Author response to Reviewer #1

The manuscript presents a comprehensive comparison of different methods for measuring particle lung deposited surface area (LDSA) in ambient air, focusing on the challenges and uncertainties associated with these measurements. The study provides valuable insights into the performance of various LDSA measurement techniques under different environmental conditions and particle characteristics. The authors have conducted a thorough analysis, considering factors such as particle effective density and hygroscopicity, which are often overlooked in LDSA measurements.

- We thank you for commenting our manuscript. We believe that your comments have helped us to improve the discussion and clarity of the manuscript. Our responses are provided below. We have also made changes in the revised manuscript (which will be submitted later after all reviewer comments). However, all the major changes are mentioned and shown in this response document. We hope that our responses and changes are satisfactory.

General Comments:

The abstract could benefit from a more detailed explanation of the challenges in estimating lung deposition of accumulation mode particles and the acceptable differences between methods when considering only ultrafine particles (UFP) and soot.

- Thank you for this suggestion. The last sentences of the abstract were modified: *"The challenges were especially related to the accumulation mode particles roughly larger than 200–400 nm* ***for which the dominant deposition mechanism in the lung changes from diffusion to impaction, and the particle effective density and hygroscopicity tend to increase****. On the other hand, the results suggest that the differences between the methods are reasonably low when considering only ultrafine and soot particles****, which have effective density closer to the standard (1.0 g/cm^3) and are more hydrophobic****, highlighting the suitability of LDSA^{al} as a monitored metric when estimating spatial differences in the particulate pollution within cities."*
- Also, some parts of the abstract were slightly shortened due to the added text.

Some statements in the introduction require revision or additional context to avoid oversimplification.

- We have carefully checked the introduction. Detailed changes are mentioned later in our responses to the Specific comments.

The manuscript would benefit from more quantitative analysis to support some of the key conclusions, particularly regarding the effects of particle effective density and hygroscopicity corrections.

- We have added additional analysis regarding the size-dependence of particle effective density. Also, the discussion of the results has been modified in the revised manuscript. Please, see our responses to Specific comments.

Some technical aspects of the measurement devices and data processing methods need further clarification.

- We have added information of the devices and the methods according to the Specific comments (see our responses there).

The discussion of the impact of particle effective density and hygroscopicity on LDSA measurements needs to be supported by additional data analysis.

- As mentioned, we have modified the discussion of the results in the revised manuscript. Please, see our responses to Specific comments.

Specific Comments:

Line 64: The statement about PM2.5 being relatively more harmful near local pollution sources like traffic is oversimplified and should be revised or removed.

- The statement has been changed to: *"For example, it has been suggested that within-city $PM_{2.5}$ dose-response gradients are steeper than between-city gradients, emphasising the role of near-source exposure (e.g., to traffic) in terms of adverse health effects of particles (Segersson et al. 2021)."*

Line 70: The concept of LDSA should be more precisely defined, acknowledging that it can refer to different regions of the respiratory system, not just the lung alveoli. It should also be clarified that LDSA refers to a surface area concentration.

- In the revised manuscript, it is mentioned that in different studies LDSA can be referred also to other respiratory tract regions than the alveoli. It is also mentioned that LDSA refers to surface area concentration. Here, we utilise $LDSA^{al}$ notation to highlight that we refer only to alveolar LDSA (which is also the most commonly measured). The new text: *"It's worth noting that, in different studies, LDSA can also be referred when considering other respiratory tract regions than the alveoli (e.g. Liu et al. 2023). Here, the notation $LDSA^{al}$ is used to clarify that only alveolar deposition is considered in this study (see Lepistö et al. 2023)."*

Line 133: More information about the Partector's design, particularly regarding ion trapping, would be helpful to understand potential influences on the charging current and calculated LDSA. The authors should address how the extrinsic charging efficiency, which is affected by particle losses in the charger, impacts the measured charging current and, subsequently, the calculated LDSA. This is crucial because particle losses can significantly alter the relationship between the charging current and the actual LDSA, potentially leading to inaccuracies in the final LDSA measurements.

