw. Ice core sections (50 cm long, 1/4 cut) were
 96 taken at every 1 m for the upper 25 m and at every 4–5 m for
 97 the layers deeper than 25 m. Approximately 1.0 cm thickness of
 98 the outer core surface was mechanically removed using a
 99 precleaned ceramic knife in a cold clean room to avoid
 100 potential contamination.

101 **Bulk Analysis.** Each sample section was melted in a
 102 precleaned Pyrex beaker (2 L). The samples were poisoned
 103 with $HgCl_2$ to prevent potential microbial degradation of
 104 organic compounds and stored at 4 °C in precleaned brown

glass bottles prior to analysis. In this study, we use 59 samples
 collected from 1.1 to 152.6 m in depth (1997–1693); the data
 of deeper sections (Table S1) were not used because of the
 presence of many sand layers.

The meltwater samples were transferred to a pear-shaped
 flask and concentrated to almost complete dryness using a
 rotary evaporator under a vacuum. The total organic matter in
 the dried samples was extracted with a 2:1 v/v solution of
 CH_2Cl_2/CH_3OH using an ultrasonic bath. The extracts were
 concentrated and passed through a glass column packed with
 quartz wool and further eluted with CH_2Cl_2 and CH_3OH to
 extract the organics potentially adsorbed on the particles. The
 eluents were then combined with the extracts, transferred to 1.5
 mL glass vials, and dried under a pure nitrogen gas stream.
 Polar organic markers in the extracts were derivatized with 99%
 N,O -bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 1%
 trimethylsilyl chloride for 2 h at 70 °C in a sealed glass vial
 (1.5 mL). The derivatives were then diluted by the addition of
 n -hexane containing C_{13} n -alkane as an internal standard prior
 to the determination by gas chromatography–mass spectrometry
 (GC-MS).

GC-MS Measurement. GC-MS analyses were performed
 on a Hewlett-Packard model 6890 GC coupled to a Hewlett-
 Packard model 5973 MSD with a programmed GC oven
 temperature. Target compounds were identified by comparing
 the mass spectra with those of authentic standards or data in
 the literature.^{24,34} Recoveries for the standards or surrogates
 were better than 80%. The analytical errors in triplicate analyses
 were within 15%. A laboratory blank was measured using Milli-
 Q water and showed no contamination for any target species.

135 ■ RESULTS

The total concentrations of biogenic SOA tracers (Figure 2A,B
 and Table S2) detected in the Ushkovsky ice cores range widely
 (50.2–18,400 pg/g-ice; mean 2890 pg/g-ice), covering the
 period between 1693 and present day (1997). The enlarged

