



Nephelometer Sensitivities for the Determination of PM_{2.5} Mass Concentration in Ambient and Indoor Air

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ABSTRACT

Simple algorithms are presented for the relationships between the gravimetrically measured PM_{2.5} mass concentration and a nephelometer particle scattering coefficient, for three different environments: two outdoor locations (an urban and a suburban) and one indoors. With these algorithms, the aerosol light scattering coefficients of the nephelometer (provided on line with a time step of seconds) can be related to PM_{2.5} mass concentrations. The effect of the relative humidity on the nephelometer readings was also evaluated with two models. In the last two campaigns (in the suburbs of the city and in a laboratory), a drying device before the aerosol entrance to the nephelometer was used, a Nafion™ dryer. In the indoor environment, the two methods (gravimetry and nephelometry) were compared with the readings of an aerosol light scattering spectrometer, which provided PM_{2.5} volume concentrations and thus it was possible to calculate the PM_{2.5} density indoors.

Keywords: PM_{2.5} gravimetric mass concentrations, Aerosol light scattering coefficient, Nephelometric measurements, Indoor aerosol density

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1 INTRODUCTION

Indoor and outdoor aerosol present a significant risk factor for the human health, as it has been asserted in numerous studies (Cohen *et al.*, 2017; Nagel *et al.*, 2018; Vardoulakis *et al.*, 2019). The main effort nowadays is to reduce the atmospheric concentrations of the PM_{2.5} (particulate matter with aerodynamic diameter < 2.5 μm), because it is deleterious to health and is associated with respiratory and cardiopulmonary diseases, as well as lung cancer (Kim *et al.*, 2015; Feng *et al.*, 2016; Melki *et al.*, 2017). Such an effort is mirrored, for example, in the European project “Urban PM_{2.5} Atlas - Air Quality in European cities”, which provides information on the levels of air pollution (specifically PM_{2.5}) in 150 European cities (Thunis *et al.*, 2017). The determination of the atmospheric concentrations of PM_{2.5} is regulated by national and international legislation and their monitoring is an imperative necessity.

Monitoring the atmospheric PM_{2.5} can be an expensive, time consuming and/or tedious task. Gravimetric methods are the standard reference methods (EU, 1999; EN, 2005). However, proxy methods that need calibration have been used by scientific groups worldwide, because of the ease of use, low purchase price and more importantly their continuous operation (recording time step of minutes) (Holstius *et al.*, 2014; Budde *et al.*, 2018). Such instrumentation may be based on the principle of β radiation attenuation by the collected aerosol, change in the frequency of oscillation in tapered oscillating microbalance, or the intensity of the light that is scattered by the aerosol flowing through an optical cell (Huang, 2007; Allen *et al.*, 2011; Kulkarni *et al.*, 2011; Kim, 2015). Comparison of these techniques and instruments, against each other and against international and European standard norms, is crucial to facilitate the PM_{2.5} monitoring (Waggoner and Weiss, 1980; Sioutas *et al.*, 2000; Liu *et al.*, 2002; Allen *et al.*, 2003;

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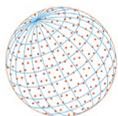
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Chow *et al.*, 2006; Grimm and Eatough, 2009; Dinoi *et al.*, 2017). In the present study, relationships between the gravimetrically measured PM_{2.5} mass concentration by an impactor and the PM_{2.5} light scattering coefficient as recorded by a nephelometer, were derived for three different environments: two outdoor locations (an urban and a suburban) and one indoors. The results will provide a simple and cost-effective method to estimate the PM_{2.5} mass concentrations on line (with a time step of minutes), albeit significant only for the above named, geographically defined locations. The effect of the relative humidity on the nephelometer readings was also evaluated (Liu *et al.*, 2002; Chow *et al.*, 2006) and it was the trigger to introduce an almost constant RH stream into the nephelometer. Furthermore, in the indoor environment, the PM_{2.5} mass concentrations (measured gravimetrically and estimated by the nephelometer data) were compared with the readings of another light scattering instrument (an aerosol light scattering spectrometer). This spectrometer provided also the PM_{2.5} volume concentrations that permitted the calculation of the PM_{2.5} density. The instrumental set up follows the philosophy of minimum cost and intervention.

