



Inter-Comparisons of Major Ions and Organic Matter Using Aerodyne Aerosol Mass Spectrometer, Ion Chromatography and Sunset Lab Carbon Analyzer in Aged Aerosols from Okinawa in the Western North Pacific Rim

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Citation: Kunwar, B.; Torii, K.; Takami, A.; Kawamura, K. Inter-Comparisons of Major Ions and Organic Matter Using Aerodyne Aerosol Mass Spectrometer, Ion Chromatography and Sunset Lab Carbon Analyzer in Aged Aerosols from Okinawa in the Western North Pacific Rim. Separations 2022, 9, 430. https://doi.org/10.3390/ separations9120430

Academic Editors: Yunqiao Zhou, Sheng Zhang, Bin Shi and Yueqing Zhang

Received: 3 October 2022 Accepted: 7 December 2022 Published: 11 December 2022

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Abstract: Inorganic components were measured in the aged ambient aerosols from Cape Hedo, Okinawa, an outflow region of East Asia, using online quadrupole Aerodyne aerosol mass spectrometer (Q-AMS) and offline ion chromatography (IC) and Sunset Lab carbon analyzer. Here, we performed an inter-comparison study on nitrate (NO₃⁻), ammonium (NH₄⁺) and sulfate (SO₄^{2–}) that were measured by IC and AMS. Sulfate and ammonium showed a good agreement between two instruments. However, abundances of NO₃⁻ by AMS are on average twice overestimated compared to nitrate obtained by IC. We also found that a significant amount of organic nitrogen (ON) was detected in the filter samples from Okinawa. The online measurement (Q-AMS) data and offline filter based-NO₃⁻ data need to be carefully evaluated when ON is abundantly present in aerosols. The OM/OC ratios derived from AMS are consistent with the bulk OM_{AMS}/OC_{Sunset} ratios (2.1). This study demonstrates that the OM/OC of 2.1 is the reasonable criteria for more aged aerosols.

Keywords: ion chromatography; Sunset Lab carbon analyzer; Aerodyne AMS; organic nitrogen; long-range atmospheric transport

1. Introduction

The importance of atmospheric aerosols has been widely documented in various fields and laboratory studies [1–3]. Atmospheric aerosols have significant impacts not only on local and regional air pollution, but also on the global climate. Recent measurement techniques have greatly improved to understand aerosols' chemical and physical parameters [4–6]. In particular, Aerodyne Research has developed a mass spectrometric analyzer for aerosol's real-time measurements, which is referred to as the Aerosol Mass Spectrometer (AMS) [7–9]. The AMS provides a size-resolved chemical composition of non-refractory submicron aerosols, with an integration time of the order of seconds/minutes [10-12]. Several studies evaluate the performance of the AMS based on intercomparison with other aerosol measurements. AMS is an advanced aerosol composition measurement technology that was widely used, but it needs to be calibrated or compared with standard instruments before use in different environments (e.g., urban or remote) [8,9,13–17].

Inorganic and organic nitrogen compounds are present abundantly in the atmosphere and contribute to the total atmospheric nitrogen budget [18–22]. The nitrogen deposition in aerosols mainly emphasizes only the inorganic fraction (i.e., NH_4^+ and NO_3^-) [23]. Recently, more studies on organic nitrogen (ON) can constitute a significant fraction of total (inorganic + organic) nitrogen in ambient aerosols [24–27].

We conducted aerosol measurements in Cape Hedo, Okinawa using an AMS to compare the online measurements to other offline measurements such as Sunset Lab carbon analyzer for organic carbon (OC) and elemental carbon (EC) and ion chromatography (IC) for major cations and anions. The ion and OC/EC data are used for the inter-comparison with AMS-derived organic matter (OM). The principal purpose of this paper is to evaluate an agreement and disagreement between AMS data and major ions and organic carbon (OC).

