Response to reviewers

Thanks for reviewers' helpful comments and suggestions again. We made every effort to respond to reviewers' questions point to point, and revised our manuscript and appendix according to their comments. For clarity, reviewers' comments are shown in *black italic font*. The response is shown in blue normal font. The modified content in the manuscript and/or the appendix is shown in **green bold font**.

Anonymous Referee #1

General comment:

The authors replied most of the reviewer's questions sufficient and the manuscript is greatly improved, however, there is in Review#1 and Review#2 the open question of the novelty of the study. I.e., in Review#1 "The study will profit from a more detailed comparison to previous studies, both on ambient aerosol properties and the HRT deposition. This comparison will also allow the authors to clearly define the novelty of their study" and in Review#2 "the extent of new insights is limited". This point is not addressed in the reply and revised manuscript. I recommend the authors to consider these open questions raised by the two reviewers.

[Response]: Thanks for the reviewers' suggestion. To better understand the novelty of this study, a literature survey about ambient particle hygroscopic properties and the particle deposition in the HRT was conducted.

(1) As for the particle hygroscopicity, the result measured by HH-TDMA at RH = 98% in this study was similar to those measured by H-TDMA or HH-TDMA at RH = 87% - 98.5%. Detailed description can be found in the appendix (see Line 19-29). Although the difference of the particle hygroscopic property determined between RH = 90% and RH = 98% cannot be evaluated due to the lack of simultaneous measurements, previous studies have found that the presence of surface active, slightly soluble substances, and the co-condensation of semi-volatile soluble organic compounds can result in the humidity-dependent characteristic of κ (Topping and Mcfiggans, 2012; Wex et al., 2009; Wu et al., 2013). Therefore, the result measured by HH-TDMA at RH = 98% ought to be closer to the hygroscopicity in the HRT-conditions.

(2) Up to now, the published research which assessed the particle deposition in the HRT with considering hygroscopicity are mostly based on the assumed values of the hygroscopic parameter (Voliotis and Samara, 2018) or estimations by parametric methods (Ching and Kajino, 2018; Hussein et al., 2013; Mitsakou et al., 2007; Haddrell et al., 2015; Vu et al., 2018). By comparison, the direct particle hygroscopicity measurements can capture the real and high-time-resolution features of ambient particles' hygroscopic growth in the HRT, and reveal the diurnal variations of the particulate matter deposition in human bodies.

(3) To our best knowledge, there are only limited studies exploring the impact of the hygroscopic growth of ambient particles on the particle deposition by direct hygroscopicity measurements. Moreover, hygroscopicity measurements using the H-TDMA (Londahl et al., 2009; Farkas et al., 2022; Vu et al., 2015; Kristensson et al., 2013)

or DASH-SP (Youn et al., 2016) in these studies were all conducted at relatively lower RH (~ 90%) compared to that in the HRT (RH = 99.5%).

(4) Besides, the field campaign was carried out in the North China Plain, a polluted area with high population density and strong primary emissions. The particle deposition estimation with considering hygroscopicity in this area has not been reported yet.

In conclusion, this study first combined the explicit hygroscopicity measurements at HRT-like conditions by HH-TDMA with the MPPD model, which enriches the understanding of the influence of water uptake and hygroscopic growth on submicron particles deposition in the HRT.

[Revise]: Line 19-29 in the appendix:

"The particle hygroscopicity parameter (Kappa, κ) in this study and previous studies measured in rural sites in the North China Plain (NCP) was shown in Table S1. The average size-resolved κ was in the range of 0.24 - 0.32 during the sampling period. The hygroscopic properties of particles in this study was similar to those determined in the NCP in summer, such as in Wuqing (Liu et al., 2011) and Xianghe (Zhang et al., 2016), which was higher than that measured in winter, such as in Dingxing (Shi et al., 2022). It can be explained that the mass fraction of organic matters with relatively weak hygroscopicity was higher in winter, while secondary inorganic aerosols with strong hygroscopicity made higher contribution in summer (Sun et al., 2015). Besides, the particle hygroscopicity increased as the particle diameter increasing, which was in accordance with previous studies measured in urban and rural sites (Swietlicki et al., 2008)."

