REVIEW

Aerosol Mass Spectrometer (AMS)-Based Real-Time Physicochemical Characterization of Atmospheric Aerosols

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Abstract : Atmospheric aerosols have become a major environmental concern because of their adverse effects on human health, air quality, and climate change. Over the last few decades, several mass spectrometry (MS)-based techniques have been developed and applied in the field of atmospheric aerosol research. Particularly, real-time measurement of ambient aerosols using an aerosol mass spectrometer (AMS) has become one of the most powerful tools for aerosol chemistry. This review provides a brief description of AMS and its applications for understanding the physicochemical properties of atmospheric aerosols, as well as its sources and evolution processes.

Keywords : atmospheric aerosols, aerosol mass spectrometer, non-refractory particulate matter, real-time measurement

Introduction

Atmospheric aerosols are liquid, solid, or mixed particles suspended in the atmosphere. They are composed of complex chemical compounds with various size distributions.[1] It has become one of the major environmental issues due to its impacts on public health and climate change.[2-7] The environmental impacts of atmospheric aerosols vary depending on the chemical composition, particle size, and mass concentration of the airborne particles. Aerosols have natural and anthropogenic sources, and they are either emitted directly into the atmosphere (primary aerosols) or produced from precursor gases (secondary aerosols).[1,4,8] Atmospheric aerosols continuously evolve in the atmosphere and alter their physicochemical properties. Therefore, both qualitative and quantitative characterizations of atmospheric aerosols are necessary to identify their sources and evolution processes, as well as their impacts on the environment and human welfare.

Mass spectrometry (MS) is one of the most powerful tools for characterizing various chemical compounds in the environment. Over the last 30 years, a variety of MS-based approaches have been developed and applied in atmospheric science.[9-15] It has become the most essential and fast-growing analytical technique in atmospheric research because of its dynamic nature, which provides high-throughput qualitative and quantitative information on analytes. Figure 1 shows the number of publications and citations of articles on MS-based aerosol studies over the past 30 years. Their numbers steadily increased over time and peaked in 2018.

Until recently, most of aerosol research was conducted by collecting particles and gaseous pollutants in ambient air.[16-21] Typically, these filter-based measurements have a low time resolution varying from hours to days. However, aerosols are complex mixtures, and their chemical properties may change on a timescale of seconds to minutes, which makes it difficult to identify their chemical properties. The application of real-time measurement techniques with a high time resolution can provide a variety of advantages in the field of aerosol research. In recent decades, state-of-the-art MS techniques capable of on-line/real-time measurements have been developed to characterize the physicochemical properties of aerosols.[22-27] Among them, the aerodyne aerosol mass spectrometer (AMS) has been widely applied to investigate the chemical and physical properties of submicron aerosol particles.[28-33] A complete review of on-line mass spectrometry for atmospheric science is beyond the scope of this paper, and thus the characteristics of the AMS and its applications are discussed.

AMS Instrumentation

There are several types of aerosol mass spectrometers (AMS), including quadrupole AMS (Q-AMS),[34,35] compact
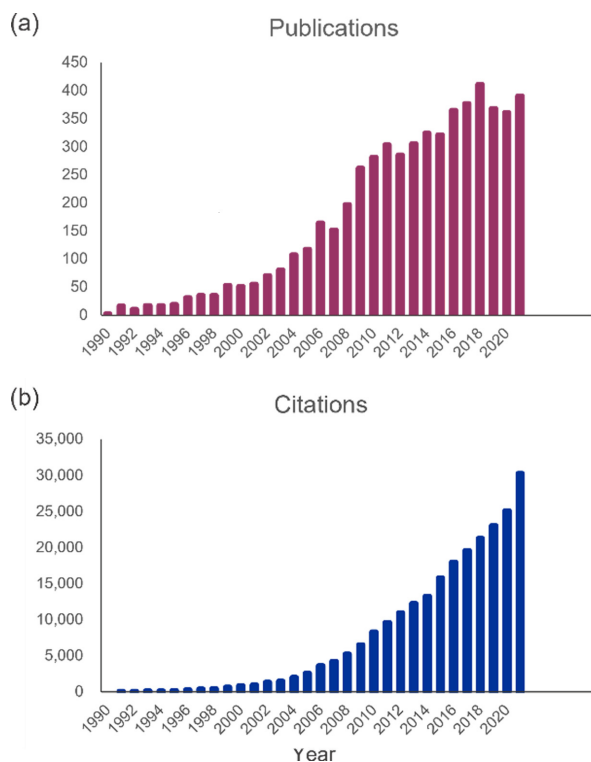

