



Review

Biogenic secondary organic aerosols: A review on formation mechanism, analytical challenges and environmental impacts



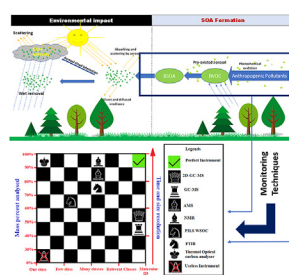
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HIGHLIGHTS

- The BSOA exhibit distinct day and nighttime formation mechanism.
- Analytical advancements and their ability to examine SOA are compiled and compared.
- SOA can cause significantly enhanced radiating forcing.
- Anthropogenic gaseous pollutants have strong influence over BSOA formation.
- Meteorological variables can effectively control BSOA formation.

GRAPHICAL ABSTRACT



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ABSTRACT

The review initiates with current state of information on the atmospheric reaction mechanism of biogenic volatile organic compounds (BVOCs) and its fate in the atmosphere. The plants release BVOCs, i.e., isoprene, monoterpenes, and sesquiterpenes, which form secondary organic aerosols (SOA) upon oxidation. These oxidation reactions are primarily influenced by solar radiations along with other meteorological parameters viz.; temperature and relative humidity, therefore, the chemistry behind SOA formation is different during day than the night time. The review throws light upon the day and nighttime formation mechanism of SOA, recent advancements in the analytical techniques available for the measurements, and its impact on the environment. Studies have revealed that day time SOA formation is dominated by OH and O₃, however, NO_x initiated SOA production is dominated during night. The formation mechanism addresses that the gaseous products of VOCs are firstly formed and then partitioned over the pre-existing particles. New particle formation and biomass-derived aerosols are found to be responsible for enhanced SOA formation. 2-Dimensional gas chromatography-mass spectrometer (2D-GC/MS) is observed to be best for the analysis of organic aerosols. Radiative forcing (RF) SOA is observed to be a useful parameter to evaluate the environmental impacts of SOA and reviewed studies have shown mean RF in the ranges of -0.27 to $+0.20$ W m⁻².

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1. Introduction

Aerosols play important roles in atmospheric process via scattering and absorbing solar radiation, influencing cloud formation and participating in heterogeneous chemical reaction, thereby affecting the distribution and abundance of atmospheric trace gases (Andreae and Crutzen, 1997; Haywood and Boucher, 2000; Choi et al., 2015). Moreover, they affect the radiative balance in the Earth's atmosphere and ultimately the climate (Ramanathan et al., 2001; Novakov and Penner, 1993; Ram et al., 2012; Pani et al., 2016; Tsay et al., 2016; Malavelle et al., 2019; Mahilang et al., 2020). Atmospheric aerosols are categorized into two parts based on their sources; anthropogenic (derived from combustion activities using biomass, fossil fuels, and household solid fuels) and natural (volcanic eruptions, wind-driven soil re-suspension, and mineral dusts (Majumdar et al., 2012)). The secondary aerosol particle is reported to be formed by the gas-to-particle conversion processes, nucleation, condensation, and various multiphase chemical reactions (Moffet and Prather, 2009; Riemer and West, 2013; Mahilang and Deb, 2020).

Plant produced biogenic volatile organic compounds (BVOCs) are extremely reactive in the troposphere with their lifetime ranging from minute to hours. When BVOCs come in contact with atmospheric oxidants the formation of SOA occurs via stepwise heterogeneous reactions (Poschl, 2005; Kawamura et al., 2017; Gunsch et al., 2018; Sinha et al., 2019; Tajuelo et al., 2019). Plants emitting significant monoterpene and isoprene are reported to belong to the families of flowering plants, ferns, conifers, and bryophyte plants (Harley et al., 1999). Some plant species, known for higher emissions of VOCs (emission rate > 5 $\mu\text{g g}^{-1}$ dry leaf h^{-1}), are *Ficus religiosa*, *Adhatoda vasica*, *Eucalyptus species*, *Adhatoda vasica*, *Casuarina equisetifolia*, *Syzygium jambolanum*, *Psidium guajava*, *Lantana camara* (Padhy and Varshney, 2005). Out of the total BVOCs emissions, isoprene comprises nearly 50% of it; other emitted BVOCs are monoterpenes and sesquiterpenes. The BVOCs undergo photochemical degradation to form gas phase oxidation products and as a result of various heterogeneous reactions of gaseous precursors, SOA are formed, i.e., called biogenic secondary organic aerosols (BSOA) (Xu et al., 2015; Marais et al., 2016; Boy

et al., 2019). The extent of BVOCs emission in the atmosphere generally depends upon the geographical location and meteorological conditions (Kourtchev et al., 2008; Helmig et al., 2013). The geographical sites which have sunny, warm tropical conditions and high vegetation biomass density (including plants such as oak, coniferous plants, pine trees), release greater BVOCs in the atmosphere. Above are the reasons why most of the studies were concerned with atmospheric chemistry in sub-tropical areas and the forests (Rissanen et al., 2006; Hoyle et al., 2011). Goldstein and Galbally (2007) reported the measurement of around 10,000–1,000,000 different organic compounds in atmosphere. The VOCs undergo several stepwise degradation processes and further lead to formation of extremely low volatile organic compounds (ELVOC). Many researchers have reported building of, an intermediate, highly oxidized multifunctional (HOM) compound in the gaseous phase of troposphere during the SOA formation process (Kulmala et al., 1998; Ehn et al., 2012). ELVOC compounds are of extremely low volatile nature due to the presence of very large number of functional groups (O/C ratio > 0.7) in HOM causing very low volatility (Mutzel et al., 2015). Jokinen et al. (2014) reported formation of gas-phase HOM, an important channel of monoterpene oxidation, via autooxidation of alkyl peroxy radical by intramolecular hydrogen atom shift. It is believed that HOM may contain many hydroperoxide groups (Mutzel et al., 2015).

Once SOA is formed in the particle phase its fate in the atmosphere continues with the particle growth, aging and ultimately removal either via volatilization or dry and wet deposition processes (Wong et al., 2019). SOAs form HOM organic compounds as intermediates throughout its life cycle (Ehn et al., 2014, 2012; Mentel et al., 2015; Mutzel et al., 2015). At the beginning, BVOC forms the primary products as ELVOC that is detectable using on-line measurement and characterizable using mass spectrometer. The ELVOC are then condensed into pre-existed atmospheric particles, onto which the rest of the process of SOA formation occurs. Isoprene derived SOA formation in the atmosphere was not considered until 2-methyltetrols was first found in atmospheric aerosols of Amazon forest in 2004. Thereafter many chamber experiments were performed worldwide to determine the SOA composition (Edney et al., 2005; Ion et al., 2005; Clements et al.,

2007; Song et al., 2019). Pinic and pinonic acids (α and β pinene SOA tracers) were also detected in the atmospheric aerosol samples worldwide (Yu et al., 1999; Sheesley et al., 2004; Bhat et al., 2007).

The review initiates with a current state of knowledge of the atmospheric reaction mechanism of BVOCs released and the altering overall SOA budget. The next part of the review throws a light upon the oxidation mechanism for SOA precursors and the analytical techniques used for characterization of biogenic aerosols. The review also discussed condensed phase reactions, sulfate aerosols interactions, cloud condensation nuclei (CCN) and future recommendations. There are lots of chamber studies and field works done regarding BSOA but understanding the dynamics of formation and characterization of BSOA are still challenging and also it is important to comprehend their indirect effects in climate and human health (Oberdorster et al., 2005; Mauree et al., 2019). Thus, the objective of this review is to discuss about the recent advancements based on earlier works of BSOA.

2. Atmospheric chemistry of secondary organic aerosols

2.1. Formation of SOA via degradation of VOC

The degradation of the emitted VOC is initiated either by the oxidants present in the atmosphere viz. OH, NO₃, O₃ radicals or by the photolysis. Under certain condition chlorine (Cl) radical also initiates oxidation of VOC. In geographical locations with low amounts of Cl radicals in the atmosphere, the VOC oxidation proceeds via OH initiated mechanism. The Cl radical is believed to be evolved from heterogeneous reaction over sea surface. Many researchers have reported high Cl loading over continental areas (Wennberg et al., 2018; Guo et al., 2020). Hence, the Cl radical initiated VOC degradation completely depends on the geographical locations (availability of Cl radical in the atmosphere). These competitive oxidation processes are either dependent on the nature of parent VOC or on the atmospheric condition (Atkinson and Arey, 2003; Bianchi et al., 2019). Stepwise degradation has been predicted in which the initial oxidation promotes the formation of first-generation products, which includes a set of organic products containing single or multiple oxygenated functional groups like,

–CHO, –OH, >CO, –NO₂, –COONO₂, –COOH, –OOH and –COOOH, etc. A generalized mechanism of SOA formation from VOCs is shown in Fig. 1. The further oxidation of these compounds results in the production of high volatile and soluble second-generation organic compounds, in which further oxidized functional group are added. The lower chain oxygenated products are more volatile than higher or long chain products. The fate of such organic compounds is decided by three stepwise processes viz., fragmentation to CO₂, functionalization to form lower volatility products or by deposition either wet or dry (Atkinson et al., 2006). Many researchers have found the traces of organosulfates and oligomers as SOA in lab and field research both.

