

Chapter 3

Organic Compounds in Atmospheric Aerosols

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Abstract

Organic compounds in the atmospheric aerosols and suspended particulate matter (PM) are a vital component of the atmosphere. Most of these compounds are volatile which affects their transport and distribution in the atmosphere. The presence of these compounds has become an issue of serious concern in recent times due to their toxic impact on human health and the environment at large, and their indispensable role as a driving force for various environmental issues. Polyaromatic hydrocarbons, polychlorinated compounds and some other components have been proven to be mutagenic and carcinogenic. Organic aerosols have also been reported to significantly affect climate and visibility. This chapter critically reviews organic compounds in the atmospheric aerosol. It discusses the occurrence and sources of these compounds, classes of organic compounds in aerosols, their impact on

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the environment and human health, recent reports on their distribution and concentrations in atmospheric aerosols. An attempt is also made at highlighting the future trends in this regard.

Keywords: organic compounds, atmospheric aerosols, particulate matter

Introduction

Organic compounds make up a considerable portion (20-80%) of the bulk of fine particulate matter in atmospheric aerosols (Tefera et al., 2021). Organic molecules are obtained through various ways, including the combustion of vegetation along with organic matter as well as photo-oxidation mechanisms in the atmosphere. Major organic compounds in atmospheric aerosol include polyaromatic compounds, chlorinated compounds, aliphatic compounds, amongst others produced mainly from anthropogenic sources even though a few are of biogenic origin (So et al., 2019).

Aerosols in the atmosphere are known to have a significant impact on climate. The many indirect and direct impacts of aerosol particles mostly on Earth's radiative balance and ecosystems have received a lot of attention. Numerous research has been carried out on certain effects, such as the absorption and scattering of solar radiation, adjustments of atmospheric biochemical processes, changes in cloud properties, and the involvement of aerosol particles in providing essential minerals to ecological systems, all of which are encapsulated inside the International Council on Climatic Change reports. Climate factors, in turn, impact mechanisms that regulate atmospheric aerosol distributions, such as transport, emissions, deposition and transformation of aerosol particles, in addition to the impact of aerosols on climate (Tegen, and Schepanski, 2018).

Atmospheric aerosol, particulate matter suspended in the air we breathe, exerts a strong impact on our health and the environment. Controlling the amount of particulate matter in the air is difficult, as there are many ways particles can be formed by both natural and anthropogenic processes. A substantial portion of atmospheric aerosol is organic, and this organic matter is exceedingly complex on a molecular scale, encompassing hundreds to thousands of individual compounds that distribute between the gas and particle phases. Because of this complexity, no single analytical technique is sufficient. However, mass spectrometry plays a crucial role owing to its combination of high sensitivity and molecular specificity. Both offline and

online approaches are covered, and molecular measurements with them are discussed in the context of identifying sources and elucidating the underlying chemical mechanisms of particle formation. There is an ongoing need to improve existing techniques and develop new ones if we are to further advance our knowledge of how to mitigate the unwanted health and environmental impacts of particles (Johnston and Kerecman, 2019).

Organic compounds constitute up to a large portion of the suspended particulate mass in different parts of the earth. These types of particulate matter are essential in a variety of environmental as well as geophysical challenges, from local difficulties to world problems (for example, climate change). However, due to the complexity of organic chemistry and also the wide range of physical properties associated including both artificial and natural organic particles, sampling and acquiring chemical information on such substances is extremely difficult. As a result of these roadblocks, we have an imperfect depiction of a possibly important aspect of atmospheric chemistry, as well as limited knowledge of the aerosol's environmental as well as geophysical effects. Given the insufficiency of quantified molecular techniques, the goal of this work is to provide a foundation for determining whatever information is required, rather than to quantify the role of organic aerosols in ecological problems (Jacobson et al., 2000; Rushdi et al., 2014).

