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Aerosol hygroscopic growth and the dependence of atmospheric electric field measurements with relative humidity

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ABSTRACT

A simple formulation is developed to model the influence of the aerosol hygroscopic growth in the dependence of the atmospheric electric field measurements with relative humidity. The formulation uses the Petters and Kreidenweis's model for the hygroscopic growth factor of aerosols with relative humidity and assumes that the ion–aerosol attachment coefficient is linearly proportional to the particle radius according to Gunn's calculation. A formula which describes the atmospheric electric field increase with relative humidity in the regime expected for the aerosols to grow hygroscopically is found; between 60% and 90%. It also relates the microphysical parameter of aerosol hygroscopicity, κ, with the macrophysical measure of the atmospheric electric field. Historical data of atmospheric electric field and relative humidity recorded in the meteorological station of Portela (near Lisbon airport, Portugal) are used to fit the model. The electrical measurements were done with a Benndorf electrograph and the 1980–1990 period was considered. Due to the high pollution levels the atmospheric electric field measurements were divided in four wind sectors, NW, NE, SE, and SW. The sector least affected by pollutant aerosols, NW, was used in the fitting and the goodness found is $r^2 \sim 0.97$, the aerosol concentration number is $\sim 3280\ \mathrm{cm}^{-3}$ and the hygroscopic growth parameter $\kappa \sim 0.094$. These are very reasonable values consistent with an urban environment, which typically has high aerosol number concentration with small hygroscopicity. The limitations of the model are presented throughout the sections.

1. Introduction

Radiative forcing caused by aerosols (e.g. Charlson, Anderson, & Rodhe, 1999; Foster et al., 2007; Kaufman, Hobbs, & Kirchhoff, 1998; Li, 1998; Lyamani, Olmo, Alcántara, & Alados-Arboledas, 2006; Markowicz, Flatau, Ramana, Crutzen, & Ramanathan, 2002; Obregón et al., 2015) is of relevance to the Earth's radiation balance and consequently to the Earth's climate. Special emphasis has been given to the direct radiative effect, in which aerosols scatter and absorb radiation, and the indirect effect, in which aerosols as

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cloud condensation nuclei (CCN) are able to modify cloud droplet number concentration, size, and distribution (Pruppacher & Klett, 2010). Moreover, in CCN processes the increase in aerosol size with relative humidity (RH) through particle hygroscopic growth is of fundamental importance. For example, as aerosol particles become larger in size than their dry equivalents, they scatter more light because of the increase in the particle cross-section, e.g. (Carrico et al., 2000; Fierz-Schmidhauser et al., 2010; Koloutsou-Vakakis et al., 2001; Pilat & Charlson, 1966; Seinfeld & Pandis, 1998; Titos et al. 2014a, b). Considering the hygroscopic growth patterns, aerosol particles can be split into three categories. Some aerosol species like soot or mineral dust are insoluble; therefore do not grow significantly in size with increasing RH (Sjogren et al., 2007; Weingartner, Burtscher, & Baltensperger, 1997). On the contrary, some aerosol species like H_2SO_4 and some organics are hygroscopic, thus being able to take up water and grow or shrink smoothly as the RH increases or decreases. Finally some aerosol species, e.g. sea salt, are also hygroscopic, but show hysteresis behavior and are called deliquescent aerosols. In fact, aerosol hygroscopic growth has been a research topic of considerable interest. Work has been done in field campaigns (e.g. Duplissy, DeCarlo, & Dommen, 2011), laboratory experiments (e.g. Rickards, Miles, Davies, Marshall, & Reid, 2013), and modeling (e.g. Petters & Kreidenweis, 2007). In this context, it is usual to refer to the aerosol growth factor, $GF = R(RH)/R_0$, where $R(RH)$ stands for the particle wet radius for a given RH and R_0 is the particle dry radius. Various models have been used to describe GF; Petters and Kreidenweis's model (Petters & Kreidenweis, 2007) is commonly used in literature. This model is a key aspect of the formulation that will be presented below and is given by

