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A new method to measure real-world respiratory tract deposition of inhaled ambient black carbon☆

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ABSTRACT

In this study, we present the development of a mobile system to measure real-world total respiratory tract deposition of inhaled ambient black carbon (BC). Such information can be used to supplement the existing knowledge on air pollution-related health effects, especially in the regions where the use of standard methods and intricate instrumentation is limited. The study is divided in two parts. Firstly, we present the design of portable system and methodology to evaluate the exhaled air BC content. We demonstrate that under real-world conditions, the proposed system exhibit negligible particle losses, and can additionally be used to determine the minute ventilation. Secondly, exemplary experimental data from the system is presented. A feasibility study was conducted in the city of La Paz, Bolivia. In a pilot experiment, we found that the cumulative total respiratory tract deposition dose over 1-h commuting trip would result in approximately 2.6 μg of BC. This is up to 5 times lower than the values obtained from conjectural approach (e.g. using physical parameters from previously reported worksheets). Measured total respiratory tract deposited BC fraction varied from 39% to 48% during walking and commuting inside a micro-bus, respectively.

To the best of our knowledge, no studies focusing on experimental determination of real-world deposition dose of BC have been performed in developing regions. This can be especially important because the BC mass concentration is significant and determines a large fraction of particle mass concentration. In this work, we propose a potential method, recommendations, as well as the limitations in establishing an easy and relatively cheap way to estimate the respiratory tract deposition of BC.

1. Introduction

Black carbon (BC), a product of incomplete combustion from coal, internal combustion engines, or biomass burning is linked to depraved air quality, acute health effects, and premature deaths (Janssen et al., 2011; Lelieveld et al., 2015). In economically advanced countries, successful measures are being taken to reduce the harmful effects of BC by introducing low emission zones, improving the vehicular fleet, and stiffening the emission standards (e.g. Rasch et al., 2013). In parallel, extensive research unveil the effects of BC pollution in laboratory tests, epidemiological, and toxicological studies (Janssen et al., 2011; WHO, 2012; Künzi et al., 2013). Contrarily, the developing or poorer regions still fall behind in terms of BC emission control. Here, although some studies on particle exposure and respiratory tract deposition do exist (e.g. Varghese et al., 2005; Huang et al., 2013), the colossal BC pollution is often neglected in favor of economic growth (Liu, 2012). Cultural behavior (e.g. observance) was also found to play an important role in many environmental problems, including air quality (Ye et al., 2016). It creates a paradox – pollution is least constrained in the regions where it is most prevailed. From the scientific perspective, on the other hand, present methodologies and sophisticated instrumentation to measure inhaled particles (e.g. Löndahl et al., 2006; Thompson and Finlay, 2012; Jakobsson et al., 2016) may be out of reach for many indigent societies and thus limit the research.

The exposure to air pollution is often referred to as a measure to understand its effect to personal health (e.g. Dons et al., 2012;

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Williams and Knibbs, 2016). For example, Huang et al. (2013) showed that exposure to traffic-related air pollution and noise are associated with alteration of heart rate variability. However, the exposure itself, although being used in epidemiological studies, does not provide any direct quantification of the fraction of pollutant that deposits in the respiratory tract after inhalation. Particle dosimetry models (e.g. Multiple-Path Particle Dosimetry Model, Chemical Industry Institute of Toxicology, Research Triangle Park, NC) can be used to estimate the deposited dose (DD) of aerosol particles (e.g. Hussein et al., 2013; Williams and Knibbs, 2016), however, it requires additional parameters such as particle number size distribution, minute ventilation, time to exposure, particle hygroscopicity etc. Unfortunately, these parameters are usually not known, and thus may contribute to significant uncertainties in DD calculations if generalized values from the references are used (Dons et al., 2012; Hussein et al., 2013).

Contrary to models, direct measurements offer data of the respiratory tract deposition dose of inhaled particles including all aspects of the exposure situation. Measurement techniques for respiratory tract deposition of airborne particles were critically reviewed by Löndahl et al. (2014). No commercially available instruments directly measure the deposition dose of airborne particles, with exception for medical techniques used for control of drug delivery or diagnosis of lung disease. Custom-built systems utilizing mobility particle sizers, gamma cameras, particle counters, etc., have mainly been developed to measure lung deposition of inhaled particles under laboratory conditions, although a few exception exists (Löndahl et al., 2014; and references therein). The device with closest resemblance to our proposed apparatus for monitoring of respiratory tract deposition was developed by Goldoni et al. (2009). Their device was, however, not optimized to measure the deposition of black carbon.

In this work we aim to: (1) develop a method and a platform for direct, simple, and cheap measurements of respiratory tract DD of BC; (2) test the system's ability to quantify an individual's DD.

2. Materials and methods

2.1. Measurement location

We performed the study in La Paz, the capital city of Bolivia (~3000–4000 m above sea level). The population of La Paz is estimated to be more than 0.8 million residents, which makes it the third-most populous city in Bolivia. The number of registered vehicles is approx. 428000 (INE, 2017). However, the real number is expected to be much higher due to unregistered automobiles (INE, 2017). The vehicular fleet in Bolivia is dominated by gasoline driven engines (84% of total fleet). Diesel and natural gas vehicles comprise the 13% and 3% of the fleet, respectively.