- Description of the diffusion charging efficiency and its size dependence has been added in the revised manuscript. We agree that ion trapping is an important factor in the operation of a diffusion charger sensor. However, in a study by Fierz et al. (2014), which represents the Partector operation principle, the ion trapping of the device is not further described. However, the role of ion trapping is now shortly mentioned by citing Fissan et al. (2006) in the revised text. It's worth noting that some other particle sensors (like the new Partector 2 Pro), may alter the parameters of the charger (like the ion trap) to estimate particle sizes better, but this is not the case with the original Partector (used in

this study), and therefore, this topic is not discussed in-detail. The changes:
"*The Partector (Naneos GmbH, Fierz et al. 2014) represents the electrical particle sensor measurement method for LDSA^{al}* ***which is based on detecting the electric current caused by the sampled particles after a diffusion charger. The diffusion charging efficiency is determined as a multiplication of the number of elementary charges of a particle after charging (n), and the probability of a particle to penetrate through the charger (P). The product, Pn, is dependent on the particle mobility equivalent size with an exponent varying typically between 1.1– 1.9 (Dhaniyala et al. 2011, Järvinen et al. 2014). Due to lucky coincidence, the charger efficiency correlates reasonably well with LDSA^{al} of a single particle in a size range roughly from 20 nm to 400 nm, which can, however, be altered slightly by adjusting the ion trap voltage of the charger (Fissan et al. 2006)***."

Line 147: The statement about ELPI+ measurement requiring estimation of particle effective density needs clarification or correction. ELPI+ particle size distribution measurements are based on aerodynamic sizing, which inherently incorporates information about particle density. Therefore, it's not immediately clear why additional estimation of particle effective density would be required. The authors should explain this apparent discrepancy or revise their statement if it's not accurate. If there are specific reasons why effective density estimation is still necessary for LDSA calculations with ELPI+ data, these should be clearly explained.

- In ELPI+, the charger efficiency depends on the on the mobile equivalent size, but the size classification depends on the aerodynamic size. When measuring e.g., particle number, it is needed to know an average current caused by one particle collected onto the impactor stage to convert the electrical current data to particle number. As only the aerodynamic size is known, the effective density needs to be estimated to know the average current caused by a single particle, and, therefore, to convert the measured electric current into the wanted quantity accurately. In the revised manuscript: "*As the particle charge after the diffusion charger,* ***and, therefore, the measured electric current****, is dependent on the particle mobility equivalent diameter, and the size classification is dependent on the aerodynamic diameter, the ELPI+ measurement requires estimation of the particle effective density* ***to estimate the average electric current caused by a single particle collected onto a impactor stage and to convert the measured current to other quantities accurately***."

Line 155: A brief description of the ICRP model used for the lung deposition function should be included.

- In the revised text, parameters for the ICRP-model calculations (gender and physical activity) are provide in new Table S1. Also, the ICRP-model is shortly introduced: "*The ICRP-model is a semi-empirical regional compartment lung-deposition model which considers the human respiratory tract as a series of filters and utilises measured data with human volunteers*".
- We hope that the readers find the citations to Hinds (1999) and ICRP (1994) for the detailed information of the model.

Table S1: Parameters utilised in the ICRP model calculation (ICRP 1994, Hinds 1999)

	Functional Reserve Capacity, FRC (l)	**Breathing rate (m^3/h)**	**Breathing Frequency (1/min)**	**Tidal Volume (l)**
Female				
Sitting	*2.68*	*0.39*	*14*	*0.46*
Light Exercise	*2.68*	*1.25*	*21*	*0.99*
Heavy Exercise	*2.68*	*2.7*	*33*	*1.36*
Male				
Sitting	*3.30*	*0.54*	*12*	*0.75*
Light Exercise	*3.30*	*1.5*	*20*	*1.25*
Heavy Exercise	*3.30*	*3*	*26*	*1.92*

More detailed information about the conversion factor/process for the Partector is needed better to evaluate the differences between its measurements and other methods.