$$GF(rh) = \left(1 + \kappa \frac{a_w}{1 - a_w}\right)^{1/3}. \tag{1}$$

In Eq. (1) a_w is the water activity (related with RH) and κ is the hygroscopicity parameter. According to Petters and Kreidenweis (2007) the hygroscopicity of atmospheric particles is in the range from 0.1 to 0.9. Moreover, the authors show that if κ of each of the components is known it is possible to calculate the hygroscopicity of the mixture by weighting the component κ with the correspondent volume fractions. This implies that the κ of the mixture can also be obtained from measurements in the absence of information on its chemical composition. Such "effective hygroscopicity parameter" can then be used in modeling CCN activity. In this context, the possibility of assessing κ from historical records of the Potential Gradient (PG) seems highly likely.[1] In fact, PG records go back to the mid-nineteenth century in different parts of Europe, e.g. London (Harrison, 2006), Paris (Harrison & Aplin, 2003), and Glasgow (Aplin, 2012). Valuable historical information about aerosol properties (not only concentration) can be accessed this way. On one hand, the sensitivity of atmospheric electric parameters to pollutant aerosols has long been proven, e.g. (Retalis, 1977; Manes, 1977), and widely used to retrieve pollution dynamics in urban environments (Silva et al., 2014). On the other hand, it was previously shown that marine aerosol size increase with relative humidity is responsible for the decrease in atmospheric electric conductivity (AEC) (e.g. Deshpande & Kamra, 2004; Kamra, Deshpande, & Gopalakrishan 1997). To relate aerosol hygroscopic growth and PG measurements a simple model is proposed here. In the literature, simple models relating aerosols and PG exist (e.g. Harrison, 2012; Harrison & Aplin, 2002), and give very useful information about the atmospheric processes under study. In a basic view, PG is a result of the action of the Global Electric Circuit (Odzimek, Lester, & Kubicki, 2010; Williams & Mareev, 2014; Wilson, 1920) and the local joint effect of ions, aerosols and water droplets (Harrison, 2012). Ions act as charge carriers in the atmosphere and are the major contributors to electric conduction (Matthews, Ward, Keitch, & Henshaw, 2010; Wright, Buckley, Matthews, Shallcross, & Henshaw, 2014). In the lower troposphere the most representative negative ions are O_2^-, CO_3^-, NO_3^-, HSO_4^- while the positive ones are: H_3O^+, H^+, NO^+, NO_2^+, NH_4^+ (Harrison & Carslaw, 2003). These are known to form small ion clusters, like $O_2^-(H_2O)_n$, via hydration by water molecules (Harrison & Carslaw, 2003). This process reduces ion mobility and consequently decreases the AEC, which causes the PG to increase with RH. This is a possible mechanism explaining the RH dependence of the PG, at least in low RH, RH ~ 20%. The change in the local ionization rate with RH is another mechanism to explain the dependence of the electrical parameters with RH (Israël, 1970, 1973); these two works go deep into the complexity of the processes being discussed here. Nevertheless, in urban environments the presence of aerosols alters significantly the electrical properties of the atmosphere (Manes, 1977). In this context, Harrison (2012) explored the induced effect of aerosols on the atmospheric electric field in cases of reduced visibility, with the presence of water droplets, and did not consider the change in the local ionization rate with RH. Aerosols scavenge conducting atmospheric ions and reduce AEC such that, through Ohm's law (for a constant conduction current), an increase in the PG is observed (Retalis, 1977). It should be mentioned here that this is a simplistic view in the sense that the charge is still present, but is carried by larger and less mobile charged aerosols, which contributes much less to conductivity (Wright, Holden, Shallcross, & Henshaw, 2014). Besides, it is known that the ion–particle attachment coefficient (β) depends on the radius (R) of the particles (Gunn, 1954) as

$$\beta = \frac{4\pi k_B T \mu_m}{e} R, \tag{2}$$

where k_B is the Boltzmann constant, T is the ambient temperature (considered here as 293 K), μ_m mean ion mobility and e electron charge. Thus it is expected that the increase in the aerosol size with RH would imply the scavenging of more ions and consequently the decrease in AEC and increase in PG; such process is expected to dominate the relative humidity dependence of the PG mainly in the RH range where aerosols grow hygroscopically (Kamra et al., 1997). Different types of aerosols would give different contributions according to their hygroscopicity; only the aerosols that grow hygroscopically would contribute. In particular, soot, a common pollutant aerosol in urban environments, does not grow hygroscopically and for that reason it is

[1] The convention is that $PG = dV_l/dz$, V_l is the potential difference between the Ionosphere and Earth's surface and z the vertical coordinate. It is defined to be positive for fair-weather days and is related with the vertical component of the atmospheric electric field by $E_z = -PG$.

expected that will not contribute to the PG dependence with RH. This aspect will be discussed in subsequent sections. Moreover, RH between ~60% and ~90% can be considered as a reasonable range where aerosols grow hygroscopically (Kamra et al., 1997; Petters & Kreidenweis, 2007; Rickards et al., 2013). For high RH, especially close to saturation, CCN processes will dominate and droplet formation will start (Nicoll & Harrison, 2010). A simple model is developed to describe the contribution of hygroscopic aerosol growth to the Relative Humidity dependence of the Potential Gradient for RH between ~60% and ~90%. The historical observations of PG taken at the meteorological station of Portela at Lisbon airport, Portugal (Serrano, Reis, Rosa, & Lucio, 2006; Silva et al., 2014), are used for this purpose.