Figure 1. (a) Number of Publications and (b) citation data reported in response to a search on "atmospheric aerosol mass spectrometry" or "atmospheric aerosol mass spectrometer" in Web of Science as of June 2022.

time-of-flight AMS (C-ToF-AMS),[36,37] high resolution time-of-flight AMS (HR-ToF-AMS),[26,31] aerosol chemical speciation monitor (ACSM),[25,38] and soot particle AMS (SP-AMS)[28,39]. Figure 2 shows a schematic of the HR-ToF-AMS. Typically, AMS instrumentation is composed of four main sections: an aerosol inlet, aerosol sizing chamber (PToF region), ionization region, and mass analyzer.[40] The aerosol inlet couples the aerodynamic lens to the vacuum system. The aerodynamic lens focuses particles into a narrow beam (< 1 mm diameter) with approximately 100% transmission efficiency to the detector, for particles in the size range of 70-500 nm.[34,41,42]

In the aerosol sizing chamber, each particle acquires a size-dependent velocity created by gas expansion into high vacuum, and their aerodynamic diameters are determined by particle time-of-flight (PToF) measurements. In the ionization region, the particles are vaporized on a heated tungsten surface at around $600^{o}C$. The non-refractory components of aerosol particles are vaporized and ionized using electron ionization (EI), formerly known as electron impact ionization, with an energy of 70 eV. "Non-refractory" components are empirically defined as compounds that rapidly evaporate under the operational conditions (for example, ammonium nitrate, ammonium sulfate, ammonium chloride, and organic compounds). Among the several types of AMS, SP-AMS is the most advanced type of AMS that can detect refractory components such as black carbon and trace metals as well as non-refractory components with two vaporization modes; a standard tungsten vaporization and an additional laser vaporization, respectively.[39] The positively charged ions generated by EI are introduced to the mass analyzer, and then separated and analyzed according to their mass-to-charge (*m/z*) ratios. HR-ToF-AMS can be operated in V- or W-mode. The V-mode is more sensitive
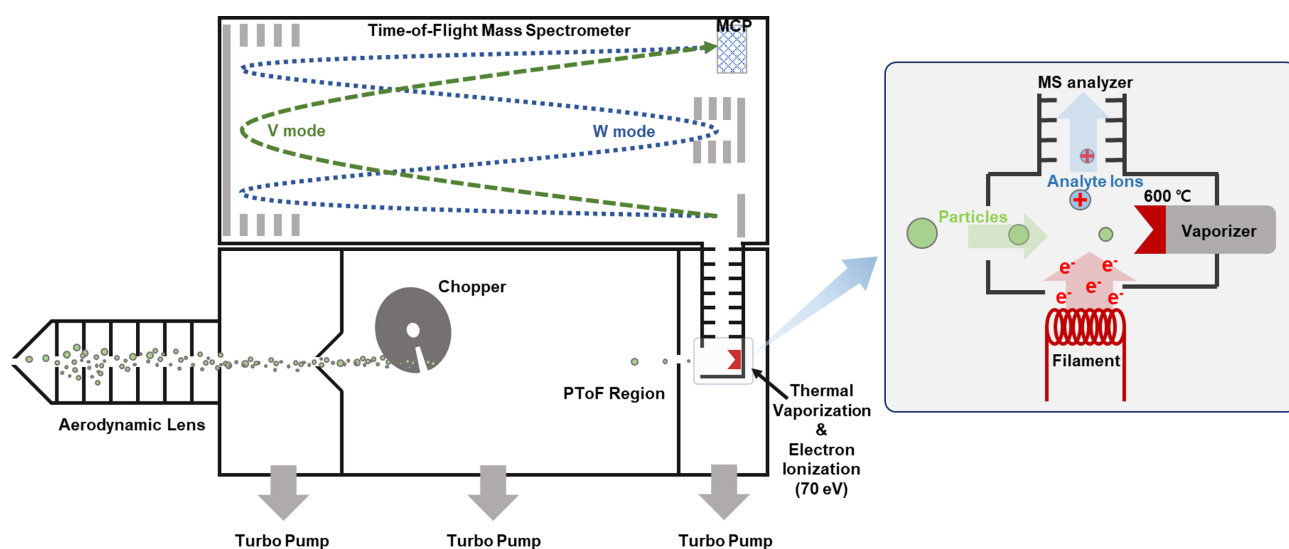