2 METHODS

The relationship between the mass concentration of PM_{2.5} and the aerosol light scattering coefficient of PM_{2.5} (B_{sp}) were examined during three monitoring campaigns in the city of Xanthi, Greece. The first period of measurements was conducted in the city centre of Xanthi, Greece (September 2013 and November 2014; referred to as “urban”). A Radiance Research M903 nephelometer (hereafter referred to as RRN-903; Radiance Research, Seattle, WA, USA), without drying the aerosol laden stream, was operated in parallel with a high volume PM_{2.5} sampler (TE-6001-2.5-I, Tisch Environmental Inc., Village of Cleves, OH, USA). The PM_{2.5} mass concentrations and the B_{sp} were monitored at the adult breathing height (~1.7 m), adjacent to the pavement of a busy road. Temperature and relative humidity (RH) were also recorded (Vaisala HUMICAP®, Helsinki, Finland). During this campaign the effect of RH on the nephelometer readings was established. During June and July 2014 the nephelometer recorded data every 5 min in the centre of the city (the high volume sampler was not used during this period). From these data, eleven days had $RH \leq 40\%$ and were used in the ANOVA presented in the results, for the case of the urban site.

During 2019, the sampling station was installed in the University campus, in the suburbs of Xanthi. Initially, the sampling was conducted outdoors (referred to as “suburban”) and finally inside a laboratory (referred to as “indoors”). During, these two campaigns the nephelometer operated with a Nafion™ dryer in place (see Fig. S1, in the supplementary material). The whole length of ½” I.D. tubing together with the length of the Nafion™ dryer was 2.5 meters, as determined by the algorithm of von der Weiden *et al.* (2009). The truncation error for PM_{2.5} is small, below 1.06 and for our data treatment was ignored (Anderson and Ogren, 1998; Müller *et al.*, 2009).

Additionally, particle number, volume and mass concentrations were monitored inside the laboratory with a PALAS Promo 2000 light scattering spectrometer (which can classify particles in 40 size bins between 200–2500 nm, PALAS GmbH, Greschbachstraße 3b, 76229 Karlsruhe, Germany). Aerosol mass concentrations provided by the PALAS Promo 2000 are calculated by the software of the instrument with a default PM_{2.5} density of 1 g cm⁻³. The 24 h average mass concentrations, acquired gravimetrically, along with the PM_{2.5} readings by the PALAS Promo, provided the opportunity to calculate the indoor PM_{2.5} densities. Also, the correlation of the readings of the two collocated light scattering instruments was examined.

Details for the monitoring methods can be found in the supplementary material.

3 RESULTS AND DISCUSSION

3.1 The B_{sp} – RH Relationship

The relationship of the B_{sp} and the atmospheric water content, as expressed with the RH, was examined for the experimental data acquired during the first campaign, i.e., during 2013 and 2014. In Fig.1 the measured B_{sp} values are plotted against RH. Two models were applied: a simple linear model and an exponential model, presented in Table 1, along with the estimated fitting