2. Formulation

Keeping in mind these arguments a formulation of the influence that aerosol hygroscopic growth has on PG will be presented. The RH range of validity of the model is between ~60% and ~90% (as discussed above) and the limitations of the model are discussed during the formulation. The first step is to consider the equation for ion balance in an environment containing aerosols. The key aspect for the validity of the formulation is that the majority of ion loss is via aerosol attachment not recombination; for this to be true does not necessarily require very high concentrations of aerosols. According to Tammet, Hõrrak, Laakso, and Kulmala (2006) it is estimated that ion–ion recombination contributes about 9–13% and ion–aerosol attachment around 65–69% (i.e. 5–7.6 times that of recombination) to ion loss for aerosol concentrations ~4000 cm^{-3} (similar values will be found when fitting the present model to PG data). In fact, "nanoparticle–nanoparticle coagulation", encompassing "ion–ion recombination", was neglected in a recent empirical formulation (Tammet & Kulmala, 2014). The formalism developed by Hoppel (1985) uses effective parameters to simplify the equation for ion balance in the presence of a more realistic aerosol size distribution. Thus, the steady-state equation for ion formation and loss in the presence of aerosols can be written as

$$q-\alpha n^2-\beta_a Z_a n=0, \tag{3}$$

where n is the mean ion concentration number, q is the ion production rate, α is the ion recombination rate, β_a is the "effective" ion–aerosol attachment coefficient for the aerosol size distribution in question, and Z_a aerosol number concentration. It is worth mentioning here that Eq. (3) is a simplification because it neglects the positive to negative ion concentration imbalance; which is crucial in highly perturbed regions where space charges form (Matthews et al., 2010). Nevertheless, the present formulation assumes a quasi-equilibrium state perturbed by the presence of aerosols. The solution of Eq. (3) is straightforward:

$$n=\frac{1}{2\alpha}\left[\sqrt{(\beta_a Z_a)^2+4\alpha q}-\beta_a Z_a\right]. \tag{4}$$

Now it is possible to make a change in the variables to transform Eq. (4) into:

$$n=n_\infty\left(\sqrt{x^2+1}-x\right), \tag{5}$$

where $n_\infty=\sqrt{q/\alpha}$ is the steady state ion concentration when no aerosols or droplets are present (Harrison & Carslaw, 2003), and x is given by

$$x=\frac{\beta_a Z_a}{2\sqrt{\alpha q}} \tag{6}$$

It is assumed that the AEC is given by $\sigma_t=2\mu_m e n$; here the contribution of charged aerosols to the total atmospheric electric conductivity is neglected. This is an approximation required to maintain the simplicity of this model, but it is reasonable to do so, as it is known that charged aerosols contribute less to conduction due to their lower mobility, as compared with atmospheric ions (Wright et al., 2014). Actually, this contribution is often neglected in similar models (e.g. Harrison, 2006, 2012; Harrison & Aplin, 2002). Thus, using Ohm's law it is possible to relate σ_t and PG:

$$PG=\frac{J_z}{\sigma_t}=\frac{J_z}{2\mu_m e}\left[n_\infty\left(\sqrt{x^2+1}-x\right)\right]^{-1}, \tag{7}$$

where J_z is the air-Earth density current. Using standard values of $J_z\sim 2$ pA m^{-2}, $\mu_m\sim 1.2$ cm^{-2} V^{-1} s^{-1}, $\alpha\sim 1.6\times 10^{-6}$ cm^3 s^{-1} and $q\sim 10$ cm^{-3} s^{-1} (Harrison & Carslaw, 2003) and assuming a typical PG ~ 100 V/m, it is found that $x\sim 2.3$. In fact, in cases with aerosol number concentration around ~4000 cm^{-3} it is expected that $x\gg 1$ and Eq. (5) can be written as

$$n=n_\infty x\left(\sqrt{1+x^{-2}}-1\right)\approx\frac{n_\infty}{2x}=\frac{q}{\beta_a Z_a}. \tag{8}$$

The approximation in Eq. (8) is accomplished by a Taylor series expansion of the square root, neglecting $O(x^{-4})$. Hence Eq. (7) becomes simply:

$$PG\approx\frac{J_z}{2\mu_m e q}\beta_a Z_a=\frac{2\pi J_z k_B T}{e^2 q}R_a Z_a. \tag{9}$$

In Eq. (9) the ion–aerosol attachment coefficient β_a was substituted by the formula derived by Gunn (1954) and presented in Eq. (2). Notice that the particle radius should not be seen as a real particle size of a monodisperse aerosol size distribution, rather as an "effective attachment radius" representative of a polydisperse aerosol size distribution subjected to electrostatic forces