Figure 2. Schematic diagram of a high resolution time-of-flight aerosol mass spectrometer (HR-ToF AMS) and an ionization technique used in the AMS.

than the W-mode, whereas higher mass resolution can be achieved in the W-mode (m/Δm = 5000). With the high resolution of HR-ToF-AMS, it is possible to distinguish isobaric compounds with the same nominal mass but different molecular formula, for example, C_2H_3O and C_3H_7 at m/z 43.[26,43]

Data Processing of AMS

Aerosol mass spectrometers are designed to continuously measure atmospheric aerosols for a period of few weeks to several months. Therefore, automated mass calibration without the use of standard materials is required. Methodologies developed for automated mass calibration of HR-ToF-AMS were well described by DeCarlo et al. (2006).[26] Briefly, mass calibration was performed using known peaks that are highly reproducible in the background spectra. Typical peaks used for mass calibrations are m/z 12 (C^+), 17 (OH^+), 18 (H_2O^+), 28 (N_2^+), 32 (O_2^+), 40 (Ar^+), 44 (CO_2^+), 149 ($C_8H_5O_3^+$), 182 ($^{182}W^+$), and 184 ($^{184}W^+$). The intensities of the peaks measured by AMS are converted into mass concentrations of chemical species using the ionization efficiency (IE) calibration.[30, 34, 44, 45] The IE calibration are performed using ammonium nitrate before every measurement. The transmission efficiency and detection efficiency of particles vary depending on the chemical species, and this collection efficiency (CE) affects the quantification results of each species. To compensate for this, collection efficiency has been determined by intercomparison of the AMS and other aerosol instruments.[46-48] It was reported that the CE values could vary depending on the properties of aerosols such as particle acidity, nitrate fraction, and water content.[49-51] In many field studies, however, CE values of 0.5 has been applied to be representative for ambient particles and showed good agreements.[52-54]

The AMS quantifies the peaks in the mass spectrum into several major chemical species: organics, sulfate, nitrate, ammonium, and chloride. The total mass concentration of organic components is determined by subtracting the signals originating from ambient inorganic components, gas-phase compounds, and instrumental artifacts.[55] Some

Table 1. Major chemical species observed in the AMS and main fragment ions for identification of chemical species.

Species	Fragment ions	m/z
Water	O^+, HO^+, H_2O^+	16, 17, 18
Ammonium	NH^+, NH_2^+, NH_3^+	15, 16, 17
Nitrate	NO^+, NO_2^+, HNO_3^+,	30, 46, 63
Sulfate	SO^+, SO_2^+, SO_3^+, HSO_3^+, $H_2SO_4^+$,	48, 64, 80, 81, 98
Chloride	Cl^+, HCl^+	35, 36
Organics	$C_cH_hN_nO_oS_s^+$	All other m/z >11

of the main fragments observed by the AMS for chemical classification are summarized in Table 1.

Allan et al. developed a generalized technique for separating ensemble mass spectra into chemically resolved partial mass spectra using user-defined fragmentation tables.[55] This new method facilitated the calculation of mass concentration and enabled the investigation of many different chemical types and sub-groups within types.

Data Interpretation of AMS

The high-resolution mass spectra obtained by HR-ToF-AMS provide detailed chemical information on submicron aerosols and it makes possible to quantify the elemental composition of bulk organic aerosols (OA). There are some representative fragment ions to estimate the source of organic compounds. The fragment ions at m/z 43 mainly correspond to $C_3H_7^+$ for the hydrocarbon-like organic aerosol (HOA) or $C_2H_3O^+$ for the oxygenated organic aerosol (OOA).[56] The $C_2H_3O^+$ ion is thought to be dominated by non-acid oxygenates. The fragment at m/z 44 (mainly CO_2^+) originates from the organic acids such as carboxylic acids and acid-derived species.[57,58] The fragment at m/z 57 ($C_4H_9^+$) is a typical fragment of saturated hydrocarbon compounds and used as a good tracer for vehicle emissions.[57,59] The contribution of biomass burning can be evaluated by high peak intensities at m/z 60 ($C_2H_4O_2^+$) and m/z 73 ($C_3H_5O_2^+$), that are considered as indicative ions of the biomass burning of levoglucosan.[60, 61]