Line 61-85 in the manuscript:

"To date, many studies have assessed the effects of hygroscopicity on ambient particle deposition in the HRT based on assumed values of the hygroscopic parameter (Kappa, κ) representing non-hygroscopic, nearly hydrophobic, and hygroscopic particles (Voliotis and Samara, 2018) or estimations by parametric methods (Ching and Kajino, 2018; Hussein et al., 2013; Mitsakou et al., 2007; Haddrell et al., 2015; Vu et al., 2018) . However, it is well-known that continental aerosols typically show an external mixing state and size-dependent hygroscopicity (Zong et al., 2021). Thus, in order to capture the real and high-time-resolution features of ambient particles' hygroscopic growth in the HRT, direct particle hygroscopic growth measurements are a matter of necessity.

To our best knowledge, there are only limited studies exploring the impact of the hygroscopic growth of ambient particles on the particle deposition by direct hygroscopicity measurements. Moreover, hygroscopicity measurements using the Humidity Tandem Differential Mobility Analyzer (H-TDMA) (Londahl et al., 2009; Farkas et al., 2022; Vu et al., 2015; Kristensson et al., 2013) or Differential Aerosol Sizing and Hygroscopicity Spectrometer Probe (DASH-SP) (Youn et al., 2016) in these studies were all conducted at relatively lower RH (~ 90%) compared to that in the HRT (RH = 99.5%). For example, Farkas et al. (2022) modelled DFs of aerosol particles with four different diameters and studied in their dry state and after their hygroscopic growth at RH = 90% using a H-TDMA. Youn et al. (2016) examined

size-resolved hygroscopicity data by DASH-SP for particles sampled near mining and smelting operations to study the effects of particles' hygroscopic growth on the HRT deposition of toxic contaminants. It was further assumed that κ was independent of RH on the premise that the effective molar volume of the solute does not vary with RH. However, the presence of surface active, slightly soluble substances, and the co-condensation of semi-volatile soluble organic compounds can result in the humidity-dependent characteristic of κ (Wu et al., 2013; Wex et al., 2009; Topping and Mcfiggans, 2012). For instance, Liu et al. (2018) showed that κ could vary from about 0.1 at RH < 20% to less than 0.05 when RH ≈ 90% due to the non-ideal mixing of water with hydrophobic and hydrophilic organic components. Therefore, an explicit hygroscopicity measurements at HRT-like conditions will make the deposition estimation more accurate."

Line 95-97 in the manuscript:

"The field campaign was conducted from June 8 to July 6 in 2014 at an ecological park in the rural area of Wangdu County (38.666°N, 115.210°E) in the North China Plain, a polluted area with high population density and strong primary emissions."

1. Specific comments on the reply to review#1 to comment 3.

Response 1: The statement "only the comparison of κ measured simultaneously at the same sampling site makes sense." This is not what is the case. Why should the rural air masses at the measurement site be very different to other rural places. The κ value is a quantity commonly compared between different measurement sites. It only has to be clarified how the measurements were conducted and the RH or supersaturation need to be included into a comparison.

[Response]: Thanks for the reviewer's comment. The result measured by HH-TDMA at RH = 98% in this study was similar to those measured by H-TDMA or HH-TDMA at RH = 87% - 98.5% in other rural sites in the North China Plain in summer. The related statement was added as follows.