(Hoppel, 1985). In the formulation being developed here the attachment coefficient is modeled to retrieve "effective aerosol properties" from *PG* values, in particular aerosol concentration. Equation (9) reveals that the *PG* is proportional to the product of aerosol radius and concentration, $R_a Z_a$, and does not depend (in first order) on the ion mobility. This is a significant result from the model as a reduction in ion mobility with RH could be a possible cause for AEC decrease (PG increase) with RH in clean environments. It is expected that humidity changes in the 60–90% range would not change considerably the ion mobility (e.g. Harrison & Aplin, 2007; Wright et al., 2014). Actually, Eq. (9) is similar to the one found by Harrison and Aplin (2002). The last step in the formulation is to describe the R_a growth with RH. To do that Eq. (1) is used and a simplification is made assuming that water activity is given by $a_w = rh = RH/100$. This is a good approximation in the regime of validity of the present model where RH is restricted from 60% to 90% (Rickards et al., 2013). Similarly to the discussion presented for the "effective aerosol radius", in real atmospheres *GF* will vary accordingly to the dry size and composition of the aerosols, thus here the hygroscopicity parameter, κ, should be interpreted as an "effective hygroscopicity parameter" representative, in a statistical sense, of the actual polydisperse aerosol size distribution. Finally, the equation relating PG and RH through aerosol growth is found:

$$PG \approx \frac{2\pi J_z k_B T}{e^2 q} Z_a R_{a,0} \left(1 + \kappa_a \frac{rh}{1-rh}\right)^{1/3}. \tag{10}$$

In Eq. (10) Z_a, $R_{a,0}$ and κ_a are the number concentration of aerosols, the dry radius, and the hygroscopicity parameter, respectively. This equation relates, in a simple formulation, three significant microphysical aerosol parameters: number concentration, dry radius and hygroscopicity parameter with two macrophysical measurements: Potential Gradient and Relative Humidity. Obviously the microphysical parameters must be considered as "effective parameters" in the statistical sense described above and not "precise parameters". Here the significant point is that in macrophysical radiative modeling the "effective parameters" are more relevant than the precise measurements of those microphysical parameters (Petters & Kreidenweis, 2007).

3. Data

A Benndorf electrograph was coupled to a radioactive probe to secure equality of potential between the sensor and the air and also improving the time response of the electrograph. It was installed at 1 m above ground in a cement base recorded the PG at Portela meteorological station (Lisbon Airport, Portugal, as shown in Fig. 1). Its sensitivity was checked using an electronic electrometer with standard voltage source between ± 200 V and the same calibration procedure was used in all periods of operation. The analog records of the electrograph were digitalized afterwards (Serrano, 2010). Further details on the dataset can be found in Serrano et al. (2006), Silva et al. (2014) and Conceição et al. (2015). Measurements with similar devices were made worldwide (e.g. Shigeno, Takizawa, Itoh, Yokoyama, & Owada, 2001). In the present study data from 1980 to 1990 is used and only non-negative values of PG were selected because negative PG values are not a consequence of RH as they are linked to rain and shower clouds. On the contrary, positive values of PG ~ 400 V/m, are found under high RH condition, for example, in the case of fogs (Deshpande & Kamra, 2004). Thus when studying the dependence of the PG with RH, it is important to include these cases, that are usually rejected under the fair-weather conditions (Voeikov, 1965). This is the reason why a strict fair-weather selection is not fully appropriate to the present study. It should be mentioned that positive charged clouds also exist and affect the PG, though

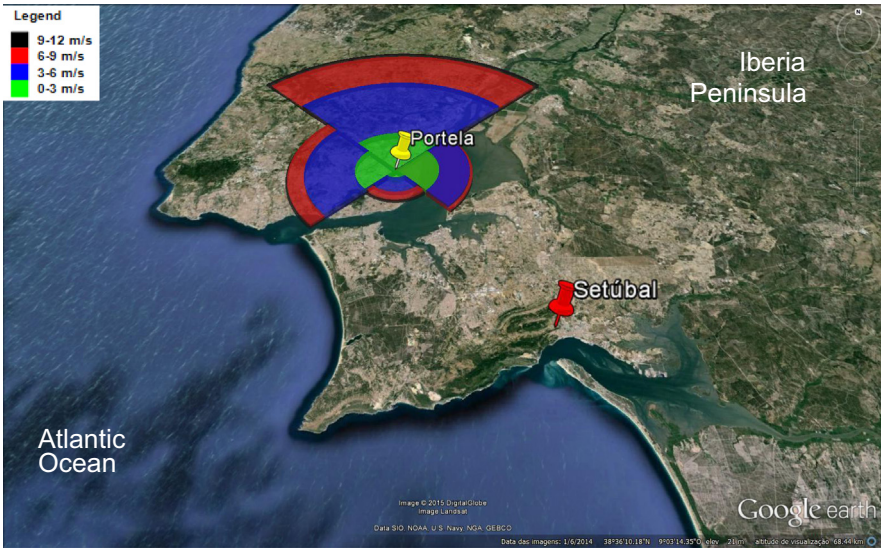

Fig. 1. Location of the Portela meteorological station (yellow pin) and the industrial region of Setubal (red pin) are marked. The Atlantic Ocean and Iberian Peninsula are also indicated. A wind rose measured at Portela is also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