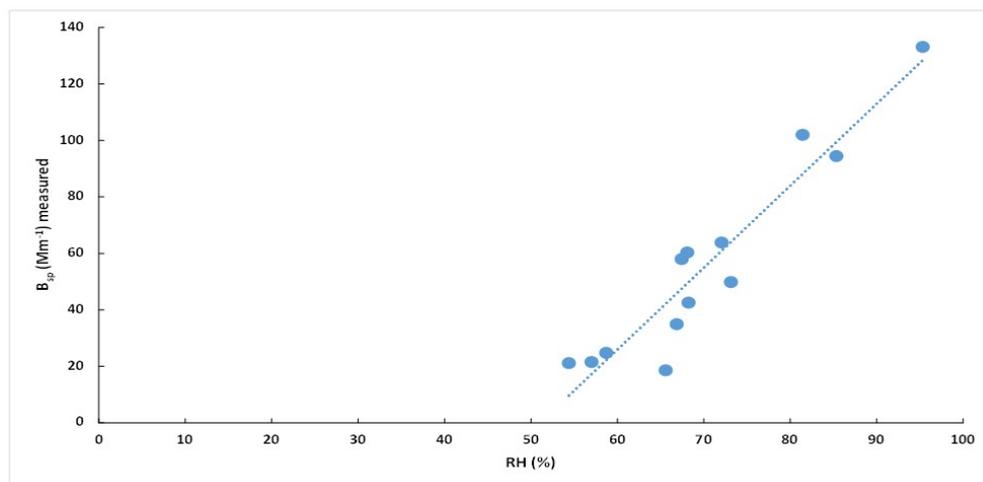
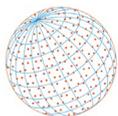


Fig. 1. The B_{sp} values dependency on RH (urban site, ambient RH).

Table 1. The estimated parameters for two models applied for the relationship of B_{sp} (m^{-1}) with RH (%).

$B_{sp} = a \times RH + b$			$R^2 = 0.887$	
Parameter	Estimate	Std. Err.	t-value	p-value
b	-1.48E-04	0.000021	-6.99445	0.000023
a	2.90E-06	0.000000	9.74869	0.000001
$B_{sp} = k \times (1 - RH/100)^{-\gamma}$			$R^2 = 0.726$	
Parameter	Estimate	Std. Err.	t-value	p-value
k	0.000024	0.000000	0.00	0.00
γ	0.583789	0.095106	0.00	0.00

parameters of each model. The best fit model in our data was the linear model, probably due to the low RH levels (most of the time below 65% during this first campaign) and due to the small number of samples. The B_{sp} dependence on the RH was not unexpected and it has been extensively reported in the literature with several proposed algorithms to account for this dependence (Vincent, 2007; Zieger *et al.*, 2013; Tryner *et al.*, 2019). However, these relationships cannot be universal solutions, because atmospheric aerosol composition (and water affinity) varies with source, sampling point, season, day and minute.

During the other two campaigns in our study, the aerosol laden air stream was dried by a Nafion™ drier in the inlet of the nephelometer to a RH less than 40% for a flow of 2 L min^{-1} . The flow rate and the size of the tubing (diameter and length) were calculated using the algorithms and the graphical user interface given by von der Weiden *et al.* (2009).

3.2 The B_{sp} Dependence on the Location of the Monitoring Station

The dependence of the B_{sp} values on the location of the nephelometer was evaluated through an Analysis of Variance (one-way ANOVA), which tested for significant differences between the means of the B_{sp} values for one categorical predictor (urban, suburban and indoors). For this analysis, the data from the urban environment (uncontrolled RH) that corresponded to days with a 24-h average $RH \leq 40\%$ were used. The results of the ANOVA are statistically significant and corroborate that the nephelometer readings depended on the location of the monitoring station, ($F = 6.38488$ and $p < 0.005194$).

3.3 The Relationship between the B_{sp} and the Mass Concentrations of $PM_{2.5}$

In Fig. 2 the average B_{sp} values were plotted against the respective average, gravimetric mass concentrations of $PM_{2.5}$ for each sampling location, i.e., urban, suburban and indoors. The coefficient of determination (R^2) for each linear model fitting was above 0.70, pointing out to a