Scatter plots between these well-defined fragments have been used as diagnostics to assess the aging or mixing state of ambient aerosols.[53,56,61] Ng et al. developed a new mass spectral diagnostic for following the aging of OA by plotting the fractional contribution of m/z 44 (f_{44}) as a function of that of m/z 43 (f_{43}). In the scatter plot between f_{44} and f_{43} (Figure 3a), highly oxygenated compounds (low-volatility oxygenated organic aerosol, LV-OOA) are observed in the upper half of the triangular region, whereas relatively less oxygenated compounds (semi-volatile oxygenated organic aerosol, SV-OOA) are positioned in the lower half.

By determining the chemical compositions of OA, further elemental analyses such as atomic H/C, O/C, S/C, and N/C ratios can be performed to evaluate its sources and oxidation status. The van Krevelen diagram, originally proposed for coal sample analysis, has been widely used to visualize and interpret complex organic compounds in environments.[62-64] The diagram cross-plots the atomic H/C ratio as a function of the atomic O/C ratio of organic compounds. Heald et al. applied the van Krevelen diagram to organic aerosol analysis and found implications for the atmospheric aging and involving processes such as volatilization and oxidation. Lines with slopes of 0, -1, and -2 in the van Krevelen diagram indicate the addition of the alcohol/peroxide, carboxylic acid, and ketone/aldehyde
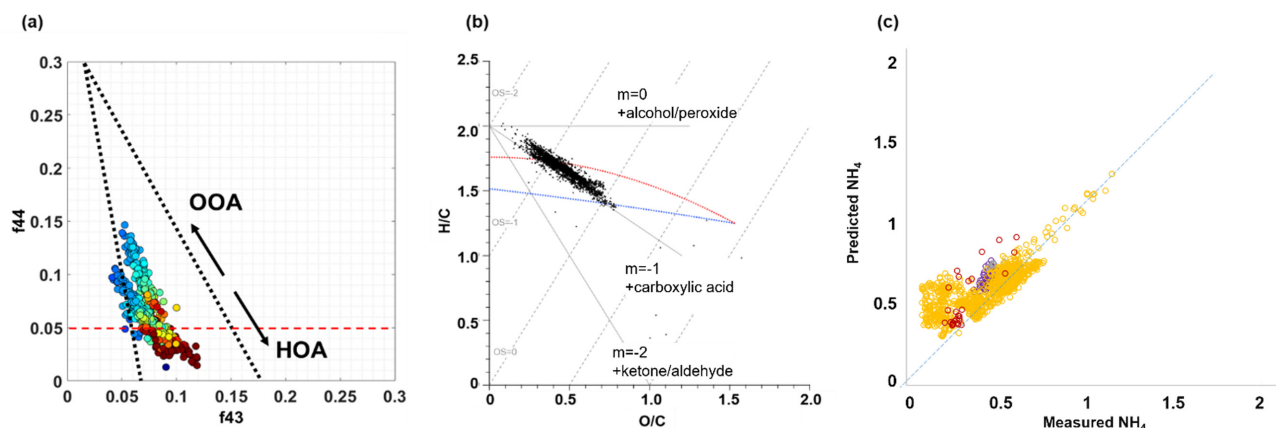
Figure 3. (a) Scatter plot of f_{44} vs. f_{43}, (b) Van Krevelen diagram, and (c) scatter plot of the predicted NH_4^+ vs. measured NH_4^+ concentrations from HR-TOF-AMS measurements.

functional groups, respectively, during OA evolution (Figure 3b).