2. Samples and Analytical Procedure

2.1. Site Description and Aerosol Sampling

Aerosol samples (PM_{1.0}, n = 28) were collected from 17 March 2008 to 13 April 2008 using low volume air sampler (URG-2000-30EHB; URG Corp) at a flow rate of 16.7 L/min. and pre-combusted (450 °C, 4 h) quartz fiber filters (Pallflex 2500QAT, 47 mm in diameter) at the roof top of Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS, 26°9' N, 128°2' E) [28,29]. Cape Hedo is located on the northwest coast of Okinawa Island, Japan, an outflow region of East Asia (Figure 1). Each sample was collected for 24 h. Blank filters (n = 4) were collected every week. Each sample was collected for 24 h. The filter samples were stored in a preheated glass vial (50 mL) with a Teflon-lined screw cap in darkness at -20 °C until the analysis. At the same time, we operated the Aerodyne quadrupole aerosol mass spectrometer (AMS) for the real time measurements [29]. Figure 2a,b show the back trajectory analysis and wind speed.



Figure 1. Sampling location, Cape Hedo, Okinawa Island.

2.2. Offline Chemical Analysis

Filter samples (PM_{1.0}) were analyzed for OC and elemental carbon (EC) using a Sunset Laboratory carbon (OC/EC) analyzer following Integragency Monitoring Protected Visual Environments (IMPROVE) thermal/optical evolution protocol [28]. Major ions (NO₃⁻, SO₄²⁻ and NH₄⁺) were determined by ion chromatography (IC, 761 Compact IC, Metrohm, Switzerland). The detection limits for anions and cations were ca. 0.1 ng m⁻³. SO₄²⁻ (0.003 ng m⁻³) is detected in the field blanks whereas NO₃⁻ and NH₄⁺ are not detected in the blanks. The analytical errors in the replicate analysis of authentic standards were within 5% for major ions, OC and EC. The detection limits of OC and EC are 0.2 μ g/cm². EC was not detected in the field blanks.



Figure 2. (a) Five-day back trajectory analysis using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Hess, 2003). (b) Wind direction recorded in Okinawa during study period. Color code labels in rose plot (0–2, 2–4, etc.) indicate the recorded wind speed in m/s. The meteorological data were obtained from the Japan Meteorological Agency.

The concentration of total nitrogen (TN) was measured using an elemental analyzer (EA) (Carlo Ebra, EA 1500). A small filter disc with the known area (3.14 cm^2) was placed in a tin cup and combusted at 1400 °C in an oxidation column of EA system. All the nitrogen species are converted to NO and then reduced to N₂ in a reduction column. The reduced N₂ was measured with a thermal conductivity detector after the purification using a packed GC column to isolate N₂ from CO₂ [30-32]. The analytical error for duplicate analysis is less than 10%. Organic nitrogen (ON) can be calculated using the following equation [32].

$$ON = TN (EA) - IN (IC)$$

where IN means inorganic nitrogen obtained by the summation of nitrogen contents of NH_4^+ and NO_3^- measured by IC. Measurements of OC, TN and major ions were completed in 2009.

2.3. Online Aerodyne AMS Measurements

At the Cape Hedo station in Okinawa Island, the Aerodyne quadrupole AMS was operated with a time resolution of 10 min [29]. In AMS, aerosols are separated from gaseous species by an aerodynamic lens and vaporized at 600 °C on a vaporizer. Vaporized molecules are ionized by the standard electron impact ionization at 70 eV. The positive ions are analyzed in a quadrupole mass spectrometer by providing the mass spectra of aerosol components. The size cut of the aerodynamic lens is approximately PM1.0 [14].

