Field observations of aerosol physical and chemical properties in the Netherlands

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Chapter 5 Discussion and outlook

This thesis focused on field observations of aerosols in the Netherlands, incorporating both campaign data and long-term observational data. The first task of this thesis involved evaluating the performance of various instruments, with a special focus on a relatively new configuration of the aerosol chemical speciation monitor. Following this critical assessment, the study investigated various aerosol characteristics, including chemical composition, particle size distribution, optical properties, and new particle formation.

In this chapter, we will summarize and discuss the main findings of the thesis research, address the questions posed in section 1.6 of Chapter 1, as well as provide insights into future research directions. The sequence of the discussion aligns with the order of the chapters presented in this thesis.

5.1 Aerosol instrumentation evaluation and mass quantification

Ensuring accurate measurements is crucial in aerosol research. ACSM is one of the most widely used techniques for measuring the mass concentration of aerosol chemical components. Compared to the quadrupole ACSM (Q-ACSM), the time-of-flight ACSM (TOF-ACSM) offers superior mass resolution ($M/\Delta M = 600$) and improved detection limits on the order of < 30 ng m^{-3} with 30 minutes time resolution (Fröhlich et al., 2013). The commonly used standard vaporizer in older configurations, has a conical structure that causes particle bounce, resulting in incomplete vaporization and reduced detection efficiency (Hu et al., 2017). Moreover, the standard aerodynamic lens system in the traditional ACSM has a transmission efficiency of approximately 100% only for particles with diameters of 50-600 nm. For particles larger than 600 nm, the efficiency decreases significantly, dropping to only 30-40% for 1 μm particles (Liu et al., 2007; Takegawa et al., 2009). This limitation restricts its detection capability to $PM_{1.0}$. The objective of Chapter 2 was to evaluate the performance of the TOF-ACSM with an improved vaporizer and lens configuration, namely a capture vaporizer and a $PM_{2.5}$ aerodynamic lens, aiming to advance the ACSM technique for quantitative measurements of $PM_{2.5}$. The goal was to determine how well this configuration performs in field observations and how accurately it can quantify $PM_{1.0}$ and $PM_{2.5}$. The research was conducted by performing a series of mass closure analyses involving multiple measurement instruments during an intensive field measurement campaign (RITA 2021). These instruments encompassed online chemical composition measurement using different principles, particle size distribution measurement, and offline filter analysis. Based on these measurement results, we also discussed the aerosol concentration and chemical composition in the Netherlands.

For all inorganic chemical substances, the daily average results showed that the difference between TOF-ACSM and filter measurements was less than ± 10% for both $PM_{1.0}$ and $PM_{2.5}$. This level of accuracy is significantly higher than the nominal specification of ± 30 %, suggesting a substantial improvement in measurement precision. The enhanced accuracy of $PM_{1.0}$ and $PM_{2.5}$ measurements enables an accurate quantification of their chemical

compositions. In general, during the measurement period, the $PM_{1.0}$ fraction constituted approximately 70%–80% of the $PM_{2.5}$ mass concentration. However, as particle size increased from $PM_{1.0}$ to $PM_{2.5}$, the mass fraction of nitrate increased by 7.2% (from 38.3% to 45.5%), while the organic mass fraction decreased by 4.8% (from 19.9% to 15.1%), indicating a size-dependent variation in chemical composition. As also reported in other studies, within the $PM_{2.5}$ range, as particle size increases, the mass fraction of organic matter decreases, while the mass fraction of nitrates increases, and the sulfates and ammonium typically increase as well (Zhang et al., 2018; Shao et al., 2018). Additionally, it was also observed that the size dependence of chemical components also varies by their sources, where the contribution of secondary formation aerosols is more evident in $PM_{1.0}$, whereas natural sources contribute more significantly in $PM_{2.5}$ (Luo et al., 2022).