Different types of oligomers can be formed over aerosols, such as association of low carbon containing species (oxidation products of glyoxal), epoxides of isoprene and high carbon containing precursors (pinene oxidation products) (Hall and Johnston, 2011). Lin et al. (2014) also reported oligomers formation in aqueous phase glycolaldehyde, glyoxal and methylglyoxal via oxidation of these gaseous species with NO_x and OH.

Organosulfates are sulfate derivatives of SOA and its formation increases as the acidic content of aerosols increases. Surratt et al. (2007) reported that increasing acidity of sulfate seed can significantly enhance the sulfate derived SOA formation. They reported organosulfates formation from C₅-alkene triols, 2-methyltetrols, 2-methylglyceric acid (2-MGA), hydroxyacetone, glyoxal, methylglyoxal and methacrolein present in aerosols. The volatility of the formed product is not only the responsible factor but also some atmospheric parameters like, water contents, cations, anions and relative humidity play vital role in the chemistry of SOA formation (Dommen et al., 2006; Surratt et al., 2006; Denkenberger et al., 2007). There are myriad of organic compounds in the atmosphere which grow or degrade. The most studied aspect of degradation chemistry of the VOC is the OH·(OH radical) initiated chemistry which is dominant in the day time (Pagonis et al., 2019). The OH· initiated mechanism is mostly preferred for the SOA formation in which radical forms of RO₂ (Peroxy) and RO (Oxy) are reacted wherein RO is formed from RO₂ in presence of high NO_x in the atmosphere. It is also concluded that the formation of product is strongly dependent upon the structure of emitted VOC and also

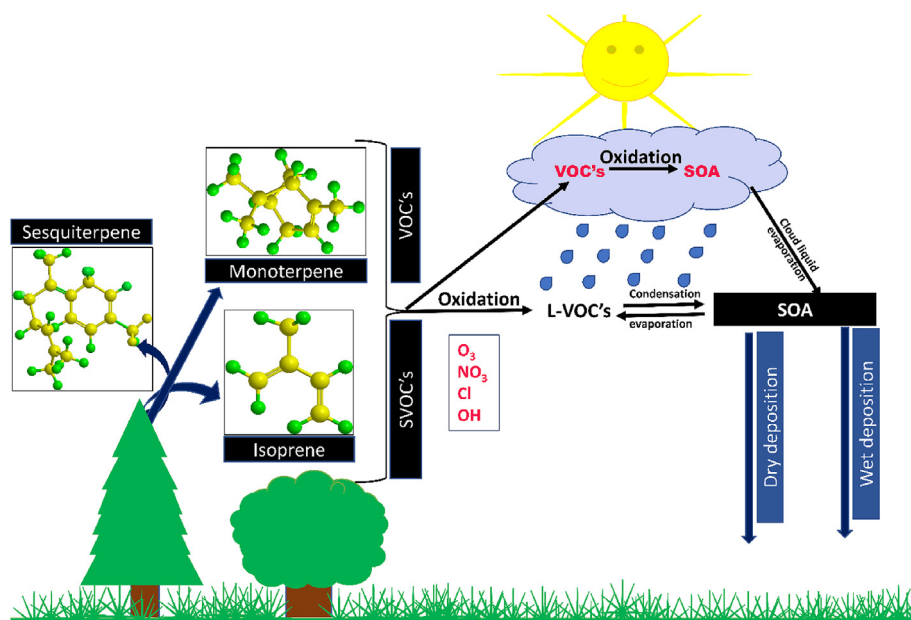


Fig. 1. BSOA formation pathways via biogenic volatile organic compounds.

meteorological variables, i.e., temperature and relative humidity etc. (Atkinson et al., 2007). There are three routes by which RO reacts, (1) formation of carbonyl groups and HO₂, (2) decomposition via formation of smaller carbonyls and radical of organic compounds, (3) formation of hydroxy derivatives of carbonyls and HO₂ via isomerization followed by hydrogen atom shift reaction. NO forms RONO₂ on interaction with RO₂, whereas NO₂ on reaction with RO₂ leads to the formation of atmospheric stable peroxy nitrates (RO₂NO₂). NO₃ plays crucial role in nighttime atmospheric chemistry, whereas O₃ acts as an oxidant both in day and night hours. Somewhere, especially in marine atmosphere, Cl[•] acts as active oxidant and participates in VOC degradation (Guo et al., 2020).

2.2. Effect of anthropogenic pollutants on VOC degradation

Various studies show that atmospheric chemical reactions of degradation mostly depend on the emission strength of VOC in particular geographical location, temperature, and availability of oxidants (Zhou et al., 2019). Increasing atmospheric aerosols can also trigger the condensation of gaseous species onto particle-phase, e.g., BVOC derived gas-phase products are easily condensed over particles phase. Hence, anthropogenic pollutants can significantly enhance the extent of BSOA formation. Another phenomenon that explains the enhancement of BSOA is new particle formation occurring from sulfuric acid and gaseous organic pollutants. Condensation of organic gaseous species over new particles also indicates the growth mechanism of atmospheric aerosols via anthropogenic emission (Bonn et al., 2008; Boy et al., 2008). Hence, the formation of new particles also provides a path for enhanced BSOA formation. The extent of sulfur-containing species can also alter the SOA formation. Xu et al. (2015) reported that isoprene derived SOA (SOAI) is mediated by the atmospheric sulfate loading rather than aqueous contents and aerosols acidity. The NO_x mostly contributes nighttime atmospheric chemistry and trigger the formation of nitrate-containing SOA species of monoterpenes. They reported that NO_x and sulfate alone mediated 43–70% of total OA at the southeastern US during the summer season and suggested that the reduction in emissions of sulfate and NO_x may help reduce the SOA burden. The anthropogenic pollutants affect the transformation of biogenic VOC and formation of SOA through several mechanisms at low NO_x condition. The vapor phase atmospheric reaction of the pollutants, viz., SO₂ with peroxy radicals promotes the formation of sulfate aerosols, which changes the acidity and water contents and hence coupling occurs between the product formed from biogenic VOC and sulfate aerosols. This coupling results in the regional cooling in the southwestern United States (Zhu et al., 2019). The pathways of reaction as well as the viscosity are affected via the meteorological conditions and presence of oxidants in the atmosphere. As a result, the particle surface available for condensation increase and hence the phenomenon promotes myriad of atmospheric reactions.

2.3. Effect of biomass burning on SOA

Huge amounts of atmospheric pollutants are released globally from biomass burning that contributes around half of the overall worldwide emissions (Bond et al., 2013). The optical properties and cloud processing efficiencies of these biomass burning emissions significantly influence the radiation budget of the Earth and affect the global climate (Ramanathan et al., 2001; Vakkari et al., 2018). Smoke plumes emitted from biomass burning emissions, which significantly harm the atmosphere, contain carbonaceous components, water-soluble ions, carbonyls, and sugar alcohols (Pani et al., 2019, 2018; Thepnuan et al., 2019). In northern Southeast Asia,

significantly high concentration of carboxylates, carbonyl and aliphatic carbon derivatives was found in the smoke released from biomass burning (Popovicheva et al., 2016). A lab study found methylfuran that was produced from epoxides of isoprene under low NO_x conditions (Allan et al., 2014). Methylfuran was also found in field research study, conducted by Hewitt et al. (2010) during the Southeast Asian tropical rain forest campaign. Kelly et al. (2018) reported global annual SOA contribution of isoprene, monoterpene, biomass combustion, and anthropogenic emission to be 19.6, 19.9, 9.5 and 24.6 Tg (SOA) a⁻¹, respectively, during 2017. Enhanced global SOA production was reported due to the photochemical degradation of biogenic and biomass-derived precursors. The aging processes and SOA formation from non-methane organic gases are greatly influenced by OH exposure that regulates the heterogeneous oxidation reaction during SOA formation (Pandey et al. 2018, 2020; Lim et al., 2019). Significant atmospheric warming and surface cooling was reported due to enhanced biomass burning emissions (organic carbon ratio > 90%) with high loading of NO₃⁻, OC3 and EC1-OP; ultimately leading to a severe haze in northern peninsular Southeast Asia (Pani et al., 2018). Thepnuan et al. (2019) obtained a good correlation between NH₄⁺ and SO₄²⁻, as an indication of secondary formation, and established a link between biomass burning and high correlation between NO₃ and levoglucosan in the upper South East Asia region. They also found high loading of oxalate ions due to biomass combustion. Vakkari et al. (2018) found a significant enhancement in SOA formation and doubled PM₁ loading due to biomass burning emission in southern African fires. Ciccioli et al. (2014) reported about the release of β-caryophyllene, which resides over wood and leaf surface due to low volatility, upon the burning of biomass. A strong correlation between β-caryophyllene and levoglucosan also indicated an association between biomass burning and secondary formation (Wang et al., 2019).