- Partector utilises a constant conversion factor from electric current to $LDSA^{al}$. This factor has been determined based on the response coefficient at 100 nm size (see Fierz et al. 2014). This point is also added to the revised text:
  "The Partector first charges the sampled particles in a diffusion charger and then converts the detected electric current caused by the sampled particles into $LDSA^{al}$ concentration with a single calibration factor. ***The chosen calibration factor is the response coefficient between the electric current and $LDSA^{al}$ at 100 nm, which typically is close to the peak size of $LDSA^{al}$ size distributions in urban environments (Fierz et al. 2014)."***

Table 1: The low PN concentration and high density reported for Prague require attention/explanation and careful interpretation.

- The site micro-environment is the most likely explanation for the lower PN measured in Prague compared to Helsinki. Also, note that geometric mean is used in the results, which typically gives slightly lower values than the arithmetic mean. In the revised manuscript, we have added additional information of the Prague site:
  "*In comparison with the Helsinki street canyon site, the measurement site was in an open environment in a preschool yard behind a fence, which limited the direct effects from the nearby traffic.*"
  Also in the results:
  "In general, the contribution of the nearby road traffic was clearer in Helsinki than in Prague ***due to the shorter distance from the passing vehicles to the measurement site, partly explaining the*** *relatively higher average PN, NO and BC concentrations compared to $PM_{2.5}$."*
- About the particle effective density, we acknowledge that the effective density determination includes necessary approximations (e.g., the averaged density for all particles). This approach and its limitations are explained in our responses to later comments. Also, the limitations of effective density estimations are addressed in the Strengths and limitations: "*In this study, it was possible to estimate the average effective density of particles by comparing the ELPI+ and DMPS/SMPS size distributions as well as the effects of hygroscopicity based on a review by Vu et al. (2015). However, these parameters have spatiotemporal variability, and they depend on the particle size and composition. In general, these factors are challenging to determine* ***(like ρ_{eff} in Prague),***

especially when considering the typical air quality monitoring measurements. Hence, not all the effects of particle effective density nor hygroscopicity were recognised in the analysis, and thus the results of these parameters should be considered to be indicative."

Lines 343-346: The conclusion about uncertainty related to particle effective density estimation needs stronger support from the data presented. Several issues should be addressed:

The unusually low PN concentration in Prague needs explanation.

- Please, see the response to the previous comment.

The limitations of using an average constant effective density over a wide size range should be discussed more thoroughly.

- The use of average constant density can be justified based on the instrument operation principles. The DMPS and SMPS results could be corrected by using a size-dependent effective density, but, with the ELPI+, the operation principle does not fundamentally enable the use of size-dependent effective density in the analysis (because the cascade impactor: collection efficiencies of different stages would overlap) without extensive simulation which has not been provided by the manufacturer according to our knowledge. The use of size-dependent effective density is not possible with the device software/operation either. Thus, the constant effective density estimation is the best that can be done with the data (and this is also very common issue with all urban aerosol measurements as there are only rarely enough instrumentation in monitoring sites to measure size-dependent density). We are however interested to hear approaches of how to take varying particle density profiles into account with ELPI+ data.

- We have added discussion of this limitation in the manuscript under Section 3.2.2. We also conducted an additional sensitivity analysis (new Fig S12) for the DMPS and SMPS data by utilising size-dependent effective density (approximated according to the studies of Virtanen et al. (2006), Rissler et al. (2014), Yin et al. (2015) and Lu et al. (2024)). In Fig S12, it can be seen that the size-dependent effective density does not considerably change the DMPS/SMPS results, which can be explained because of the dependence of mobility equivalent diameter with both the measurement method and lung deposition (also discussed in the manuscript). The scaled effective density function is not based on our data and is only an approximation, but we believe that this additional analysis shows that the average effective density approach does not cause considerable uncertainties with the DMPS and SMPS. Still, with the ELPI+, this uncertainty cannot be estimated in a justifiable way. However, the ELPI+ result can be compared to the DMPS/SMPS results, which do not have major uncertainty related to effective density. Also, it needs to be mentioned that, with ELPI+, constant effective density is always required, and thus, it is also reasonable to consider ELPI+ results with an average effective density.