The volume concentrations obtained by the ACSM and MPSS were very well correlated ($R^2 > 0.9$, slope = 1.0). However, the slope (ACSM data as x-axis, MPSS data as y-axis) appeared to vary with relative humidity conditions: it tends to increase at higher RH. This was due to the $PM_{2.5}$ size selection at the inlet of the ACSM occurring at ambient conditions, thus the upper limit of the dry particle size depended on RH. Higher RH resulted in a smaller dry cutoff diameter because of aerosol hygroscopic growth, consequently leading to lower mass concentrations in the ACSM $PM_{2.5}$ measurements. Previous studies have demonstrated that the impact of RH on the size cutoff in ACSM measurement is more significant at oceanic or coastal stations compared to inland sites, and this impact is more pronounced for $PM_{2.5}$ than for $PM_{1.0}$ (Poulain et al., 2020). This effect of RH was much less pronounced in MPSS measurements because the particles were pre-screened by a PM_{10} inlet and dried to a RH below 40%, and the upper size limit was approximately 830 nm. Therefore, at high RH the volume concentration estimated from the MPSS measurement stayed the same, while the volume estimated by ACSM measurement decreased, leading to a larger slope of MPSS vs. ACSM volume concentration. In addition, using different particle size cut-off methods, such as cyclones and impactors, may also lead to inconsistencies in particle size cut-off results. When considering the size cutoff curves for $PM_{2.5}$ particles, impactors typically exhibit a sharper cutoff curve compared to cyclones. Impactors operate by collecting particles through inertial impact onto a solid surface, resulting in high efficiency for particles near the collection orifice size and a rapid decline in efficiency for particles significantly larger or smaller than this diameter. Cyclones, on the other hand, utilize centrifugal forces to separate particles, leading to a more gradual cutoff curve where separation efficiency changes more uniformly with particle size. These findings highlight the critical importance of considering the size cutoff, which can significantly impact the accuracy of measurements. For long-term measurement consistency, we recommend using the same size cut-off methods to ensure comparability of measurements.

Overall, the introduction of the capture vaporizer and $PM_{2.5}$ aerodynamic lens has significantly improved the performance of the ACSM, in particular for the quantification of $PM_{2.5}$. This improvement is particularly important given that daily air quality standards in

many countries, such as the United States, China, and Canada, are based on $PM_{2.5}$ levels. The World Health Organization (WHO) also sets guidelines for $PM_{2.5}$ concentrations. Therefore, it is recommended that this new configuration be adopted to achieve more accurate and reliable air quality monitoring. However, the introduction of the capture vaporizer has also led to additional thermal decomposition of organic and inorganic compounds. A few studies have discussed fragmentations in the capture vaporizer, but further research is still needed to fully understand these effects (Hu et al., 2018a, b). This is particularly crucial for interpreting the composition of organic matter using the Positive Matrix Factorization (PMF) approach, which has been extensively applied in measurements using the standard vaporizer, but its application with the capture vaporizer has been limited and requires more investigation (Zheng et al., 2020; Joo et al., 2021). Additionally, further distinguishing between organic and inorganic nitrates and sulfates may help to further reduce discrepancies (± 10%) between ACSM measurements and filter analysis results. Future research can focus on the aforementioned aspects to enhance the accuracy of measurements and deepen our understanding of the results.

5.2 Aerosol optical properties: combining in-situ and remote sensing measurements

Through the evaluation of in-situ aerosol instrument performance, assurance of data quality, and understanding of the local aerosol chemical composition in the first chapter, we established a solid foundation for subsequent research. In Chapter 3, we introduced remote sensing measurements to gain insights into the vertical distribution of aerosols, thus extending our analysis to a spatiotemporal dimension. The Caeli Raman lidar was used to retrieve vertical profiles of aerosol optical properties. However, this measurement technique has certain limitations. Firstly, Raman lidar retrievals are typically only available in the late afternoon or at night due to interference from strong sunlight during the day. Secondly, although Raman lidar has the advantage over conventional elastic lidar of directly measuring backscatter and extinction coefficients without assuming a lidar ratio, it can only retrieve the extinction profiles above a certain height due to overlap issues.

Therefore, in this study, we calculated the optical properties of aerosols using ground-based in-situ aerosol measurements, exploring the optical closure between ground-based measurements and lidar results. From May to October 2021, Raman lidar measurements were conducted on 20 days, resulting in 26 time periods of optical profiles, each typically lasting about 1 hour. By comparing the vertical profiles of backscatter and extinction coefficients derived from our calculations with those retrieved from the Raman lidar, approximately only about 35% of the profiles were found to be comparable. That is, in these cases, we can predict the vertical profiles of aerosol optical properties using ground-based measurements. This is particularly useful for extending the extinction profiles to lower altitudes (below 800 meters) where they cannot be retrieved by the Raman lidar, thereby bridging the gap between ground-based and remote sensing measurements. However, even in the cases where the calculated

and retrieved backscatter and extinction coefficient profiles differed, the lidar ratio profiles predicted from ground-based in-situ measurements connected reasonably well with the retrieved lidar ratio profiles starting from 800 meters. For all cases, the difference between the calculated and retrieved lidar ratios was generally less than ± 30%.