2.4. Day time atmospheric chemistry

2.4.1. OH initiated mechanism

During daytime high temperature with intense sunlight enhances the biogenic VOC (isoprene and monoterpenes) productions, i.e., high SOA loading are generally found during daytime. Li et al. (2019) found that average atmospheric temperature is strongly correlated with isoprene ($R^2 = 0.84$) and monoterpenes ($R^2 = 0.91$) emissions in the atmosphere. A study conducted at coniferous forest found that the concentration of hydroxyl radical was comparatively higher (10^5 – 10^6 molecules cm⁻³) during daytime. Hence, OH radical initiated chemistry dominates during daytime (Bates et al., 2019). When OH radicals are formed and interact with biogenic VOC (emitted from the vegetations), a series of oxidation reaction get started, and the biogenic VOC are degraded to produce low volatile organic compounds (products). Fig. 2 displays atmospheric degradation pathway of biogenic volatile organic compounds. Fig. 3 shows the detailed mechanism of gas phase oxidation of isoprene as an important constituent of VOC. The oxidation of isoprene by OH radical at low NO_x concentration produces hydroxyhydroperoxide that further produces isoprene epoxydiol (IEPOX) as an important intermediate in atmosphere reactions (Xu et al., 2015). Then further degraded RO₂ radical is produced, which further yields carbonyl and hydroxycarbonyls. The fate of these RO₂ radical is dependent on NO_x (mixture of NO and NO₂) concentration. High BSOA with low NO conditions yield RO₂ radical that further undergoes transformation to RO₂NO₂ and RONO₂. This finally ends up to alkoxy radicals and smaller volatile fragments. However, at elevated NO_x conditions methanecaryloperoxynitrates (MPAN) are formed as intermediate, which tend to generate a mixture of product dominated by peroxy acetyl

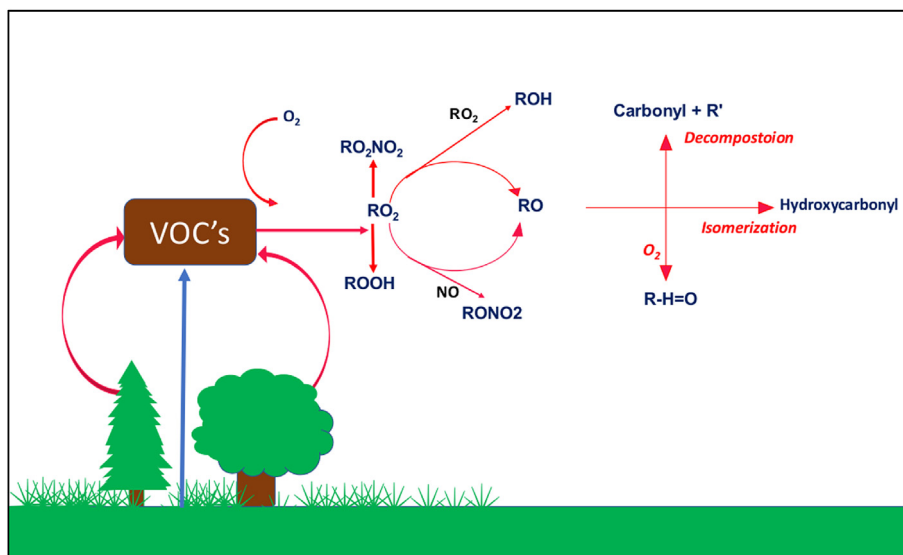


Fig. 2. Atmospheric degradation pathway of biogenic volatile organic compounds.

nitrate (PAN), carbonyls, hydroxyl carbonyl and organic nitrates (Liu et al., 2019a). PAN, an important constituent of the photochemical smog, is organic peroxy nitrate that is formed by the reaction of RO_2 radical and NO_2 .

2.4.2. O_3 initiated mechanism

Ozone gas generally comes to the troposphere from stratosphere via eddy flux processes. Besides this, it can also be formed via photochemical reaction between VOC (biogenic and anthropogenic) and NO_x (Calfapietra et al., 2013). Due to high isoprene emission flux and formation of ozone during the daytime, it can be stated that the ozone degradation dominates at day time. Ozone is also produced by photochemical oxidation of CO, CH_4 and non-methane VOC in presence of NO_x . The loss of tropospheric O_3 takes place through dry deposition and various other chemical reactions. The term photochemical indication, used in order to evaluate the extent of ozone formation, depends upon the concentration of H_2O_2 , HNO_3 and reactive nitrogen species (Gen et al., 2019). The chemistry initiated by O_3 tends to feed into similar mechanism as those of NO_3 and OH by virtue of the formation of OH, RO_2 and RO radicals (Faiola et al., 2019).

Johnson and Manston (2008) described that O_3 initiated chemistry is generally believed to take place by Criegee intermediates (carbonyl oxides) formation. These intermediates are formed by decomposition of primary ozonides of isoprene via two pathways to give a carbonyl along with it. A carbonyl substituted Criegee intermediate can be also formed through α -pinene (Zhou et al., 2019). Initially formed energy rich Criegee intermediate gives further reaction by a number of pathways, i.e., A) collisional stabilization of thermalized Criegee intermediate and, B) for dialkyl and monoalkyl substituted Criegee intermediate, isomerization to a 'hot' hydroperoxide followed by decomposition (Atkinson and Arey, 2003). In the stepwise photooxidation of isoprene and α -pinene, generally, epoxides are observed as end product (Ng et al., 2006). Ozone alkene reaction system involves both OH radical and O_3 as oxidants (Atkinson et al., 1993). At the end of the process, product distribution includes carboxylic acid and hydroxyalkyl hydroxyperoxide, which are sensitive to both NO_x and H_2O and also to scavengers such as carbonyl and acid scavengers (Hallquist et al., 2009).

2.5. Nighttime atmospheric chemistry

2.5.1. OH, and NO_x initiated mechanism

During night time, the levels of the OH radical is almost minimized, hence the nighttime chemistry is mainly dominated by NO_3 radicals, which are formed via reaction of NO_x with ozone. Further, NO_3 reacts with NO_2 to form N_2O_5 and establishes equilibrium between them, thus both NO_3 as well as N_2O_5 affect degradation at night. Ng et al. (2008) performed chamber experiments and observed that the organic nitrates were formed from reaction between NO_3 radical and BVOC. However, along with NO_2 and NO the OH radicals are also formed even at night upon decomposition of nitrate substituted peroxy radicals, which also contribute in degradation of VOC. The oxidation products (SOA) of NO_3 are mainly multifunctional organic nitrates containing carbonyl, alcohol and peroxide groups or of compounds of lower vapor pressure. The N_2O_2 initiated chemistry also operates and much of its chemical reactions completes on the particle phase of aerosols.

The formation of ammonium nitrate in the ambient atmosphere accounts for the removal of NO_x from the atmosphere. This nighttime mechanism can remove as much as NO_x as the day time gas phase reaction with OH with NO_2 to produce HNO_3 . Nighttime loss of N_2O_5 thus limits the availability of NO_2 for the photochemical production of O_3 the following day (Xia et al., 2019).

At high NO_x condition RO radicals are formed, the fate of which is dependent on the structure of parent VOC. All these degradations can result into carbonyl, HO_2 or it may also decompose through C–C bond breaking via formation of smaller carbonyls and organic radicals. Isomerization through H-atom shift may also take place to produce hydroxy carbonyl compounds and HO_2 . When OH radical interacts with isoprene then there are possibilities of both self and cross reactions to take place. The later results 1,2-diols formation in the natural tropical atmosphere at both low as well as high NO_x conditions during high biomass burning activity (Anthropogenic activity) (Liu et al., 2019a).

Surrat et al. (2006) investigated the chemical composition of products formed by isoprene oxidation both under high and low NO_x condition and concluded that formation of high MW product was dependent on the concentration of NO_x . At low NO_x condition organic peroxides were produced and significantly contributed to the SOA mass, which further decreased with time and thus also