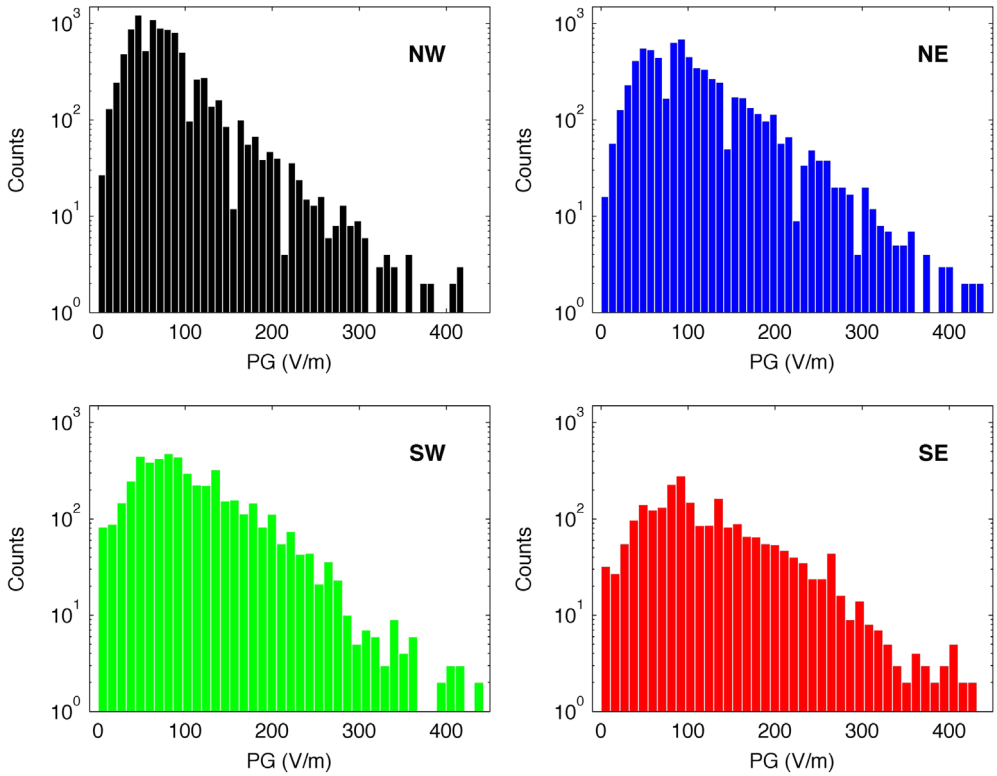

Fig. 2. Distributions of the hourly PG values, in logarithmic scale, for the four wind sectors: NW, NE, SE, and SW.

less statistically significant in Lisbon with low cloud cover percentages (ranging from 28% in summer and 61% in winter). Precipitation and snow further perturb the PG and for that reason "manually observed present weather" (MW) was used. PG values having MW in the range of 50–99; which corresponds to "precipitation at the station at the time of observation" were excluded. Relative humidity was calculated from the air temperature and dew point measured in Portela meteorological station (the same station where PG was recorded). The former Portuguese Institute of Meteorology (IM) did the measurements and the data was retrieved from the NNDC Climate Data Online website supported by NOAA. During the 1980s most of the industries and main pollution sources in the region were located to the south of Tagus River, in Setubal region. Therefore using the station as a geographic reference, the mentioned main pollution sources can be found in the southern sector while in the northern sector such sources are scarcer (and population is lower). The Tagus river basin and the Iberian Peninsula are located to the East whereas the Western sector is covered by the Atlantic Ocean. Pollution has the effect of increasing the PG (Silva et al., 2014, and the references therein), thus it is expected that south winds correspond to higher PG values than northern ones. Furthermore, westerly winds transport marine air, which is known to bring ions with higher electrical mobility than those transported from continental regions (Wilding & Harrison, 2005). Moreover, typically marine air contains fewer but larger aerosol particles which would have a lower mobility and higher "effective attachment coefficient" but a lower total influence on ion concentration, and hence conductivity, because of their very low number (Hoppel, 1985). For that reason lower PG values are expected to be associated to winds from the west as compared with those from east. These features were observed in Silva et al. (submitted for publication) and according to that procedure, PG is divided into four wind sectors:

1) NW, $270^\circ \leq \theta \leq 360^\circ$;
2) NE, $0 \leq \theta \leq 90^\circ$;
3) SE, $90 \leq \theta \leq 180^\circ$;
4) SW, $180^\circ \leq \theta \leq 270^\circ$.

Matthews (2012a, 2012b) previously applied this methodology to study the impact of high voltage power lines on the local PG. It is worth mentioning that the prevailing winds in Lisbon are from NW (Fig. 1) and result from the Iberian thermal depression (Costa et al., 2010). From the considerations presented thus far it is expected that the NW sector corresponds to lower PG values than those associated to the NE and SE sectors; regarding the SW sector, where winds bring both marine and polluted air, the PG values are expected to be higher than in the NW, but smaller than in the SE. These results are depicted in the histograms of Fig. 2, and further statistical parameters are presented in Table 1. The median PG values are consistent with the previous arguments: NW, 67.0 V/m; NE, 90.0 V/m; SE, 100.0 V/m; and SW, 90.0 V/m. Additionally, the daily variation of PG corresponding to the four

Table 1
Mean, median, median absolute deviation (MAD), skewness, kurtosis, and number of hours for the period between 1980 and 1990. The atmospheric electric field measurements are divided in: NW, NE, SE, and SW.