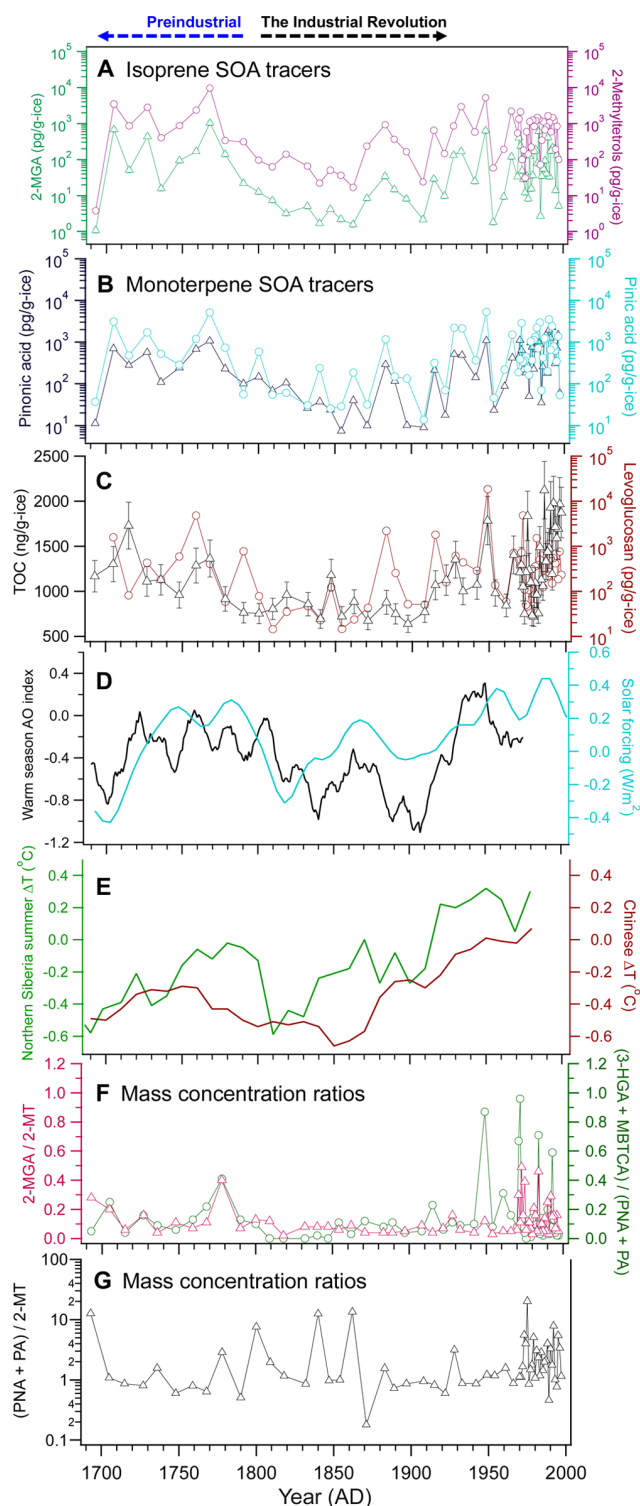


Figure 2. (A) and (B) Historical trends in the concentrations of isoprene secondary organic aerosol (SOA) tracers and monoterpene SOA tracers in the Ushkovsky ice core, respectively. (C) Historical trends in the concentrations of total organic carbon (TOC) and levoglucosan, as reported by Kawamura et al.⁴ (D) Reconstructed warm season Arctic Oscillation (AO) index⁵⁴ and solar radiative forcing.⁷⁰ (E) Reconstructed Northern Siberian and Chinese summer temperatures.⁵¹ (F) and (G) Historical changes in the mass concentration ratios among different organic marker compounds measured in the Ushkovsky ice core.

figure covering the period of 1950–1997 is provided in the 140
 Supporting Information (Figure S2). The data are strongly 141
 positively skewed (median 3750 pg/g-ice; 10th and 90th 142
 percentiles, 179 pg/g-ice and 6230 pg/g-ice, respectively) due 143
 to anomalously high concentrations in a handful of years during 144
 the preindustrial (1693–1790) and the 20th century (1908– 145
 1997) periods, notably 1768 and 1949. Concentrations of total 146
 organic carbon (Figure 2C) as well as those of individual tracers 147
 were lowest in the 19th century and, in particular, during the 148
 peak of the Little Ice Age in Europe (early mid 1800s), when 149
 temperatures were low throughout the biogenic source regions 150
 suppressing emissions.^{35,36} On the whole, there is a strong 151
 correlation between ice core SOA tracer concentrations and the 152
 Northern Hemisphere high-latitude temperature anomaly and a 153
 weak correlation with solar irradiance (Figure 2A–E). While 154
 concentrations of the individual tracers fit this general pattern, 155
 there are also notable differences, which are discussed later. 156

Isoprene SOA Tracers. Oxidation products of isoprene, the 157
 most prevalent nonmethane hydrocarbon emitted to the 158
 atmosphere,³⁷ have been shown to be significant contributors 159
 to global organic aerosol mass.^{24,38} Concentrations of 2- 160
 methyltetrols (2-MT), the sum of 2-methylthreitol and 2- 161
 methylerythritol, in the Ushkovsky ice core ranged from 3.8 to 162
 9710 pg/g-ice (median 587.5 pg/g-ice; Table S2). 2-MT, 163
 together with C₅-alkene triols and 3-methyltetrahydrofuran-3,4- 164
 diols (3-MeTHF-3,4-diols) neither of which were detected in 165
 the Ushkovsky ice core, are higher generation products formed 166
 from the photooxidation of epoxydiols of isoprene (IEPOX = 167
 β -IEPOX + α -IEPOX) under low-NO_x (NO_x = NO + NO₂) or 168
 NO_x-free conditions.³⁹ In this study, 2-MT concentrations in 169
 the preindustrial period were about double those in the 20th 170
 century and more than 30 times higher than those during the 171
 end of Little Ice Age (early-to-middle 1800s). As expected, a 172
 strong correlation ($R^2 = 0.95$, $p < 0.05$) was found between 2- 173
 methylerythritol and 2-methylthreitol (Figure S1), with the 174
 isomeric fractions of 2-methylerythritol in 2-MT varying little 175
 between the different periods ($\sim 0.70 \pm 0.04$). 176

