Photochemical aging of aerosols contributes significantly to the production of atmospheric formic acid

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Abstract

Formic acid (HCOOH) is one of the most abundant organic acids in the atmosphere and affects atmospheric acidity and aqueous chemistry. However, the formation mechanisms of HCOOH remain poorly understood, and current air-quality models largely underestimate observed atmospheric concentrations of HCOOH. In particular, HCOOH production from condensed-phase or heterogeneous reactions is not considered in current models. In a recent field study, we measured atmospheric HCOOH concentrations at a coastal site in South China. The average concentrations of HCOOH were 191.1 ± 167.2 ppt in marine air masses and 996.3 ± 432.9 ppt in coastal air masses. A strong linear correlation between HCOOH concentrations and the surface area densities of submicron particulate matter was observed in coastal air masses. Post-campaign laboratory experiments confirmed that the photochemical aging of ambient aerosols promoted by heterogeneous reactions with ozone produced a high concentration of HCOOH at a rate of 0.185 ppb h⁻¹ under typical ambient conditions at noon time. HCOOH production was strongly affected by nitrate photolysis, as this efficiently produces OH radicals that oxidise organics to form HCOOH. We incorporated this particle-phase source into a photochemical model and found that it explained 81% of the peak concentration of ambient HCOOH and reproduced the diurnal variation in HCOOH concentrations. These findings demonstrate that the photochemical aging of aerosols is an important source of HCOOH that must be included in atmospheric chemistry-transport models.
1. Introduction

Organic acids are ubiquitous in the troposphere and constitute a significant fraction of the total organics in both the gas and particle phases (Chebbi & Carlier, 1996). They also participate in the aqueous-phase chemistry of clouds, contribute to secondary organic aerosol (SOA) formation through reactions within the condensed phase (Carlton et al., 2007; Ervens et al., 2004; Lim et al., 2010), and are proposed to enhance the formation of new particles in the atmosphere (Zhang et al., 2004). Formic acid (HCOOH) is among the most abundant organic acids in the atmosphere (Khare et al., 1999) and accounts for over 60% of the free acidity in precipitation in remote areas and more than 30% of that in polluted areas (Andreae et al., 1988; Keene et al., 1983; Keene & Galloway, 1988; Khare et al., 1999; Stavrakou et al., 2012). This contribution is increasingly important due to the decline in the concentrations of anthropogenic nitrogen oxides (NO\textsubscript{x}) and sulfur dioxide. HCOOH serves as a significant sink of in-cloud hydroxyl radicals (·OH) and stabilised Criegee intermediates (SCIs) (Jacob, 1986), and thus influences aqueous-phase chemistry by affecting pH-dependent reaction rates, oxidant concentrations, and solubilities (Vet et al., 2014). HCOOH also plays a role in the formation of cloud condensation nuclei (Yu, 2000), due to its comparatively higher hygroscopicity at low critical supersaturations when incorporated into aerosols (Novakov & Penner, 1993). This, in turn, affects total indirect radiative forcing. Additionally, HCOOH may be involved in halogen chemistry through its heterogeneous reaction with solid sodium chloride in sea-salt aerosols (Xia et al., 2018).

Considering the abovementioned roles of HCOOH in atmospheric chemistry, it is essential to understand its sources and sinks. However, the budget of HCOOH is currently poorly quantified, with state-of-the-art chemistry-transport models significantly underestimating field-observed concentrations of HCOOH (Baboukas et al., 2000; Bannan et al., 2017; Chaliyakunnel et al., 2016; Le Breton et al., 2012; Millet et al., 2015; Yuan et al., 2015). HCOOH is primarily removed from the atmosphere through wet and dry deposition, with a minor sink of being photo-oxidation by ·OH (Atkinson et al., 2006). The main sources of HCOOH include direct emissions from terrestrial vegetation (Andreae et al., 1988), biomass and biofuel burning (Akagi et al., 2011; Goode et al., 2000; Yokelson et al., 2009), fossil-fuel combustion (Kawamura et al., 2000; Zervas et al., 2001b, 2001a) and soil emissions (Sanhueza & Andreae, 1991). Moreover, secondary formation from the oxidation of volatile organic compounds (VOCs) is considered the major source of HCOOH at the global scale (Paulot et al., 2011). Despite the inclusion in models of various gas-phase mechanisms of HCOOH formation, such as ozonolysis of terminal alkenes (Neeb et al., 1997), alkyn oxidation (Bohn et al., 1996), OH-initiated isoprene oxidation (Paulot et al., 2009), monoterpane oxidation (Larsen et al., 2001), keto-enol tautomerisation (Andrews et al., 2012; Shaw et al., 2018) and ·OH oxidation of methylldioxy radicals (CH3O2·) (Bossolasco et al., 2014), HCOOH
concentrations remain significantly underestimated (Millet et al., 2015; Yuan et al., 2015), indicating that a substantial missing source of HCOOH remains unidentified.

Current models do not consider HCOOH production from heterogeneous or condensed-phase reactions, but these could be an important source of HCOOH. Aqueous reactions of formaldehyde (HCHO) (Chameides & Davis, 1983; Jacob, 1986), glyoxal (Carlton et al., 2007), and other species with ·OH (aq) can produce HCOOH, particularly in moderately acidic environments (Jacob, 1986). A multiphase cloud-processing pathway involving methanediol oxidation was proposed that reconciles model predictions with measured concentrations of HCOOH (Franco et al., 2021). Moreover, Gao et al. (2022) recently proposed a new bidirectional deposition-emission process, whereby HCOOH deposits rapidly in night-time dew and is re-emitted from the dew as it evaporates on the following day. They found that this process explained most of the concentrations of HCOOH that they observed. Laboratory chamber studies have demonstrated that the photochemical aging of organic aerosols can also produce HCOOH (Henry & Donahue, 2012; Malecha & Nizkorodov, 2016; Mang et al., 2008; Pan et al., 2009; Walser et al., 2007; Zhang et al., 2021), but the importance of this process as a source of atmospheric HCOOH has not been quantified, and this source is not considered in current models.