Forested areas of countries such as Egypt, Amazonian regions, IGP, China and Europe are an ideal habitat to research secondary organic aerosols because of complex atmospheric properties, which are frequently within photochemical circumstances. Investigate the content of aerosols in situ, notably in photo-oxidation processes of organic carbon volatile compounds, while accounting for natural and anthropogenic sources, and also to understand how some of these molecules occur in the aerosols. The secondary organics detected are di-, oxo- and monocarboxylic acids, alkene derivatives, thia and aza arenes, oxy-aromatics, and several terpene photo oxidation products. This in situ experiment permitted the existence of secondary components to be confirmed, which had previously only been researched in synthetic experimental conditions (Alves and Pio, 2005).

Occurrence and Sources of Organic Compounds in Atmospheric Aerosols

Despite significant advancements in the past few years, predictive and quantitative knowledge of atmospheric aerosol chemical composition,

sources, environmental consequences and transformation processes remain a key research problem in atmospheric science. This overview starts with a historical context on scientific problems about atmospheric aerosols from over decades, then moves on to a characterization of their distribution, transformation processes, sources, and physical and chemical characteristics since they are now recognized (Calvo et al., 2013).

Winter/autumn could see a rise in monocarboxylic acids, polycyclic aromatic hydrocarbons (PAH), bisphenol A and biomass burning tracers whereas summer had seen an increase in dicarboxylic-, BSOA tracers as well as hydroxycarboxylic acids. Diverse sources and production pathways for heterocyclic acids have been identified, with phthalic, benzoic, and trimellitic acids peaking in the summer and isophthalic, p-toluic, among terephthalic acids peaking in the winter/autumn. The carcinogenic, carcinogenic power and mutagenic activities of Benzo[a]pyrene-equivalents were computed and showed substantial ($p > 0.05$) improvements over the wintertime (Kanellopoulos et al., 2021).

In the study of PM_{2.5}, which was a case study of Jinan, a generally polluted city in the North China Plain, in the winter to explore the chemical compositions, origins, and development mechanisms of organic aerosols (OAs) (NCP). PM_{2.5}, organic components (such as fatty acids, sugars, oxygenated-PAHs (OPAHs) and polycyclic aromatic hydrocarbons (PAHs)) and carbonaceous species were 1.8–2.7 times greater in hazy episodes compared to clear episodes. Furthermore, the CWT data revealed that even during haze periods, the majority of OAs came from the surrounding as well as local areas (Li et al., 2021).

Anthropogenic activities are responsible for 60 to 80 percent of sulphur emissions. The huge quantity of pollutants emitted in various phases of industrial applications, as well as the wide diversity of contaminants, characterise industrial contamination. This kind of contaminant produced is mostly determined by the manufacturing process, technologies, or raw materials employed. Several industries that produce bricks, cement, ceramics, mining, quarrying and foundries, all emit considerable amounts of primary aerosols, whether during the manipulation or production and transportation of the raw resources used (Manisalidis et al., 2019).

Steelworks are key point-source emitters of metallic pollutants, according to the study, which was based on an investigation of an incident of pollutants from industry plumes. Because metal-rich particles were detected internally mixed with marine and/or continental chemicals, the authors stressed the importance of coagulation procedures among industrial particles and particles

from other sources. Energy generation from fossil fuels is a significant source of gases that function as secondary aerosol precursors. Primary particles are created by coal waste products including sulphur, clay, chlorides, metals, and carbonates primarily mercury, as well as unburned char or coal in power plants (Csavina et al., 2011).

Emission of sea spray, discharge of soil and mineral dust (rock debris) and emission of biomass burning smoke, biogenic aerosols, and injection of volcanic material to tropospheric heights through severe eruptions are all major ecological surface primary sources of aerosol particles. Space, in the form of cosmic aerosols, contributes a tiny amount to total atmospheric aerosol load distribution, although these fine particles are thought to have only a little impact on the aerosol properties of high-altitude atmospheric regions, where the intensity of particles is always really low. As a result, cosmic rays have little effect on the low stratosphere's air characteristics of the human-environmental condition mostly in the troposphere. These morphological characteristics, optical properties, chemical composition, as well as deposition processes of the many kinds of particles generated at the surface of the planet are all distinguished through well-diversified chemical composition, deposition patterns and morphological features (Viana, et al., 2014).