The AMS data are averaged for the integration time of filter samples, i.e., 24 h. AMS quantified data were converted to organic aerosol masses using the following equations [14]

$$M_{m/z} = \frac{1}{\overline{CE_{org}}} \frac{1}{\overline{RIE_{org}}} \frac{MW_{NO3}}{\overline{IE_{NO3}}} \frac{10^{12}}{QN_A} S_{m/z}$$
(1)

$$OA = \sum_{m/z} M_{m/z} (m/z = 1 - 300)$$
(2)

where \overline{CE}_{org} and \overline{RIE}_{org} denote the average particle collection efficiency and relative ionization efficiency (RIE) for organics, respectively. MW_{NO3} (62 g mol⁻¹) indicates the molecular weight of nitrate, whereas IE_{NO3} indicates ionization efficiency of ammonium nitrate. Q denotes a sample flow rate in cm³s⁻¹, and N_A represents Avogadro's number. S_{m/z} (Hz)

is the signal of count rate at the m/z originating from organic compounds and obtained by subtracting the signals from the ambient gas molecules, inorganic species and instrumental artifacts. On the other hand, IE_{NO3} represents the determined monodispersed ammonium nitrate particles from the calibration unit. The uncertainty in determining IE_{NO3} was estimated to be 14% [16]. The uncertainty in the RIE values for major inorganic compounds (sulfate, nitrate, chloride and ammonium) is considered to be small because the mass spectra of these compounds are well defined. The \overline{RIE}_{org} is 1.4, and the CE value is assumed to be 1 for inorganics [29].

The molar ratio of ammonium to sulfate is generally less than 2, and sometimes less than 1. SO_4^{2-} is present as a mixture of $(NH_4)_2SO_4$ (molar ratio = 2) and NH_4HSO_4 (molar ratio = 1) and H_2SO_4 (molar ratio = 0). In this study, the average molar ratio of NH_4^+ to SO_4^{2-} is 1.14. Thus, the major chemical state is NH_4HSO_4 . Deliquescence point of NH_4HSO_4 is 40% relative humidity (RH) at 25 °C [29]. In Okinawa, RH of ambient air was in between 40 and 87% and RH at the inlet of Q-AMS was between 17.2% and 69.1%. Thus, we consider that NH_4HSO_4 is present as liquid phase and that CE for liquid phase aerosols is 1 [8]. Therefore, aerosols that are measured in Okinawa during the study period mainly exist as liquid phase and thus CE = 1 is suitable. CE = 1 is used for all the species.

3. Results and Discussion

3.1. Comparison of Ions Obtained from Aerodyne AMS and Ion Chromatograph

Table 1 shows the data obtained from AMS, IC and Sunset Lab carbon analyzer. $SO_4^{2^2}$ and NH_4^+ are mainly formed in the atmosphere via secondary processes [33,34]. The concentrations of $SO_4^{2^-}IC$ and NH_4^+IC , which were both measured by IC, ranged from 1.7 to 18 µg m⁻³ (av. 7.7 ± 4.2 µg m⁻³) and 0.43 to 5.0 µg m⁻³ (2.3 ± 1.2 µg m⁻³), respectively, whereas those of $SO_4^{2^-}AMS$ and NH_4^+AMS ranged from 1.7 to 15 µg m⁻³ (6.2 ± 3.0 µg m⁻³) and 0.60 to 5.0 µg m⁻³ (2.1 ± 1.0 µg m⁻³), respectively. Figure 3 presents temporal variations of $SO_4^{2^-}$ and NH_4^+ measured by two methods. Figure 4 shows the scatter plots of NO_3^- , NH_4^+ and $SO_4^{2^-}$ between two instruments. As shown in Figure 4, the Pearson's "r" values are 0.93 for $SO_4^{2^-}$ and 0.95 for NH_4^+ (Press et al., 1992). However, we observed some difference in the concentrations of sulfate between AMS and IC: those by AMS are slightly lower than those by IC (Figure 5). The differences in NH_4^+ concentrations between two methods are smaller than those of $SO_4^{2^-}$. The F-test can be used for determining whether the variances of two samples (or groups) differ from each other. We performed statistical F-test using IBM SPSS statistics 25 software to compare between the two measurements.