	NW	NE	SE	SW
Mean (V/m)	75.4	101.1	119.5	104.1
Median (V/m)	67.0	90.0	100.0	90.0
MAD (V/m)	30.7	43.7	54.7	47.4
Skewness	2.03	1.34	1.13	1.20
Kurtosis	9.81	5.48	4.61	5.10
Number of days	385	283	95	204

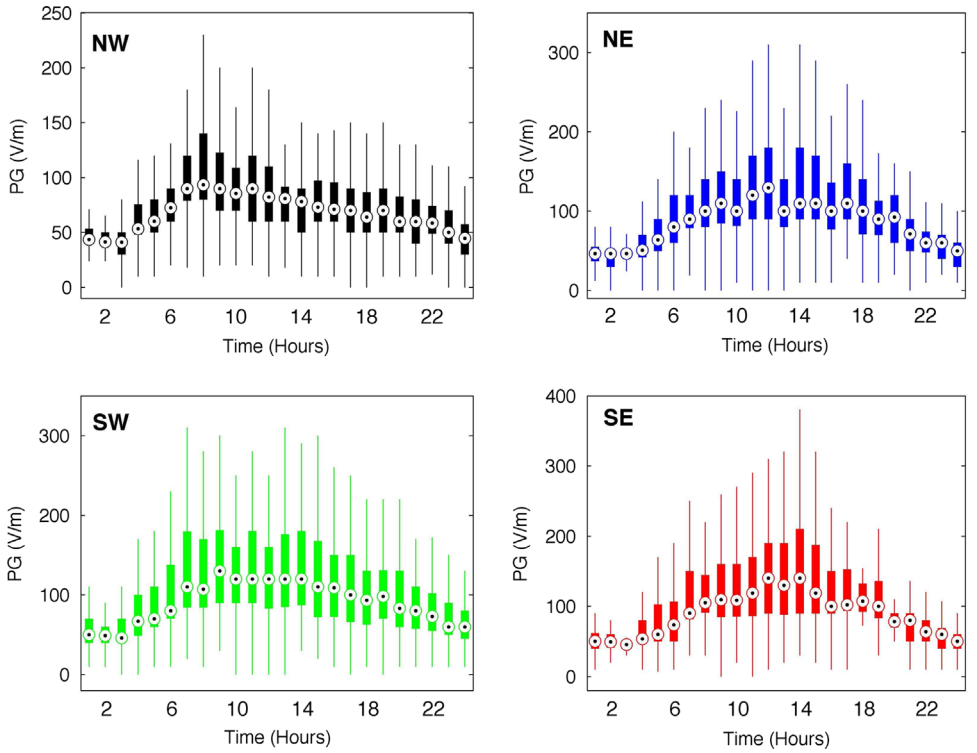

Fig. 3. Daily behaviour of hourly PG values in a boxplot representation. The four wind sectors are considered: NW, NE, SE, and SW.

wind sectors is presented in a boxplot[2] representation (Fig. 3), and show similar behaviour. It is verified that at the beginning and end of the day low values of PG are observed, around ~50 V/m. Daily PG curves measured inland often differ from the Carnegie curve mainly due the action of local phenomena, for example, convective currents (Tacza et al., 2014). Convective currents due to the presence of the Atlantic Ocean could, in fact, be a reason explaining such low values measured at Portela; nevertheless investigation of such mechanism is out of the scope of this paper. The daily behaviour for the NW is slightly different from the other three sectors as it shows less variability and the peak observed in the other wind sectors at 18UT is reduced in this one. In fact, for PG measurements carried out in urban environments, the peak at 18UT is a combination of the maximum of the Global Electric Circuit activity, Carnegie curve (Harrison, 2013) and of the air pollution generated at the end of the workdays (Harrison, 2009). Also winds from the NW sector are most likely to occur during this time of the day (known as *Nortada*, Alcoforado, Andrade, Lopes, Vasconcelos, & Vieira, 2006). Hence, the reduction of the 18UT peak for NW sector can be an indication of a more efficient removal of air pollution. Finally, daily averages are calculated for both PG and RH, reducing the variability of these parameters.

[2] On each box, the central dot is the median, the limits of the box are the 25th (first quartile, q_1) and 75th (third quartile, q_3) percentiles and the whiskers (solid lines) extend to the most extreme data points not considered outliers. Maximum whisker length (w) is set to 1.5 and outliers are defined to be larger than $q_3+w(q_3-q_1)$ or smaller than $q_1-w(q_3-q_1)$.