The results indicate that our proposed method can directly provide the vertical distribution of aerosol optical properties to some extent. More significantly, it can provide a representative lidar ratio that can be used to extend the extinction profile to lower altitudes where it cannot be retrieved by Raman lidar. One of the limitations of our study is the assumption that aerosols are homogeneously distributed within the atmospheric boundary layer. This condition is more likely to occur during the daytime, whereas Raman lidar measurements are typically conducted at night. Therefore, we anticipate that the prediction of the optical properties would be closer to the measurements during the daytime.

Overall, our study represents to our knowledge the first instance where a satisfactory lidar ratio can be obtained using only ground measurements and meteorological forecasts. This significantly expands the potential applications of our methodology. Previously, there have been a few studies that attempted to predict the aerosol vertical optical properties, which relied on airborne measurements (Düsing et al., 2018, 2021; Ferrero et al., 2019). Düsing et al.(2018) conducted flight experiments to collect airborne in-situ measurement data. They found good agreements between the calculated and lidar retrieved backscattering coefficients, with the R^2 values of 0.928, 0.955, and 0.819 for wavelengths of 355 nm, 532 nm, and 1064 nm, respectively. However, due to the limitations of flight experiments, comparisons were restricted to two flight cases. Our approach provides a more generalizable methodology for predicting the optical properties with the routine aerosol measurements that are available at most of the atmospheric monitoring sites, such as ACTRIS stations.

As mentioned, we assumed a well-mixed boundary layer in the calculations and changes in aerosol properties with altitude were only due to hygroscopic growth. This assumption generally gave results that are sometimes consistent with Raman lidar retrievals. However, there are several scenarios where this assumption may be less applicable or lead to large uncertainties. **Firstly**, in cases where discrepancies were observed between the calculated and retrieved profiles of backscatter and extinction coefficients, they are typically attributed to different aerosol layers aloft, making ground-level aerosol concentrations less representative. As a possible way to solve this problem, Zhang et al. (2024) obtained aerosol in situ data aloft based on unpiloted aerial vehicle (UAV) measurements, but the correlations between calculated and lidar retrieved backscatter coefficients were lower, with a Pearson correlation coefficient of only 0.241. This indicates the substantial challenges in calculating aerosol optical properties through drone in situ measurements. While both backscatter and extinction coefficients are sensitive to variations in aerosol concentration and their hygroscopicity growth, the calculated lidar ratio does not depend on aerosol concentration and is only weakly affected by hygroscopic growth. Thus, a representative lidar ratio can still

be obtained from the ground-based measurements even though the backscatter and extinction coefficients could be biased.

Secondly, the chemical composition data utilized in this study was based on measured data for fine mode ($PM_{2.5}$) and assumed data (entirely sea salt or entirely mineral dust) for coarse mode ($PM_{2.5-10}$). This could introduce large uncertainties, particularly when the coarse mode dominates. Ferrero et al. (2019) found that under Icelandic dust background from transportation in the Arctic, the backscatter coefficients estimated by Mie scattering theory using the chemical composition measured by tethered-balloon (including ionic water-soluble components, elemental carbon and organic matter), resulted in substantial underestimation of lidar backscatter coefficient measurements by up to 76%, 53%, and 45% at wavelengths of 355, 532, and 1064 nm, respectively. However, good agreement was achieved with negligible underestimation when dust was accounted for in the calculations. In addition, we assumed internally mixed organic and inorganic aerosols with externally mixed black carbon. Düsing et al.(2021) employed a core-shell mixing approach in their optical closure between Mie calculations and lidar measurements. Zhang and Thompson (2014) reported that the average difference in extinction efficiency between the internally mixed model and core-shell model is 24%, with a maximum of 115%, primarily due to differences in absorption efficiency. It would be beneficial for future research to explore how different mixing states impact our calculations.

Lastly, but equally important, accurate relative humidity profiles are important for predicting the vertical distribution of aerosol optical properties. In this study, we compared various measured and estimated relative humidity profiles and ultimately adopted the ECMWF hourly resolution data. The advantage of this data is its immediate availability without measurement constraints. However, the usefulness of ECMWF data is limited by its lower temporal and vertical resolution. Incorporating relative humidity data with higher temporal and spatial resolution in the future could further improve the accuracy of the predictions.