The photochemical aging of aerosols occurs through the reactive uptake of oxidants onto particle surfaces, altering their chemical compositions and physical properties (George et al., 2015). In the condensed organic phase, this aging process can produce volatile compounds, such as HCOOH, through the photodegradation of SOA (Henry & Donahue, 2012; Malecha & Nizkorodov, 2016). Furthermore, the photolysis of particulate nitrate (NO₃⁻) produces oxidants such as ·OH, nitrogen dioxide (NO₂), and nitrite ions/nitrous acid (HONO), which efficiently oxidise glyoxal to HCOOH (Zhang et al., 2021). Paulot et al. (2011) observed a marked positive correlation between HCOOH concentrations and submicron organic aerosol masses in three coastal, urban, and polar regions, and suggested that aerosol aging produces HCOOH. However, another field and model study estimated that this aging process makes only a minor (<5%) contribution to concentrations of HCOOH, although large uncertainties in the result were noted (Yuan et al., 2015). Overall, the aforementioned results show that there is a need for the determination of improved constraints on HCOOH production from the photochemical aging of aerosols, as this will enable assessment of the significance of this process as a source of HCOOH in comparison with other sources.

In this study, we measured HCOOH concentrations at near-ground level at a coastal site in Hong Kong, China, for 2 months during autumn 2021. We examined the characteristics of HCOOH concentrations and their correlation with related species’ concentrations or other parameters. We showed that the use of current gas-phase mechanisms in a photochemical box model underpredicted the observed concentrations of HCOOH at our site. We then conducted a chamber study to measure the rate of HCOOH production during the aging of ambient aerosols.
aerosols and extrapolated the results to the real atmosphere. We incorporated this HCOOH-formation mechanism into a model using a parameterisation involving fine particulate matter concentration, surface area density, light intensity, and ozone (O3) concentration, and then performed simulations to evaluate the contribution made by the photochemical aging of aerosols to HCOOH production. Furthermore, we showed that NO3− photolysis acted as a crucial source of ·OH during the aging process. Our results enhance the understanding of HCOOH sources and model simulations of ambient HCOOH concentrations.

2. Methods

2.1. Field observations

Ambient measurements of the atmospheric concentrations of HCOOH and related species/parameters were conducted from 13 August to 31 October 2021 at the Hong Kong Environmental Protection Department’s Cape D’Aguilar Super Site (CDSS; 22.21°N, 114.25°E), which is situated a few hundred meters away from the nearest coastline of the South China Sea (Fig. S1). During the study period, this coastal site was initially predominantly influenced by marine air masses and subsequently by coastal air masses. The site was also affected by biogenic emissions (from deciduous and evergreen trees) and ship emissions (from ships in nearby waters). There were no other significant anthropogenic sources nearby.

The species quantified were HCOOH, HONO, trace gases (nitric oxide, NO2, carbon monoxide (CO), sulfur dioxide (SO2), and O3), volatile organic compounds (VOCs), oxygenated VOCs, aerosol mass concentrations (1-µm particulate matter (PM1), PM2.5, and PM10 concentrations), aerosol size distributions, aerosol ionic compositions, NO2 photolysis frequency (j(NO2)), and meteorological parameters (temperature (T), relative humidity (RH), wind direction, and wind speed). A detailed description of the measurement of HCOOH concentration is provided below, and information on other measurements is summarised in Table S1.

The concentration of HCOOH was measured at 172.91 atomic mass unit (amu) using an iodide-adduct time-of-flight chemical ionisation mass spectrometer (I-TOF-CIMS, Aerodyne Research), as we used in our previous study at the same site (M. Xia et al., 2022). A comprehensive description of the use of the I-TOF-CIMS can be found in previous studies (Aljawhary et al., 2013; Lee et al., 2014). Briefly, humidified iodomethane-containing N2 air was passed through an inline ioniser (containing polonium-210) to generate iodide ions (I−) and iodide–water ions, which served as the reagent ions, and the HCOOH produced was detected as IHCOOH. The background concentration of HCOOH was determined every 2 days by injecting zero air and was found to be 60.9 ppt. HCOOH calibration was performed three times on-site and once in the laboratory immediately following the field campaign using diluted gas standards generated by a permeation tube (KIN-TEK) with a permeation rate of 90.87 ng min−1.
HCOOH sensitivity varies with RH as water competes with HCOOH for I\(^{-}\) (Lee et al., 2014). Thus, the HCOOH sensitivity was measured at various RHs, as shown in Fig. S2. The sensitivity remained stable at a given RH, with a variation of less than 5\% throughout the campaign.

The ToF-CIMS was housed in an air-conditioned shelter at an indoor air T maintained at 25–28\(^\circ\)C. The shelter was located approximately 15 m away from the CDSS station. The sampling tube was a 0.5-m long perfluoroalkoxy-Teflon tube (1/2 in. outer diameter), the inlet of which was situated on the sidewall of the shelter, 1.5 m above the ground. To achieve laminar flow in the sampling tube, a flow rate of 25 Lpm was adopted, with a residence time of 0.1 s. The ToF-CIMS drew ~2 Lpm sample air, and the remaining airflow was discarded. The sampling tube was replaced with a new tube every 2 days to reduce inlet artifacts. We investigated possible inlet artifacts by injecting known concentrations of HCOOH into a used sampling inlet and found that the artifacts had a negligible effect on the measured HCOOH concentration (difference < 3\%). The remaining instruments were housed in the CDSS station, with their sampling inlets located ~1.5 m above the roof.

2.2. Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) and Extended Aerosol Inorganic Model IV (E-AIM IV) models

Hourly 24-h backward trajectories were obtained using the HYSPLIT model (https://www.ready.noaa.gov/hypub-bin/trasrc.pl). The input parameters were Global Data Assimilation System 1\(^{\circ}\) for the meteorology data; 22.21\(^{\circ}\)N and 114.25\(^{\circ}\)E for the location; and 100 m for the endpoint height, which is slightly higher than the site’s altitude. Air masses were classified as marine or coastal, based on their source regions. A unique period was identified as a haze period, during which there was a transition from marine air masses to coastal air masses under stagnant conditions (wind speed < 3 m s\(^{-1}\)). A detailed classification can be found in Fig. S3.