- Added text: "*On the other hand, with DMPS and SMPS, the approximation of one averaged effective density for all the particles does not cause considerable uncertainties in the results due to the fact that both measurement method and lung* *deposition are mainly dependent on the mobility equivalent size of particles. This is demonstrated in Fig. S12, where example comparisons of DMPS and SMPS data with averaged, standard, and size-dependent effective densities in Helsinki and Prague are shown. However, with the ELPI+, the operation principle does not fundamentally enable utilisation of size-dependent effective density (see 2.3), which should be acknowledged. Still, this uncertainty of ELPI+ can be estimated by comparing the density-corrected results to the DMPS/SMPS results which are not as vulnerable to errors in terms of varying effective density."*

Also, in Methods -section:

"Also, with the ELPI+, data analysis with size-dependent effective density is not straightforward due to the cascade impactor measurement."

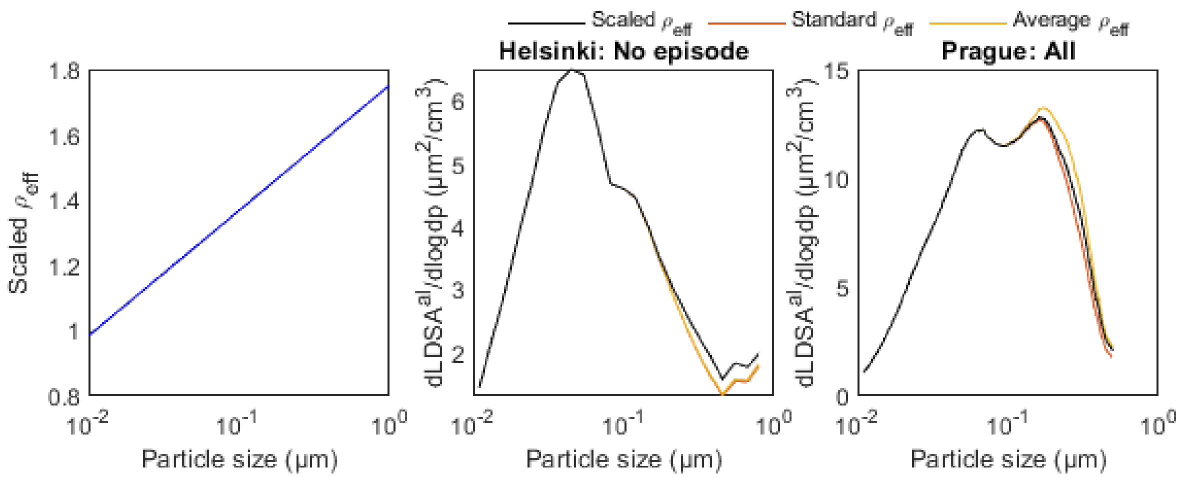

Figure S12: Comparison of average LDSA^{al} size distributions with Helsinki: All (DMPS) and Prague: All (SMPS) data by using scaled size-dependent effective density (ρ_{eff}), standard ρ_{eff} (1.0 g/cm^3) and averaged ρ_{eff} for all sizes (Helsinki: 1.1 g/cm^3, Prague 2.0 g/cm^3). Scaled ρ_{eff} function is showed in the first figure panel and is based on studies by Virtanen et al. (2006), Rissler et al. (2014), Yin et al. (2015) and Lu et al. (2024).

A sensitivity analysis showing how variations in effective density across different size ranges impact LDSA calculations would strengthen the argument.

- Thank you for this suggestion. Please, see the response to the previous comment.