In summary, our proposed method shows promise in providing vertical distributions of aerosol optical properties and extending extinction profiles to lower altitudes using predicted lidar ratios. Future applications of this methodology can be developed in two main directions. On one hand, it can be applied to long-term measurements to assess its performance under aerosol backgrounds in different seasons. As mentioned, the vertical mixing of aerosols is typically more effective during the daytime and in the summer months, while it tends to be less effective during nighttime and winter periods. Therefore, applying this methodology to longer measurement periods could further investigate limitations of the model. On the other hand, it also can be implemented at different locations. For sites that do not have advanced Raman lidar, this method offers the possibility of deriving extinction coefficient profiles using the calculated lidar ratio and measured backscatter coefficient profiles from the simple elastic backscatter lidar. By integrating the vertical profiles of the extinction coefficient, the aerosol optical depth (AOD) can be obtained and further compared with AOD measurements

from sun photometers. These further studies would provide better validation of the effectiveness and applicability of the model to different geographical locations.

5.3 Aerosol particle size distribution at rural and coastal sites in the Netherlands

In Chapter 4, we focused on long-term observations instead of intensive field campaign measurements. The objective of this study was to achieve a more comprehensive understanding of aerosol characteristics in the Netherlands, with a particular focus on particle size distribution - a crucial characteristic for understanding the impact of aerosols on the environment and climate. In this study, we provided an overview of aerosol particle size distributions in typical environments (regional background and a more remote coastal area) in the Netherlands over the past two years, with emphasis on ultrafine particles (UFPs) and new particle formation (NPF).

The results showed that from July 2021 to December 2022 the average total particle number concentration (from 10 nm to 800 nm) was 6780 cm^{-3} (standard deviation 4020 cm^{-3}) at Cabauw, which is approximately twice that of Lutjewad (3390 cm^{-3} with standard deviation 2560 cm^{-3}). Mamali et al.(2018) reported that the average particle number concentration (from 10 nm to 500 nm) at Cabauw from January 2008 to December 2015 (excluding 2012) was 9200 cm^{-3} (standard deviation 4900 cm^{-3}), with an increasing trend from 2008 to 2011 and a decreasing trend between 2013 and 2015. For 2012 a value of approximately 9600 cm^{-3} was reported by Keuken et al. (2015). This suggests that the particle number concentration may have shown a decreasing trend in recent years.

For UFPs, the average number concentration in our study was 5930 cm^{-3} at Cabauw (standard deviation: 3810 cm^{-3}) and 2680 cm^{-3} at Lutjewad (standard deviation: 2240 cm^{-3}), which accounted for over 80% of the total particle number concentration at both sites. Notably, elevated concentrations of UFPs at Cabauw were associated with wind directions from the Schiphol airport, Rotterdam port, and Utrecht city. In particular, airports are increasingly recognized as a significant primary source of UFPs. Keuken et al. (2015) found that particle number concentrations at Adamse Bos (7 km from Schiphol airport), increased threefold from 14100 cm^{-3} (other wind directions) to 42000 cm^{-3} (airport direction) during March to May 2014, with particles primarily in the 10-20 nm range. In contrast, at Cabauw (40 km from Schiphol airport), particle concentrations increased by only 20% during wind from the airport direction with an average UFP concentration of approximately 7500 cm^{-3}. This is likely due to dilution during particle transport. Compared to the observations in Amsterdamse Bos, the particle size in Cabauw during wind from the airport was shifted towards larger particles in the 20-40 nm range, probably due to condensation and coagulation growth processes (Hofman et al., 2016; Keuken et al., 2015). The previous records of both total number concentration and UFP concentration are all higher than the average values we observed approximately a decade later. This might be due to general pollution reduction due

to stricter emissions standards. However, it might also be related to lower traffic volume due to several COVID-19 lockdown periods during 2021 and 2022 and a general trend to work from home.