The aerosol water content (AWC) and pH were predicted by the E-AIM IV online in batch mode (http://www.aim.env.uea.ac.uk/aim/model4/model4d.php). The thermodynamic model was constrained by hourly field-measured molar concentrations of NH\(_{4}\)^{+}, sodium ions (Na\(^{+}\)), sulfate ions (SO\(_{4}\)\(^{2-}\)), NO\(_{3}\)^{−}, and chloride ions (Cl\(^{-}\)) in PM\(_{2.5}\); gas-phase ammonia concentrations; ambient T; and RH. Initial concentrations of protons (H\(^{+}\)) and hydroxide ions were estimated based on the ion balance of the major water-soluble ions. The input of Na\(^{+}\) into the model (Na\(^{+}\)\(_{\text{eq}}\)) was calculated as a sum of the equivalent concentrations of Na\(^{+}\), potassium ions, magnesium ions, and calcium ions (Eq. (1)). The model also considered water dissociation and allowed all possible solids to form in the system. Parameters p, q, r, and s (options in batch mode) were set to 3, meaning that the input portions of ammonium (NH\(_{4}\)^{+}), NO\(_{3}\)^{−}, SO\(_{4}\)\(^{2-}\), and Cl\(^{-}\) always remained in the condensed phase and did not produce corresponding gas-phase species, such as nitric acid (HNO\(_{3}\)) and hydrochloric acid. The aqueous-phase NO\(_{3}\)^{−} concentration was calculated by dividing the AWC by the moles of aqueous NO\(_{3}\)^{−}. Aerosol pH
was calculated as the negative logarithm of the concentration of H⁺.

\[ [Na^+]_{eq} = [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] \]  

(1)

2.3. Chemical box model

The Framework for 0-D Atmospheric Modeling (F0AM version 4.2.1) (Wolfe et al., 2016) coupled with Master Chemical Mechanism (MCM v3.3.1, http://mcm.york.ac.uk) (Jenkin et al., 2015) was employed to investigate the formation of HCOOH at the field site. We followed Yuan et al. (2015) by enhancing the simulation of the secondary formation of HCOOH by modifying the HCOOH yields obtained by the ozonolysis of alkenes and other unsaturated species, and by adding chemical processes (vinyl alcohol oxidation; photo-tautomerisation of vinyl alcohol; and the reactions of HCHO + HO₂ and CH₃O₂⁻ + ·OH) to the MCM. A single typical episode day, 28 September 2021, was selected as an example to run the model, as the critical model-input data were available on this day. The measured concentrations of O₃, NOₓ, CO, SO₂, HONO, VOCs, and OVOCs were averaged or interpolated to 5-min resolution and constrained in the model. We also run the model using hourly averaged data of another typical day in coastal air masses, 28 October 2021, and diurnal variations during the whole campaign. The methane concentration was assumed to remain constant (2000 ppb; Peng et al., 2022), due to a lack of measurement data. The dilution process was treated as a first-order loss with a dilution loss rate coefficient of 1/86,400 s⁻¹, consistent with previous studies (Li et al., 2014; Yuan et al., 2015). The dry deposition rate was determined based on the deposition velocity and the boundary layer height (BLH). For HCOOH, a deposition velocity of 1 cm s⁻¹ was employed (Müller et al., 2018). A sensitivity analysis of the deposition velocity was also conducted. The diurnal profile of BLH was acquired from a previous study at another coastal site in Hong Kong (Su et al., 2017). Wet deposition was not considered as there was no rainfall on 28 September 2021. The model was executed for three replicates to stabilise the intermediate species it generated, and the results from the final run were used for further analysis. Primary emissions and transportation from other regions were not considered in the box model; thus, the production rate of HCOOH was utilised to evaluate the significance of various chemical pathways.

2.4. Laboratory experiments

We illuminated ambient aerosols collected on filters or aqueous solutions in a dynamic chamber to mimic HCOOH formation in the atmosphere. The overall experimental setup is illustrated in Fig. S4. The dynamic chamber has a dimension of 25-cm length × 15-cm width × 4-cm height with the top side sealed by a transparent Teflon film. Each aerosol filter or solution sample was placed in a quartz Petri dish (inner diameter: 35 mm, inner height: 7 mm) at the chamber’s centre. Aerosol filter sampling details can be found in Text S1. A high-pressure xenon (Xe) lamp was used to simulate sunlight and its spectral irradiance is displayed in Fig. 6d. Compared with standard air mass 1.5 solar irradiation (AM 1.5) corresponding to a solar zenith angle of 48.2°, the Xe lamp exhibited a smaller flux at 300–326 nm but a larger flux at
326–420 nm. An air stream from a zero-air generator (Environics, model 7000) served as the carrier gas that delivered reaction products to the chamber’s outflow. The weather conditions that prevailed during the field campaign were mimicked by maintaining the reactor’s T at approximately 28 °C and adjusting the RH in the chamber to 70% by passing the carrier gas through a water bubbler. Prior to the introduction of a sample into the chamber, the background HCOOH concentration was monitored for 10 min with the light on and zero air added. After 1 h of irradiation, 100 ppb of O3 was introduced via a dynamic calibrator (Environics® Series 6100) and monitored using an O3 analyser (Thermo Scientific Model 49i). An AM 1.5 filter (which removes light below 360 nm) and a 300–800 nm filter (which allows the passage of 300-800 nm light) were applied to the Xe lamp to investigate the effect of the irradiation wavelength on the formation of HCOOH.

A sample solution was prepared by mixing formaldehyde (HCHO, Sigma-Aldrich, 37 wt% in water) and sodium nitrate (NaNO3, Honeywell, 99.5% purity). The resulting solution contained 0.15 wt% HCHO and 0.2 M NaNO3, and was adjusted to pH 2.7 by the addition of sulfuric acid (H2SO4, Sigma-Aldrich, 98% purity), as this was the E-AIM model’s prediction of the average aerosol acidity during the entire campaign. We assumed that ·OH produced by NO3– photolysis was the rate-limiting species and HCHO was taken as an example of one of the possible precursors of HCOOH.

The average rate of production (ppb·s⁻¹) of HCOOH (P_HCOOH) during the 1-h irradiation was calculated by the following equation (Eq. (2)), derived from (Peng et al., 2022):

\[
P_{\text{HCOOH}} = \frac{\int_0^{60} (C_{\text{HCOOH}} - C_{\text{HCOOH-bkg}}) \, dt \times \frac{Q}{V}}{60}
\]  

(2)

where Q is the carrier gas flow rate (4 L min⁻¹); V is the reactor chamber volume (1.875 L); and \( C_{\text{HCOOH}} \) and \( C_{\text{HCOOH-bkg}} \) (ppb) are the concentrations of HCOOH in the chamber after and before adding the sample, respectively. The photolytic loss of HCOOH was ignored, as the cross-section of HCOOH was beyond the spectral range of the Xe lamp (Burkholder et al., 2020).