By contrast, 2-methylglyceric acid (2-MGA) is a C₄- 177
 dihydroxycarboxylic acid that is formed via methacrylic acid 178
 epoxide (MAE) and has been identified as a key gas-phase 179
 intermediate resulting in isoprene SOA formation from the 180
 high-NO_x pathway.^{40,41} In the preindustrial period, NO_x 181
 emissions were limited to wildfires, soil denitrification, and 182
 lightning.⁴² The large rise in anthropogenic NO_x emissions 183
 since the start of the industrial revolution⁴³ have increased 184
 atmospheric NO_x concentrations; yields of 2-MGA would have 185
 been expected to be more substantial in the present day than in 186
 the preindustrial period. However, 2-MGA was found to be less 187
 abundant than 2-MT in all core samples, varying from 0.03 to 188
 0.86 (mean ratio of 2-MGA:2-MT ~ 0.13). The mean ratios of 189
 2-MGA/2-MT showed only negligible differences between the 190
 present (0.13) and the preindustrial period (0.15) but were 191
 slightly lower in the early-to-middle 1800s (~ 0.08). These 192
 results suggest that the low-NO_x pathway via IEPOX^{39,41,44–46} 193
 has dominated isoprene photooxidation at the high latitudes in 194
 the Northern Hemisphere throughout the past three centuries. 195

Monoterpene SOA Tracers. We detected four mono- 196
 terpene oxidation products in the ice core samples: 3- 197
 hydroxyglutaric acid (3-HGA), pinonic acid, pinic acid, and 198
 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). Pinic and 199
 pinonic acids (PA and PNA) are first-generation products 200
 formed from the oxidation of α - and β -pinene, the most 201
 abundant monoterpenes, by hydroxyl radical (OH), O₃, or 202

203 nitrate radical (NO_3);^{11,47} 3-HGA and MBTCA are higher-
204 generation products.^{11,15} On a global scale, the majority of
205 monoterpene SOA is believed to be formed from initialization
206 reactions involving ozone rather than OH or NO_3 radicals;^{48–50}
207 although NO_3 chemistry is an important source at night and in
208 some regions, links between yields and atmospheric NO_x
209 concentrations are less clear than for isoprene SOA.

210 Total concentrations of these tracers range from 24 to 12,000
211 pg/g-ice (mean 1780; median 10th and 90th percentiles, 788,
212 73.2, and 418 pg/g-ice, respectively) with pinic acid dominating
213 (Table S2). Concentrations of PA (mean 932, median 409 pg/
214 g-ice) are double those (mean 482, median 281 pg/g-ice) of
215 PNA, consistent with laboratory-reported relative yields of the
216 two species.⁴⁸ 3-HGA and MBTCA are less abundant than PA
217 and PNA with a median ratio of (3-HGA + MBTCA):(PA +
218 PNA) of 0.09 (mean 0.15). The ratios (Figure 2F) were
219 significantly lower during the Little Ice Age (~ 0.03) than in the
220 preindustrial period (0.16), reflecting the trends seen in total
221 organic carbon (TOC) concentrations (Figure 2C). The
222 average ratio (0.18) for the last 100 years is higher (Table
223 S2), and while not significantly different from preindustrial
224 levels, appears to show an increasing trend (Figure 2F).