The measurements to determine the deposition dose (DD) of black carbon (BC) took place between 13.00 and 16.00 local time, on June 6, 2018 (dry-season, Soruco et al., 2015), as a separate part of a bigger air-quality-oriented measurement campaign. Two most common modes of transportation in the city, micro-bus and walking, were chosen for our experiment. Approximately 25, 15, and 20 min were spent for walking in Busch Avenue, transit-transport in Arce Avenue, and walking in Arce Avenue, respectively. The walks in both avenues were downhill (approx. 7% grade), while the drive with a micro-bus was uphill. The Busch Avenue is a 4-lane road (2 lanes each direction, separated by a lawn) with a moderate traffic load and is located in a more residential part of La Paz. The traffic congestions were noticed only at bigger intersections and roundabouts. On the other hand, Arce Avenue can be characterized as one of the main arteries running through La Paz center and connecting it with suburbs, and other cities (e.g. El Alto). From the roundabout at Isabel La Catolica it continues northwest as 4 lanes, reduces to 2 lanes as Avenue Villazon. It changes its name once again to 2-lane Avenue of Mariscal Santa Cruz, where it is joined by an opposite direction, 2-lane road separated by a lawn with a pedestrian ways. In contrary to Busch Avenue, immense traffic and large number of people regularly block these avenues.

2.2. Instrumentation

Two identical portable micro-aethalometers (AethLabs model MA200, San Francisco, USA) have been used to measure equivalent black carbon (BC) mass concentration in 1 s time resolution at a flow rate of 150 mL/min. The MA200 measures the rate of change of transmitted light due to particle deposition on filter relative to an adjacent reference (particle-free) point. The optical attenuation increment is then converted to a mass concentration of BC using the known optical absorbance per unit mass of BC material (Cheng and Lin, 2013). Like the previous generation of the instrument (AE51), the measurements at 880 nm are interpreted as the concentration of BC. The measurement principle of MA200 closely resembles to that of AE51, with the main differences being in the number of wavelengths (5 versus 1), filter material (polytetrafluoroethylene membrane versus fiber filter), and measurement modes (DualSpot® in MA200).

We used a single board computer (Hardkernel model Odroid C1+, GyeongGi, South Korea) with a high sensitivity GPS module (Navilock model NL-8004U, Berlin, Germany) to log the BC mass concentration and position. The GPS position was recorded in 1-s time resolution.

2.3. The new approach

The experimental setup to measure the respiratory tract deposition of equivalent black carbon is shown in Fig. 1. It comprises of mouthpiece, mixing chamber, flowmeter, dryer, and a portable MA200 micro-aethalometer. The ambient aerosol, inhaled exclusively through the nose, was exhaled through the mouthpiece and conductive rubber tubing (length 10 cm, inner diameter 0.8 cm) into the mixing chamber, which was designed to reduce pressure fluctuations and ensured a steady flow for the micro-aethalometer. This was achieved by installing an air-tight flexible membrane (Fig. 1, 1b) inside the housing (Fig. 1, 1a), which had the open ports allowing the membrane to expand during the exhalation cycle. This prevented the disturbance from over-pressure due to air resistance in the particle filter (Fig. 1, 3). The diameter of tubes for exhaled air from mouth to mixing chamber, mixing chamber to flowmeter, and mixing chamber to filter (Fig. 1, 7) were 0.8 cm. While the lines after the filter and those for the particle sampling were 0.2 cm. The differences in tube diameters are reflected in Fig. 1 by different line widths. This ensured that the majority of exhaled air passed through particulate filter into the flowmeter and out of the system (due to higher air resistance in lower diameter tubes). An open end after the filter (Fig. 1, 7) was left for condensate release. The influence of the micro-aethalometer sampling flow and open end for condensate (after filter 7) onto estimating the breathed air volume (from measurements of flowmeter) was investigated in the laboratory prior the measurements. It was found that the measured flow rate of breathed air is less than 5% lower than the actual value. Given the fact that exposure to BC in developing regions might be up to 10 times higher than in Europe and/or United States (e.g. Kecorius et al., 2017; Alas et al., 2018), we consider the underestimation of breathed air volume, and thus, the total respiratory tract deposition dose by less than 5% to be negligible.

To measure the BC mass concentration in the exhaled air, the measurement setup shown in Fig. 1, was placed inside the backpack

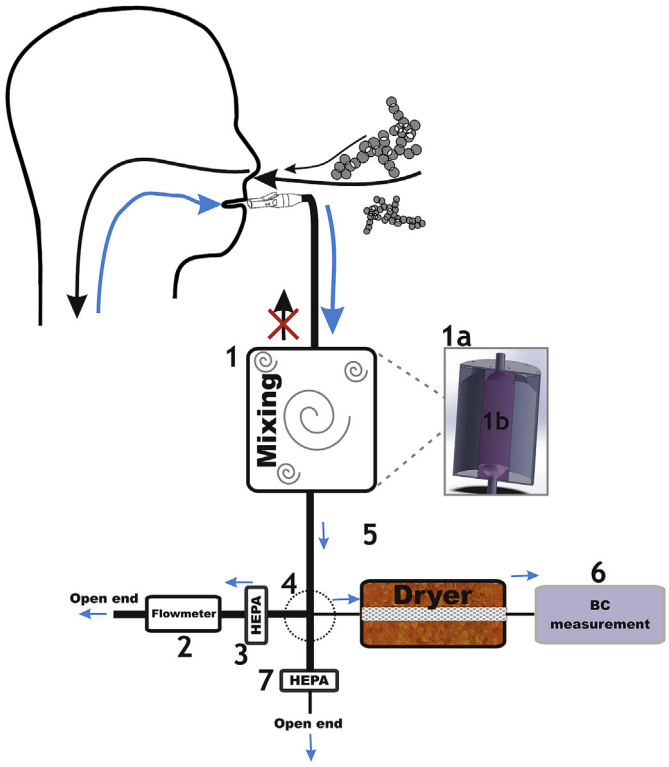

Fig. 1. The experimental setup to measure respiratory tract deposition of black carbon. 1 – mixing chamber (1a – housing, 1b-flexible latex membrane); 2 – mass flowmeter; 3, 7 – high efficiency particulate air filters; 4 – four way flow splitter; 5 – silica gel dryer; 6 – MA200 micro-aethalometer. Note: An identical micro-aethalometer, not shown in this figure, was used to record ambient BC mass concentration.

and carried along the commuting routes. A system measuring the ambient BC mass concentration was placed in a second backpack, which was then taken along the side of the first system. Both backpacks were equipped with micro-aethalometers, GPS, and data acquisition hardware. All sample lines in contact with aerosol (except mouth-piece and mixing chamber membrane) were made of conductive rubber material or stainless steel.