We attempted to extrapolate the laboratory results to account for the field-observed concentrations of HCOOH. As photochemical aging occurs on aerosol surfaces and a strong correlation between the surface area (Sa) and the concentration of HCOOH observed in the field, the extrapolation was conducted based on Sa. The Sa in the chamber was calculated as the Sa of the filter divided by the chamber’s volume, assuming that only the first layer of the aerosols was illuminated. Although this might have resulted in an underestimation of the Sa density in the chamber, this assumption was reasonable, because particles in the lower layers would receive less light than those in the uppermost layer due to the light-screening effect of the first layer (Ye et al., 2017). The aging process was also influenced by light intensity, and as we discovered that the major oxidant was generated by the photolysis of particulate NO3⁻ (See Results, section 3), the light intensity was normalised based on the photolytic frequency of
aqueous NO$_3^-$ ($J_{\text{NO}_3\text{(aq)}}$) due to the absence of an absorption coefficient for particulate NO$_3^-$. Although there is a redshift of the particulate NO$_3^-$ absorption wavelength compared with the aqueous-phase NO$_3^-$ absorption wavelength, our results should be reliable because we used $J_{\text{NO}_3\text{(aq)}}$ as a reference for normalisation rather than for calculating an accurate $J_{\text{NO}_3\text{(aq)}}$ (Du & Zhu, 2011; Zhu et al., 2008). The $J_{\text{NO}_3\text{(aq)}}$ under the Xe lamp was $8.85 \times 10^{-6}$ s$^{-1}$ and the daytime average $J_{\text{NO}_3\text{(aq)}}$ in the ambient air at our site was $1.12 \times 10^{-5}$ s$^{-1}$ (Text S3). Both $J_{\text{NO}_3\text{(aq)}}$ values were calculated assuming a quantum yield equal to 1. The normalised HCOOH production rate in the ambient air ($P_{\text{HCOOH-amb}}$) was calculated using the following equation (Eq (3)):

$$P_{\text{HCOOH-amb}} = P_{\text{HCOOH}} \times \frac{S_{\text{amb}}}{S_{\text{cha}}} \times 1.266 \quad (3)$$

where $S_{\text{amb}}$ represents the field-measured Sa density; $S_{\text{cha}}$ denotes the Sa density calculated for the chamber; and 1.266 is the ratio of the ambient $J_{\text{NO}_3\text{(aq)}}$ to the chamber $J_{\text{NO}_3\text{(aq)}}$. For the aging process involving O$_3$, the photolytic rate constant of O$_3$ generating O$_1D$ ($J_{\text{O}_3\text{--O}_1D}$) in the chamber ($1.31 \times 10^{-5}$ s$^{-1}$) was also normalised to the average daytime $J_{\text{O}_3\text{--O}_1D}$ ($1.84 \times 10^{-5}$ s$^{-1}$) under ambient conditions (Text S3). For the results of the aqueous solution, the concentrations of HCHO and NO$_3^-$ were also normalised.

3. Results and Discussion

3.1. Field measurements of HCOOH concentrations

The field site was exposed to two distinct types of air masses; initially, it was largely exposed to marine air masses, and later to coastal air masses. Marine air masses ($T = 29.4 \pm 2.0 \, ^\circ\text{C}$, RH = 85.8 $\pm$ 7.0 %) were warmer and more humid than coastal air masses ($T = 25.7 \pm 2.3 \, ^\circ\text{C}$, RH = 77.0 $\pm$ 6.0 %), and exhibited low concentrations of O$_3$ (15.0 $\pm$ 8.9 ppb) and high concentrations of NO$_x$ (6.2 $\pm$ 4.5 ppb). Conversely, coastal air masses were characterised by high concentrations of O$_3$ (53.6 $\pm$ 14.2 ppb) and low concentrations of NO$_x$ (1.9 $\pm$ 1.6 ppb). The high concentrations of NO$_3^-$ in the marine air masses are attributable to the emissions from ocean-going container ships that passed the site approximately 8 km to the south. A haze event occurred from 24 September to 2 October, due to a transition from marine to coastal air masses under stagnant conditions. O$_3$ concentrations steadily increased during the first 5 days, peaked on 29 September, and remained high until the end of the haze period (Fig. 1). Therefore, the potential HCOOH formation mechanism was analysed separately for these three distinct periods.

Ambient HCOOH concentrations significantly varied during the three periods. The average HCOOH concentration in marine air masses was 191.1 $\pm$ 167.2 ppt; this was higher than those over the remote ocean, due to local emission sources, but significantly lower than those in urban environments (Table 1). In contrast, the ambient HCOOH concentrations in coastal air...
masses were substantially higher, averaging 996.3 ± 432.9 ppt, comparable with other measurements at rural or urban background sites. During the haze period, the concentrations of HCOOH displayed a pattern similar to the concentrations of O₃, with the daytime peak concentration increasing from 673.5 to 2789.9 ppt. A pronounced diurnal variation in the concentration of HCOOH was observed throughout the entire campaign, as illustrated in Fig. 2, consistent with other studies (Millet et al., 2015; Yuan et al., 2015). HCOOH concentrations rapidly increased after sunrise, peaking at approximately 1 pm (local time), and then quickly decreasing in the late afternoon, due to the weaker sunlight and lower BLH than earlier in the day.

HCOOH is widely recognised as a secondary photochemical product. Table 2 presents the Pearson correlation coefficients between the concentration of HCOOH and those of other air pollutants or other meteorological parameters during the three distinct periods. The concentration of HNO₃ was strongly correlated with the concentration of HCOOH throughout the entire field campaign, consistent with other studies (Bannan et al., 2017; Millet et al., 2015). This finding suggests that HCOOH is predominantly generated through secondary photochemical mechanisms at this site, as HNO₃ is a secondary photochemical product resulting from the reaction between ·OH and NO₂. The positive linear relationship between the concentrations of O₃ and HCOOH also implies the secondary source of HCOOH.