Aerosols can be anthropogenic or natural, dependent upon their source. Its primary components of anthropogenic aerosols mostly in the atmosphere are industrial and urban areas, and this can as a result of traffic (road surface abrasion, exhaust emissions, tyre and brake wear, particle resuspension from pavements motorways), various industrial operations (emissions from oil refineries, power plants, and mining), construction (soil movement, excavations, and demolitions), as well as emissions from residences in this context (food cooking and heating). Biomass emissions and burning from different farming operations, on the other hand, are the principal producers of aerosols in rural regions. Oceans and seas, soil, deserts, vegetation, volcanoes, lightning and wildfires are all-natural producers of aerosols. Particles from a broad variety of sources have significantly varied chemical components, which are usually connected to their source (Penkala et al., 2018).

Secondary organic aerosol influences the burden of the particles in the atmosphere, affecting climate and air quality. Biologically active volatile organic compounds released by plants, including terpenoids, are part of the key secondary organic aerosol precursors, having isoprene leading biogenic volatile organic compound global emissions. Furthermore, as related to other terpenoids, its particle mass-produced by isoprene oxidation is rather small. Researchers show that in combinations of air vapours, isoprene, methane as

well as carbon monoxide may all reduce the instantaneous mass and total mass yield produced from monoterpenes. Isoprene scavenges hydroxyl radicals, inhibiting their interaction through monoterpenes, and to ensuing isoprene peroxy radicals scavenger highly oxygenated monoterpene compounds, according to research. The yield of low-volatility substances which might normally produce secondary organic aerosol is reduced as a result of all these effects. As a result, highly reactive chemicals that create just a little quantity of aerosol aren't always net producers of secondary organic aerosol mass, and their oxidation in combinations of atmospheric vapours might reduce both the number and mass of secondary organic aerosol particles (McFiggans et al. 2019).

Major Classes of Organic Compounds Present in Atmospheric Aerosols

Organic aerosols make up a major portion of fine-mode aerosols in the atmosphere (with *particle* diameters in the *range* of 10^{-9} to 10^{-4} m). Models of secondary organic aerosol (SOA) production and aging presume that SOA is made up of liquid particles having rapid adequate condensed phase diffusion coefficient to keep the gas phase in balance (O'Brien et al., 2014).

In the same vein, Heald, & Kroll, (2020) examines available knowledge about Organic Aerosol (OA) that is important for global climate studies and identify crucial gaps that must be filled to decrease the associated assumptions. Most of the parts needed to describe OA in a global climate model are sketched out, with such a specific focus on SOA: The main carbonaceous aerosol emission estimates, as well as SOA precursor gas emission estimations, are summarized. The most recent knowledge of condensable organic material chemical production and change is presented. The hygroscopicity of OA is reported, as well as observations of optical characteristics of organic aerosol particles. The mechanics of OA contacts between clouds, as well as parameterizations for wet and dry removal processes in global models, are discussed. This data is compiled to offer a continuous examination of the movement from the released material to the atmosphere, up to the point where the created organic aerosol has a climatic influence. At each phase of the process, the sources of uncertainty are indicated as regions that need more research.