The pilot study was performed by a 33-year old, non-smoking male (medical examination documents, e.g. lung function, are available on request from corresponding author). The person himself carried all the instrumentation necessary for this study.

In the following, we provide a detailed description on measurements and data analysis procedures to obtain the respiratory tract deposition dose of BC. This also includes the discussion on some relevant critical aspects for particle lung deposition measurements as described by Löndahl et al. (2014).

2.3.1. Initial steps

Prior to measurements, flow calibration of both MA200 has to be performed *in situ* atmospheric pressure. This can be done with a flow calibration kit provided together with the instrument. Additionally, the flow rates at the inlet of the instrument are recommended to be checked every time before the instrument is deployed using low backpressure external flowmeter. If this step is neglected, the measured BC mass concentration can be biased. For example, at higher altitudes air density and pressure decreases. This will result in instruments pump running at a higher speed to pull a larger volume of air in order to obtain constant mass flow. We recommend setting the flowrate to 150 mL/min and time resolution to 1 s. This will ensure the highest instrument sensitivity and acceptable time base for exhalation measurements.

The instruments measuring BC mass concentrations in exhaled and ambient air must be synchronized. This is important for later data analysis.

Leaks have to be tested using a particle-free air. For the experimental setup shown in Fig. 1, inhalation of particle-free air can be achieved by high efficiency particulate filter. Please note that the micro-aethalometers will show high noise levels when measuring low BC mass concentrations. It is important not to exclude negative values from the measurements, when the average is calculated and zero is checked.

2.3.2. Particle losses

It is necessary to estimate particle losses in the experimental setup, as they may otherwise lead to overestimation of the respiratory tract DD. Short tubing made of conductive materials was used to reduce particle losses due to diffusion and electrostatic deposition, respectively. The remaining particle losses was characterized and corrected for. In case of unknown particle size spectra (e.g. particle number size distribution) and the measured physical particle property is mass (in our case, BC mass concentration), information about particle losses inside the experimental setup can be achieved through the instrument inter-comparison either in laboratory or *in situ* (e.g. Alas et al., 2018). In this study, we intercompared our experimental breathing set-up versus ambient BC measurements in both environments. The results are shown in Fig. 2.

It can be seen that in our case, the two micro-aethalometers (with and without breathing setup) agree reasonably well (within 3%). Such a small BC mass losses inside the experimental setup were considered negligible in this context. Please note that such a method is recommended only when inter-instrument variability is minimal (less than 1%).

2.3.3. Breathing pattern

Breathing pattern should be monitored during the measurements. In our case, the commercially available mass flowmeter (TSI model 4000, Shoreview, MN, US) was used to measure exhaled air flowrate (Fig. 3).

The flowrate has to be corrected for pressure, temperature, and humidity effects. It is a medical standard to report flows and volumes at body temperature and pressure, saturated (BTPS, which are the conditions in the lung). To account for these conditions, we therefore performed the correction according to TSI handbook (TSI, 2018). It was found that the values recorded for standard conditions had to be corrected by 10% to obtain mass flowrate including the water vapor correction. This is later translated into 10% lower deposition dose values. From the breathing pattern, personal physical parameters, such as tidal volume (volume of air displaced between normal inhalation) and breathing frequency can be obtained. These values can then be used to calculate the minute ventilation.

2.3.4. Data analysis procedure

The proposed method to obtain the respiratory tract deposition dose (DD) of equivalent black carbon (BC) relies on the measurement of the ambient BC mass concentration, the exhaled air flowrate, and the BC mass concentrations of the exhaled air. The last two parameters are directly measured with the experimental setup shown in Fig. 1. From the measured variables, the respiratory tract deposition dose can be calculated as:

$$DD = (BC_{ambient} - BC_{exhaled}) \times V_{air\_breathed}, \quad (1)$$

where $BC_{ambient}$ and $BC_{exhaled}$ is BC mass concentration in ambient and exhaled air (in ng/m^3), respectively. $V_{air\_breathed}$ is the volume of