A previous laboratory study revealed that HCOOH can be produced by the photochemical aging of aerosols (Malecha & Nizkorodov, 2016), which may be an important process in ambient air. In the coastal air masses and haze period, there was a strong correlation between the concentrations of HCOOH and PM, particularly between the concentrations of HCOOH and PM₁. This was also observed by Paulot et al. (2011) and suggests that HCOOH may be produced from PM. The Sa of PM₁ was also highly correlated with the concentration of HCOOH in both coastal air masses and haze periods, indicating that HCOOH is mainly produced from reactions on aerosol surfaces. However, in the marine air masses, the concentration of HCOOH was not related to aerosols due to the low particle concentrations in such masses. To further explore the potential role of aerosol aging in HCOOH production, we plotted the correlation of HCOOH concentrations with Sa × O₃, Sa × NO₃⁻, and Sa × O₃ × NO₃⁻ for the coastal air masses (Fig. 3). We discovered that the correlation coefficient significantly increased when Sa was combined with the concentration of O₃ or NO₃⁻ or with the concentrations of both species, compared with these three factors being considered separately. This finding suggests that the HCOOH observed in the coastal air masses was not predominantly derived from gas-phase O₃ oxidation of VOCs; rather, it was derived from heterogeneous or condensed-phase reactions on aerosol surfaces. The results during the haze period were similar. Therefore, photochemical aerosol aging may play a key role in HCOOH production as the aging process involves the reactive uptake of oxidants onto particle surfaces.
3.2. Box model simulation

A box model was utilized to evaluate the formation mechanisms of HCOOH using the measurement data from a typical haze day (28 September 2021). The peak HCOOH concentration on that day was approximately 2 ppb, and occurred at approximately 3:30 pm. The base model, incorporating only the default mechanism of MCM v3.3.1, significantly underestimated the HCOOH concentration: the highest simulated concentration was 0.256 ppb, representing only 14.5% of the observed value. We made modifications to the formation mechanisms following Yuan et al. (2015) and these resulted in the simulated peak daytime concentration increasing to 0.363 ppb, accounting for 20.1% of the observed value (Fig. 4). Therefore, an additional HCOOH formation mechanism is required to account for the difference between the measured and simulated values.

A comprehensive analysis of HCOOH sources and sinks was conducted for both the base and modified cases (Fig. 5a & 5b). The reaction of CH$_2$OO Criegee intermediate biradicals with H$_2$O was identified as the major source of HCOOH, accounting for over 90% of the current known sources for both cases. CH$_2$OO is formed from seven excited biradicals that originate from the O$_3$ oxidation of various alkenes and unsaturated compounds (Saunders et al., 2003). Among these, CH$_2$O is the largest contributor to the production of CH$_2$OO (Fig. S5) and is generated by the ozonolysis of isoprene. The primary loss of HCOOH is via deposition, owing to its high solubility in water. To account for uncertainty in the deposition velocity ($V_d$) of HCOOH, we conducted a sensitivity test of HCOOH production to various $V_d$ values (Fig. 5d). The results revealed that the simulated HCOOH concentration was insensitive to $V_d$ when it was higher than 1.00 cm s$^{-1}$. The daytime peak concentration increased by 60% when $V_d$ decreased from 1.00 to 0.50 cm s$^{-1}$, but the model still largely underestimated the HCOOH concentration. The field-observed $V_d$ of HCOOH ranges from 0.43 cm s$^{-1}$ to 1.10 cm s$^{-1}$ (Müller et al., 2018), and thus given the high humidity at the study site, the observed $V_d$ of HCOOH of 0.5 cm s$^{-1}$ should have been close to the lower limit. The simulated net HCOOH production (sources – sinks) became positive at approximately 9 am, while the ambient concentration of HCOOH started increasing at 6 am, which is aligned with sunrise (Fig. 2). These results indicate that there are pathways for the photochemical generation of HCOOH that are distinct from O$_3$ oxidation and these may include the photochemical aging of aerosols. We also executed the model on 28 October 2021, another day that was exposed to coastal air masses, and obtained similar outcomes (Fig. S6).

3.3. Laboratory experiments

Figure 6a presents the results of a typical aerosol-filter irradiation experiment. Upon turning on the light, HCOOH was instantaneously produced, indicating a rapid transfer from the condensed-phase to the gas phase through photochemical reactions. Within 3 minutes, the HCOOH concentration reached 11.1 ppb, but when the light was turned off, the HCOOH concentration quickly returned to nearly background concentrations. This suggests that
HCOOH was produced predominantly via photochemical reactions. The HCOOH concentration exhibited a logarithmic decay after its first peak concentration and this decay also occurred continued after its second peak concentration, which may be attributable to either the evaporative loss of HCOOH or the photochemical loss of oxidants (Ye et al., 2017). When the AM 1.5 filter was added, the HCOOH concentration decreased by approximately 48.1% within 5 min, and after the filter was removed, the HCOOH concentration returned to the logarithmic decay line. This suggests that there was only minor evaporation of HCOOH from the condensed-phase due to the increased temperature of aerosol surfaces under light irradiation. However, the addition of the 300–800 nm filter reduced the HCOOH concentration by only 13.2%, indicating that the photochemical production of HCOOH primarily occurs at wavelengths lower than 360 nm. Given the agreement between the wavelength at which NO₃⁻ absorbs light (290–350 nm) and the wavelength of HCOOH production (< 360 nm), and the high correlation between the ambient HCOOH concentration and the product of Sa density and NO₃⁻ concentration (as shown in Fig. 3), we infer that ·OH produced from NO₃⁻ photolysis were the major oxidants in the particle phase and thus drove HCOOH production. The production of HCOOH was also found to be dependent on O₃, as the concentration of HCOOH increased by 64.7% after the addition of 100 ppb of O₃.