Real-time measurement data from the AMS can provide valuable information on the dynamic changes in particle acidity during the aerosol evolution process. The aerosol ion balance can be used as an indicator for aerosol acidity estimation and is expressed by the ratio between the measured and theoretically predicted ammonium concentrations (Figure 3c).[29,65-67] The equation for calculating the predicted mass concentration of ammonium ($NH_4^+(p)$) is as below:

$$NH_4^+(p) = 18 \times \left(2 \times \frac{SO_4^{2-}(m)}{96} + \frac{NO_3^-(m)}{62} + \frac{Cl^-(m)}{35.5} \right)$$

Where $NH_4^+(m)$, $SO_4^-(m)$, $NO_3^-(m)$, and $Cl^-(m)$ are mass concentrations of ammonium, sulfate, nitrate, and chloride ions, respectively, measured by AMS. In many studies, ion balances for inorganic particulate matter (PM) were evaluated to elucidate the neutralization state of the aerosols.[50,68-70] When the aerosols are long-range transported from their sources, the freshly produced acidic compounds may have sufficient time to react with basic compounds, therefore more neutralized aerosols can be formed. Although it is difficult to generalize site-specific characteristics in relation to the degree of neutralization, this parameter can help discriminate between locally produced acidic components and regionally transported aerosols.[71]

Providing reliable information on the sources of ambient aerosols is critically important in terms of establishing the effective policies for the reduction and management of PM. Highly time-resolved chemical composition data can be further analyzed in conjunction with various statistical analysis methods such as positive matrix factorization (PMF), chemical mass balance (CMB), principal component analysis (PCA), and partial least squares (PLS). Among these methods, the combination of AMS data and PMF has become a powerful tool for identifying the potential sources of organic aerosols and evaluating source contributions.[72,73] PMF developed by Paatero is a multivariate factor analysis technique to estimate the quantitative contributions of air pollution sources.[74] A detailed description of PMF and its mathematical algorithm can be found in other publication.[74,75] Lanz et al. applied PMF to aerosol mass spectra for the first time and identified six factors and their source profiles.[76] The number of OA factors vary depending on the characteristics of the study sites, such as spatial, seasonal, and meteorological conditions. Figure 4 shows an example of typical PMF results of HR-ToF-AMS data. OA factors are generally separated into three primary organic aerosols (POA); hydrogen-like OA (HOA), cooking-related OA (COA), and biomass burning OA (BBOA) and two secondary organic aerosols (SOA); semi-volatile oxygenated OA (SV-OOA) and low-volatility oxygenated OA (LV-OOA). HOA factor is characterized with the predominance of $C_xH_y^+$ ions, high H/C ratio, and low O/C ratio.[77-79] This factor shows good correlation with primary combustion emissions, such as black carbon (BC) and NOx. COA is a cooking activity-related factor that generally shows two peaks at lunch and dinner time in its diurnal profile. It is characterized by high ratio of m/z 55 ($C_4H_7^+$ and $C_3H_3O^+$) to m/z 57 ($C_3H_5O^+$ and $C_4H_9^+$), high fraction of $C_3H_3O^+$ ion, and the O/C ratios similar to those of fatty acids.[52,80-82] BBOA factor shows high contribution in winter and is characterized by high abundance of $C_2H_4O_2^+$ ion at m/z 60, which is used as an indicator of biomass burning of levoglucosan.[67, 83] Both SV-OOA and LV-OOA are characterized by dominant peaks of $C_xH_yO_z^+$ derived from oxygenated compounds, especially at m/z 43 (mostly $C_2H_3O^+$) and m/z 44 (mainly CO_2^+).[53,56] Highly oxidized OOA (LV-OOA) shows the highest O/C ratio, high fraction of m/z 44 (CO_2^+), and correlates well with the sulfate. In the diurnal profile of LV-OOA, it generally shows the peak during the daytime, corresponding to the formation of significant SOA by photochemical reactions. In contrast, intermediately oxidized OOA (SV-OOA) exhibits lower O/C ratio, and higher fraction of m/z 43 compared with that of LV-OOA, and correlates well with the nitrate.