[Revise]: Line 19-29 in the appendix:

"The particle hygroscopicity parameter (Kappa, κ) in this study and previous studies measured in rural sites in the North China Plain (NCP) was shown in Table S1. The average size-resolved κ was in the range of 0.24 - 0.32 during the sampling period. The hygroscopic properties of particles in this study was similar to those determined in the NCP in summer, such as in Wuqing (Liu et al., 2011) and Xianghe (Zhang et al., 2016), which was higher than that measured in winter, such as in Dingxing (Shi et al., 2022). It can be explained that the mass fraction of organic matters with relatively weak hygroscopicity was higher in winter, while secondary inorganic aerosols with strong hygroscopicity made higher contribution in summer (Sun et al., 2015). Besides, the particle hygroscopicity increased as the particle diameter increasing, which was in accordance with previous studies measured in urban and rural sites (Swietlicki et al., 2008)."

Table S 1 Particle hygroscopicity parameter (Kappa, κ) in this study and previous studies

Rural site	Kappa, mean ± SD (Dry diameter, nm)						Instrument	RH	Reference
Wangdu	0.24 ± 0.09 (30)	0.24 ± 0.07 (50)	0.27 ± 0.06 (100)	0.28 ± 0.07 (150)	0.30 ± 0.08 (200)	0.32 ± 0.10 (250)	HH-TDMA	98%	This study
Wuqing	0.25 ± 0.06 (50)	0.28 ± 0.04 (100)	0.33 ± 0.05 (200)	0.35 ± 0.05 (250)			HH-TDMA	98.5%	(Liu et al., 2011)
Xianghe	0.29 ± 0.09 (50)	0.30 ± 0.06 (100)	0.31 ± 0.06 (150)	0.33 ± 0.04 (200)	0.35 ± 0.08 (250)	0.37 ± 0.09 (350)	H-TDMA	87%	(Zhang et al., 2016)
Dingxing	0.16 (60)	0.18 (100)	0.16 (150)	0.15 (200)			H-TDMA	90%	(Shi et al., 2022)

2. Specific comments on the reply to review#1 to comment 14. L.363:

Response 2: What allows the conclusion that the measured BC is "pure BC"? It is an ambient measurement with many committed species. Thus, I would expect some aging of the BC particles. There are quite some studies focusing on the hygroscopicity of BC. E.g., Liu et al., 2013. https://acp.copernicus.org/articles/13/2015/2013/acp-13-2015-2013.pdf The statement "The κ of BC with Dp = 50 nm was 0.20 ± 0.12" should be rephrased. It is the κ of the aerosol population, not of BC. The mass ratio can be strongly influenced by relatively few larger particles, whereas κ depends on the whole size distribution.

[Response]: Thanks for the reviewer's comment. As the expression was not rigorous, relevant statements have been deleted.

3. Fig. S8 BC and hydrophobic particles cannot be used synonymous. There are also other hydrophobic particles. Please be clear.

[Response]: Thanks for the reviewer's comment. The related statements and Figure S8 were deleted.

Comments on the revised manuscript:

1. 253: Are there differences between Figure 2 and S2, S3? They look very comparable so a statement on the comparison will be nice.

[Response]: Yes. Due to the similar physiological parameters (such as the FRC, URT volume, TV, and BF) of the adults (Figure 2 in the manuscript) and the elderly (Figure S3 in the SI), their regional and total deposition functions were similar to each other. While, for the reason that the FRC is positively correlated with the body weight, the FRC of the children was about one third of those of the adults and the elderly, leading to the different DF curves of the children (Figure S2 in the SI). Therefore, the statement of comparing the DFs of all age groups was added as follows.

[Revise]: Line 244-252 in the manuscript:

"As shown in the three figures, the regional and total DFs of all age groups respectively followed the same trends regardless the particle hygroscopicity. Due to the similar physiological parameters (such as the FRC, URT volume, TV, and BF, as shown in Table 1) of the adults (Figure 2) and the elderly (Figure S3), their regional and total DF functions were similar to each other. While, for the reason that the FRC is positively correlated with the body weight, the FRC of the children was nearly one third of those of the adults and the elderly, which may lead to the different DF curves of the children (Figure S2). Compared with the adults and the

elderly, the children had lower DFs of ultrafine particles in the head and higher DFs of submicron particles in the P region, resulting in higher total DFs of submicron particles."