225 Ice core profiles of monoterpene and isoprene SOA tracers
226 are similar (Figure 2A,B), with monoterpene-derived SOA
227 tending to dominate (mean ratios of total monoterpene:total
228 isoprene tracers 2.6, median 1.4). Concentrations of PA and
229 PNA, in particular, resemble those of isoprene SOA tracers,
230 although there were substantial fluctuations in the relative
231 abundances. Ratios of PA and PNA (from monoterpene
232 oxidation) to 2-MT (from isoprene oxidation under low- NO_x
233 conditions) were similar (mean 2.3, median 1.2; Figure 2G),
234 suggesting isoprene and monoterpene SOA at Ushkovsky were
235 derived from similar source regions during the period covered
236 by the ice core samples.

237 ■ DISCUSSION

238 Concentrations and relative abundances of the isoprene and
239 monoterpene SOA tracers detected in the Ushkovsky ice core
240 are determined by the combination of local BVOC sources and
241 long-range transport of both the tracers and their precursors
242 including reactive nitrogen. Emission rates of BVOCs are
243 strongly dependent on plant species and distribution and
244 environmental conditions such as temperature and light levels.
245 Transport of atmospheric compounds to the region is
246 influenced by the origin of the air mass arriving at the sample
247 site, which is determined by prevailing air circulation in the
248 Northern Hemisphere. Understanding and identifying the
249 relative contributions of the various sources and the causes of
250 the fluctuations in the ice core concentrations is vital to
251 ongoing efforts to elucidate and predict the evolution of
252 tropospheric composition and climate.

253 The general trends of isoprene and monoterpene SOA
254 tracers in the Ushkovsky ice core agree with climate records
255 such as mean annual temperature records from China and the
256 warm season temperature from Northern Siberia⁵¹ (Figure 2E).
257 As would be expected given the exponential temperature
258 dependence of biogenic emissions on temperature, concen-
259 trations of biogenic SOA tracers and TOC were low during the
260 Little Ice Age. Our ice core records of monoterpene SOA
261 tracers significantly correlate with historical temperatures in
262 proximal regions climate records including Chinese and
263 Northern Siberian temperatures ($r = 0.63$ to 0.40 , $p < 0.01$)
264 (Table S3). However, isoprene SOA tracers showed relatively

265 weak correlations with mean annual temperature in China and
266 Siberia ($r = 0.54$ to 0.35 , $p < 0.01$). Relatively higher
267 correlations of the ice core SOA tracers with the Chinese
268 temperatures ($r = 0.63$ to 0.47 , $p < 0.01$) than those with
269 summer temperatures in Northern Siberia ($r = 0.59$ to 0.35 , $p <$
270 0.01) suggest a strong empirical relationship between the ice
271 core records of biogenic SOA and midlatitude climate.
272 However, the historical temperature change in this region
273 (~ 1 °C) is too small to account fully for the large variations of
274 biogenic SOA tracers observed in the ice core samples during
275 the past 300 years.

276 The SOA tracers generally show very little correlation with
277 solar irradiance ($r = 0.25$ to 0.32 , $p < 0.05$ for isoprene tracers,
278 PA and PNA), although the higher generation monoterpene
279 tracers (3-HGA and MBTCA) may be weakly influenced ($r =$
280 0.42 to 0.45 , $p < 0.01$). Although isoprene emissions are
281 strongly light dependent, those of most monoterpenes are
282 driven only by temperature,^{36,52} and it is likely that the
283 correlations seen are driven by the effect of solar irradiance on
284 subsequent photochemistry combined with relationships
285 between solar irradiance and surface temperature. The effect
286 of changes in solar forcing on surface temperature is highly
287 uncertain and also highly localized,⁵³ making it hard to draw
288 firm conclusions on causality.

289 This variability is likely to be driven primarily by fluctuations
290 in atmospheric circulation patterns driven by the warm-season
291 Arctic Oscillation (AO)⁵⁴ (Figure 2D). All the ice core records
292 of biogenic SOA tracers correlate well with the AO index ($r =$
293 0.51 to 0.43 , $p < 0.01$) (Table S3); for example, lower
294 concentrations of isoprene and monoterpene SOA tracers were
295 observed in 1693, the early-to-middle 1800s, and early 20th
296 century coincident with negative AO conditions, which reduce
297 westerly jet intensity and deliver cold and clean air masses from
298 the Arctic to middle and high latitudes in the Northern
299 Hemisphere. Under such conditions, not only are local biogenic
300 emissions low but also SOA tracer compounds and precursors
301 are not advected from more distant sources. High concen-
302 trations of biogenic SOA tracers in samples dating from the
303 early 18th century and present day (the 20th century) (Table
304 S2) occur during periods with the positive AO patterns. Under
305 such circulation patterns, air masses at Ushkovsky originate
306 mainly from lower latitudes in Asia, bringing warmer (and for
307 the present day, more polluted) conditions.