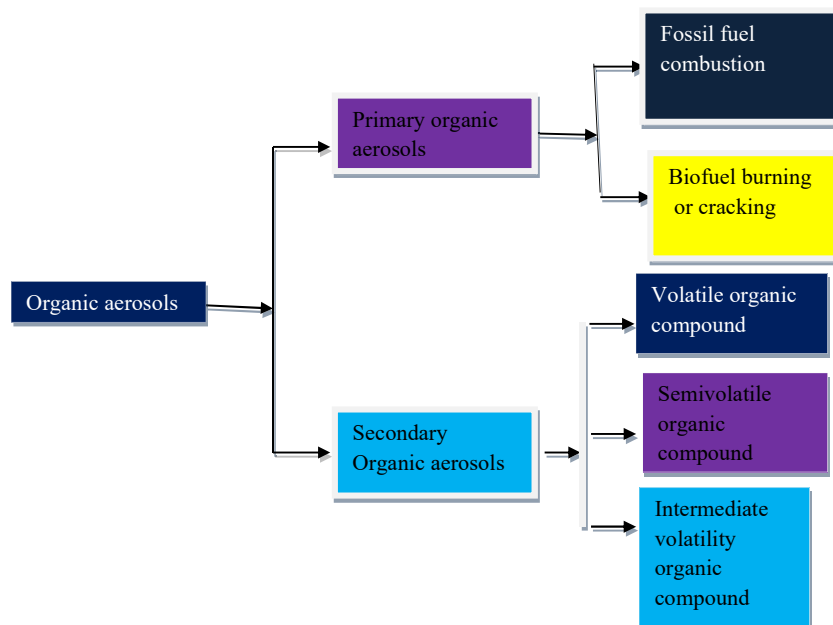


Figure 1. Major classes of organic aerosols.

However, Huang et al. (2021) discovered secondary organic aerosol (SOA), secondary inorganic aerosol (SIA) and Primary organic aerosol (POA) can all be found in a single atmospheric particle (SIA). Research on the quantity but also kinds of phases available in such complicated multicomponent particles is essential to forecast their involvement in climate and air quality. On the other hand, SIA+POA+SOA particles can include three different liquid phases: a higher-polarity organic-rich phase, an aqueous inorganic-rich phase as well as a low-polarity organic-rich phase, as seen here. Based on their findings, three liquid phases could persist inside the same particle across a broad humidity levels scale whenever the SOA's elemental oxygen-to-carbon (O: C) ratio is much less than 0.8. When the SOA's O: C ratio is larger than 0.8, however, three phases do not emerge. It also shows that the existence of three liquid phases in these kinds of particles affects overall equilibration timing also with nearby gas-phase utilizing kinetic and thermodynamic simulations. The capacity of these particles to function as nuclei for liquid cloud droplets, their reactivity and the process of SOA creation and development in the atmosphere will all be influenced by three stages.

Marine aerosol, which contains both inorganic and organic constituents of secondary and primary origin, is among the most significant natural aerosol processes on a worldwide scale. The current research compares novel secondary and primary organic marine aerosol data obtained during the EU project Marine Aerosol Production (MAP) with some of those reported in the previous research. Following prior studies, marine aerosol samples taken at the coastal location of Mace Head, Ireland, indicate a chemical properties pattern that is impacted mostly through the oceanic biological activity cycle (Rinaldi et al., 2010).

Physicochemical Properties of Organic Aerosols

The study of Hays, (2014), stated that the chemical makeup of aerosols is complicated. Several organic molecules, black carbon and refractory brown, cations, heavy metals, salts, anions, and other inorganic phases could be found in ignition aerosols. Semivolatile component divides among the liquid, gas, as well as particle phases in aerosol organic compounds, a process governed by either interfacial mass or dynamic equilibrium transfer concerns. Photo-oxidation of semivolatile and volatile organic materials in the atmospheric could result in the formation of growing particles or particle nuclei through condensation. This heterogeneous particle nanostructure and morphology is produced by the different chemistry along with the processing of anthropogenic emissions aerosols, that impacts to an aerodynamic nature, optical characteristics, and hence the destiny and movement of aerosols. The complicated chemical composition of burning aerosols necessitates the application of several advanced scientific measuring methods. The study focuses on the measures that have emerged in the combustion and aerosol research community for accurately evaluating the chemical and physical characteristics of anthropogenic particles.

Because aerosol particles have such limited air lives, their chemical composition can fluctuate greatly depending on local sources and sinks. Submicron aerosol is made up of organic compounds, inorganic compounds, mineral species and elemental carbon. The bulk of nitrate, sulphate, elemental carbon and ammonium in today's atmosphere come through anthropogenic emissions; organic molecules come through both natural and anthropogenic sources (Allen et al., 2019).