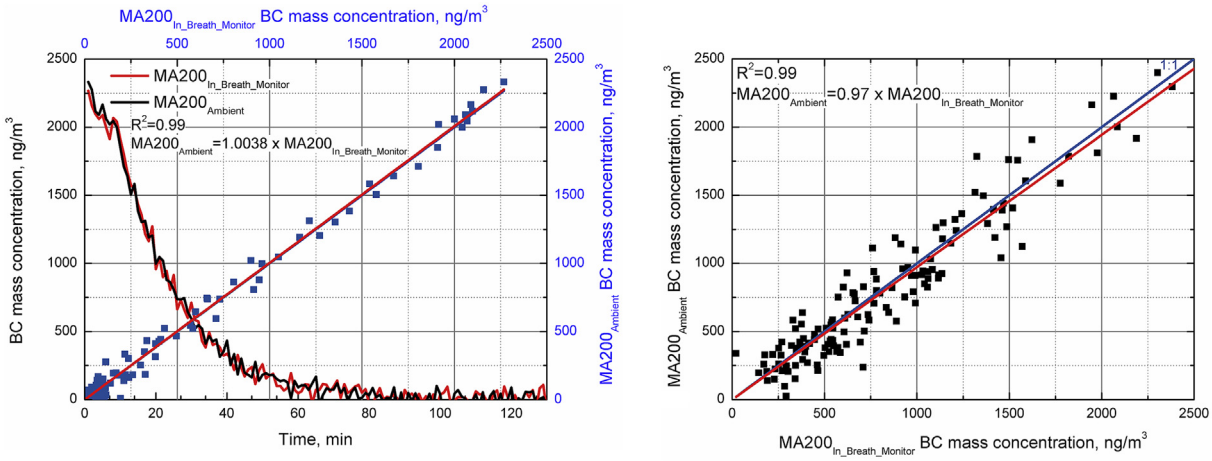

Fig. 2. Left – Micro-aethalometer inter-comparison using laboratory generated soot (Mini-CAST, Moore et al., 2014). Black and red lines show the BC mass concentration decay measured by both micro-aethalometers after the mixing chamber was filled with soot. Right - instrument inter-comparison under real-world conditions. In both cases instruments were set to 30 s data averaging. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

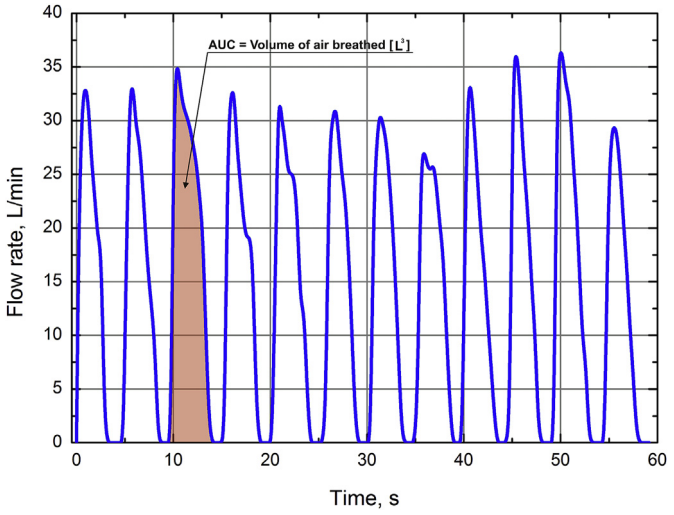

Fig. 3. An example of measured flowrate of exhaled air. The exhaled air volume (in liters) can be retrieved by integrating the flowrate (calculating the area under curve (AUC), shaded area in the figure). Start-end times (start and end time between two zero flow measurements) were defined for each exhalation cycle for calculating the average deposited BC mass concentration for each breathing cycle.

air breathed (in m^3). In this work, we have used an exhaled air flowrate to estimate the volume of air breathed. $V_{air\_breathed}$ was calculated from the flowrate measurements as:

$$V_{air\_breathed} = \int_{t_0}^{t_1} Q dt, \quad (2)$$

where Q is measured flowrate of exhaled air (in L/min), t_0 and t_1 is the start and end time of exhalation. We recommend the following procedure to evaluate the DD:

1. The measurements from both instruments have to be merged together to calculate cross-correlation function. It is important that instrument times are synchronized prior measurements.
2. An optimal alignment after determining the maximum lag has to be performed for both time series of the BC mass concentrations (Fig. 4)
3. When both of the BC time series are aligned, the difference between BC mass concentrations in exhaled and ambient air can be calculated to determine the deposited BC mass concentration (Fig. 5, panel a).
4. From the exhaled air flowrate measurements (Fig. 3), the start and end times (in milliseconds) for each exhalation cycle have to be defined. This time interval is then used to calculate the average deposited BC mass concentrations for each breathing cycle.
5. By integrating the flowrate of exhaled air (Eq. (2)), the volume of air breathed per one cycle is obtained. It has to be corrected for humidity effects onto flowmeter (depending on the type of flowmeter used). In this work, we have corrected the flowmeter for pressure, temperature, and humidity effects following the handbook provided by the flowmeter manufacturer.
6. Using Eq. (1), deposition dose (in ng) per one breath can be calculated by multiplying the deposited BC mass concentration and volume of air breathed (per 1 cycle).

The results can be illustrated as a cumulative deposition dose of black carbon in the respiratory tract during the whole commuting distance.

2.3.5. Limitations

There are several design aspects, summarized by Löndahl et al. (2014), which may influence the measurement results. Firstly, soot restructuring (collapse) upon exposure to high humidity environment followed by the rapid water evaporation was observed in a laboratory study by Ma et al. (2013). As the relative humidity inside human airways is nearly 100% (Ferron et al., 1988), the changed optical properties of measured BC particles (Radney et al., 2014) may introduce some uncertainty due to restructuring even if measured dry. However, we were not able to find any published results on the effect of soot particle restructuring in the airways and its effect on optical properties. Secondly, measured flowrate, and thus estimated inhalation rate and DD could be affected by a changed chemical composition of the exhaled air. A significant increase of CO_2 in exhaled air (from 0.04% in clean ambient air to approx. 3.3% in exhaled air) was observed in previous studies (e.g. Boyer and Bailey, 1942). As most of the flowmeters are calibrated to measure regular air, this might influence the measured flowrate. In our study we do not expect these uncertainties to be high, as it was demonstrated that 3% error is