Species	$Av \pm SD$	Range (Min-Max)
	$(\mu g m^{-3})$	
Total organics by AMS	2.5 ± 1.2	1.0–5.9
OC by Sunset Lab	1.2 ± 0.59	0.41-2.5
EC by Sunset Lab	0.36 ± 0.23	0.41-2.5
SO_4^{2-} by AMS	6.2 ± 3.0	1.7–15
NO ₃ ⁻ byAMS	0.11 ± 0.05	0.03-0.31
NH4 ⁺ byAMS	2.1 ± 1.0	0.6–5.0
TN by elemental analyzer	2.2 ± 1.2	0.5–5.1
SO_4^{2-} by IC	7.7 ± 4.2	1.7–19
NO_3^- by IC	0.06-0.13	ND-0.58
NH4 ⁺ by IC	2.3 ± 1.2	0.43–5.0

Table 1. Concentrations of organic and inorganic species measured by different methods during the same study period.



Figure 3. Temporal variations of (a) NO_3^- , (b) NH_4^+ and (c) SO_4^{2-} measured by two instruments (IC and AMS) in aerosols collected from Cape Hedo, Okinawa.



Figure 4. Scatterplots of (**a**) NO_3^- , (**b**) NH_4^+ and (**c**) SO_4^{2-} measured by two instruments (IC and AMS) in aerosols collected from Cape Hedo, Okinawa.



Figure 5. Temporal variations of organic nitrogen (ON) in aerosols collected from Cape Hedo, Okinawa.

We further performed an F test for two variances to identify whether difference is significant or not. F-test (one tail) is a statistical analysis used to evaluate the hypothesis test with the help of variance of two datasets or population. By the calculation, we can decipher

whether the null hypothesis (H0) for the given data set is true or not. The standard *p* value is 0.05 (95% probability). If $F > F_{Critical}$, then we will reject the null hypothesis, which means that the selected data sets are not equal. For F test (one tail), our null hypothesis is "both instruments measure the same thing." For NH₄⁺ (AMS) and NH₄⁺ (IC), and SO₄²⁻ (AMS) and SO₄²⁻ (IC), F is <F_{Critical} and *p*-value is less than or equal to 0.05. Hence, we accept our null hypothesis. Thus, there is no difference between the two measurements (see Tables 2 and 3). Good correlations of NH₄+ and SO₄²⁻ between two instruments together with F-test demonstrate that the concentrations measured by two instruments are similar or equal.

	$\mathrm{NH_4}^+\mathrm{AMS}$	$\rm NH_4^+{}_{\rm IC}$
Mean	6.2	7
Variance	9.4	18
Observations	28	28
df	27	27
F	0.5	
$P(F \le f)$ one-tail	0.04	
F Critical one-tail	0.5	

Table 2. Result of F-test between $NH_4^+(AMS)$ and $NH_4^+(IC)$.

Note: F < Fcrit and p value is less than or equal to 0.05. Therefore, there is no significant difference between two measurements.

Table 3. Result of F- test between SO ₄	$^{2-}$ (AMS) and SO ₄ $^{2-}$ (IC).
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	${\rm SO_4}^{2-}{\rm AMS}$	SO ₄ ²⁻ _{IC}
Mean	7.8	6
Variance	18	10
Observations	27	27
df	26	26
F	1.9	
$P(F \le f)$ one-tail	0.05	
F Critical one-tail	1.9	

Note: F < Fcrit, *p* value is less than or equal to 0.05. Therefore, there is no significant difference between two measurements.