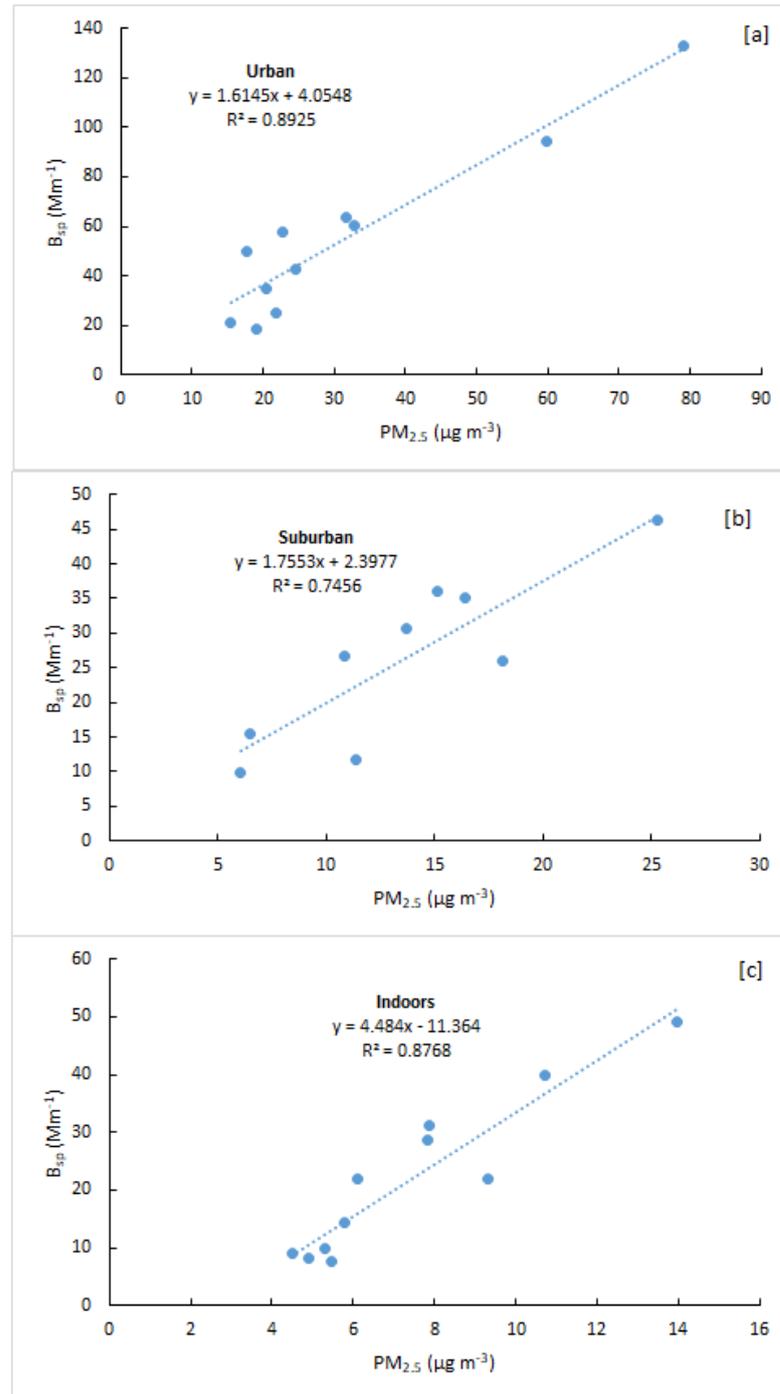
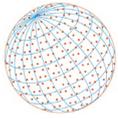


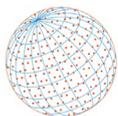
Fig. 2. The relationship B_{sp} - $PM_{2.5}$ (gravimetrically measured).

satisfactory relationship between the two variables. The slope of the regression line varied between $1.6 m^2 g^{-1}$ to $4.5 m^2 g^{-1}$, values that are similar to those reported in other studies (Liu *et al.*, 2002; Chow *et al.*, 2006; Hand and Malm, 2007).

