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

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Supporting Information

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

INTRODUCTION

Palaeoclimate archives containing annual layers (e.g., ice cores, tree rings, speleothems, and coral reefs) have played a central role in reconstructing decadal-scale climatic oscillation of the past. This insight has proved an invaluable tool to constrain climate model projections of future climate change by validating model hindcasts. Similarly, analysis of particles preserved in ice cores provides an unprecedented opportunity to elucidate the distribution, concentration, size distribution, and even chemical composition of atmospheric aerosols in the past. Such data would allow us to deduce the influence of aerosol radiative forcing on past climate change. Previously, aerosol particles preserved in high altitudinal or high latitudinal ice cores have been examined for inorganic species (e.g., sulfate), black carbon, and organic species such as polycyclic aromatic hydrocarbons, carboxylic acids, biomass burning tracers, and humic-like substances. To date, little was known about the historical trends of secondary organic aerosols at a molecular level.

Here, we present the findings of the analysis of ice cores for evidence of organic compounds formed from biogenic trace gases. Terrestrial vegetation emits large quantities (∼1 Pg C y⁻¹) of biogenic volatile organic compounds (BVOCs), including reactive species such as isoprene and monoterpene, to the atmosphere. The role of their atmospheric reactions in governing the production and loss of tropospheric ozone is well studied and relatively well understood, but BVOC oxidation has also been shown to lead to aerosol formation. Organic particles formed by the photooxidation of BVOCs are considered “secondary” organic aerosols (SOA) and are believed to be more abundant than directly emitted “primary” organic aerosols (POA) in the Earth’s atmosphere. It is believed that SOA could be a significant source of new nanoscale particles, especially in pristine remote regions, that can grow into the accumulation mode and act as CCN, influencing local climate and radiative forcing. However, the uncertainties are substantial. Estimates of biogenic SOA production range from 9−910 Tg C y⁻¹ with a best estimate of 60−240 Tg C y⁻¹ and even a guess of 1,011,19−21. The radiative forcing effect of SOA has been estimated as −0.03 W m⁻² (−0.27 to +0.20 W m⁻²), but this is highly dependent on assumptions of the total atmospheric burden of SOA.

Given the ubiquity and influence of organic particles in the atmosphere, there is an urgent need to better understand and constrain the processes leading to the formation of SOA and to...
elucidate the role of aerosols in governing global and regional climate. Studies of production, transformation, and removal processes have been extensively conducted for ambient aerosols and simulated in laboratory conditions. Relationships between the phases of organic aerosols and their reactivity have been investigated. Model simulations have been performed to identify trends in SOA concentrations and distributions and to quantify modern and past SOA budgets. However, the uncertainties of such estimates are substantial, and better constraints are required.

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

## MATERIALS AND METHODS

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

**Bulk Analysis.** Each sample section was melted in a precleaned Pyrex beaker (2 L). The samples were poisoned with HgCl$_2$ to prevent potential microbial degradation of 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 (1997–1969); 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$_2$Cl$_2$/CH$_3$OH using an ultrasonic bath. The extracts were concentrated and passed through a glass column packed with quartz wool and further eluted with CH$_3$Cl$_2$ and CH$_2$OH 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$_2$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 C13 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. 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.

## 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
The data are strongly positively skewed (median 3750 pg/g-ice; 10th and 90th percentiles, 179 pg/g-ice and 6230 pg/g-ice, respectively) due to anomalously high concentrations in a handful of years during the preindustrial (1693−1790) and the 20th century (1908−1997) periods, notably 1768 and 1949. Concentrations of total organic carbon (Figure 2C) as well as those of individual tracers were lowest in the 19th century and, in particular, during the peak of the Little Ice Age in Europe (early mid 1800s), when temperatures were low throughout the biogenic source regions suppressing emissions.35,36 On the whole, there is a strong correlation between ice core SOA tracer concentrations and the Northern Hemisphere high-latitude temperature anomaly and a weak correlation with solar irradiance (Figure 2A−E). While concentrations of the individual tracers fit this general pattern, there are also notable differences, which are discussed later.

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

By contrast, 2-methylglyceric acid (2-MGA) is a C\textsubscript{4}-dihydroxycarboxylic acid that is formed via methacrylic acid epoxide (MAE) and has been identified as a key gas-phase intermediate resulting in isoprene SOA formation from the high-NO\textsubscript{x} pathway.40,41 In the preindustrial period, NO\textsubscript{x} emissions were limited to wildfires, soil denitrification, and lightning.42 The large rise in anthropogenic NO\textsubscript{x} emissions since the start of the industrial revolution43 have increased atmospheric NO\textsubscript{x} concentrations; yields of 2-MGA would have been expected to be more substantial in the present day than in the preindustrial period. However, 2-MGA was found to be less abundant than 2-MT in all core samples, varying from 0.03 to 0.86 (mean ratio of 2-MGA:2-MT ~ 0.13). The mean ratios of 2-MGA/2-MT showed only negligible differences between the present (0.13) and the preindustrial period (0.15) but were slightly lower in the early-to-middle 1800s (~0.08). These results suggest that the low-NO\textsubscript{x} pathway via IEPOX39,41,44−46 has dominated isoprene photooxidation at the high latitudes in the Northern Hemisphere throughout the past three centuries.