We next extrapolated the production rate of HCOOH observed in the chamber to ambient conditions, using the method described in Section 2.4, to assess the role played by the photochemical aging of aerosols in HCOOH production. Table 3 summarises the HCOOH concentrations and production rates observed in the chamber experiments, and the normalised HCOOH production rates in ambient air under light and light + O₃ conditions, respectively. The average $P_{\text{HCOOH-nml}}$ without the addition of O₃ was determined to be 0.106 ppb h⁻¹, equivalent to 138.5% of the peak HCOOH production rate in the modified case. The addition of 100 ppb of O₃ increased $P_{\text{HCOOH-nml}}$ by 0.079 ppb h⁻¹, indicating that the heterogenous reaction between O₃ and aerosols made a non-negligible contribution to HCOOH production. By comparing the net $P_{\text{HCOOH-nml}}$ via the photochemical aging pathway with and without O₃, it was found that the incorporation of these two conditions into the model should improve the model results by factors of 2.89 and 1.51, respectively. These results highlight the importance of HCOOH production via the aging of aerosols, which we found generated more HCOOH than gas-phase reactions at our observation site.

We established a relationship between $P_{\text{HCOOH-nml}}$ and three parameters: PM$_{2.5}$ concentration (cPM), which represents the reactant concentration; Sa, which represents the available reaction area; and jNO₂, which represents the light intensity. After multiplying these three factors, we discovered a strong linear correlation between $P_{\text{HCOOH-nml}}$ and cPM × Sa × jNO₂ (Fig. 6b). The intercept was set to zero, as there should be no HCOOH production when cPM × Sa × jNO₂ is zero. Based on the correlation, we derived an equation (Eq. (4)) for calculating $P_{\text{HCOOH-nml}}$. Additionally, we assumed that $P_{\text{HCOOH-nml}}(O₃)$ increased linearly with O₃.
concentration. Incorporating this equation into the F0AM model by treating the photochemical production of HCOOH from particles as an emission resulted in significantly improved predictions: they explained 81% of the peak concentration, as illustrated by the black line in Figure 4. The production of HCOOH from particles was the largest source of HCOOH, accounting for 76% of the total production (Fig. 5c). Moreover, the model also reproduced a rapid increase in the concentration of HCOOH in the morning and a sharp decrease in the concentration of HCOOH in the late afternoon (Fig. 4). The different trend at midnight is attributable to the continuous deposition of HCOOH concomitant with no production in the model at that time. We also evaluated the model’s performance in simulating HCOOH production for 28 October 2021. The particle-phase production narrowed the gap significantly and constituted over 70% of the total production (Fig. S6), which is consistent with the results for 28 September 2021.

In summary, the inclusion of HCOOH production from the photochemical aging of aerosols significantly improved the performance of the model. Although there may be limitations to the assumptions made in the parameterisation, particularly in environments containing with different chemical compositions of particles, this new parameterisation provides a general form constrained by four factors for calculating HCOOH production from the condensed phase.

\[
\dot{P}_{\text{HCOOH}} = 0.0091x + 0.01O_3 \times 0.0064x, \quad x = cPM \times S_a \times jNO_2 \quad (4)
\]

Photolysis of particulate NO$_3^-$ is an important source of ·OH (Mack & Bolton, 1999; Zellner et al., 1990). To investigate the potential production of HCOOH from this source, an irradiation experiment was conducted on a solution (Fig. 6c). The concentration of HCOOH increased linearly with time and did not reach a stable state after 90 min of illumination. This differs from the aerosol experiments and might have been due to the continuous evaporation of water from the solution caused by the heating effect of the light source, which would have concentrated the solution. To determine the appropriate time to calculate \(P_{\text{HCOOH}}\), we also plotted the time series of HONO concentrations. This showed that the HONO concentration stabilised after 1 h of irradiation, suggesting that NO$_3^-$ photolysis also reached a steady state. As ·OH produced from NO$_3^-$ photolysis were the only oxidants present in the system, the actual HCOOH production rate at the initial HCHO concentration should have followed the same trend as the HONO concentration. Therefore, we chose 1 h after turning on the light as the appropriate time to quantify \(P_{\text{HCOOH}}\), and found that at this time, \(P_{\text{HCOOH}}\) in the chamber was 21.9 ppt s$^{-1}$. We also attempted to extrapolate the results to ambient air, similar to the aerosol filter experiments. To do so, in addition to normalising \(S_a\) and light intensity, we needed to normalise the HCHO and NO$_3^-$ concentrations. The average concentration of gas-phase HCHO (HCHO$_{(g)}$) measured on 28 September was 2.35 µg cm$^{-3}$. By using a ratio of 0.03 between the concentration of HCHO in the particle phase (HCHO$_{(p)}$) and the concentration of HCHO in the gas phase (Toda et al., 2014), the concentration of HCHO$_{(p)}$ was calculated to be 0.07 µg cm$^{-3}$, which is comparable to the concentrations that have been reported in previous studies (Klippel...
Based on the aqueous volume of aerosol calculated by the E-AIM model (0.02 µl m⁻³), the HCHO mass concentration in the aqueous phase was found to be 3.5 g L⁻¹. The NO₃⁻ concentration on the aerosol surface was determined to be 0.98 mol L⁻¹. Therefore, the PₕCOOH in ambient air attributable to the aqueous oxidation of HCHO was estimated to be 0.41 ppb h⁻¹, which is 285% higher than the PₕCOOH attributable to the photochemical aging of ambient particles. This greater-than-100% contribution could be attributable to the simplicity of the solution system. In ambient air, other oxidisable species, such as halides (Peng et al., 2022; M. Xia et al., 2022) could also react with the ·OH produced from NO₃⁻ photolysis, which competes with HCHO. In summary, NO₃⁻ photolysis appears to be a critical source of oxidants during the photochemical aging process of aerosols.

4. Conclusion and implications

This study provides the first estimate of high rates of HCOOH production from the photochemical aging of real ambient particles and demonstrates the potential importance of this pathway in the formation of HCOOH under ambient conditions at a coastal site in Hong Kong. Incorporating aerosol photochemical aging significantly improved the performance of a widely used chemical model, which underscores the significance of condensed-phase photochemistry and the necessity of incorporating its mechanisms into atmospheric models. The substantial production of HCOOH from condensed-phase photochemical reactions altered both the composition and the volatility of SOA. Moreover, other low-molecular-weight organic acids, such as acetic acid, may be produced via this mechanism, as observed in our irradiation experiments. Improving the constraints on this photochemical aging of aerosols will not only aid the understanding of the budget of these organic acids but also affect their SOA chemistry.