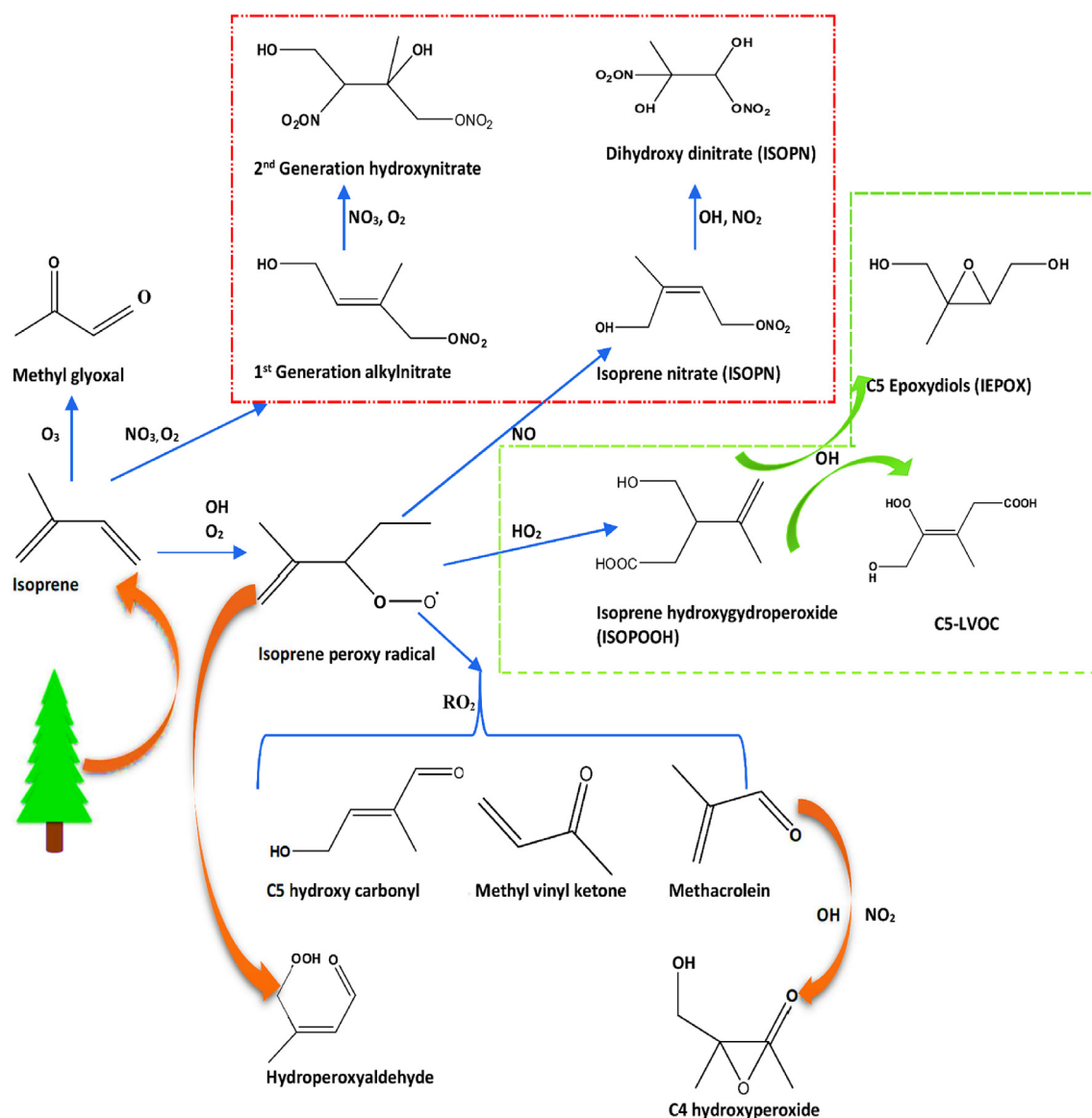


Fig. 3. Gas phase isoprene oxidation and formation of first and second-generation products. Here red box indicates night time dominated process and green box indicated day time dominated process. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

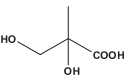
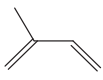
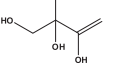
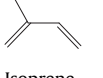
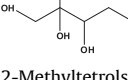
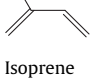
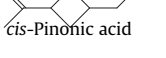




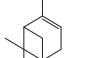
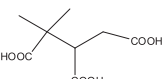
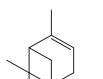
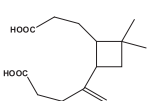
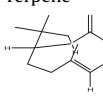
indicated photochemical aging. The major products were 2-methyltetrols, C₅-alkene triols, and the minor products identified were 2-methyltetrol oxyformate derivatives, hemiacetal derivatives and C₅-trihydroxyl monocarboxylates. These compounds were also identified in the PM_{2.5} (matrix) in ambient air matrix of Amazonian forests. Different BSOA tracers with their precursors and mass fragments are given in Table 1. At high NO_x condition, major products formed are acidic oligoesters with 2-methylglyceric acid as a key monomeric acid unit and residues formed by esterification of OH groups with acetic/formic acid (Cui et al., 2019; Surratt et al., 2006). Table 2 illustrates different studies regarding BSOA and their concentration levels in the ambient atmosphere.

2.6. Role of ammonia in SOA formation

The extent of ammonia (NH₃), generally present as a trace gas in troposphere (Zaveri et al., 2020), depends upon the source and strength of emission in the atmosphere (Li et al., 2020). NH₃ in the atmosphere comes from nature as well as anthropogenic sources.

NH₃ can be emitted mostly from livestock like cows, beef, chicken and hogs (Yu et al., 2020; Zhang et al., 2020a). However, NH₃ from mobile emission sources and soil emissions are also significant (Zhu et al., 2020). The atmospheric nitric (HNO₃) and sulfuric acids (H₂SO₄) react with NH₃ and form NH₄HSO₄, NH₄NO₃ and (NH₄)₂SO₄ (Wang et al., 2020a). The fate of atmospheric NH₃ is generally finished by OH radical initiated oxidation, wet and dry deposition (Aguilar-Dodier et al., 2020). NH₃ is less reactive in the troposphere, hence its removal via gas phase oxidation process is less significant (Fairlie et al., 2020). Its reaction with HNO₃ and H₂SO₄ leads to formation of secondary inorganic aerosols (Agarwal et al., 2020). Researchers also reported the interaction of atmospheric NH₃ with organic acids leading to enhanced SOA formation (Du et al., 2020). SOA formation from NH₃ occurs via formation of condensable salt formation through acid-base atmospheric reactions (Jang et al., 2020). Organic aerosols are ubiquitous in nature and covers major fraction of atmospheric aerosols (Wu et al., 2020). An earlier work has reported that fog and hazy atmosphere include significantly high organic aerosols loading due to their highly polar nature (Izhar

Table 1
BSOA, Precursors, mass fragments and their day & night-time dominance

S.N.	SOA Tracer Name	Precursor	Mass of SOA	Mass Fragments	Mechanism of formation Dominated in	References
1.	 2-Methylglyceric acid	 Isoprene	134	321, 203, 293, 219, 337	Day	Fu et al., 2010
2.	 C5-Alkene triols	 Isoprene	118	NA	Day	Wang et al., 2005; Kourtchev et al., 2005
3.	 2-Methyltetrols	 Isoprene	180	409, 219, 319, 293, 203	Day	Edney et al., 2005; Claeys et al., 2004,
4.	 cis-Pinonic acid	 Terpene	184	257, 121, 139, 167, 187	Day	Fu et al., 2010
5.	 cis-Norpinic acid	 Terpene	NA	NA	Night	Fu et al., 2010
6.	 Pinic acid	 Terpene	186	241, 315, 151, 197, 331	Night	Fu et al., 2010
7.	 MBTCA ^a	 Terpene	NA	NA	Night	Fu et al., 2010
8.	 β-Caryophyllinic acid	 β-caryophyllene	254	309, 383, 399, 427, 439	Day & Night	Fu et al., 2010

^a 3-methyl-1,2,3-butanetricarboxylic acid

et al., 2020). Acetic and formic acids are well known conventional organic acids present in gas and particle phase in the atmosphere (Link et al., 2020). These organic acids are derived from biogenic as well as anthropogenic sources. Among the various organic acids, dicarboxylic acid is formed via oxidation reaction between atmospheric hydrocarbons and ozone (Zhang et al., 2020b), and the pinic and pinonic acids are formed from oxidation reactions of α -pinene. Researchers have reported that the pinic acid is the most abundant species in particle as well as gas phase in the atmosphere (Babar et al., 2020; Kołodziejczyk et al., 2020). The organic acids produced in gaseous phase react with NH_3 and form condensable salts (Qi et al., 2020). This phenomenon indicates the enhanced SOA formation in NH_3 rich atmosphere (Sorooshian et al., 2020). Some exceptional cases are also reported in which acetic and formic acids do not form condensable salts with NH_3 (Abbatt and Wang, 2020).

In one of the chamber studies, α -pinene was primarily allowed to react with O_3 until the aerosol formation and thereafter NH_3 was added in the reaction chamber (Bagchi et al., 2020). This caused significant enhancement in the numbers and aerosol mass concentration and indicated the triggering of gas-to-particles conversion process in the reaction chamber. They observed that adding NH_3 enhanced the particles size from 242 to 248 nm, which indicated the condensation of SOA (formed from α -pinene, ozone and

NH_3) over pre-existing particles. Similarly, enhanced SOA (e.g., pyruvic acid and 2-methylglyceric acid) formation was reported during the reaction of VOC (isoprene) with ozone and NH_3 (Chen et al., 2020; Wang et al., 2020b). Firstly, energy rich ozonide is formed via oxidation reaction of double bond of alkene with ozone. The ozonide is then decomposed in carbonyl substituted C10–C1. The norpinic acid, pinonic acid, pinic acid and norpinonic acid were found to be produced via α -pinene, ozone and NH_3 reactions (Winterhalter et al., 2003; Lengyel et al., 2020).