Monoterpene SOA Tracers. We detected four monoterpene oxidation products in the ice core samples: 3-hydroxyglutaric acid (3-HGA), pinonic acid, pinic acid, and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). Pinic and pinonic acids (PA and PNA) are first-generation products formed from the oxidation of α- and β-pinene, the most abundant monoterpenes, by hydroxyl radical (OH), O\textsubscript{3}, or...
nitrate radical (NO₃)\(^{11,47}\). 3-HGA and MBTCA are higher-generation products.\(^{1,15}\) On a global scale, the majority of monoterpene SOA is believed to be formed from initialization reactions involving ozone rather than OH or NO₃ radicals,\(^{48–50}\) although NO₃ chemistry is an important source at night and in some regions, links between yields and atmospheric NOₓ concentrations are less clear than for isoprene SOA. Total concentrations of these tracers range from 24 to 12,000 pg/g-ice (mean 1780; median 10th and 90th percentiles, 788, 73.2, and 418 pg/g-ice, respectively) with pinic acid dominating (Table S2). Concentrations of PA (mean 932, median 409 pg/g-ice) are double those (mean 482, median 281 pg/g-ice) of PNA, consistent with laboratory-reported relative yields of the two species.\(^{48}\) 3-HGA and MBTCA are less abundant than PA and PNA with a median ratio of (3-HGA + MBTCA):(PA + PNA) of 0.09 (mean 0.15). The ratios (Figure 2F) were significantly lower during the Little Ice Age (~0.03) than in the preindustrial period (0.16), reflecting the trends seen in total organic carbon (TOC) concentrations (Figure 2C). The average ratio (0.18) for the last 100 years is higher (Table S2), and while not significantly different from preindustrial levels, appears to show an increasing trend (Figure 2F).

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

### DISCUSSION

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

The general trends of isoprene and monoterpene SOA tracers in the Ushkovsky ice core agree with climate records such as mean annual temperature records from China and the warm season temperature from Northern Siberia\(^{31}\) (Figure 2E). As would be expected given the exponential temperature dependence of biogenic emissions on temperature, concentrations of biogenic SOA tracers and TOC were low during the Little Ice Age. Our ice core records of monoterpene SOA tracers significantly correlate with historical temperatures in proximal regions climate records including Chinese and Northern Siberian temperatures (r = 0.63 to 0.40, p < 0.01) (Table S3). However, isoprene SOA tracers showed relatively weak correlations with mean annual temperature in China and Siberia (r = 0.54 to 0.35, p < 0.01). Relatively higher correlations of the ice core SOA tracers with the Chinese temperatures (r = 0.63 to 0.47, p < 0.01) than those with summer temperatures in Northern Siberia (r = 0.59 to 0.35, p < 0.01) suggest a strong empirical relationship between the ice core records of biogenic SOA and midlatitude climate. However, the historical temperature change in this region (~1°C) is too small to account fully for the large variations of biogenic SOA tracers observed in the ice core samples during the past 300 years.

The SOA tracers generally show very little correlation with solar irradiance (r = 0.25 to 0.32, p < 0.05 for isoprene tracers, PA and PNA), although the higher generation monoterpene tracers (3-HGA and MBTCA) may be weakly influenced (r = 0.42 to 0.45, p < 0.01). Although isoprene emissions are strongly light dependent, those of most monoterpens are driven only by temperature,\(^{54,56}\) and it is likely that the correlations seen are driven by the effect of solar irradiance on subsequent photochemistry combined with relationships between solar irradiance and surface temperature. The effect of changes in solar forcing on surface temperature is highly uncertain and also highly localized,\(^{53}\) making it hard to draw firm conclusions on causality.

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

Biogenic isoprene SOA tracers at the beginning of the 18th century were more abundant than those of the present day (Table S2). The high levels of biogenic SOA tracers in the preindustrial period relative to the present day were probably caused by atmospheric transport and deposition of the tracers to high latitudinal regions in the Northern Hemisphere during a period when the lower latitudes were still thickly forested. Anthropogenic emissions (of NOₓ and sulfate in particular) are known to play a strong role in enhancing biogenic SOA from isoprene and to a lesser extent monoterpens,\(^{55,56}\) but our findings indicate other factors contribute substantially to the total SOA at Ushkovsky. This is to be expected given the myriad of factors that contribute to SOA formation, evolution, and transport, and the highly complex and nonlinear nature of atmospheric chemistry and SOA formation in particular. Short- and long-term changes in climate and land cover alter biogenic emissions from local source regions. Global development has altered emission rates and concentrations of anthropogenic pollutants. Natural variability in middle- to high-latitude atmospheric dynamics and circulation patterns shifts the source
regions of transported species. Differences in temperature affect the rates of all the various processes involved to greater and lesser extents. The extreme complexity of the dependencies and relationships between these competing processes further emphasizes the need for data sets such as the ice core records presented here to constrain emissions and elucidate the processes involved in chemical transformation and transport over long time scales.