Nitrate, ammonium as well as sulphate are the three frequent inorganic aerosol components. Ammonia (NH_3) is launched as a gas through both

anthropogenic and natural sources, with agricultural practices seeming to be the most prevalent. Once before in the environment, it reacts using different acids to generate ammonium salts. Sulphate has been most typically created when sulphur dioxide, which is produced by anthropogenic activity, the volcanoes or sea, is oxidized. Sulphuric acid (H_2SO_4) could persist as either a particle mostly in the atmosphere, although in the presence of ammonia, it neutralizes to create salts such as ammonium bisulphate (NH_4HSO_4) and ammonium sulphate ($\text{NH}_4)_2\text{SO}_4$. Nitrate is generated in the atmosphere when NO_2 is neutralized. Particulate ammonium nitrate (NH_4NO_3) is formed when there is an accumulation of ammonia in the environment once sulphate has now been neutralized (Zhu et al., 2015; Farah, 2018).

Tropospheric aerosols have an impact on global temperature, air quality and atmospheric compounds. According to current assessments, organic chemicals in this haze account for about half of the total aerosol fine mass concentration worldwide. Although, the well-constrained mechanisms that produce sulfate or nitrate aerosol, oxidation of volatile organics in the atmosphere could produce hundreds of persistent chemicals in the aerosol phase. Modeling the organic aerosol's influence on global warming requires the development of such an amenable system that takes into account the physical and chemical development of the organic aerosol. Researchers explain how to combine a three-dimensional coordinate system described through heteroatom mass, double bond equivalents (D.B.E.) and molecular weight with high-resolution molecular mass data. The use of spectrometry to describe important features of organic aerosols is a strong tool. The technique is simple in principle yet complicated enough to work with quantitative structure-property relationships (QSPRs), which are utilized to estimate physical and chemical factors that regulate aerosol behavior (Yiyi et al., 2012).

If methane or ethane condensate clouds exist, they are patchy, thin, and ephemeral. The pole shadow appears to be connected with, but not contained in, stratospheric clouds of compressed hydrocarbons and nitriles, implying that abundances might change by the season. Crystallizing condensate particles again from the stratosphere is most likely crystallizing centers for the creation and fast expansion of methane ice particles in the troposphere, where even the gas phase is extremely fully saturated. Some hailstones have a fallout period of 2 hours or less once generated. Melting and the possible breakup of methane droplets should happen at a depth of 12 km or less (McKay et al., 2001).

Transport Mechanisms of Organic Compounds in Atmospheric Aerosols

Aerosols in the atmosphere include a large amount of water in the form of thin water films and bulk water. Organic molecules with low vapor pressures and limited solubility give adsorptive surfaces and very large surface areas. They likewise provide very active surface area for the oxidation process in the gaseous environment utilizing singlet oxygen, ozone species as well as hydroxyl. As a result of the interaction at the air-water interface of cloud/fog droplets and in the thin water layer organic molecules and atmospheric aerosols are easily converted (Kalliat et al., 2015).

For responses to the questions "What is there and also how did it get there," atmospheric aerosol research has depended primarily on measurements. Furthermore, researchers have depended on the principles of aerosol research for the assessment of atmospheric particle properties, in addition to recording the composition of atmospheric aerosols. Even by the 1990s, the prominent components of the scientific research that apply to atmospheric particles had become well documented. Theoretical aspects of aerosol scientists that piqued my interest were chemical and mechanics mechanisms (Hidy, 2019).

Secondary organic aerosols are the type of aerosol that forms in the atmosphere when low vapor pressure organic contaminants condense (SOA). SOA is thought to provide an impact mostly on affecting climate change, the atmosphere's radiation budget, public health as well as visibility. Previous research has shown that SOA may considerably influence the fine particle load in the atmosphere in metropolitan areas, particularly when strong smog events (Song et al., 2005).