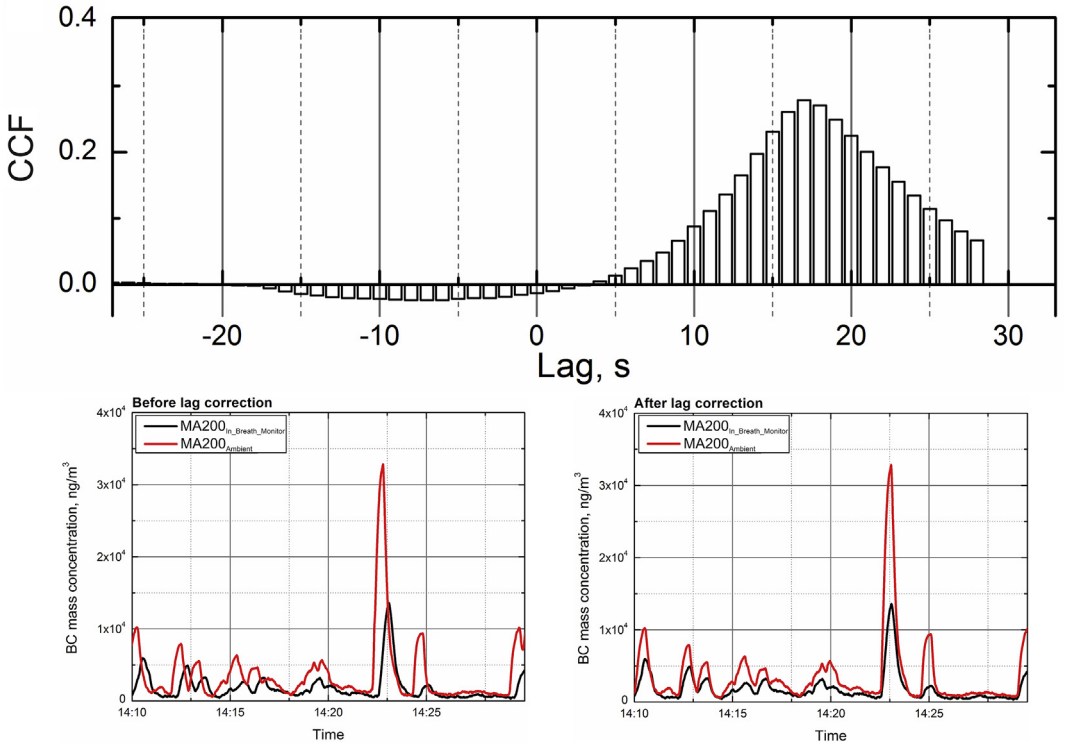

Fig. 4. The example of cross-correlation function (CCF, top panel) of two time series of BC mass concentrations measured in exhaled and ambient air. The BC measurements before (bottom-left) and after optimal alignment after determining the maximum cross-correlation lag (bottom-right) are shown in the lower panel. For cross-correlation function calculation, see Dean and Dunsmuir (2016).

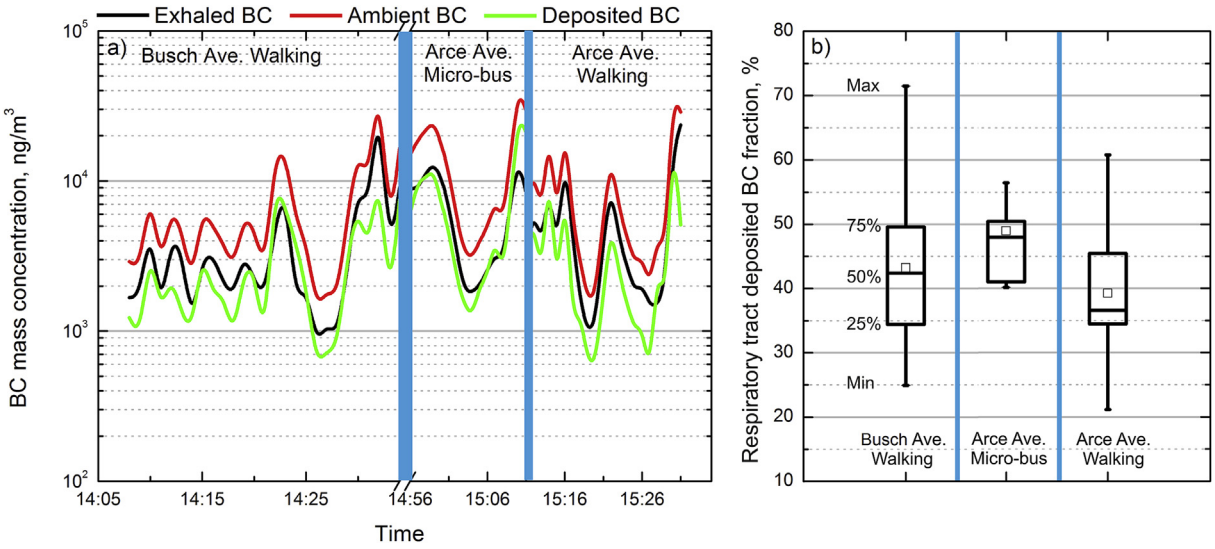

Fig. 5. Equivalent black carbon (BC) mass concentration measured in ambient (red line) and exhaled (black line) air (panel a). Deposited BC mass concentration was estimated by calculating the difference between ambient and exhaled BC (green line). The respiratory tract deposited fraction of BC is shown in panel b. The deposited BC mass concentration was used (multiplied by volume of air breathed) in estimating the deposition dose of BC. Here, BC is presented as 1 min average (squares in panel b). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

expected in the mass flowmeter when the CO_2 content is at 10% (Lotus Consulting, 2018). Having CO_2 content at approx. 3% this error converges to zero. Evaluation of previously mentioned effects would further improve our proposed method accuracy.

Information on regional deposition fraction/dose is considered to be crucial due to differences in anatomy, physiological function, clearance mechanisms, etc. in distinct areas of the respiratory tract (Löndahl et al., 2014). One of the most important parameters needed to retrieve the information on regional particle deposition is particle size distribution (e.g. number, surface area, volume or mass). In this study, however, due to the choice of the instrumentation, only total black carbon mass concentration was measured. Meaning, the information on particle size is lost. It disables the retrieval of regional dose, and only the total respiratory tract

deposition dose can be recovered. This limitation could be overcome by mobile measurements of black carbon particle size distribution. Unfortunately, up to the date of this study, no such instruments are available. On the other hand, total deposition dose/fraction still remains a viable parameter to understand the effects of particle exposure, and is frequently reported in scientific literature (e.g. Löndahl et al., 2012; Kristensson et al., 2013) as regional deposition can only be measured with high uncertainty and by use of radiolabeled particles.