308 Biogenic isoprene SOA tracers at the beginning of the 18th
309 century were more abundant than those of the present day
310 (Table S2). The high levels of biogenic SOA tracers in the
311 preindustrial period relative to the present day were probably
312 caused by atmospheric transport and deposition of the tracers
313 to high latitudinal regions in the Northern Hemisphere during a
314 period when the lower latitudes were still thickly forested.
315 Anthropogenic emissions (of NO_x and sulfate in particular) are
316 known to play a strong role in enhancing biogenic SOA from
317 isoprene and to a lesser extent monoterpenes,^{55,56} but our
318 findings indicate other factors contribute substantially to the
319 total SOA at Ushkovsky. This is to be expected given the
320 myriad of factors that contribute to SOA formation, evolution,
321 and transport, and the highly complex and nonlinear nature of
322 atmospheric chemistry and SOA formation in particular. Short-
323 and long-term changes in climate and land cover alter biogenic
324 emissions from local source regions. Global development has
325 altered emission rates and concentrations of anthropogenic
326 pollutants. Natural variability in middle- to high-latitude
327 atmospheric dynamics and circulation patterns shifts the source

328 regions of transported species. Differences in temperature affect
329 the rates of the all the various processes involved to greater and
330 lesser extents. The extreme complexity of the dependencies and
331 relationships between these competing processes further
332 emphasizes the need for data sets such as the ice core records
333 presented here to constrain emissions and elucidate the
334 processes involved in chemical transformation and transport
335 over long time scales.

336 Biomass burning is one of the most important emission
337 sources of gases and particles into the atmosphere.^{57,58} Like
338 those of 2-methyltetrols and 2-MGA, relatively high concen-
339 trations of monoterpene SOA tracers were found at Ushkovsky
340 in 1949. In the same ice core, Kawamura et al.⁴ reported the
341 highest concentration (18.6 ng/g-ice) of levoglucosan, a
342 biomass-burning tracer,⁵⁹ in the year 1949. Interestingly, the
343 intensive biomass-burning episode in 1949 may have been
344 associated with the civil war that spread out all over
345 northeastern to central China in the period 1948–1949.
346 During the war fires, much land vegetation was burned in these
347 regions, generating massive amounts of smoke aerosols and
348 VOCs including isoprene,⁵⁸ which could have contributed to
349 the peak of biogenic SOA tracers in 1949. Recent smog
350 chamber experiments have demonstrated that nonmethane
351 organic gases from combustion sources are a major class of
352 SOA precursors.⁶⁰ Positive correlations were found between
353 levoglucosan and a few higher generation oxidation products
354 (e.g., 3-HGA and MBTCA) in the Ushkovsky ice core (Table
355 S4), suggesting that biomass-burning activities have had
356 sporadic influence in Northeast Asia, especially for mono-
357 terpene SOA tracers.

358 The ratios of PA and PNA (monoterpene SOA tracers) to 2-
359 MT (isoprene SOA tracers associated with low NO_x
360 conditions) are not significantly higher in the present day
361 samples (mean 2.7, median 1.7) than the preindustrial period
362 (mean 2.4, median 0.84; Table S2), in spite of increasing NO_x
363 concentrations in source regions. This indicates concomitant
364 changes in BVOC concentrations at the site and in source
365 regions, pointing to the complexity of disentangling the
366 contributory factors. BVOC emissions at high latitudes tend
367 to be dominated by monoterpenes due to plant species
368 distribution. Monoterpene SOA tracers would therefore be
369 expected to be more abundant relative to isoprene SOA tracers
370 during periods when air masses to the region originate in the
371 Arctic regions. The relatively high average ratio of (PNA +
372 PA)/2-MT (mean 3.8, median 1.2) found during the Little Ice
373 Age is therefore likely a reflection of air mass origin,^{15,37,61} in
374 keeping with the extremely cold conditions experienced in
375 Europe at this time.