Recent field data reveals that organic compounds constitute a large constituent of atmospheric aerosols, which supports this concept. A "reversed micelle" with an aqueous core encased in an inert, hydrophobic organic monolayer is suggested as the model organic aerosol. Surfactants of natural material cover the aerosol particles with organic components. They suggest a chemical mechanism in which air radicals interact through the organic surface layer to metabolize it. When an organic aerosol is subjected to an oxidizing environment, an optically active hydrophilic layer and an inert hydrophobic coating transform into a reactive one. As a result, water accumulation could cause packaged organic aerosols to develop and form cloud deposition nuclei, affecting atmospheric radiative transmission. The chromophores that

remained on the surface of the aerosol following chemical conversion might alter radiant transmission significantly. The chemical model generates predictions that may be verified through observation. A curve of percentage organic content as a function of particle diameter, for example, indicates that such upper tropospheric aerosol would include a large proportion of organic substances. Organic aerosol processing in the atmosphere will result in the release of tiny organic pieces into the troposphere, which will then play a role (Ellison et al., 1999; Dobson et al., 2000; Su et al., 2020).

Impact of Organic Contaminants on Human Health and the Environment

Combustion of fossil fuels, transportation, chemical industries, chlorination water purification and pesticides utilized in agriculture are only a few of the forms of organic contaminants released into the environment. The presence of these compounds presents a serious threat to human health, the environment, and other beings (Patel et al., 2020).

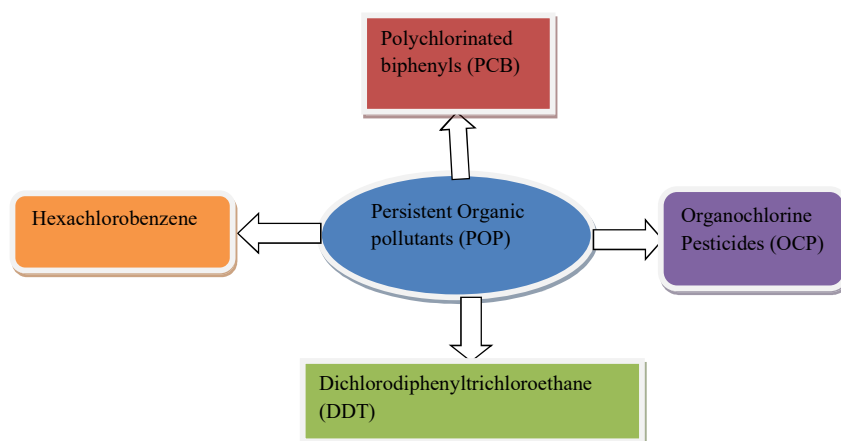


Figure 2. The major class of toxic organic compounds.

Persistent organic pollutants (POPs) are a type of harmful organic chemical that is released into the environment as a result of various human activities. Due to various durability, bioaccumulation, toxicity, and vulnerability, these chemical compounds have become a significant source of

worry. POPs include compounds including polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), (Figure 2) as well as by-products including furans and dioxins, among others. Continuous releases of hazardous chemicals into the water, soil, and sediments have far-reaching consequences for the whole planet (Kudom, 2019).

PCBs, organochlorine insecticides, hexachlorobenzene, DDT, and other industrial by-products such as dibenzofurans, polychlorinated dibenzo-p-dioxins as well as polynuclear aromatic hydrocarbons, are all examples of POPs. Synthetic, lipophilic, persistent, extremely poisonous organic contaminants that accumulate in the food system. POPs bioaccumulate in adipose tissue, raising the likelihood of negative health impacts in children (Thakur and Deepak, (2020).

Recent Reports on Concentrations and Distributions of Various Organic Compounds in Atmospheric Aerosols

The current state of knowledge on the source, composition, impacts and transformations of water-soluble organic aerosol (OA) has still been restricted to outdoor situations. The research, which was influenced through investigations on environmental OA, analyzes but also highlights topics connected to domestic water-soluble OA and its implications on human wellbeing, laying the groundwork for future research on the subject. The following are the three primary subjects that are discussed: the present condition on WSOM from the indoor particles in the air, including the major opportunities and challenges for cytotoxicity evaluation and chemical characterization; what is known about the mass contribution, origin as well as health effects of WSOM in outdoor air particles; and why the aerosol WSOM should have been suggested for future indoor air quality research findings. While difficult, research on the WSOM component in particles of the air is critical for a complete understanding of its fate, origin, long-term dangers inside as well as toxicity (Duarte and Duarte, 2021; Haque et al., 2019).