The significant variation between ELPI+ and SMPS size distributions in Prague, especially for accumulation mode particles, warrants a more detailed explanation, considering factors beyond effective density.

- In Figure 2, it can be seen that the differences between ELPI+ and SMPS are much less significant after the density correction for the data, so it is reasonable to consider that it is the main reason for the difference in the results without any corrections.
- One additional reason is the varying operation principles: SMPS measures particles based on their number concentration (CPC), and then LDSA is calculated by assuming spherical particle shape (which of course is an approximation as explained in the methods section). ELPI+ (also Partector), however, measures concentrations based on the particle charge, and, therefore, particle shape also affects the measured concentrations. Especially with larger particles, agglomerated structures can cause considerable differences between the detection methods of a CPC and electric current,

which is also discussed in the method sections. Even though some device-related uncertainties can slightly affect the obtained results, these two points are most likely the main reason behind the difference.

- These explanations are discussed thoroughly in the manuscript, but we added reference to section 2.1.1. in the text, to help the reader to find further explanations for the mentioned behaviour of the size distributions.

Line 359: Quantitative analysis should be provided to support the conclusion about decreased differences after peff-correction.

- By comparing size distributions in Figure 1 and 2, it can be seen that the difference between ELPI+ and DMPS/SMPS is clearly less significant after the density correction. Also, Figure 4 and (original Figure S13, new Fig S14) support this idea in terms of total concentrations. The data behind the figures is provided in original manuscript Table S1, and also main numbers of the results have been provided in Section 3.2.2. Thus, we believe that it is rather evident, that the differences between the methods decreased after the effective density correction. It is not clear what kind of additional quantitative analysis is requested in this comment. It is also worth considering, that $LDSA^{al}$ has not strictly defined reference measurement method, and all the common $LDSA^{al}$ methods have both strength and weaknesses (as shown in the manuscript). Therefore, it is not straightforward to quantitatively state which methods are the most correct, nor the exact effect of different corrections, as there is no reference method available. One main point of this study is to show how the results with different methods vary in different conditions and what factors influence the obtained results, which is crucial when comparing $LDSA^{al}$ results with different instrumentation, and not yet well understood. However, additional discussion related to the effective density correction is added in the revised text (see previous comments) to help readers to evaluate the effect of corrections.

Figure 3: The opposite trends of overestimation and underestimation for ELPI+ and SMPS require more in-depth discussion.

- Thank you for this suggestion. In the revised manuscript, in-depth discussion about the over/underestimations have been added: ***The overestimation of total $LDSA^{al}$ concentration of the ELPI+ with the standard ρ_{eff} assumption (Fig. 3) can be explained with the conversion from electric current into to $LDSA^{al}$, as the calculation considers the particles to have larger mobility equivalent size than they have in reality, causing the conversion factors into to $LDSA^{al}$ to be too high (see also Lepistö et al. 2020)****. As seen, the majority of $LDSA^{al}$ concentration in the studied sites was attributable to particles smaller than 500 nm (mobility equivalent diameter). Thus, the DMPS, SMPS and Partector are less vulnerable to errors related to the effective density if the concentration of particles larger than 500 nm is not high* ***as both the measurement (charging efficiency and size classification) and lung deposition efficiency are dependent on the same quantity (mobility equivalent size). The slight underestimation in Fig. 3, is related to the concentrations of particles larger than about 500 nm, where the dominant deposition method changes from diffusion to impaction, causing the DMPS and SMPS to underestimate the deposition efficiency***."

Lines 408-412: The statement about hygroscopicity-corrected size distributions for SMPS and DMPS should be reconsidered:

The changes before and after corrections may be more related to particle size distribution than hygroscopicity or chemical composition.