Relative humidity also plays crucial role in SOA formation (Sun et al., 2013; Cheng et al., 2015). Fick et al. (2003) reported that formation of pinonaldehyde and pinic acids are significantly enhanced at higher relative humidity. However, pinonic acid formation decreases with higher relative humidity (Kammer et al., 2020). They also reported that the SOA yield under dry condition is higher than the yield obtained for humid condition. However, a kinetic modeling study conducted by Kamens et al. (1999) reported that water vapor increased the gaseous SOA formation and condensation over particle phase. The enhanced SOA formation under humid conditions are significant than dry conditions (Liu et al., 2020; Pratap et al., 2020). Humid conditions are also reported for acidic SOA product formation (Geng et al., 2020). To investigate the role of acidity, the oxidation reaction of VOC with

Table 2
Concentration (ng m^{-3}) of BSOA form difference studies.

S.N.	Study site	Event	Particle Size	Isoprene SOA tracers			Monoterpenes SOA tracers			β -caryophyllene		References
				MGA	C5-alkene triols	MTL	3-HGA	PA	Pinic acid	MBTCA	CPA	
1.	Qinghai Lake	Summer	TSP	1.0 \pm 0.35	1.2 \pm 0.81	1.6 \pm 0.84	3.7 \pm 2.1	11 \pm 4.2	0.72 \pm 0.23	0.22 \pm 0.22	ND	Ren et al. (2018)
2.	Shanghai, China	Winter	TSP	2.5 \pm 0.58	0.44 \pm 0.24	0.81 \pm 0.29	4.4 \pm 1.2	8.0 \pm 1.7	3.9 \pm 1.2	ND	ND	Ren et al. (2018)
3.	Alaska, USA	Summer	TSP	0.5 \pm 0.1	7.7 \pm 2.1	15.2 \pm 3.1	0.59 \pm 0.07	1.34 \pm 0.6	5.18 \pm 1.2	2.65 \pm 0.3	0.62 \pm 0.1	Haque et al. (2016)
4.	Alaska, USA	Winter	TSP	0.09	0.02	0.04	0.23	0.68	1.3	0.1	0.04	Haque et al. (2016)
5.	Mumbai, India	Winter	PM ₁₀	1.2 \pm 0.80	0.95 \pm 1.2	1.4 \pm 0.45	14 \pm 11	1.9 \pm 0.73	2.7 \pm 1.9	0.49 \pm 0.37	5.6 \pm 2.9	Fu et al. (2016)
6.	Chennai, India	Winter	PM ₁₀	0.67 \pm 0.45	2.18 \pm 2.93	2.75 \pm 2.78	6.24 \pm 6.68	0.82 \pm 0.36	1.00 \pm 0.82	0.25 \pm 0.30	2.76 \pm 1.92	Fu et al. (2010)
7.	Central China	Annual	PM ₁₀	4.1 \pm 2.2	8.1 \pm 9.8	8.5 \pm 6.4	2.1 \pm 1.1	3.0 \pm 1.4	NA	1.6 \pm 1.1	2.2 \pm 1.2	Li et al. (2013)
8.	South China	Fall-winter	PM _{2.5}	2.04 \pm 1.9	NA	27.6 \pm 15.1	0.43 \pm 0.59	3.60 \pm 3.76	1.25 \pm 0.79	1.16 \pm 0.99	0.54 \pm 0.56	Ding et al. (2011)
9.	Beijing, China	Winter	PM _{2.5}	3.63	2.38	1.17	4.27	NA	NA	NA	NA	Shen et al. (2018)
10.	Tianjin, China	Summer	PM _{2.5}	20.09	15.32	34.42	15.58	NA	NA	NA	NA	Shen et al. (2018)
11.	Shanghai, China	Summer-Spring	PM _{2.5}	1.29 \pm 0.92	NA	6.07 \pm 3.86	0.39 \pm 0.46	0.92 \pm 0.93	NA	1.45 \pm 1.17	0.58 \pm 0.75	Zhu et al. (2018)
12.	Guangzhou	Annual	PM _{2.5}	2.05 \pm 2.07	17.7 \pm 22.2	8.14 \pm 10.8	11.8 \pm 8.09	5.82 \pm 5.92	1.34 \pm 0.92	9.25 \pm 7.94	9.25 \pm 7.94	Yuan et al. (2018)
13.	East China	Summer	TSP	1.4	2.2	4.8	2.2	NA	3.4	5.6	2.9	Kang et al. (2018)
14.	Jinan, China	Annual	PM _{2.5}	7.5 \pm 12.6	8.8 \pm 24.2	26.7 \pm 56.6	11.6 \pm 6.2	12.4 \pm 5.0	NA	NA	NA	Liu et al. (2019a)
15.	Southeastern China	Annual	PM _{2.5}	1.38 \pm 0.72	11.3 \pm 18.1	32.5 \pm 48.8	13.3 \pm 9.36	0.41 \pm 0.95	1.22 \pm 1.25	7.8 \pm 6.08	5.99 \pm 7.25	Hong et al. (2019)

NA – Not Available, ND– Not Detected

ozone and NH_3 was performed at pH 9.0 (Jang et al., 2002). High SOA yields were obtained under humid (31%) and acidic conditions. The proposed reasons were increasing in gaseous organic acid and subsequent condensation and particle phase SOA formation under NH_3 rich environment.

2.7. Effect of acidic aerosols

Atmospheric aerosols may have acidic nature depending upon the concentration of water-soluble inorganic ions. These acidic aerosols have significant impact on atmosphere like lower visibility, cloud processing and human health impacts (Zhang et al., 2007). Increased SOA loading is also reported in many works due to the presence of acid catalyzed aerosols (Tsigaridis and Kanakidou, 2003). A chamber study of reactions, between isoprene and oxidants at different $[\text{H}^+]$ acidity, was conducted by Surratt et al. (2007) towards finding the influence of aerosol acidity on isoprene derived SOA formation. They found that the obtained mass of the SOA was linearly correlated with acidity, hence concluded that higher acidity caused more SOA formation. Yields of 2-methyl erythritol and 2-methyl threitol present in particle phase were also found to increase with increasing acidity. High isoprene derived SOA with acidic aerosols is also reported in ambient air (Jaoui et al., 2004). Formation of one of the isoprene products, i.e., 2-MGA, however, was reported to be unaffected by acidic aerosols (Edney et al., 2005; Kleindienst et al., 2009). In another study, Zhang et al. (2007) reported a 25% increase in secondary organic carbon yield with high acidity of ambient aerosols at Pittsburgh. They reported the acid catalyzed effect on SOA formation. Offenberg et al. (2009) conducted a laboratory study of SOA formation derived from β -caryophyllene and α -pinene by varying $[\text{H}^+]$ concentration and keeping NO_x and precursor concentration constant at simulated condition of ambient atmosphere. Isoprene and β -caryophyllene both were allowed to oxidize with NO_x onto smog chamber. The SOA yields were reported to be high with increasing aerosols acidity for β -caryophyllene, while inverse results were reported for α -pinene derived SOA yield which showed less SOA yield with high aerosols acidity.

2.8. Gaseous and liquid phase interactions during SOA formation

Atmospheric gases and their uptake towards liquid phase play key role in the extent and nature of SOA formation (Gorkowski et al., 2020). Most of the reactions occur at the interface between the atmospheric gases and liquid phase of aerosols (Qian et al., 2019). Brüggemann et al. (2020) reported about inadequacy of the only liquid phase mechanism to explain SO_2 initiated oxidation mechanism, as it occurred via bound complex formation between gas and liquid interface. Zhang et al. (2019) also reported that glyoxal and acetaldehyde uptake mechanism also undergo complex reactions at the interface. Enhanced reactivity at the interface is reported due to photochemical activity. A study reported that presence of light between 300 and 500 nm strongly enhances the NO_2 initiated SOA formation process due to photosensitized transfer of electron (George et al., 2015). The photo induced reaction is stronger on humic acid in which a light induced reduction of NO_2 leads to gaseous nitrous acid (HONO) formation. The chambers experiment also indicated the HONO formation on humic acid aerosol. A similar chambers experiment revealed the occurrence of a photo induced reaction with strong absorption band appearing at 450 nm for benzophenone and phenol when exposed to ozone (Zhang et al., 2020b). The similar shift of band was also observed for photochemical oxidation of limonene during the SOA formation process in the atmosphere (Shiraiwa et al., 2019). Chambers experiments revealed that carbonyls undergo aldol condensation in

sulfuric acid containing solution forming oligomers (Mekic et al., 2019). The ammonium sulfate and amino acid in aqueous phase were found to form light-absorbing “humic-like” substances (Grace et al., 2019).