Additionally, the application of this new method for determining the mass of deposited particles in the respiratory tract should be done within the detection limit of the instrument to be used (e.g. micro-aethalometer). While the BC mass concentration in many developing regions is sufficiently high to be measured by our experimental setup, this may not be true for other locations.

We would also like to emphasize some issues that could also be improved in the future to advance the DD measurement and personal comfort of an individual, who performs such kind of experiment. For example, we noticed that an extended inhalation, without exhalation through the nose gave a distress to nasal cavity and throat. This is due to extensive drying, which is a result of the absence of the exhaled air (and moisture in it). Another issue that was discovered during the experiment was the accumulation of excess secretion. Because of the mouthpiece, the swallowing of saliva became somewhat disrupted. The inhalation through nose could be replaced by inhalation through mouth, solving all previously mentioned problems. This, however, would require redesigning of the presented experimental setup and introduce problems with instrumental dead-space (re-inhalation of previously exhaled air). Although the mentioned discomfort was tolerable, the reduction of it would be desirable. To simplify the flow measurements, the relative humidity in the lines after the exhaled air should be lowered. This could be achieved by measuring the inhaled, and not the exhaled air flow. In our present setup this cannot be achieved due to the specifications of the used flowmeter (particulate filter is needed upstream the flowmeter). For example, pressure drop or ultrasound could be used to measure inhaled air flowrate without particle filter (e.g. Demir et al., 2018), reducing the problem of water vapor condensation.

Further, we present the very first results from a pilot study in La Paz, Bolivia, during which the new experimental setup was used. The experiment was conducted under real-world conditions: approx. 45 min of walking, and 15 min of transit inside natural gas powered micro-bus (with open door and windows).

3. Results of the feasibility study

The information on ambient equivalent black carbon (BC) mass concentration, as well as 1-min deposition dose (DD) along the avenues are summarized in Table 1. An STP (standard temperature and pressure; 273 K and 1013 hPa) correction was applied to BC mass concentration values following the Alvarez et al. (2013). For better representability, we have split the data set into two parts. A rather stable background BC mass concentrations and a sudden increase in concentration due to collectively passing vehicles and/or measurements directly at intersections, were split at a value of 5 $\mu g/m^3$. BC values less than 5 $\mu g/m^3$ were designated as base level of BC, while values above 5 $\mu g/m^3$ – as high level of BC. Such a separation was done to distinguish high and low pollution episodes, and was done after evaluating all the measurement data. We also note that during the commuting inside the micro-bus, the levels of BC mass concentration were not only higher, but also less variable than those recorded while walking. For this reason, we did not split this data set as described previously. The data for DD was split at 10 and 50 ng for 1 breath and 1 min, respectively. In addition, arithmetic mean for the whole data set (with no data subset), standard deviation, and median value were also calculated (see Table 1). The highest average BC mass concentration in ambient air was recorded inside the micro-bus (natural gas powered). The BC mass concentration along the Arce Avenue (inside micro-bus) was 13.7 $\mu g/m^3$ (SD = 18.0 $\mu g/m^3$). The reasons for that were: a) being directly at the source of emission; and b) the micro-bus windows and doors were open, allowing an efficient infiltration of BC into the vehicle. This also determined the highest respiratory tract deposited mass concentration fraction of BC (48% of total exposure mass concentration was deposited inside the respiratory tract, Fig. 5, panel b). Somewhat lower average concentrations were measured while walking (8.3 $\mu g/m^3$ in Busch Ave.; 9.5 $\mu g/m^3$ in Arce Ave.). It resulted in lower respiratory tract deposited mass concentration fraction (approx. 40%). It can also be seen that while walking, the variability in BC mass concentration was somewhat higher (22–23 $\mu g/m^3$ versus 18.0 $\mu g/m^3$). After splitting the measurement data as described previously, a rather stable pattern of BC at the street emerged. The average mass concentrations of 2.0 and 2.3 $\mu g/m^3$ were recorded in Busch and Arce Avenues, respectively. These values can be considered as the street-site background concentrations of BC. An episodic cases of extremely high concentrations (up to 360 $\mu g/m^3$), which determined high BC variability, was the result of individual soot plumes being recorded from passing diesel vehicles, and/or the situations when the experimenter had to stop at a busy intersection. We would also like to note that in both avenues the experiment was carried out on the dedicated pedestrian zones, which were located on the lawns separating opposite direction routes. This means that the subjects were exposed equally to traffic moving on both sides.

The amount of air breathed per one cycle (tidal volume) ranged from 0.8 L (while inside the micro-bus) to 1.1 L (while walking). In Busch Avenue (walking), average breathing rate was 12 breaths/min. In Arce Avenue (walking) the average breathing rate was 13 breaths/min. The breathing rate while riding the micro-bus was 11 breaths/min. Despite the lower ventilation rates, the highest DD of BC, received in 1 min, was during a micro-bus ride - 52.5 ng/min.

Table 1
Summary of ambient equivalent black carbon (BC) mass concentration (in $\mu g/m^3$), BC deposition dose (in ng) in different avenues (summarized from 1 s time resolution measurements), and volume of air breathed (in liters). Note: M = overall arithmetic mean; SD = standard deviation; Mdn = median; MB = arithmetic mean of base BC levels; SDB = standard deviation of base BC levels; MdnB = median of base BC levels; MH = arithmetic mean of high BC levels; SDH = standard deviation of high BC levels; MdnH = median of high BC levels. Statistics for the deposition dose is calculated from 1 min values.