In contrast, the correlation coefficient of nitrate (NO_3^-) between the two instruments is weaker (r = 0.31) than NH₄⁺ (0.95) and SO₄²⁻ (0.93). Being different from the cases of SO₄²⁻ and NH₄⁺, we found that the average concentration of NO₃⁻_{AMS} is twice that of NO₃⁻_{IC}. Such a difference could not be explained by the analytical errors of the two methods. The thermal alteration of organic nitrogen (ON) in the ionization chamber of AMS may produce nitrate [35]; therefore, these differences between NO₃⁻_{AMS} and NO₃⁻_{IC} may suggest that ON is abundantly present in aerosols (PM_{1.0}) from Okinawa, an outflow region of Chinese pollutants. In fact, we found a significant amount of ON in the Okinawa aerosols (Figure 5). Our previous studies also showed a substantial amount of ON in the TSP aerosols from Cape Hedo, Okinawa [32] and in the alpine snow samples collected from Mt. Tateyama, central Japan [36]. Significant amounts of ON have been reported in Chinese aerosols [37]. However, we cannot exclude the possible evaporative loss of NO₃⁻ from the filters during sampling, which may cause a potential underestimate of NO₃⁻_{IC}.

We found strong correlation (r = 0.72) and similar temporal trends between ON and NO_3^-AMS . Strong correlation and similar temporal trends suggest that NO_3^-AMS has significant contribution from ON. We found very good correlation (r = 0.62) between NO_3^-AMS and $ON + NO_3^-IC$. There are several studies that showed coal combustion, biomass burning and anthropogenic activities produced nitrophenols and amino nitrogen-containing organic compounds and contribute to ON [38–41]. Large amounts of nitrophenols, aminophenols and are transported to Okinawa via long range atmospheric transport [42]. Recently, Li et al. [42] reported the

significant amount of proteinaceous organic matter in Okinawa aerosol. High concentrations of $NO_3^{-}AMS$ and OM were observed on March 23, April 2 and Apri 7. During March 17 and 18, and April 6 and 9, air masses arrived from the Pacific Ocean over the study area. Except for these dates, air masses arrived from East Asia, Russia, Mongolia and north China (Figure 2a) [28]. The concentration of NO_3^{-} is higher in TSP samples and that of ON is higher in PM₁ samples during spring in Okinawa.

3.2. OM_{AMS} versus OC_{Sunset}

It is very difficult to understand organic matter (OM) concentrations using National Institute for Occupational Safety and Health (NIOSH) thermal optical transmittance (TOT) and Interagency Monitoring of Protected Visual Environment (IMPROVE) thermal optical reflectance (TOR) protocols. These programs measure OC, but not OM. OM can be estimated using OC concentration. The OM/OC ratio can vary widely depending on sources, locations, atmospheric aging and meteorology [43,44]. The presence of aliphatic hydrocarbons in particulate matter showed a lower OM/OC ratio [43,45]. Secondary formation of atmospheric aerosols contains more oxygenated organics and, thus, has a higher OM/OC ratio [46]. An OM/OC ratio is critical to obtain mass closure between gravimetric PM measurements and colocated measurements of PM constituents which can be reflect the role of OM in regional and local air quality management plans and to improve model predictions of OM [47]. The OM/OC ratio also helps to estimate atmospheric aging and chemical processing in the atmosphere [48].

After the recent development of high-resolution aerosol mass spectrometer (HR-AMS), the OM/OC ratio in ambient air has been measured in real-time and measurements of the elemental composition of nonrefractory PM_1 aerosol are reported using HR-AMS elsewhere [49–51]. Hence, the hydrogen-to-carbon (H/C), oxygen-to-carbon (O/C) and nitrogen-to-carbon (N/C) ratios of OM can be directly measured in the ambient aerosols. OM/OC ratios have also been determined for a number of specific sources such as vehicular emissions. Chirico et al. [52] found that the OM/OC ratio from vehicular emissions can vary between 1.26 and 1.40. Reff et al. [53] estimated OM/OC ratios of 1.4 to 2.7 in laboratory-generated secondary organic aerosol (SOA).