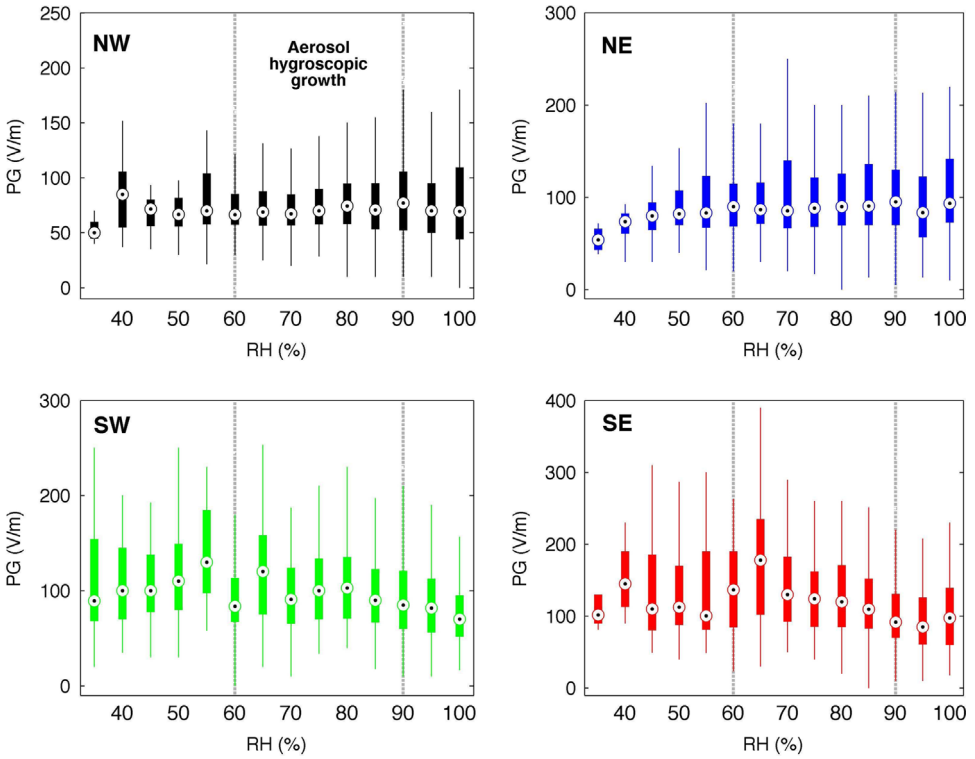

Fig. 4. RH dependence of daily averaged PG values of all sectors: NW, NE, SE, and SW. Bins with $\Delta RH = 5\%$ in the RH range from 30% to 100% were used. The label attributed to a bin corresponds to its upper limit. Vertical lines mark the hygroscopic growth region, in which the analysis is focused.

4. Results and discussion

PG as a function of RH is shown in a boxplot representation in Fig. 4 for the four wind sectors. PG values are separated into RH bins with a given width, $\Delta RH = 5\%$, from $RH = 30\%$ up to 100%. The condition for each i-bin is

$$RH_{ini} + (i-1)\Delta RH < RH(i) \leq RH_{ini} + i\Delta RH, \tag{11}$$

The choice of the ΔRH was made as a trade-off between statistical representativeness of each bin and sufficient number of bins to have enough values to guarantee the validity of the analysis. It is seen in Fig. 4 that for low RH the PG values tend to fair-weather values around ~ 80 V/m and a diversity of behaviors is observed for higher RH. On one hand, in the heavily polluted southern sectors, SW and SE, it is observed that the PG tends to decrease with RH; which is an unexpected result. These should result from the presence of high levels of pollutant aerosols and two possibilities can be considered: (1) precipitation of air pollution particles by charged water aerosols (Balachandran, Krupa, Machowski, Jaworek, 2001) reducing ion–aerosol attachment and increasing AEC; (2) increased partitioning of charge to the larger aerosols implying that charged aerosols would contribute to AEC (the assumption made in the formulation assuming that the charged aerosols do not contribute to AEC would not be valid). On the other hand, the northern sectors show an increase in the PG with RH in the region of aerosol hygroscopic growth. The PG for NE sector shows a slightly lower increase with RH as compared with the NW sector. This is an important result because these sectors are known to be the least polluted (Silva et al., submitted for publication) and more hygroscopic marine aerosols, coming from the Atlantic Ocean, influence the NW sector. Marine aerosols are known to have high hygroscopicity (Carrico et al., 2000; Titos et al., 2014b) and will dominate the non-hygroscopic behaviour of the pollutant aerosols. To progress with the analysis the median values of the PG corresponding to the northern sectors, for each RH bin, are represented against the median RH of the respective bin. The data is fitted to the model in Eq. (10) in the RH region defined for aerosol hygroscopic growth between $\sim 60\%$ and $\sim 90\%$. In the fitting it was assumed that the dry size of the aerosols is $R_{a,0} \sim 0.1$ μm, and the following parameters are used: $J_z \sim 2$ pA m^{-2}, $T \sim 293$ K, and $q \sim 10$ cm^{-3} s^{-1} (Harrison & Carslaw, 2003). The fits are presented in Fig. 5a and b. The error bars represent the median absolute deviation (MAD), the solid-line is the fitted curve and the dashed-lines are the model curve using κ 40% above (upper limit) and below (lower limit) of the fitted values, respectively. The model describes well the RH evolution of the PG for the northern wind sectors in the region of aerosol hygroscopic growth. The results are presented in Table 2. These are very reasonable values consistent with an urban environment; which has high aerosol concentration number with small hygroscopicity. They are probably a result of the mixture between the non-hygroscopic pollutant aerosols resulting from the activity of the city of Lisbon and the hygroscopic marine aerosols. This is more evident for the NW sector. The fitting procedure is robust against the $R_{a,0}$ used and would only affect the value estimated for Z_a because these two quantities appear as a product in