2. Figure 3: I recommend to merge fig. 3 and S5 to one figure. Figure 3 alone gives somehow misleading indications. The driving factor is the exposure time with not corresponding activities. As stated in the authors reply to the review, the activities for the exposure time are not only resting, it should be made clear that this figure represents the literature exposure time to ambient pollution for a certain region not for all activities but only for resting.

[Response]: Thanks for the reviewer's suggestion. The former Figure S5 was incorporated into Figure 3. The related content was modified as follows.

[Revise]: Line 184-189 in the manuscript:

"It should be noticed that the exposure time data came from the statistical results of the questionnaire survey of the outdoor activity time for the rural population in Hebei, China. While, people may rest, take light exercise, or take heavy exercise during the exposure time. Different exercise levels (e.g. sitting, walking, exercising, etc) can result in different dose estimations and are not discussed here. For instance, previous studies found that the exercise level had great impact on the minute ventilation and led to the increasing deposition dose (Londahl et al., 2007)."

Figure 3 and related statement were shown in Line 325-343 in the manuscript:

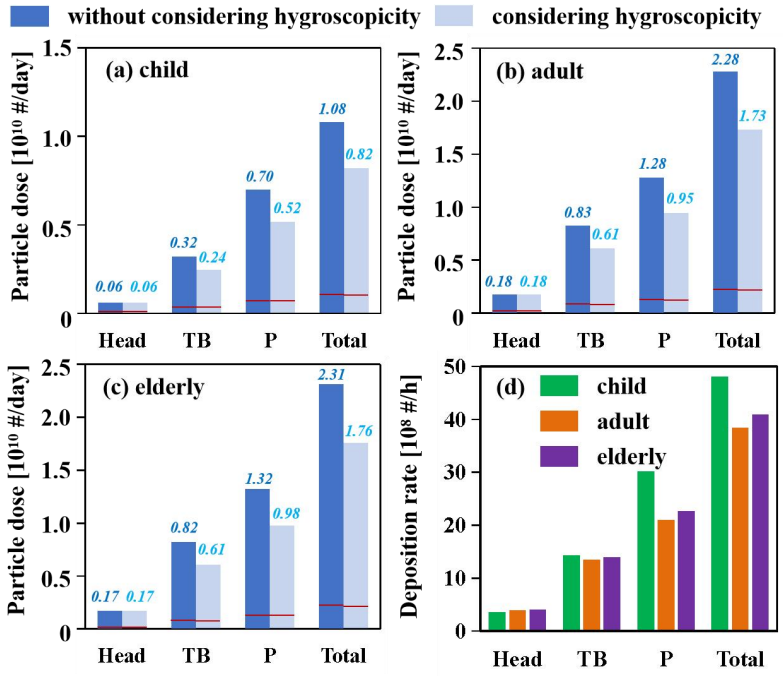

Figure 3. Regional and total deposition doses for the (a) children, (b) adults, and (c) elderly with/without considering particle hygroscopicity. The dark blue columns represent doses without considering hygroscopicity. The light blue columns

represent doses considering hygroscopicity. The red lines on the column represent the division of doses of hygroscopic (above the red line) and hydrophobic particles (below the red line). Numbers above each column mean the corresponding particle doses with a unit of 10^{10} #/day. (d) The average regional and total deposition rates considering hygroscopicity for three age groups. The green, orange, and purple column represent the children, adults, and elderly, respectively.