376 The 20th century concentrations of isoprene SOA tracers in
377 the Ushkovsky ice core (mean 1060 ± 1120 pg/g-ice) are
378 substantially lower (although not significantly so, due to the
379 high fluctuations observed during both periods) than those of
380 the preindustrial period (mean 2390 ± 3260 pg/g-ice), whereas
381 concentrations of monoterpene SOA tracers show little
382 difference (Table S2). Given other indications that biogenic
383 SOA in this region is mostly derived from local sources, this
384 suggests a significant decrease in isoprene emissions at
385 Northern Hemisphere high latitudes, especially in East Asia.
386 This may be a result of the substantial rise in CO₂ levels
387 (elevated atmospheric concentrations of CO₂ have been shown
388 to directly inhibit isoprene emissions⁶²) coupled with land-use
389 change from broadleaf forests (high isoprene emitters) to
390 croplands (negligible isoprene emitters) since the industrial

391 revolution.³⁵ Model hindcasts show decreased annual global
392 isoprene emissions and increased monoterpene emissions from
393 the preindustrial era to the present day.⁶³

394 In addition to the factors outlined above, small-scale
395 meteorological, biochemical, and *in situ* glacial processes can
396 be expected to contribute to the large historical variations of
397 organics in the ice core. Local meteorological phenomena such
398 as land/sea breezes and orographic uplift will regulate local
399 transport of aerosol particles and their precursors to the
400 Ushkovsky ice cap, as observed at Mt. Fuji (3776 m a.s.l.).⁶⁴
401 Photochemical and biological aging of organic aerosols after
402 their deposition at the snow/glacier surfaces are also known to
403 modify ice core organics.^{3,65,66} Thus, organics recorded in ice
404 cores are a function of variations in external inputs of
405 atmospheric aerosols and potentially *in situ* processes such as
406 accumulation rates, summer melt events, and microbial
407 activities.⁷ However, the accumulation rates in the ice cores
408 do not significantly change over the studied periods compared
409 to the concentrations of biogenic SOA tracers.^{33,67} Seki et al.⁷
410 also stated that the TOC and biogenic primary organic tracers
411 in the same ice core samples do not significantly correlate with
412 measured melt events.⁶⁸ Thus, the concentrations of biogenic
413 SOA tracers in the Ushkovsky ice core are not significantly
414 biased by the accumulation rates and/or summer melt events.

415 The historical reconstruction of BVOC emissions and
416 biogenic SOA production is a highly complex and challenging
417 issue, regulated by many factors, including species distribution,
418 climate, the chemical composition of the atmosphere (e.g.,
419 concentrations of CO₂, NO_x, and O₃),^{42,69} and large-scale
420 atmospheric circulation. In addition, humans have altered the
421 Earth's environment with unprecedented intensity and speed
422 through land-use changes and anthropogenic emissions since
423 the industrial revolution. Given the multiplicity of factors
424 influencing SOA concentrations and properties, the substantial
425 uncertainties in current estimates of aerosol radiative forcing
426 and climate effect is unsurprising. Our ice core records provide
427 important information on biogenic SOA concentrations over
428 the past 300 years that will allow us to begin to disentangle the
429 causes of observed trends and fluctuations in atmospheric
430 aerosols and gain vital insights into the various processes
431 involved. These data are particularly useful for modelers to
432 evaluate the skill of current atmospheric chemistry and
433 transport and Earth system models to reproduce aerosol
434 concentrations under historical pristine conditions in the
435 Northern Hemisphere. The understanding gained from such
436 model-measurement comparisons will allow us to constrain
437 projections of future concentrations and hence the potential
438 influence of biogenic SOA on future climate change.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the
ACS Publications website at DOI: 10.1021/acs.estlett.6b00275.

Detailed methodology and four supplementary tables
(Table S1–S4). (PDF)

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Notes

The authors declare no competing financial interest.

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