Summary and Future Perspectives

Aerosol mass spectrometer has been widely deployed for the characterization of particulate matter because of its ability to perform real-time chemical speciation and
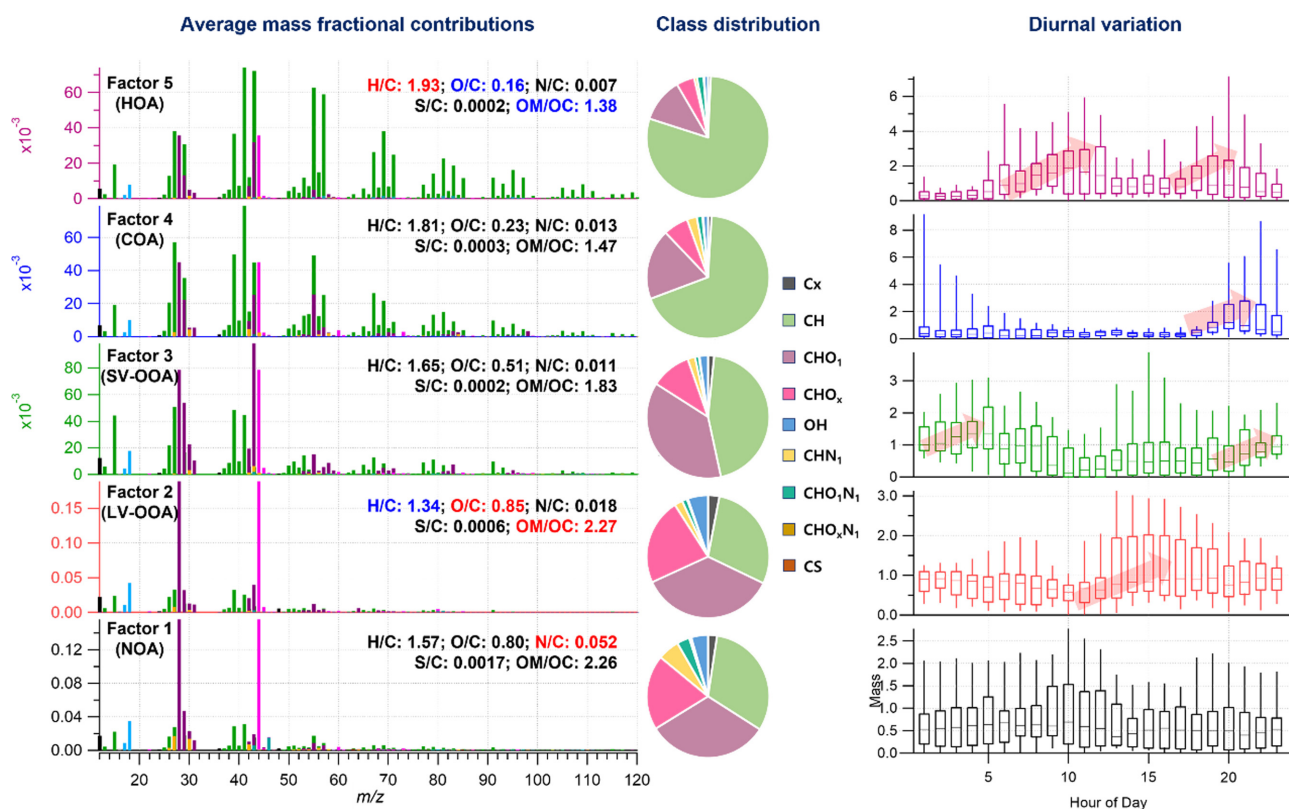
Figure 4. Overview of the results from AMS PMF analysis, major chemical distribution and diurnal variation of each OA factor.

quantitative mass loading as a function of the particle size of submicron particulate matters (PM$_1$). AMS field studies combined with various receptor models, such as PMF, conditional bivariate probability function (PBCF), and concentration weighted trajectory (CWT) enable a more in-depth investigation on the potential sources and its spatial distributions. Moreover, mobile measurements are conducted to identify the vertical and horizontal profiles of atmospheric aerosols using a mobile laboratory, ship, and aircraft. These studies have significantly broadened our understanding on aerosol chemistry.

However, many challenges remain for a complete understanding of the physicochemical properties of atmospheric aerosols and their atmospheric evolution. Particularly, technical advances to enhance the transmission efficiency for smaller particles (nucleation mode particles) are necessary to fill the gaps in our knowledge on evolution of atmospheric aerosols, such as new particle formation and gas-particle partitioning. Additionally, parallel measurements utilizing other MS techniques are required to obtain more detailed molecular information on PM. For example, high resolution mass spectrometer coupled with soft ionization techniques produces intact molecular ions without extensive fragmentation and allows for the detailed characterization of atmospheric aerosols at the molecular level. Therefore, the combination of traditional off-line

analytical techniques and real-time analysis not only provides more comprehensive information on atmospheric aerosols but also increases our understanding of the field.

Acknowledgments

Conflict of Interest

The author declares no conflict of interest.

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