PM_{2.5}, organic components (such as fatty acids, sugars, oxygenated-PAHs (OPAHs) and polycyclic aromatic hydrocarbons (PAHs) and carbonaceous species were 1.8–2.7 times greater in hazy episodes than in clear episodes (Jelena et al., 2021). One of the most prevalent saccharides has been levoglucosan, which showed substantial associations between carbonaceous species throughout the sample period, indicating that biomass burning has a

major impact on carbonaceous species amounts in PM_{2.5} in Jinan throughout the winter. During the whole sample period, the positive matrix factorization (PMF) model revealed that biomass burning had been the primary source of OAs. Research outcomes of the concentration-weight trajectory (CWT) and the potential source contribution function (PSCF) show that Shandong Province and the Beijing-Tianjin-Hebei (BTH) are contributed significantly to PM_{2.5} levels in Jinan over the winter. Furthermore, the CWT data revealed that during hazy periods, the majority of OAs came from the local and adjacent areas (Li et al., 2021).

Conclusion

Considering major recent scientific advances and efforts, significant knowledge gaps of atmospheric organic aerosols remain, impeding attempts to comprehend, mitigate and model environmental concerns including aerosol generation both in more pristine locations and polluted urban. During the last century, the experimental toolbox accessible to scientists studying atmospheric organic substances had also grown significantly, offering new insights into time resolution, speciation and identification of semi volatile and reactive molecules at trace levels. It has opened up previously unimagined possibilities while simultaneously presenting modern research obstacles. The involvement of epoxides throughout the aerosol formation, particularly from isoprene, its significance of common oxidizing, responsive organic through air-surface mechanisms (regardless of whether aerosol or atmosphere-biosphere exchanges), as well as the extensiveness of interactions between biogenic and anthropogenic emissions and indeed the subsequent influence on atmospheric organic aerosols are just a few instances of ground-breaking research. For carbonaceous aerosols, improved monitoring approaches are required, particularly for quite a better knowledge of the aging processes and chemical composition of organic aerosols. When collecting as well as analyzing organic aerosol chemicals, special care must be taken to remove errors. Because the difference between organic and black carbon is not always evident, measurements must be supported with a characterization of a quantity being measured. It is necessary to attempt to avoid discrepancies in carbonaceous aerosol readings.

Future studies should focus on basic photochemical mechanisms, enhanced chemical deposition, speciation, nitrogen budget closure, and reactive carbon and seasonal and geographical variety in chemical systems,

building on recent breakthroughs in the scientific evidence of atmospheric organic aerosols. This information should have been tailored to individual social concerns such as climate change and the effects of air pollution on human health, as well as appropriate answers such as urban growth, land use modifications, and the creation of new power generation. As a result, societal reactions will have significant feedback effects on atmospheric aerosols, which our society should work to comprehend and anticipate. Particularly tiny organic molecules might experience photochemical degradation, resulting in the creation of 10 to 1000 of those first-generation devices, which will subsequently experience additional transformation and oxidation. As a result, atmospheric researchers are unlikely to be able to detect most VOC oxygen-free radicals mostly in the environment. Therefore, scientists should aim towards diversification to fully comprehend the complexity of detectable constituents to the point from which we can grasp AOAs at the operational level. A deeper knowledge of AOAs at the borders between macro and micro scales is also required. Gas-particle interactions, including those among the biosphere and the atmosphere, hydrosphere and cryosphere, are all examples. Mechanisms in the aqueous medium, along with interactions among organic and inorganic constituents of aerosols, need to be investigated more since they are likely to disclose previously unknown mechanisms.

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