In addition, NPF, as the major secondary source of UFP, occurred on 83% (36% of type I and 57% of type II) of the observation days at Cabauw. This proportion significantly exceeded the 35% NPF events of the days between April 2008 and March 2009 at Cabauw (Manninen et al., 2010). Combined with the discussion in the previous paragraph, these data indicate an intriguing phenomenon: while the current total particle number concentration at Cabauw seems to be declining compared to the historical data, the frequency of NPF appears to be increasing. This may be due to the reduced emissions of traffic-related particles, and decreased condensation sinks, leading to an increase in nucleation events (Brines et al., 2015). Further research is essential to better elucidate the underlying causes and mechanisms driving the increase in NPF occurrence and to understand its implications for public health, air quality, and climate. Besides, the frequency of NPF events at Cabauw is also higher than those observed at other stations. Bousiotis et al.(2021) investigated NPF phenomena at 13 locations across Europe, encompassing sites with various land uses and environments, and analyzing data from each site for at least three years. They observed that the frequency of NPF occurrences ranged approximately from 5% to 20% (without specifying the types of NPF). Generally, the NPF frequency was higher in rural background areas compared to urban regions. However, it is important to consider that most current classifications of NPF events are performed manually, which may introduce human bias. Therefore, future research on NPF classification aimed at achieving systematic and automated processes will be beneficial for accurately comparing NPF events from different studies.

Our observations demonstrated that NPF events are often driven by solar radiation, and are associated with lower relative humidity, higher temperatures, and higher SO_2 and O_3 levels. This is consistent with existing literature on the characteristics of NPF (Kulmala et al., 2013; Kerminen et al., 2018). However, at Cabauw, we observed that morning NPF typically occurs before sunrise, during the morning rush hour, and on weekdays, and is associated with high concentrations of black carbon and NOx. This indicates that the morning NPF related to traffic emissions is different from most NPFs that rely on solar radiation. In addition, these newly formed particles usually do not tend to grow further. Brines et al.(2015) also reported that in urban areas (Barcelona and Madrid in Spain, and Brisbane in Australia), traffic emissions lead to particle nucleation, but these are not followed by a substantial condensation/growth phase. Yan et al.(2020) discovered through chamber experiments that NOx can influence the growth of particles by altering the chemical composition and volatility of highly oxygenated organic molecules. This inhibitory effect on particle growth was found to be more pronounced for smaller particles (2 nm), whereas the influence on larger particles (greater than 30 nm) was negligible. Therefore, we hypothesize that high concentrations of NOx from traffic emission or in the early morning (due to the shallow boundary layer), may suppress the growth of NPF. However, this mechanism has not yet been demonstrated in the

atmospheric environment, requiring further verification and research to confirm its validity and understand its implications in real-world settings.

Lastly, we observed a substantial correlation ($R^2 = 0.62$) in the concentrations and trends of large aerosol particles (100-800 nm) between two sites over 185 km apart, with one located in the northwest and the other in the middle south of the Netherlands. This finding suggests that long-range transport is a significant source of these particles. This is noteworthy because few previous publications have reported such a high correlation of particle number concentrations on such a distance scale. Given that large particles primarily determine mass concentration, this discovery may hold substantial value for the further validation and enhancement of particulate matter dispersion models.

The research also raises questions that require further investigation in the future: (i) Nucleation particles caused by traffic emissions have also been observed in other countries and cities (Brean et al., 2024; Wu et al., 2021). However, the mechanisms of NPF triggered by traffic emissions are not yet fully understood. Future research delving deeper into the impact of traffic emissions on NPF at Cabauw could be highly valuable for understanding their influences on the environment. This may require further measurements of smaller diameter particles, such as those between 3-10 nm, or measurements of molecular clusters. (ii) Additionally, conducting quantitative analyses to identify the principal factors influencing different NPFs would be very beneficial. For instance, solar radiation is crucial for the initiation of NPF, yet there are few reports on the specific radiation thresholds needed to initiate regional NPF events (Lee et al., 2008). Therefore, identifying the key drivers and their respective thresholds to initiate NPF could be crucial. This may involve statistical modeling and machine learning approaches for threshold prediction, such as threshold regression models and random forest models. (iii) Moreover, Lutjewad, a coastal observation station, offers a unique opportunity for studying both continental and marine aerosols based on different wind directions and air mass origins. Future efforts could implement advanced analytical techniques at this location, such as high-resolution mass spectrometry, to characterize the chemical composition of marine aerosols, e.g. measurements of iodine, which are closely related to marine NPF. This would significantly enhance our understanding of aerosol formation and its dynamic changes in different geographic contexts, an area that is currently not fully explored (Kerminen et al., 2018). We also found that at Lutjewad, particles reaching sizes sufficient to act as CCN are likely primarily contributed by the growth of NPF. This finding warrants further investigation to understand the role of different chemical compositions and particle sizes in acting as CCN, and their impacts on cloud and climate.