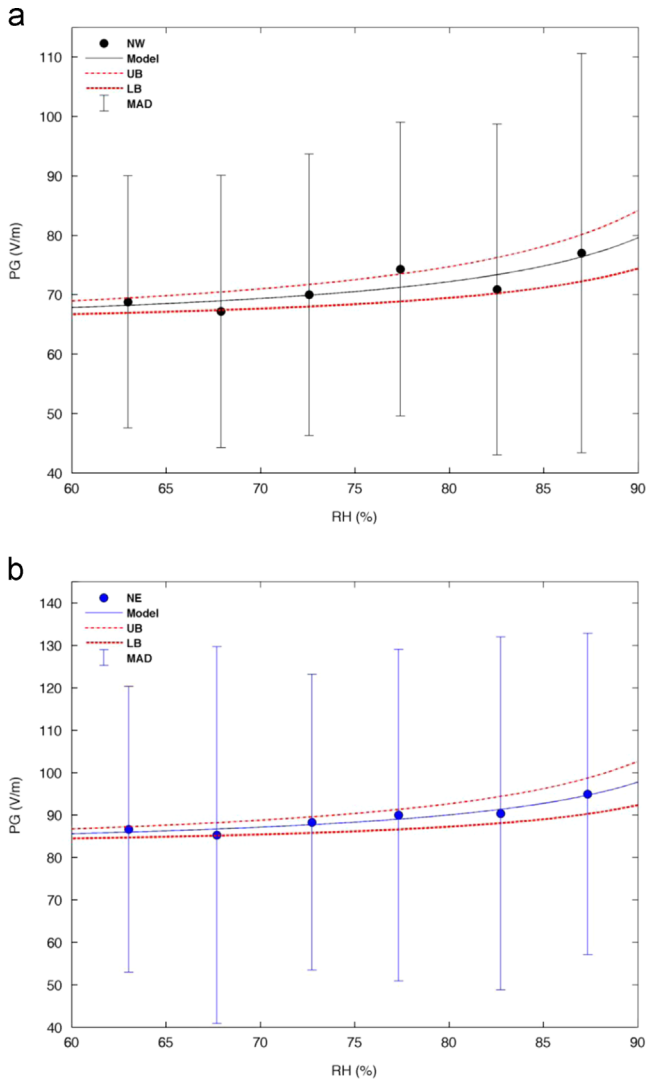

Fig. 5. The fits of the model to the wind sectors: (a) NW and (b) NE. The error bars represent the median absolute deviation (MAD), the solid-line the fitted curve and the dashed-lines the model function but with a variation in κ of 40% above and below the fitted valued.

Table 2
Results from fitting the model to the PG in the northern wind sectors: aerosol number concentration (Z_a) and aerosol hygroscopic growth parameter (κ_a). The goodness of the fit is also given (r^2). It is assumed that particle dry radius is $R_{a,0}$=0.1 μm.

	NW	NE
Z_a (cm^{-3})	3280	4179
κ_a	0.094	0.072
r^2	0.97	0.997

Eq. (10). It is important to mention that $R_{a,0}$ is expected to be small as it is the dry radius instead of the typical values measured in real atmospheric conditions where the aerosol particles are already hydrated to some extent (Deshpande & Kamra, 2004).

5. Conclusions

The formulation developed here relates in a simple way three microphysical properties of the aerosols: dry radius, concentration number and hygroscopicity; with the macrophysical measurement of Potential Gradient. As a simple formulation, it has several limitations such as neglecting the positive to negative ion concentration unbalance, the effect of electrified aerosols, the

influence of aerosol size distribution, and the change in the ionization rate with the relative humidity. Nevertheless, it describes fairly well the dependence of the Potential Gradient with the Relative Humidity for the northern wind sectors (less affected by air pollution) of the measurements done at the Portela meteorological station (Lisbon, Portugal). The values for the aerosol hygroscopicity are low, but consistent with the fact that they are probably a consequence from a mixture between non-hygroscopic pollutant aerosols (resulting from the activity of the city of Lisbon) and the hygroscopic marine aerosols. This point validates the model here developed.

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