Also, the $PM_{2.5}$ mass concentrations acquired with the impactors can be used to convert nephelometer readings, in each case of the present study, into mass concentration in order to observe the $PM_{2.5}$ variation in a time step of few minutes. These equations are:

$$PM_{2.5} (\mu g m^{-3}) = 0.55 \times B_{sp} (Mm^{-1}) + 1.13 \text{ (urban, ambient RH)} \quad (1)$$

$$PM_{2.5} (\mu g m^{-3}) = 0.42 \times B_{sp} (Mm^{-1}) + 2.47 \text{ (suburban, RH} \leq 40) \quad (2)$$



The respective equation for the indoor laboratory environment is presented below, in Fig. 3.

3.3 Indoor PM_{2.5} Densities

In the laboratory, the two light scattering instruments were run simultaneously with the impactor. Note that the laboratory was void of people during the experiment, except the instrument operator, hence there were not PM emission events, which could disturb the readings of the nephelometer (Liu *et al.*, 2002).

This experiment provided the opportunity to calculate PM_{2.5} densities. Assuming that the average PM_{2.5} mass concentration obtained indoors, gravimetrically, is the same concentration that the PALAS Promo detects, then the measured mass of PM_{2.5} divided by the total volume V of PM_{2.5} particles recorded by the PALAS Promo, will result in indoor aerosol densities, the last column in Table 2.

The calculated PM_{2.5} densities were used to correct the PALAS Promo PM_{2.5} mass concentrations (calculated by the instrument with the default density of 1 g cm⁻³). The PM_{2.5} mass concentrations (second column in the Table 2) were corrected by multiplying each value with the respective density in the last column of the Table 2. As can be seen from Table 2, the calculated indoor particle densities differed (mean = 0.95 (SD = 0.17) g cm⁻³) but not significantly from the arbitrary selected density of 1 g cm⁻³, due to absence of indoor emissions and a relatively unpolluted outdoor air in this case. The results indicate that arbitrarily selected densities of indoor aerosol for the calculation of their indoor concentrations may be erroneous, especially if an indoor environment has enhanced human activity, i.e., variable indoor sources.

The corrected PM_{2.5} mass concentrations of the PALAS Promo were better related with the gravimetrically derived values. The Relative Standard Error was 3.15% for the uncorrected and 2.46% for the corrected values. In Fig. 3, the corrected PM_{2.5} mass concentrations from the PALAS Promo and the PM_{2.5} mass concentrations from the gravimetric method are plotted against the respective the B_{sp} values to highlight the good correlation of the three methods.

4 CONCLUSIONS

The mass concentration of PM_{2.5} in a small time step is needed to trace aerosol variations. In the present study the PM_{2.5} mass concentrations were determined gravimetrically and related to the aerosol light scattering coefficient obtained by a RRN-903, during three campaigns at three

Table 2. Indoor PM_{2.5} densities.

Gravimetric mass concentration (µg m ⁻³)	*Mass Concentration (PALAS Promo) (µg m ⁻³)	**Mass per day sampled gravimetrically (kg)	***V = Sum dV of PM _{2.5} per 24 hours (PALAS Promo) (m ³)	Calculated PM _{2.5} particle densities (g cm ⁻³)
9.33	9.1	6.7176 E-8	7775.8 E-11	0.86
6.12	8.06	4.4064 E-8	4951.0 E-11	0.89
13.96	13.1	10.0512 E-8	11969.7 E-11	0.84
10.73	12.55	7.7256 E-8	7969.7 E-11	0.97
7.82	8.58	5.6304 E-8	6187.9 E-11	0.91
4.48	4.14	3.2256 E-8	3852.8 E-11	0.84
7.86	11	5.6592 E-8	7299.9 E-11	0.78
5.78	4.09	4.1616 E-8	3073.0 E-11	1.35
5.32	3.93	3.8304 E-8	3362.9 E-11	1.14
5.48	3.81	3.9456 E-8	3751.6 E-11	1.05
4.92	4.37	3.5424 E-8	4286.3 E-11	0.83

* Assuming PM_{2.5} density of 1 g cm⁻³.