2.9. Ice nucleation

Cloud phase reactions and ice nucleation both play crucial roles in maintaining the atmospheric radiation budget of the Earth (Quante, 2004). Earlier works have reported two types of nucleation phenomena, i.e., homogeneous and heterogeneous nucleation during ice nucleation (Spichtinger and Gierens, 2009). Inorganic salts, dust particles, and bioaerosols are believed to trigger the ice nucleation activity (Baustian et al., 2013). Some organic aerosols like oxalic acid, citric acid, and ethylene glycol have been reported as ice-nucleating species (when present as single-component organic aerosol) (Murray et al., 2010). Organic aerosols can exist as liquid, amorphous and glassy forms depending on the composition and water extents of aerosols (Koop et al., 2011). A laboratory study conducted by Mohler et al. (2008) found that α -pinene derived SOA is effective towards ice nucleation. Another work, however, has reported that the α -pinene SOA shows weak ice nucleation activity in the cirrus cloud presents at an upper troposphere (Ladino et al., 2014). Wilson et al. (2012) and Schill et al. (2014) found SOA and organic aerosols to be sufficiently active towards ice nucleation. The mixtures of dicarboxylic acid, raffinose, and ammonium sulfate seed aerosols are reported to be highly active towards ice nucleation at temperature <220 K (Wagner et al., 2012). SOA containing methylamine and methylglyoxal presents as glassy state and shows poor ice nucleation activity. However, adding ammonium sulfate significantly enhances their ice nucleation activity. Ammonium chloride and ammonium sulfate coated with long-chain alcohol have been found to increase the freezing temperature of solution (Cantrell and Robinson, 2006; Zobrist et al., 2008). Like the structure of ice, the alcohol-containing aerosols can assemble into 2dimensional crystal at the air-solution interface. Prenni et al. (2009) have demonstrated the none-ice nucleation-activity of 25 different alkenes molecules containing SOA at 243 K. Apart from these works, there is still a substantial knowledge gap between the SOA and ice nucleation activity. Hence much research is needed to improve the understanding of SOA formation and ice nucleation.

3. Analytical techniques employed

3.1. Molecular characterization of biogenic constituents of SOA

When molecular characterization of particular compound is done, a term tracer or marker is used that allows the chemists to gain insight into the composition of complex matrix such as the ambient aerosols (Johnston et al., 2019). In the photooxidation of isoprene, 2-methyltetrols, 2-methylglyceric acid, C₅-alkene triols and related oligomer products have been identified as tracers and have been also confirmed in the field samples from the Amazon basin, Brazil and from mixed coniferous and deciduous forest in Hungary (Claeys et al., 2004). The GC/MS with prior trimethyl silylation was used for analysis of ambient aerosol samples. The molecular formula of constituent SOA tracers can be estimated using chemical ionization mass spectrometry (CI-MS) (Wang et al., 2004).

3.2. Analytical advancements

The SOA consist of a myriad of compounds, which exhibit diversity in their physical nature in atmosphere and hence the

techniques involved in their complete characterization become complicated. Based on the capability of acquiring information on the characteristics of SOAs, the techniques employed may be explained into following categories-indirect method, online technique, and the offline technique. The difference between measured total organic aerosols and estimated primary organic aerosols (POA) forms the basis of indirect method of quantification of SOA. The offline measurement technique includes nuclear magnetic resonance spectrometer (NMR), gas chromatography-mass spectrometry (GC-MS), Fourier transform infra-red spectrometer (FTIR) and liquid chromatography-mass spectrometry (LC-MS), which give complete information about different chemical components of organic aerosols. Aerosol mass spectrometer (AMS) comes under online measurement technique that provides fast acquisition time and near real time data but they are less capable of providing information about composition (without providing details of individual fractions) (Ide et al., 2019).

The most widely used technique for characterization of SOA from complex mixture aerosols is gas chromatography coupled with mass spectrometry, which is utilized as the most powerful separation and analytical technique (Kotianova et al., 2004). The hyphenated techniques like GC-MS is usually used with electron ionization (EI) or chemical ionization (CI) detectors and similarly, LC-MS is used with atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) detectors in positive and negative ion modes. The complexity and highly oxidizing nature of SOA make some limitation to completely characterize individual components, because they can give overlapping peaks and may cause majority of mass fractions as unresolved (Williams et al., 2007). To overcome such situations, researchers have developed derivatization process that makes organic compounds available for chemical characterization using analytical techniques (Claeys et al., 2004; Jaoui et al., 2005; Szmigielski et al., 2007; Healy et al., 2008). The molecular mobility in the GC column is generally restricted by the presence of alcohol, carbonyl and carboxylic acid groups in the molecules (Liao et al., 2007). Poor detector response is obtained in GC due to interaction of such molecules with stationary phase. Moreover, some chemical species remain undetected. Derivatization process includes formation of derivatives of analytes. Derivatives formation suppresses polarity and increases volatility of the analytes. Hence, derivatization improves separation of mixtures and provides better GC response. Derivatization for GC analysis is done via three different reactions, i.e., acylation, alkylation and silylation (Flores et al., 2014). Simply in the silylation reaction, insertion of a substituted silyl group occurs. The hydrogen atom replacement via silyl group increases polarity of less volatile molecules and, hence, it makes the analytes suitable for GC separation (Flores et al., 2015). To increase the resolution, researchers have developed two dimensional GC coupled with time of flight (TOF) mass spectrometer that has the capability of detecting 10,000 organic species in the ambient atmosphere (Hamilton et al., 2004).

For characterization of high molecular weight and highly polar compounds LC is used. Mainly, LC is used for analysis of carboxylic acids (Walhout et al., 2019a). Further, the hyphenated technique, i.e., LC-MS has better detection limit, high sensitivity and good reliability over LC with fluorescence detector technique. LC does not need any derivatization techniques for analysis (Iinuma et al., 2007). To overcome the problem regarding low resolution, Iinuma et al. (2007) used two dimensional LC for characterization of organosulfates in pinene derived SOA.

Fourier transform infrared (FTIR) spectroscopy is used for the detection of functional groups in compounds, in samples collected on filters. One of the major advantages of this technique is that it is capable of measuring some functional groups, e.g., amines and organosulphates, which are difficult to measure using other

techniques. Many researchers have employed FTIR spectroscopy in field samples (Takahama et al., 2019; Wallington et al., 2019). The OA characterized by FTIR spectroscopy is also in good agreement with AMS study in many reported works (Lechevallier et al., 2019; Singh et al., 2019).

Very high-resolution techniques such as ultra-high-performance liquid chromatography electron spray ionization quadrupole-TOF-MS (Particle into liquid sampler (PILS) - Ultra performance liquid chromatography (UPLS)/ESI-Q-TOF-MS) in liquid sampling has been used for quantification of SOA. TOF/MS is used for differentiating secondary volatile organic compounds (SVOC) and particle phase species. The SOA are firstly derivatized by silylation and thereafter separated by GC enabling sequential identification and quantitative analysis of alkanolic acid, polyols, diacids, sugars and multifunctional compounds with MS detector. A good time resolution online technique for quantification of SOA includes AMS for quantitative measurements of time resolved aerosol chemical composition of atmospheric aerosols (Salcedo et al., 2006).

A direct determination of glyoxal by open path differential optical absorption spectroscopy (DOAS) has been done by researchers, which presents novel means to get information about VOC oxidation process (Volkamer et al., 2006). Chemical ionization mass spectrometers (CIMS) now-a-days is employed frequently for quantification and characterization of VOC through ionization with reactive ions such as H_3O^+ , NO_3^- , CF_3O^- , or acetate and also for characterizing organic trace gases. The multi orifice volatilization impactor (MOVI) coupled to TOF/CIMS has also been used in some works that provides the molecular mass data, but not fragmentation, to identify isomers or additionally unknown compounds (Nozière et al., 2015). Thermal desorption aerosol gas chromatography (TAG) is also a frequently used technique for separation of the organic molecules from the matrix. Since CI is a soft-technique, instead fragmentation pattern, it only provides information about the molecular mass, hence it is coupled to MOVI flux measurement device to gather more information (Isaacman et al., 2014). Measurement of ambient aerosols with good time resolution is done using aerosol mass spectrometer (AMS). The complicated mass spectra obtained with the use of electron ionization are resolved

into individual oxygenated and deoxygenated organic aerosol components using positive matrix factorization (PMF) source apportionment (Zhang et al., 2011).

The mostly employed analytical techniques used for OA, compared with each other on the basis of the three features: time and size resolution, percent of mass that can be analyzed, and chemical resolution of an instrument, are summarized logically through chess-board scheme in Fig. 4. Here, pre-eminent pieces of chess have been used as a depiction of the most powerful analytical technique. This most powerful piece was considered on the basis of number, and direction of moves and hence the overall ability to attack on the opponent. Here, Queen is considered as the most powerful piece and Pawn is considered as least powerful piece. Here Queen is representing 2D-GC/MS and Pawn is representing the assumed useless analytical technique. The positions of particular piece/analytical technique have their own importance. It can be understood as a 3Dimensional graph, containing three different scales, i.e., mass percent analyzed (Y1 scale), chemical resolution (X1 Scale) and time and size resolution (Y2 scale). Hence, the assumed perfect instrument is placed in h8 position while, the useless instrument is kept in a1 position of the chess-board. In the similar way all the analytical techniques are compared using chess-board as 3D representation.