- The hygroscopicity correction does not change the measured particle size distribution. The correction affects only the estimated particle lung deposition efficiency function (see Figure S7). Thus, the changes after the hygroscopicity correction are related to different particle lung deposition efficiency caused by the hygroscopic growth of particles in the respiratory system. Therefore, in all three cases (1. general assumptions, 2. effective density corrected, and 3. effective density & hygroscopicity corrected), the input size distribution is always the same. This point is clarified in the revised Methods - section: *"It should be noted, that the hygroscopicity correction only changes the estimated lung deposition efficiency of particles, not the initial size distribution or the surface area of the inhaled particles."*

A more detailed analysis of how the PSD itself influences the observed changes after hygroscopicity correction is needed.

- Please, see our response to the previous comment. The PSD itself does not change due to the correction. But, of course, the initial particle size distribution affects how much the hygroscopicity-correction changes the result. This is explained in the revised manuscript: "*In general, hygroscopicity correction decreased the lung deposition efficiency of particles smaller than 200 nm whereas it increased the deposition efficiency of particles larger than 200–400 nm (see also Fig. S7)."*
- Also, the discussion in Section 3.2.3 was slightly modified:
"*Even though the hygroscopicity-correction can considerably change the estimated $LDSA^{al}$ size distributions, the effect on the measured absolute $LDSA^{al}$ concentration was less significant which can be seen in Fig. 6. Note that the correction was not done for the Partector data. With the ELPI+, $LDSA^{al}$ concentration with the general assumptions was 107–114 % of the hygroscopicity-corrected result in all the cases. With the DMPS and SMPS, $LDSA^{al}$ with general assumptions was 95–104 % of the ones with the hygroscopicity-correction.* ***This result can be explained due to the balancing effects of particles smaller than 200 nm and larger than 200–400 nm in terms of the hygroscopicity correction****. Thus, by a coincidence, accuracy of the absolute $LDSA^{al}$ concentration measurement was not significantly affected due to the particle hygroscopicity.* ***However, it's worth noting that this result may depend on the location and urban environment. For example, high concentration of accumulation mode particles can potentially cause underestimation of $LDSA^{al}$ without hygroscopicity correction.*** *Also, it's important to note that the hygroscopicity correction still affected the relationship between the studied instruments (Fig. 6)."*

The relative importance of hygroscopicity versus PSD in determining the final LDSA values should be discussed.

- Please, see the responses to previous comments.

Stronger quantitative support is needed for the conclusion about the agreement between methods after hygroscopicity correction.

- Similarly, as with the response regarding the effective density correction, the lack of reference instrument for $LDSA^{al}$ challenges quantitative analysis of the strengths and weaknesses between the different methods. One of the main points of this study is to show how different factors like the effective density or hygroscopicity can affect the accuracy of different $LDSA^{al}$ instruments in ambient conditions, which is not well understood currently. In Figure 5 and 6, the changes after hygroscopicity corrections can be observed (see also original manuscript Table S1 and Figure S13). The hygroscopicity correction decreases the lung deposition efficiency of particles smaller than 200 nm, whereas it increases the deposition efficiency of larger accumulation mode particles. This phenomenon can also be observed in Figure 5. Then, the differences between instruments are discussed in terms of total concentration in the text. It is not clear what kind of additional quantitative analysis is requested in this comment.

Line 497: The conclusion about neglected hygroscopicity not considerably changing the results due to balancing effects should be presented more cautiously, acknowledging that it may only be valid under certain conditions.

- We agree, this point is now acknowledged (see responses to previous comments).

Technical Corrections:

Line 312: Add the Wu et al. (2023) reference to the reference list.

- Thank you for pointing this out. We have added the reference to the list.

Check for consistency in terminology throughout the manuscript, particularly in the use of LDSA and LDSAal.

- In the manuscript, $LDSA^{al}$ notation is used thoroughly. As mentioned in an earlier response, this notation is used to clarify that the results consider alveolar deposition, and this clarification is also mentioned in the revised manuscript. LDSA without “al” is used only once:
  “*It’s worth noting that, in different studies, LDSA can be referred also when considering other respiratory regions than only alveoli (e.g. Liu et al. 2023). Here, the notation $LDSA^{al}$ is used to clarify that only alveolar deposition is considered in this study.”*