We compared OM_{AMS} and organic carbon (OC) data obtained from the campaign, where OM_{AMS} represents the concentration of organic matter measured by AMS, whereas OC was measured by Sunset Laboratory carbon analyzer. As shown in Figure 6, temporal variations of OM_{AMS} and OC_{Sunset} are similar. A strong correlation (0.83) is found between OM_{AMS} and OC_{Sunset} (Figure 6). The mass concentrations of OM_{AMS} ranged from 1.0 to 5.9 μ g m⁻³ (av. 2.5 \pm 1.2 μ g m⁻³), whereas those of OC ranged from 0.41 to 2.5 μ g m⁻³ (1.2 \pm 0.59 μ g m⁻³). OM_{AMS} is 1.6–3.6 times more abundant than OC, which is expected because organics contain several elements (H, O, N, S, etc.) other than C. Turpin and Lim. [43] estimated the OM/OC ratio to be 1.6 \pm 0.2 for fresh urban aerosols and to be 2.1 \pm 0.2 for aged aerosols. Okinawa aerosols are significantly aged during long-range atmospheric transport from East Asia [27,28,32,55,56].

Based on the two measurements, we calculated the average OM_{AMS}/OC ratio to be 2.1 \pm 0.5. Hence, OM/OC ratios (2.1) from this study are consistent with previous studies for aged aerosols [43,57,58]. Further, we found that, based upon the estimated elemental composition measured by AMS, the organic mass to organic carbon (OM_{AMS}/OC_{AMS}) ratio was 2.1, being consistent with more aged aerosols ([24], and reference therein). The elemental estimation of OM:OC ratios from AMS is similar to the bulk OM_{AMS}/OC_{Sunset} ratios (2.1). For the elemental estimation, we only included C, H and O atoms.



Figure 6. Temporal variations of organic matter (OM) measured by AMS and organic carbon (OC) measured by Sunset Laboratory carbon analyzer (**left** panel) and correlation plots (**right** panel) between OC and organic matter measured by two instruments (Sunset and AMS) in aerosols collected from Cape Hedo, Okinawa.

Figure 7 shows the temporal variation of OM_{AMS}/OC_{sunset} ratios. The higher ratios were obtained in March 31 (3.5) and April 8 (3.3). We checked the air mass trajectory to identify the source regions. We found that air masses of March 31 and April 8 came from South Asia and oceanic regions. Trimonen et al. [41] reported OM/OC ratios of 1.5 to 2.1 for oxygenated aerosols. OM to OC ratios were reported to be 1.3–1.5 for primary OA and 1.8–2.2 for secondary OA [48]. Aiken et al. [48] showed a high OM/OC ratio (2.5) for aged, oxygenated OA. The high variability of OM/OC in our study as compared to previous studies suggests that OA are often photochemically more aged in the western North Pacific Rim. A very high OM_{AMS}/OC ratio (3.8) was reported in Cape Hedo, Okinawa, in December 2010 [56]. However, the average OM/OC ratio (2.1 ± 0.5) obtained in our study is consistent with the ratio (2.1 ± 0.2) reported for aged aerosols [38].



Figure 7. Temporal variations of mass concentration ratios of organic matter (OM_{AMS}) to organic carbon (OC_{Sunset}).

The presence of aliphatic hydrocarbons tends to lower OM/OC ratios [43,45] while particulate matter dominated by secondary formation is typically more oxygenated and, thus, has a higher OM/OC ratio [46]. OM/OC ratios were relatively low from 17 March to 27, and were relatively high from 28 March to 8 April. The higher ratios indicate more oxygenated aerosols generated during long range transport, whereas lower ratios may be associated with the presence of aliphatic hydrocarbon or less photochemical processing. Higher OM/OC ratios were observed during 16 March (2.5), 22 March (2.6), 28 March (2.4), 30 March (3.4), and April 12 (2.5), whereas lower ratios were obtained on 2 April (1.4) and 3 (1.3). During 16 March, air mass originated from the Pacific Ocean and travelled over the coastal regions before arriving in Okinawa, while air masses of 22 March, 28 March, 30 March and 12 April originated from East Asia via long-range atmospheric transport. During 2 and 3 April when lower ratios were observed, air masses were delivered from North China without severe photochemical aging.