Avenue	M	SD	Mdn	MB	SDB	MdnB	MH	SDH	MdnH
Ambient BC mass concentration									
Busch (Walk)	8.3	23.5	3.5	2.0	1.5	1.9	26.6	44.6	11.1
Arce (Micro-bus)	13.7	18.0	10.0	3.1	1.2	3.2	17.3	19.6	14.4
Arce (Walk)	9.5	22.1	4.1	2.3	1.6	2.3	20.1	36.5	9.4
Deposited Dose of BC per 1 min									
Busch (Walk)	39.6	47.0	20.0	16.7	13.0	11.8	102.0	50.0	89.0
Arce (Micro-bus)	52.5	42.4	40.8	24.9	14.5	22.8	102.1	25.1	109.4
Arce (Walk)	46.5	49.9	22.2	17.2	7.8	13.3	92.6	54.0	59.8
Deposition Dose of BC per 1 breath									
Busch (Walk)	3.2	8.6	1.3	1.4	2.1	1.0	25.7	20.5	19.1
Arce (Micro-bus)	5.0	4.0	3.6	3.8	2.8	3.0	12.3	2.0	12.1
Arce (Walk)	4.3	12.3	1.6	1.7	2.4	1.4	33.7	29.6	19.2
Volume of air breathed per 1 min (in liters)									
Busch (Walk)	13.1	1.1	13.1	–	–	–	–	–	–
Arce (Micro-bus)	8.8	1.8	8.3	–	–	–	–	–	–
Arce (Walk)	14.6	0.9	14.4	–	–	–	–	–	–
Volume of air breathed per 1 cycle (tidal volume, in liters)									
Busch (Walk)	1.1	0.2	1.1	–	–	–	–	–	–
Arce (Micro-bus)	0.8	0.2	0.8	–	–	–	–	–	–
Arce (Walk)	1.1	0.2	1.1	–	–	–	–	–	–

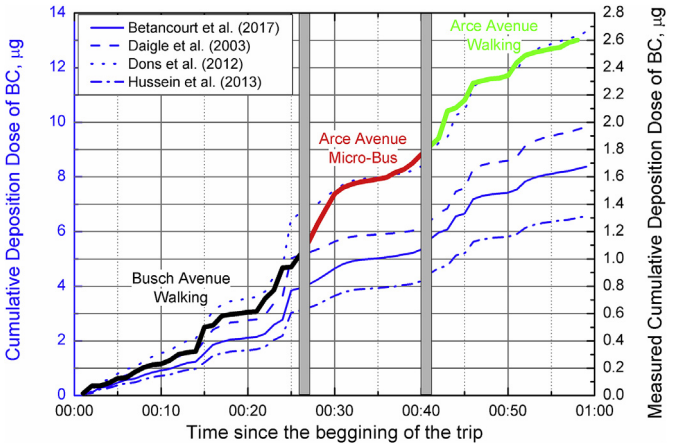

Fig. 6. Cumulative deposition dose (DD) of black carbon (BC, in ng) during 1-h commuting trip in La Paz, Bolivia. Different travel means and avenues are indicated in the figure. Additionally, cumulative DD of BC, calculated using minute ventilation from references, are shown in blue lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

This is because the exposure of BC while being inside the micro-bus was somewhat higher. Deposition doses measured while walking were in the range of 40 ng/min. It also reached values as high as 102 ng/min. This usually happened when the experimenter was exposed to extremely high concentrations of BC (mainly at intersections).

Cumulative deposition dose of the BC (in µg) is shown in Fig. 6. After 1-h of commuting in La Paz, the total DD of BC was approx. 2.6 µg. The contribution from different means of transportation were 40%, 28%, and 32%, for walking on Busch Avenue, riding a micro-bus and walking on Arce Avenue, respectively. Although the BC mass concentrations in Busch Avenue were the lowest, the DD of BC, approx. 1030 ng, was among the highest. This is because the time-spent in this avenue was 25 min that is 5–10 min longer than in other cases. Longer exposure time resulted in higher DD of BC.

4. Discussion

In our previous studies (e.g. Alas et al., 2018) we already showed that the black carbon (BC) mass concentrations in the developing regions can reach levels as high as 140 µg/m^3. In this study, on the other hand, the BC mass concentrations on the roadside and inside the micro-bus were in a range 3–26 µg/m^3. Comparing with another study from South America, the observed BC mass concentrations in La Paz were 5 times less than those observed in Bogota, Colombia (Betancourt et al., 2017). The reasons for lower BC concentrations might be the differences in vehicular fleet (in La Paz most of the fleet is gasoline and gas vehicles), meteorological conditions, topography, etc. Nevertheless, as in the study by Betancourt et al. (2017), the exposure concentrations of BC were found to be the highest inside the transit-transport.

One interesting exercise might be the comparison of measured versus modelled deposition dose (DD) of black carbon (BC). For this matter we used previously published method (Betancourt et al., 2017) to calculate potential dose of BC. The simplified calculation of DD can be written as:

$$DD = C \times IR \times \Delta t, \quad (3)$$

where DD is deposition dose (in ng), C – exposure concentration (in ng/m^3), IR – inhalation rate (also known as V_E - minute ventilation, L/min.), and Δt is exposure time in minutes. If only the exposure concentration is measured, the IR and Δt have to be obtained by different means. For example, the information about time spent in different environments (Δt) can be gained from activity surveys (e.g. Kecorius et al., 2018) or direct exposure measurements, where the subjects also records their position. Inhalation rate, contrarily, is a more complex variable. Depending on physiology, exercise level, gender, race, age, environment (e.g. high altitude), etc., inhalation rates vary both between individuals and over time for the same individual (ICRP, 1994; Frisancho et al., 1999). Nevertheless, generalized values are often used in estimating the deposition dose (e.g. Hussein et al., 2013). A semi-direct way, which relies on correlation between acceleration data and metabolic equivalent units (MEU), was also used previously to estimate the inhalation rate (Kawahara et al., 2011; Betancourt et al., 2017). By knowing the MEU, the IR can be derived. However, most IR values are still being retrieved from the generalized handbooks (e.g. US-EPA, 2011).