As mentioned in the figure, GC/MS, which provides molecular identity, is able to investigate only 40–50% of the complete aerosols mass existing in the atmosphere. The analysis of organic mixtures using GC/MS, mostly takes 1 h as reported by William et al. (2007) but the drawback is limited size resolution. Similarly, the thermal-optical carbon analyzer can determine the total OC with 1-h time resolution but with limited size resolution. However, the combination of techniques will completely be able to provide more about the composition of aerosols and their quantification with better time and size resolution in the analysis of organic aerosols (Goldstein and Galbally, 2007). PILS-WSOC, which includes the use of particles into liquid sampler (PILS) is available with the analysis of water-soluble organic carbon (WSOC). PILS has the ability to achieve the time resolution of minutes but there is also drawback of limited size resolution. This was not possible with water-soluble organic carbon analyzer alone. The other instrument, AMS

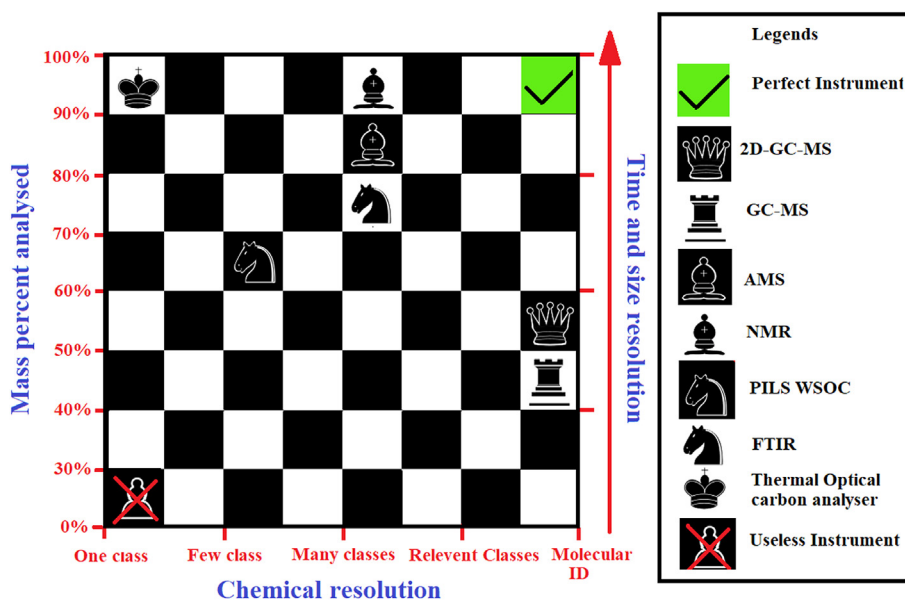


Fig. 4. 3D depiction of some of the current techniques used to analyse the aerosol's organic content on basis of their supplemental nature. The explanation and abbreviations are given in the text.

provides good time and size resolution, it can also give chemical composition, whereas the characterization done by NMR and FTIR is more directly associated with functional groups (Aiken et al., 2008; Decesari et al., 2007). Hence, the 100 percent perfect instrument with all necessary characteristics does not exist, but hyphenation of techniques is useful for characterization of OA.

4. Worldwide and seasonal variation of BSOA

In this section, the seasonal variation and worldwide estimation of three main categories of BSOA tracers derived from isoprene (SOAI), monoterpenes (SOAM) and sesquiterpenes (SOAS) are described. Zhu et al. (2017) estimated BSOA tracers in PM_{2.5} aerosols of Shanghai, China during summer-spring season. They found the SOAI tracers to be the most abundant over SOAM and SOAS. The SOAI formation was found to be temperature dependent; hence, high concentration of SOAI was reported for summer days. The study revealed a weak correlation indicating the non-dependence characteristics between relative humidity and SOAI, and a significant increase in SOAI formation with increase in the acidity of aerosols. One of the SOAI, 2-methylglyceric acid was reported to have different formation process marked by weak correlation between 2-methylglyceric acid with other SOAI. Interestingly, cis-pinonic acid was reported to be the first oxidation product of monoterpenes based on its negative correlation with all other SOA tracers. Yuvar et al. (2018) discussed the seasonal differences and the meteorological factors influencing SOA formation at Pearl River Delta. SOAI loading was found significant throughout the study period; however, SOAM and SOAS formation were dominated in the summer season. Atmospheric oxidants also played crucial role in SOAI, SOAM and SOAS formation via heterogeneous photochemical reactions onto the particles surface.

BSOA are usually found more abundant in summer over winter. Fu et al. (2016) reported Coastal region Mumbai (India) has high abundance of BSOA in winter than summer. This was reported to be due to the predominant southwest summer monsoon, which circulated clean marine air to Mumbai, India. The rise in SOA abundance and its temporal variation during winter indicated large contributions of continental aerosols via long-range transport along with local sources. Contrastingly, Fu et al. (2016) also found SOAI and SOAM to be more abundant than those of SOAI at Mumbai, India. In another work, organic molecular composition of PM₁₀ samples, collected at tropical region of India, viz., Chennai for BSOA showed the high abundance of SOAM and SOAS in late winter, whereas in summer SOAI contribution was more significant. The abundance of β -caryophyllene SOA tracers were found comparable during winter and summer at Chennai (Fu et al., 2010).

Kang et al. (2018) estimated the molecular composition and concentration of BSOA and found the significant transportation of BSOA from continental inland areas to East China Sea. Here, SOAM was found to be the dominated species over SOAI and SOAS, which indicated the formation of photochemically aged SOA through long-range transport. The concentration of SOAI tracers were reported to be higher than other SOA tracers in aerosols samples of urban site in Jinan North China (Liu et al., 2019b). The SOAI tracer was reported to be high in summer and low in the winter. In this work, the increase in SOAI and SOAM concentration was correlated with increase in atmospheric ozone concentration, and decrease in their respective concentrations with increasing NO_x concentration. In another study Hong et al. (2019) reported high SOAI abundance than other tracers in PM_{2.5} during summer season at Mt. Wuyi, southeastern China. The reason behind more abundant 2-methylglyceric acid in fall-winter season was concluded to be due

to atmospherically favored conditions like low temperature and higher NO_x concentration. Here also β -caryophyllene and levoglucosan were found strongly correlated indicating biomass burning emission as a common source. In another work, Ding et al. (2011) reported an estimate for BSOA tracers in fine particles (PM_{2.5}) over rural region Pearl River Delta (PRD) in south China. Here, 2-methyltetrols showed good correlations with atmospheric temperature. 2-Methyltetrols was also strongly correlated with aerosol acidity, which indicated the enhanced SOAI formation with aerosol acidity. The negative correlations found for α -pinene SOA tracers may produce from their transfer in particle to gas phase with the increase of aerosol acidity. Shen et al. (2018) investigated the PM_{2.5} samples from urban sites like, Beijing, Tianjin, Shijiazhuang and Xinglong (background site) over one-year time duration. The background site, Xinglong had seasonal highest SOAI and SOAM concentration over urban sites. SOAI had more abundance in summer, however, the SOAM and SOAS had more abundance in spring. They also concluded that the background site was mostly influenced by biogenic sources. However, urban sites were mostly affected by anthropogenic sources.

Haque et al. (2016) estimated total suspended particulates (TSP) samples from central Alaska, USA for BSOA. Here, SOAI was reported to be more abundant in summer; however, SOAM and SOAS were found least abundant in summer. Contrastingly, SOAM and SOAS were found more abundant in spring whereas, SOAI was least abundant in spring. Hoque et al. (2016) also reported that the β -caryophyllene was strongly correlated with levoglucosan biomass burning tracers indicating that the β -caryophyllene was also significantly contributing towards biomass burning. The Subarctic Alaska aerosols were enriched with α/β -pinene and β -caryophyllene, biogenic SOA tracers.

Ren et al. (2019) monitored PM_{2.5} aerosol samples of Mt. Wuyi and observed that the abundances of the isoprene and monoterpene SOA tracers to be higher in summer season than other seasons, whereas the β -caryophyllenic acid was found lowest in summer. Concentrations of BSOA tracers showed a positive correlation with temperature and a negative correlation with relative humidity. Moderate correlations between the gaseous pollutants (SO₂ and NO₂) and BSOA tracers observed in the mountain top of southeast China suggests that the gaseous pollutants trigger the acid-catalyzed heterogeneous reaction and SOA formation. In this work also significant correlation was observed between the β -caryophyllene and levoglucosan indicating their genesis from biomass burning. Ren et al. (2019) also concluded that anthropogenic sources in China may enhance BSOA production in the distant mountain top regions.

5. Environmental impact of SOA

The presence of SOA in the atmosphere has impact on the climate and health. Respiratory diseases, reduced visibility, haze, degradation in the air quality leading to a polluted environment and more are the results of presence of organic species in atmospheric aerosols. The regional cooling observed in the southeastern US have been attributed to them. It is expected that NO_x, SO₂, and VOC emission would be decreasing in North America, Europe and vicinity areas, whereas it would be increasing in Asian continent, in future. These changes in the climate, disturbs the global ecosystem distribution and ultimately BVOC emission rates. Consequently, ozone levels would get affected and thus the SOA formation in both regional and global scales. The vulnerable arctic environment is under special threats since it has experienced warming at a rate two times the rate of the global average. Moreover, surprising

depletion in tropospheric ozone concentration at Polar Regions was reported. The SOA so formed influence the ecosystem in many ways playing a key role in tropospheric chemistry including ozone dynamics, CO production and methane oxidation.