Our solution irradiation experiments demonstrated the importance of NO₃⁻ photolysis in HCOOH production via the production of ·OH. This suggests that NO₃⁻ photolysis not only influences the aerosol-based production of inorganic species (such as HONO (Ye et al., 2017) and halogens (Peng et al., 2022; M. Xia et al., 2022), but also the aerosol-based production of organics, particularly water-soluble organics. Thus, there is a need for future studies on the roles of NO₃⁻ photodissociation in aerosol aging processes, as such research would improve our understanding of the aging mechanisms of the condensed phase.

Data availability

The data that support the findings of this study are openly available in Zenodo at https://doi.org/10.5281/zenodo.8059231. Other raw data are also available from the corresponding author, upon reasonable request.
Authors’ contributions

T. W. arranged the field campaign and designed the laboratory irradiation experiment. Y. J. and M. X. conducted the field campaign and photochemical filter experiments. M. X. revised the model code. Y. J. conducted the photochemical solution experiments, analysed the data, ran the model, and wrote the draft manuscript. T. W. and M. X. revised the manuscript.

Competing interests

One author (Tao Wang) is a member of the editorial board of Atmospheric Chemistry and Physics. The authors have no other competing interests to declare.

Acknowledgements

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References


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Fig. 1 Times series of temperature (T); relative humidity (RH); nitrogen dioxide photolysis frequency (jNO$_2$); concentrations of ozone (O$_3$), nitrogen oxides (NO$_x$), and formic acid (HCOOH); and surface area density (SA) during the field campaign. Data were not collected from August 29 to September 10 due to the persistently clean weather conditions, similar to those during the initial stage of the campaign. The gap in data collection from October 8 to October 17 was due to a rainstorm. Any other short gaps were caused by instrument maintenance.

Table 1. Summary of worldwide field-observed formic acid (HCOOH) concentrations

<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>Time</th>
<th>HCOOH (ppb)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pasadena, USA</td>
<td>urban</td>
<td>2010.06-07</td>
<td>2.0 ± 1.0</td>
<td>(Yuan et al., 2015)</td>
</tr>
<tr>
<td>Kensington, London</td>
<td>urban</td>
<td>2012.01-02</td>
<td>0.63 (winter)</td>
<td>(Bannan et al., 2017)</td>
</tr>
<tr>
<td>London background</td>
<td></td>
<td>2012.07-08</td>
<td>1.33 (summer)</td>
<td></td>
</tr>
<tr>
<td>Shanghai, China</td>
<td>suburban</td>
<td>2017.06-12.23</td>
<td>2.08 ± 1.89</td>
<td>(Xu et al., 2020)</td>
</tr>
<tr>
<td>Yorkville, USA</td>
<td>rural</td>
<td>2016.08.15-10.13</td>
<td>1.17 ± 0.85</td>
<td>(Nah et al., 2018)</td>
</tr>
<tr>
<td>North Pacific</td>
<td>marine</td>
<td>2008.07.29-08.19</td>
<td>30 ± 39.8 ppt</td>
<td>(Miyazaki et al., 2014)</td>
</tr>
<tr>
<td>Pacific and</td>
<td>marine</td>
<td>2017.09-10</td>
<td>&lt; 0.1</td>
<td>(Chen et al., 2021)</td>
</tr>
<tr>
<td>Atlantic</td>
<td></td>
<td>2018.04-05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colorado, USA</td>
<td>forest</td>
<td>2016.02.01-03.01</td>
<td>55 ± 57 ppt (winter)</td>
<td>(Fulgham et al., 2019)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2016.04.15-05.15</td>
<td>30 ± 24 ppt (spring)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2016.07.15-08.15</td>
<td>1.2 ± 0.91 (summer)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2016.10.01-11.01</td>
<td>0.81 ± 0.48 (autumn)</td>
<td></td>
</tr>
<tr>
<td>Alabama, USA</td>
<td>deciduous</td>
<td>2013.06-07</td>
<td>2.5 (peak average daytime)</td>
<td>(Millet et al., 2015)</td>
</tr>
<tr>
<td>Hong Kong, China</td>
<td>coastal</td>
<td>2021.08.13-10.31</td>
<td>0.58 ± 0.53</td>
<td>This study</td>
</tr>
</tbody>
</table>
Fig. 2 Diurnal variation in the concentrations of formic acid (HCOOH) in different periods. (a) Diurnal cycle of HCOOH concentrations and frequency of nitrogen dioxide photolysis (jNO₂) for the whole campaign; (b) and (c) diurnal cycle of HCOOH concentrations in marine and coastal air masses, respectively. The shading represents the standard deviations of the measurements.