For comparison, we have used examples of previously reported inhalation rate values (Table 2). The results of cumulative deposition dose measured in this study, and calculated by using the inhalation rates from literature, are presented in Fig. 6. Our measured cumulative deposition dose of BC was 3–7 times lower than the values obtained by applying previously reported inhalation rates. As concentration (C) and time (Δt) was the same in each calculation, the only changing variable was the inhalation rate (IR). While at rest, our measured IR was rather close to previously reported values, except Dons et al. (2012). IR was on average two fold lower for walking. The inhalation rate, or so called minute ventilation, can be calculated by multiplying breathing frequency and tidal volume (Panis et al., 2010). In our study, the frequency of breathing was measured directly, and was 11–13 breaths/min. Tidal volume, the volume of air moved in/out of the lungs during one inhalation/exhalation, was calculated by integrating the measured exhaled air flowrate. It was found to be in the range between 0.8 and 1.1 L/min. One of the studies, where these parameters were measured in real-world conditions was conducted by Panis et al. (2010). During the field tests, breathing frequency and tidal volume in Panis et al. (2010) was measured using a commercially available calorimetry system. Although the study did not include values for walking activity, it did cover biking and trip by car. Breathing frequency of males during cycling and car ride was found to be 28 and 18 breaths/min., respectively. While corresponding tidal volumes were 2.2 and 0.8 L, respectively. It can be seen that in our study and the study by Panis et al. (2010), although the tidal

Table 2
Example of inhalation rates used in other studies to calculate the deposition dose of particulate pollutants.

Reference	Inhalation rate, sitting [L/min]	Inhalation rate, light exercise [L/min]
Daigle et al. (2003)	9.0	38.1
Panis et al. (2010)	13.4	59.1 (cycling)
Dons et al. (2012)	16.1	49.2
Hussein et al. (2013)	10.0	23.0
Betancourt et al. (2017)	13.0	29.2
This study	8.8	13.8

volume (while at rest) is comparable, the inhalation rate is noticeably different. This is because the breathing frequency in our study was considerably lower (11 versus 18 breaths/min.). The main reason for lower breathing frequency could be the sampling line/filter-induced resistance in the breathing setup. When exhaling into the measurement setup, it was noticed that the breathing was distinctly deeper and less frequent than in the case of natural breathing. In other words, when the measurement setup was used, the subject had to adjust his breathing so that he would get enough oxygen to perform the measurement tasks, as well as to ensure the optimal conditions for aerosol sampling (breathing steadily reduces pressure perturbations in the system). Finally, as DD is directly proportional to IR (see Eq. (1) and Eq. (3)), it is clear that any change in IR will result in an increase/decrease of DD. Moreover, some degree of uncertainty might also result from constant IR values used in the DD calculations. In other words, when constant IR value is used, the DD tends to be higher/lower (depending on certain conditions), rather than estimating DD for every single breath.

5. Summary and conclusions

Poor air quality in developing countries was recognized by World Health Organization, who emphasized that the black carbon is not only the major constituent of particulate air pollution, but is also linked to adverse health effects. It is thus important to bridge the gap between air pollution and health in the regions where the black carbon pollution is the highest. However, currently existing practices and methods, together with sophisticated tools are often out of reach in economically developing regions. It limits the understanding about air pollution and its health effects, and often blurs the severe problems related to air quality. Such a situation necessitates the advancement of simple and accessible tools to evaluate the health impacts of particulate pollutants.

In this study we present a simple and relatively cheap, non-invasive approach to characterize the respiratory tract deposition dose (DD) of equivalent black carbon (BC) under real-world conditions. We call this method **MERDOC** (**Me**asuring **r**eal-world deposition **do**se of black **c**arbon). It can be easily adapted and/or up-scaled to different pollutants and bigger sample size. The proposed method provides direct measurements of breathing rate, volume of air breathed, and deposited concentration of pollutants in the respiratory tract. These parameters are generally used in estimating the deposition dose of pollutants empirically.

A feasibility study was conducted in La Paz, Bolivia, to demonstrate the potential of the proposed method to determine the DD of BC. We measured DD of BC in two different environments: walking on a street and riding a micro-bus. The results showed that the cumulative deposition dose over a 1-h trip would result in approx. 2.6 μg of BC. This includes approx. 40 min. street walk in two different avenues and a micro-bus ride of 20 min. We also compared our measured DD of BC with the results of DD obtained by previously published methods. The difference between the methods was found to be too high to be ignored. By using the published inhalation rates, we found that the cumulative DD of BC was up to 5 times higher than the values measured using our proposed method. It questions the use of generalized parameters, such an inhalation rate (or minute ventilation) in estimating the DD for target population.

As a result of this study, the experimental setup and recommendations for measuring the DD of BC, is provided. It enables simple and cheap determination of DD of BC that can be easily implemented in developing regions. The method can also be extended to measure different properties of deposited particles (e.g. deposition of particle number, using portable mobility particle size spectrometers) and/or DD of other pollutants. Our proposed approach has a potential to improve understanding about the health risks of air pollution, temporal and spatial dynamics of personal exposure, and received dose under real-world conditions. Future work will focus on improving the presented setup, increasing sample rate, as well as deploying it in other highly polluted environments to determine the DD of BC.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.02.021.

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