SOA has some optical properties; it absorbs and scatters the solar radiation hence alters the radiation budget of Earth. The optical properties of SOA may depend upon the chemical complexity of atmospheric SOA, presence of atmospheric oxidants, VOC loading and aerosols aging (Moise et al., 2015). Optical properties of climate can be estimated by the parameter named radiative forcing SOA (RFSOA). The annual average RFSOA was reported to be -0.27 to $+0.20 \text{ W m}^{-2}$ (Boucher et al., 2013). This finding is also mentioned in the 5th annual assessment report by Inter-Governmental Panel on Climate Change in 2014. Many of the global climate models have been established to estimate the RFSOA of the organic aerosols in which the interaction between aerosols and radiation due to light scattering and absorbing properties of SOA have been described. Scattering of radiation has cooling effect; however, absorbing nature has heating effect on the atmosphere. Recent model studies have revealed organic aerosols to be mainly white particles having very small absorbing nature (Hoyle et al., 2009; Spracklen et al., 2011; Myhre et al., 2013). Myhre et al. (2013) made a comparative study between 16 global model results and concluded RFSOA value for cooling to be -0.4 W m^{-2} , which was higher than the heating estimates. Results indicated the dominance of scattering SOA on directly influencing the climate. In addition, light absorbing SOA also significantly contributed to influencing the climate. Absorbing SOA is a broad part of organic aerosols present in the atmosphere named brown carbon that absorbs in much stronger wavelength than black carbon (Liu et al., 2015). Shrivastava et al. (2015) reported that atmospheric burden of SOA is far higher than the black carbon because brown carbon strongly absorbs at lower wavelength. Hence, absorptivity coefficient by SOA has greater importance to evaluate atmospheric implication. Absorptivity on particular wavelength depends upon the precursors of SOA, their formation process and geography of location (Zhang et al., 2011).

Less absorbing SOA ($\text{MAC}_{405\text{nm}} < 0.02 \text{ m}^2 \text{ g}^{-1}$) was formed from oxidation of α -pinene via OH radical, whereas SOA from toluene via OH/NO_x as oxidant was more absorbing ($\text{MAC}_{405\text{nm}} = 0.4 \text{ m}^2 \text{ g}^{-1}$) nature (Lin et al., 2015). In addition, absorptivity of atmospheric SOA also depends on the presence of ammonia that increases the absorbing coefficient of SOA (Updyke et al., 2012). On the other hand, Lee et al. (2014) reported that photochemical aging could also alter the light absorbing properties of SOA. Solar radiation can decompose certain absorbing species; however, some light absorbing species may form onto particle phase via heterogeneous photochemical reactions (Hinks et al., 2016). Generally, dehydration of aerosols and cloud particles may form high light absorbing oligomers. However, water uptake may result hydrolysis and less light absorbing aerosols (Nguyen et al., 2015). Additionally, photochemical reactions of imidazole on particle phase also alter the optical properties of aerosols by influencing SOA formation and aging process (De Haan et al., 2019).

Furthermore, absorption coefficient of SOA via other sources, like biomass burning is also significant. Biomass burning is considered to be the major source of atmospheric brown carbon (Washenfeller et al., 2015). Zhang et al. (2016) also found the absorptivity of primary biomass combustion aerosols (405 nm , BBOA $\sim 0.5\text{--}1 \text{ m}^2 \text{ g}^{-1}$) to be far greater than the absorptivity of SOA. Recent global modelling studies have focused on the potential importance of primary and secondary OA from different sources (Wang et al., 2014, 2016; Lin et al., 2015). These studies also incorporated regional measurement of optical depth of aerosols and satellite-based measurement to find global brown carbon contribution. It

was concluded that the heating effect was regionally influenced by the absorbing organic aerosols from biomass combustion and non-natural emissions was comparable with evolved SOA cooling. Ultimately the absorbing nature of SOA depends upon the chemical complexity, formation mechanism, their sources and atmospheric aging.

6. Recent advances in atmospheric chemistry

Researchers across the world have focused on the novel SOA formation mechanism, cloud aerosol interaction and their environmental impacts. Garofalo et al. (2019) investigated the aerosols released from forest fire of western United States and concluded that those aerosols were the products of subsequent oxidation and condensation over particles. Faiola et al. (2019) studied the impact of stress caused by insect's attack on pine trees and their association with VOCs emissions. They also reported significant changes in VOC emissions from plant due to this stress caused by insects. Recently, laboratory research works have revealed the interaction of biomass derived 3-methylfuran and resorcinol with NO₃ radical and subsequent SOA formation in aerosols (Finewax et al., 2019). Similarly, organic nitrates containing SOA formation was reported from multistep oxidation of Δ -3-carene (Draper et al., 2019). In another work, particle phase hydrolysis reactions have been studied in the atmospheric aerosols by Zare et al. (2019). It was concluded that organic nitrates SOA are no longer identifiable due to its hydrolysis onto particles phase. Walhout et al. (2019b) studied about the photochemical aging process of pinene derived SOA. They used the combination of FTIR and UV-vis studies with the offline mass spectrometry to investigate the SOA formation. They also reported that the residence time of aerosols is of 4 days period. Recent surface science studies of aerosols revealed that the surfactants molecules can exist between the gas and particle interface of aerosols. It is reported that surfactants form a coating over particles and alter the cloud condensation activity by reducing the surface tension (McNeill et al., 2013; Ruehl et al., 2016). Cheng et al. (2019) have reported the existence of surfactants in the aerosol samples of marine atmosphere. They studied the interfacial behavior using Langmuir adsorption and the presence of surfactants was confirmed by IR spectroscopy. Vidović et al. (2020) confirmed the presence of brown carbon and SOA in the cloud droplets. A recent study conducted by Fankhauser et al. (2019) indicated the presence of bacterial traces in the aerosols over cloud droplets. The modelling studies revealed that these bacteria can degrade the complex organic compounds into fragments. However, their impacts could be less significant due to the presence of such bacteria in trace level. The physical separation of cloud droplets also limits the extent of bacterial degradation. Recently, Fe³⁺ and isoprene derived organosulfur SOA compounds have been found by Huang et al. (2019) in the atmospheric aerosols. Many research groups have also reported the presence of surface-active substances in the light absorbing compounds containing aerosols (Sareen et al., 2010; Schwie et al., 2010; Li et al., 2011). In another work, significant reduction in the interfacial tension of aerosols was reported due to photooxidation of brown carbons. Gubbins et al. (2019) investigated the influence of alcohol uptake onto organosulfur containing SOA system which revealed that alcohol uptake triggers light absorbing organic formation that leads to the increase in viscosity with increasing O:C ratio of the aerosols. Isoprene derived SOA formed via epoxydiols (IEPOX) causes high viscosity that reduces the further IEPOX uptake and results in formation of stable SOA (Olson et al., 2019; Zhang et al., 2019). All the recent advances open up new ways in atmospheric chemistry and aerosols dynamics. This would be helpful to fulfil the knowledge gaps and

also in tackling atmospheric pollution.

7. Future perspectives

Particles are formed and grow either by condensation or by partitioning on particles or by forming more volatile oxidation products. Hence, ELVOC need attention and analysis towards their formation mechanism and quantifications. The challenges as summarized could be critical requirement of authentic quantitative standards those are currently unavailable, developing more understanding about the atmospheric chemistry of interface from micro to macro level in both gas to particle interface as well as interface between atmosphere and biosphere, cryosphere and hydrosphere, and advanced investigation on interaction of organic and inorganic components. Apropos to the above, advancement in accurate methodologies and high-resolution instruments are the needs of the hours. In this review, detailed mechanisms of BSOA formation is well discussed and besides these more studies are required to estimate the link between biogenic and anthropogenic primary emissions. Faster and accurate analytical techniques are further required for quantitative determination of BSOA mainly their hourly and time series variation studies in the ambient atmosphere are required. The lifetime of BSOA, their distribution in different size ranges, their possibilities of long-range transport and their stability in the atmosphere are some challenges that should be dealt in future by researchers.

8. Conclusion

This review summarizes the different mechanism of gas phase oxidation, reactive uptake of formed gaseous species and subsequent biogenic SOA into aerosol particle surface. The significance of gaseous pollutants (NO_x , SO_2 , O_3) on the vegetation derived VOCs and their degradation under atmospheric conditions (temperature and relative humidity) are elaborated. On the basis of variability in the VOC emission rates the atmospheric chemistry are also different during day and night time. The biogenic SOA formation and their seasonal variations depend on geographical differences and sites of unique atmospheric composition like urban atmosphere, rural regions, coastal areas, mount and forest sites. These regions have great importance because of different unique cross-over between anthropogenic and biogenic pollutants. On the basis of the complexity and the optical properties of organic aerosols their environmental impacts have been discussed in terms of radiative forcing SOA. The widely used analytical techniques for estimation of organic aerosols have been summarized, and based on the information obtained by particular techniques; they are compared using 3dimensional representation onto chess-board scheme. For online measurement the AMS and for offline measurement 2D GC-MS have been considered to be the best suitable techniques for estimation of organic aerosols. Apart from the discussed analytical techniques there is still requirement of a technique with excellent chemical, time and size resolution, which could be able to estimate molecular identity, greater coverage of aerosols mass percent characterization for being able to be placed as near as possible toward the h8 position (represented as perfect instrument) of the chess board (described in results and discussion).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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