Figure 8 shows relative abundances (%) of organic matter (OM), SO_4^{2-} , NH_4^+ and NO_3^- measured by AMS, carbon analyzer or IC. The average abundance of OM_{AMS} (23%) is close to the calculated OM (2.1*OC) (21%). Similarly, the average abundances of SO_4^{2-} are 19% (AMS) and 18% (IC). Further, those of NH_4^+ are 19% and 18%, respectively. In contrast, relative abundance of NO_3^- by AMS is almost twice that by IC. The higher relative abundance by AMS is due to the presence of organic nitrogen (ON) as discussed above. The ratio of m/z 30 (NO⁺)/m/z 46 (NO₂⁺) obtained for authentic NH₄NO₃ is 1.2 [59]. We also observed similar values using the AMS instrument. Calibration of AMS was performed on 16 March 2008 at the Cape Hedo site just before the campaign. The ratio of 1.2 by AMS for authentic NH₄NO₃ is less than half of the value of 3.3 obtained by AMS for ambient aerosols from Cape Hedo, Okinawa. The higher ratio in Okinawa aerosols further supports the production of m/z 30 due to the presence of organic nitrogen [59].



Figure 8. Relative abundances of organic matter (OM), SO_4^{2-} , NH_4^+ and NO_3^- measured by (a) Aerodyne aerosol mass spectrometer (AMS), and (b) ion chromatography and Sunset Laboratory carbon analyzer. OM was calculated by 2.1*OC. The number in bracket means absolute amount in $\mu g m^{-3}$.

4. Conclusions

We compared the abundances of ions (SO_4^{2-} , NH_4^+ and NO_3^-) obtained by an ion chromatograph (IC) and by Aerodyne aerosol mass spectrometer (AMS) for the ambient aerosols ($PM_{1.0}$) from Cape Hedo, Okinawa Island: an outflow region from the Asian Continent. The abundances of SO_4^{2-} and NH_4^+ showed good correlations between IC and AMS measurements. In contrast, we found higher concentration of NO_3^- estimated by AMS than by IC. This finding suggests that abundant presence of organic nitrogen may produce nitrate during the heating and ionization in an AMS instrument. More research is needed for real time measurement (AMS) and filter-based measurement of nitrate, which requires a careful evaluation when organic nitrogen exists abundantly in the ambient aerosols. The elemental estimation of OM:OC ratios from AMS is the same as the bulk OM_{AMS}/OC_{Sunset} ratio (2.1), suggesting a good agreement between AMS and the Sunset carbon analyzer.

Author Contributions: Conceptualization, K.K.; methodology, A.T., K.T.; software, A.T and B.K; validation, A.T., K.T. and B.K.; formal analysis, A.T and K.T.; investigation, B.K.; resources, K.K.; data curation, A.T and K.T.; writing—original draft preparation, B.K.; writing—review and editing, K.K and A.T.; visualization, B.K.; supervision, K.K.; project administration, K.K.; funding acquisition, K.K. All authors have read and agreed to the published version of the manuscript.

Funding: Funded by the Environment Research and Technology Development Fund (B-0903, 2-1403) from the Ministry of the Environment, Japan.

Data Availability Statement: Data will be available upon the request.

Acknowledgments: This study was in part supported by the Japan Society for the Promotion of Science (JSPS) (Grant-in-Aid Nos. 1920405 and 24221001), and the JSPS Joint Research Program implemented in association with DFG (JRPs-LEAD with DFG: JPJSJRP 20181601). We thank K. Okuzawa, Y. Kitamori, S. G. Aggarwal, and M. Mochida for their help in aerosol sampling at Cape Hedo. We also thank the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport model and READY website (http://www.arl.noaa.gov/ready.php, accessed on 22 October 2021) used in this study. The authors appreciate the English editing by Phil Meyers of the University of Michigan.

Conflicts of Interest: The authors declare no conflict of interest.

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