Table 2. Pearson correlation coefficient ρ matrix between the concentration of formic acid and other air pollutants, and related meteorological parameters, during three distinct periods.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coastal</th>
<th>Haze</th>
<th>Marine</th>
<th>Parameter</th>
<th>Coastal</th>
<th>Haze</th>
<th>Marine</th>
</tr>
</thead>
<tbody>
<tr>
<td>jNO₂</td>
<td>0.41</td>
<td>0.58</td>
<td>0.65</td>
<td>Sa</td>
<td>0.73</td>
<td>0.68</td>
<td>-0.03</td>
</tr>
<tr>
<td>T</td>
<td>-0.27</td>
<td>0.70</td>
<td>0.72</td>
<td>Sa × NO₃⁻</td>
<td>0.85</td>
<td>0.56</td>
<td>0.15</td>
</tr>
<tr>
<td>RH</td>
<td>-0.56</td>
<td>-0.51</td>
<td>-0.65</td>
<td>Sa × O₃</td>
<td>0.83</td>
<td>0.74</td>
<td>0.31</td>
</tr>
<tr>
<td>PM₁</td>
<td>0.79</td>
<td>0.66</td>
<td>0.05</td>
<td>HNO₃</td>
<td>0.75</td>
<td>0.59</td>
<td>0.69</td>
</tr>
<tr>
<td>PM₂,₅</td>
<td>0.69</td>
<td>0.63</td>
<td>0.19</td>
<td>Cl⁻</td>
<td>-0.41</td>
<td>-0.44</td>
<td>0.09</td>
</tr>
<tr>
<td>PM₁₀</td>
<td>0.68</td>
<td>0.55</td>
<td>0.26</td>
<td>NO₃⁻</td>
<td>0.67</td>
<td>-0.10</td>
<td>0.57</td>
</tr>
<tr>
<td>HONO</td>
<td>-0.03</td>
<td>0.26</td>
<td>-0.34</td>
<td>SO₄²⁻</td>
<td>0.66</td>
<td>0.65</td>
<td>0.10</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>0.89</td>
<td>0.88</td>
<td>-0.27</td>
<td>Na⁺</td>
<td>-0.28</td>
<td>-0.50</td>
<td>0.37</td>
</tr>
<tr>
<td>NO</td>
<td>-0.12</td>
<td>0.44</td>
<td>0.13</td>
<td>NH₄⁺</td>
<td>0.72</td>
<td>0.64</td>
<td>0.24</td>
</tr>
<tr>
<td>NO₂</td>
<td>-0.24</td>
<td>0.36</td>
<td>-0.39</td>
<td>K⁺</td>
<td>0.53</td>
<td>0.32</td>
<td>0.15</td>
</tr>
<tr>
<td>NOₓ</td>
<td>-0.22</td>
<td>0.40</td>
<td>-0.27</td>
<td>Mg²⁺</td>
<td>-0.30</td>
<td>-0.38</td>
<td>0.47</td>
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<tr>
<td>O₃</td>
<td>0.69</td>
<td>0.65</td>
<td>0.68</td>
<td>Ca²⁺</td>
<td>-0.11</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.64</td>
<td>0.66</td>
<td>0.41</td>
<td>HCl</td>
<td>0.18</td>
<td>0.51</td>
<td>0.55</td>
</tr>
<tr>
<td>CO</td>
<td>0.63</td>
<td>0.51</td>
<td>0.13</td>
<td>Isoprene</td>
<td>0.03</td>
<td>0.61</td>
<td>0.63</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.37</td>
<td>0.46</td>
<td>0.16</td>
<td>Benzene</td>
<td>0.63</td>
<td>0.55</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Fig. 3 Scatter plot of the concentration of formic acid (HCOOH) and (a) the concentration of ozone (O$_3$); (b) the mass concentration of nitrate ions (NO$_3^-$) in PM$_{2.5}$; (c) the surface area density (Sa) of PM$_1$ ($\mu$m$^2$ cm$^{-3}$); (d) the product of Sa and the concentration of O$_3$; (e) the product of Sa and the concentration of NO$_3^-$; and (f) the product of Sa, the concentration of O$_3$, and the concentration of NO$_3^-$ in coastal air masses.
Fig. 4 Variations in the concentrations of formic acid (HCOOH) on 28 September 2021.

Fig. 5 Model-calculated profiles of sources and sinks of formic acid (HCOOH) on 28 September 2021 for (a) the base case; (b) the modified case; and (c) the case including the production from particles. Upper right inset: the contribution from various sources to HCOOH concentrations. Bottom right inset: the contribution from different sinks to HCOOH
concentrations. CH$_2$OO = formaldehyde oxide, a Criegee intermediate (biradical); VINOH = vinyl alcohol. d) Model-predicted concentrations of HCOOH based on various deposition velocities ($V_d$).

Fig. 6 Results of the irradiation experiments. (a) Typical variation in formic acid (HCOOH) concentrations during irradiation (in aerosols collected on 2 November 2020). AM 1.5 and 300–800 nm filters were added after the addition of 100-ppb ozone. (b) The correlation between $P_{\text{HCOOH-nml}}$ and 2.5-µm particulate matter (PM$_{2.5}$) concentration ($c_{\text{PM}}$) × surface area ($S_a$) × nitrogen dioxide photolytic frequency ($j_{\text{NO}_2}$). (c) Variations in the concentrations of HCOOH and nitrous acid (HONO) as a function of time after illumination of an aqueous solution of formaldehyde and sodium nitrite at pH = 2.7. The vertical black line indicates the time at which HONO stabilised. (d) Comparison of the irradiation spectrum of the xenon lamp used in this study and standard air mass 1.5 solar irradiation (AM 1.5).
Table 3 Summary of formic acid (HCOOH) concentrations and production rates observed in chamber experiments and normalised HCOOH production rates in ambient air under light and light + ozone (O3) conditions, respectively. HCOOH(O3) denotes the increased concentration of HCOOH after the addition of 100 ppb O3.

<table>
<thead>
<tr>
<th>Date</th>
<th>HCOOH(light) (ppt)</th>
<th>HCOOH(O3) (ppt)</th>
<th>P_HCOOH(light) (ppt s⁻¹)</th>
<th>P_HCOOH(O3) (ppt s⁻¹)</th>
<th>P_HCOOH-nml (light) (ppb h⁻¹)</th>
<th>P_HCOOH-nml (O3) (ppb h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2020.10.07</td>
<td>8420.2</td>
<td>4670.0</td>
<td>299.4</td>
<td>166.0</td>
<td>1.70E-01</td>
<td>1.33E-01</td>
</tr>
<tr>
<td>2020.10.08</td>
<td>6787.7</td>
<td>2899.0</td>
<td>241.3</td>
<td>103.1</td>
<td>1.31E-01</td>
<td>7.89E-02</td>
</tr>
<tr>
<td>2020.10.26</td>
<td>4660.9</td>
<td>3077.5</td>
<td>165.7</td>
<td>109.4</td>
<td>6.01E-02</td>
<td>5.57E-02</td>
</tr>
<tr>
<td>2020.11.02</td>
<td>6656.3</td>
<td>3507.6</td>
<td>236.7</td>
<td>124.7</td>
<td>1.55E-01</td>
<td>1.15E-01</td>
</tr>
<tr>
<td>2020.11.03</td>
<td>4490.8</td>
<td>2266.7</td>
<td>159.7</td>
<td>80.6</td>
<td>1.06E-01</td>
<td>7.55E-02</td>
</tr>
<tr>
<td>2020.11.04</td>
<td>4943.1</td>
<td>2191.5</td>
<td>175.8</td>
<td>77.9</td>
<td>7.67E-02</td>
<td>4.77E-02</td>
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<tr>
<td>2020.11.05</td>
<td>3088.0</td>
<td>2368.6</td>
<td>109.8</td>
<td>84.2</td>
<td>4.37E-02</td>
<td>4.71E-02</td>
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<tr>
<td>Average</td>
<td>5578.1</td>
<td>2997.3</td>
<td>198.3</td>
<td>106.6</td>
<td>1.06E-01</td>
<td>7.89E-02</td>
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</tbody>
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