Biomass burning is one of the most important emission sources of gases and particles into the atmosphere. Like those of 2-methyltetrols and 2-MGA, relatively high concentrations of monoterpene SOA tracers were found at Ushkovsky in 1949. In the same ice core, Kawamura et al. reported the highest concentration (18.6 ng/g-ice) of levoglucosan, a biomass-burning tracer, in the year 1949. Interestingly, the intensive biomass-burning episode in 1949 may have been associated with the civil war that spread out all over northeastern to central China in the period 1948–1949. During the war fires, much land vegetation was burned in these regions, generating massive amounts of smoke aerosols and VOCs including isoprene, which could have contributed to the peak of biogenic SOA tracers in 1949. Recent smog chamber experiments have demonstrated that nonmethane organic gases from combustion sources are a major class of SOA precursors. Positive correlations were found between levoglucosan and a few higher generation oxidation products (e.g., 3-HGA and MBTCA) in the Ushkovsky ice core (Table S4), suggesting that biomass-burning activities have had sporadic influence in Northeast Asia, especially for monoterpene SOA tracers. The ratios of PA and PNA (monoterpene SOA tracers) to 2-MT (isoprene SOA tracers associated with low NOx conditions) are not significantly higher in the present day samples (mean 2.7, median 1.7) than the preindustrial period (mean 2.4, median 0.84; Table S2), in spite of increasing NOx concentrations in source regions. This indicates concomitant changes in BVOC concentrations at the site and in source regions, pointing to the complexity of disentangling the contributory factors. BVOC emissions at high latitudes tend to be dominated by monoterpenes due to plant species distribution. Monoterpene SOA tracers would therefore be expected to be more abundant relative to isoprene SOA tracers during periods when air masses to the region originate in the Arctic regions. The relatively high average ratio of (PA + PA)/2-MT (mean 3.8, median 1.2) found during the Little Ice Age is therefore likely a reflection of air mass origin, in keeping with the extremely cold conditions experienced in Europe at this time.

The 20th century concentrations of isoprene SOA tracers in the Ushkovsky ice core (mean 1060 ± 1120 pg/g-ice) are substantially lower (although not significantly so, due to the high fluctuations observed during both periods) than those of the preindustrial period (mean 2390 ± 3260 pg/g-ice), whereas concentrations of monoterpene SOA tracers show little difference (Table S2). Given other indications that biogenic SOA in this region is mostly derived from local sources, this suggests a significant decrease in isoprene emissions at Northern Hemisphere high latitudes, especially in East Asia. This may be a result of the substantial rise in CO2 levels (elevated atmospheric concentrations of CO2 have been shown to directly inhibit isoprene emissions) coupled with land-use change from broadleaf forests (high isoprene emitters) to croplands (negligible isoprene emitters) since the industrial revolution. Model hindcasts show decreased annual global isoprene emissions and increased monoterpene emissions from the preindustrial era to the present day.

In addition to the factors outlined above, small-scale meteorological, biochemical, and in situ glacial processes can be expected to contribute to the large historical variations of organics in the ice core. Local meteorological phenomena such as land/sea breezes and orographic uplift will regulate local transport of aerosol particles and their precursors to the Ushkovsky ice cap, as observed at Mt. Fuji (3776 m a.s.l.). Photochemical and biological aging of organic aerosols after their deposition at the snow/glacier surfaces are also known to modify ice core organics. Thus, organics recorded in ice cores are a function of variations in external inputs of atmospheric aerosols and potentially in situ processes such as accumulation rates, summer melt events, and microbial activities. However, the accumulation rates in the ice cores do not significantly change over the studied periods compared to the concentrations of biogenic SOA tracers. Seki et al. also stated that the TOC and biogenic primary organic tracers in the same ice core samples do not significantly correlate with measured melt events. Thus, the concentrations of biogenic SOA tracers in the Ushkovsky ice core are not significantly biased by the accumulation rates and/or summer melting events.

The historical reconstruction of BVOC emissions and biogenic SOA production is a highly complex and challenging issue, regulated by many factors, including species distribution, climate, the chemical composition of the atmosphere (e.g., concentrations of CO2, NOx, and O3), and large-scale atmospheric circulation. In addition, humans have altered the Earth’s environment with unprecedented intensity and speed through land-use changes and anthropogenic emissions since the industrial revolution. Given the multiplicity of factors influencing SOA concentrations and properties, the substantial uncertainties in current estimates of aerosol radiative forcing and climate effect is unsurprising. Our ice core records provide important information on biogenic SOA concentrations over the past 300 years that will allow us to begin to disentangle the causes of observed trends and fluctuations in atmospheric aerosols and gain vital insights into the various processes involved. These data are particularly useful for modelers to evaluate the skill of current atmospheric chemistry and transport and Earth system models to reproduce aerosol concentrations under historical pristine conditions in the Northern Hemisphere. The understanding gained from such model-measurement comparisons will allow us to constrain projections of future concentrations and hence the potential 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, four supplementary tables (Table S1–S4) and two supplementary figures (Figure S1–S2).

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