"In both cases, the adults (Figure 3(b)) and the elderly (Figure 3(c)) groups received similar regional and total doses. In contrast, the children had the minimum total dose (Figure 3(a)), which was around half (47.4% on average) to that for the adults. As shown in Eq (4), the exposure time is an important parameter for deposition dose calculations. The exposure time of the adults and the elderly groups was more than twice than that of the children (Table 1), which resulted in the greater deposition dose for the former two groups. Therefore, to remove the impact of the exposure time, the regional and total deposition rates for three age groups were also calculated and shown in Figure 3(d). The children received the maximum total deposition rate ($(4.81 \pm 4.55) \times 10^9$ #/h), followed by the elderly group ($(4.09 \pm 3.92) \times 10^9$ #/h), and the adults received the minimum ($(3.84 \pm 3.69) \times 10^9$ #/h). The regional deposition rate in the TB and P regions for three age groups showed a same order as the total deposition rate, while the order in the head was quite different. Specifically, three age groups had the similar deposition rate in the head."

3. 453: There are already HHTDMA capable for measurements in nearly saturated conditions (up to 99.6% RH). E.g. Mikhailov and Vlasenko 2020. https://amt.copernicus.org/articles/13/2035/2020/

[Response]: Thanks for the reviewer's comment. The statement was modified as follows.

[Revise]: Line 437-443 in the manuscript:

"For instance, the HH-TDMA (Suda and Petters, 2013), the Leipzig Aerosol Cloud Interaction Simulator (Stratmann et al., 2004), the inverted streamwise-gradient cloud condensation nuclei counter (Ruehl et al., 2010), and the filter-based differential hygroscopicity analyzer (Mikhailov et al., 2011) have been used to determine the particle hygroscopicity at RHs up to 99%. In particular, Mikhailov and Sergey (2020) adopted a new method with in situ restructuring to minimize the influence of particle shape, and the RH was up to 99.6% with an RH measurement accuracy better than 0.4%."

4. 454: I recommend a broader literature research and to extend the literature review to other global regions. There are studies reporting physiological parameters in the HRT and may the authors would need to justify here why physiological parameters in the HRT are significantly different between some rural regions in China and other places.

[Response]: Thanks for the reviewer's advice. We summarized the physiological parameters in the HRT used in the previous studies as Table R1.

Table R 1 Physiological parameters of different populations

Groups	FRC / mL	URT Volume / mL	TV / mL	BF / min^{-1}	Population	Reference
Children	1330	21.91	630	22		
Adults	3338	36.31	730	18	Chinese	This study
Elderly	3259	34.01	760	18		
Adults	2950	44.70	537.5	16	Chinese	(Li et al., 2016)
Children	1330	22.79	580	32		
Adults	3389	40.78	2360	26	Greek	(Voliotis and Samara, 2018)
Elderly	3475	34.63	2270	26		
Children	1484	25	303	19		
Adults	3122	50	625	16	Chinese	(Wang et al., 2021)
Elderly	3402	50	625	16		
Adults	3300	50	1250	20	American	(Gangwal et al., 2011)
Adults	3300	50	750	12	Caucasian	(Manigrasso et al., 2015)
Adults	3301	50	750	12	Caucasian	(Vu et al., 2017)
General	3300	50	625	12	-	MPPD Help

As shown in Table R1, the physiological parameters used in this study are similar to those for Chinese in other studies and those for other populations.

Anonymous Referee #2

Thank you for the changes and responses to my suggestions and questions. The only point I think still needs to be addressed is the question of deposited dose. I understand that determining dose on a mass basis is not possible (could it be estimated?). Thus, in the abstract, I think it is important to note that the doses change on a particle number basis to avoid any misunderstanding.

[Response]: Thanks for the reviewer's suggestion. The statement was modified in the manuscript.

[Revise]: Line 19-23 in the manuscript:

"In this study, the effects of hygroscopicity and mixing state on regional and total deposition doses based on the particle number concentration for the children, adults, and elderly were quantified using the Multiple-Path Particle Dosimetry model based on the size-resolved particle hygroscopicity measurements at HRT-like conditions (relative humidity = 98%) performed in the North China Plain."

Reference

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