** Assuming that the PALAS Promo sampled indoor air of the concentration determined gravimetrically, this column lists the total mass sampled by passing through it 5 L min⁻¹ × 1440 min = 7.2 m³ of indoor air.

*** The total volume V of PM_{2.5} sampled in 24 hours.

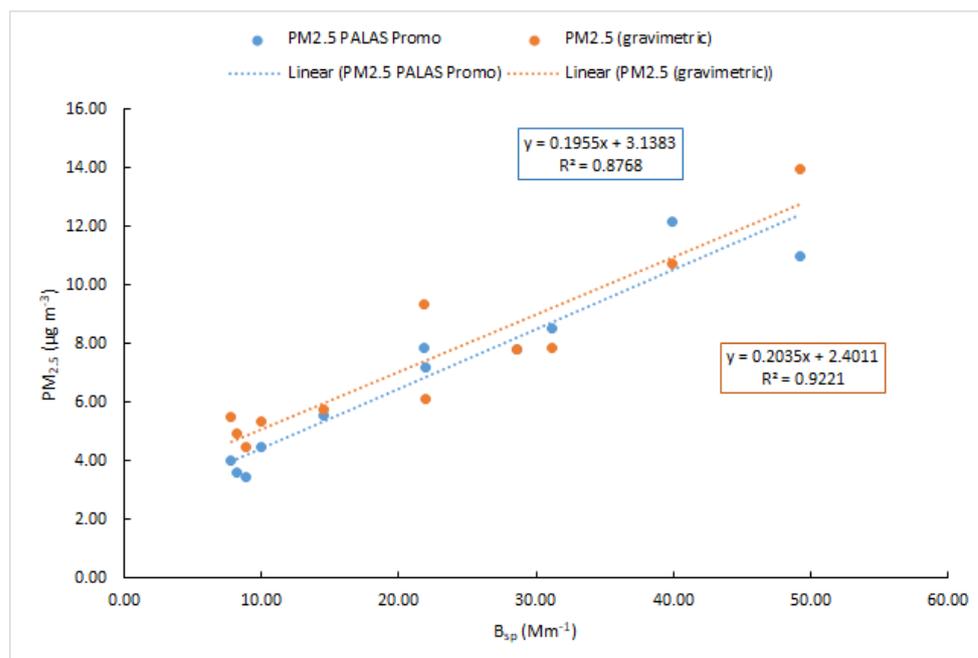
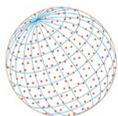


Fig. 3. The indoor relationship B_{sp} with $PM_{2.5}$ mass concentrations, as measured gravimetrically and as calculated with the PALAS Promo, corrected for particle density.

different environments, i.e., an urban, a suburban and indoors. The data from the first campaign, in the city center, confirmed, as expected, that the aerosol light scattering coefficient was sensitive to the ambient RH. Two models were tested in order to express this relationship and a simple linear model has been proved to provide the best fit in this case. Thus, in the following two campaigns (in the suburbs of the city and in a laboratory), a drying device before the aerosol entrance to the nephelometer was used. For these campaigns, relationships between B_{sp} and the $PM_{2.5}$ mass concentrations (gravimetric) were also derived. The presented algorithms can be applied in order to convert light scattering data to bulk $PM_{2.5}$ mass concentration, using the nephelometer RRN-903 as a $PM_{2.5}$ mass detector. However, as confirmed also by an Analysis of Variance, the B_{sp} is sensitive to the location of the monitoring station and there is a need for in situ calibration in each case. Furthermore, the densities of indoor particles with the same experimental set up with the cooperation of an aerosol spectrometer (PALAS Promo), which readings were well related with the nephelometer RRN-903, indicate their variability even in a supposedly controlled environment.

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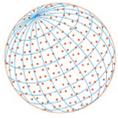
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SUPPLEMENTARY MATERIAL

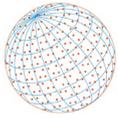
Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.2020.04.0159>

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