Problem of Ionization Rate in the Research of Atmospheric Aerosols

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ABSTRACT: We propose a new method for experimental determination of the ionization rate and the small ion sink in the ambient air. The method relies on the generally accepted theory of balance and dynamics of small ions and on the presumption that the ambient ions are in the steady state. Preliminary experimental results demonstrated that the described new method can be used to obtain the reasonable values of both parameters.

INTRODUCTION

The theory of balance and dynamics of small ions in the air is presented in the classic monograph by Israël [1970]. The essence of the theory can be summarized by general equation of small ion dynamics:

$$\frac{dc}{dt} = I - \alpha c^2(t) - S_{ion}c(t) , \tag{1}$$

where c is the concentration of small ions, t is time, I is the ionization rate, α is the coefficient of mutual recombination, and S_{ion} is the term, which characterizes the ion sink. Considering steady state conditions, the balance equation (1) can be presented in a more simple manner:

$$I = \alpha c_\infty^2 + S_{ion}c_\infty , \tag{2}$$

where c_∞ is the concentration of small air ions in the steady state.

The ionization rate has been traditionally measured by means of ionization chambers. This method was already well developed a hundred years ago when V.F. Hess carried out the measurements that were recognized with the Nobel Prize in Physics in 1936. Contemporary development has only improved the ionization chamber measurement method by automating the recording of results. However, recent research of new particle formation in the field of atmospheric aerosol studies has pointed out new and challenging problems. The ionization rate is a factor of ion-induced aerosol nucleation and is included in the models of atmospheric aerosol formation. The existing models consider the ionization rate as a homogeneous scalar, characterized by a single number. In reality, the ionizing radiation near the ground appears to be largely dependent on location and environmental conditions, especially when the ground is covered with tall vegetation (e.g., forest tree canopy). There have been several attempts to estimate the ionization rate from

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the small air ion and aerosol particle measurements using steady-state balance equation of small air ions, as well as from direct measurements of ionizing radiation.

The monograph by Israël [1970] presents in Table 21 altogether 38 values of the ionization rate I from a number of studies carried out before 1957. The mentioned values of I extend from 1.5 to 35.5 $cm^{-3} s^{-1}$. Of later studies, Dhanorkar and Kamra [1994] performed measurements at Pune, India, during 2 days in March and 2 days in May, 1991. They found a significant diurnal variation of ionization rate I. The maximum values of I were 117 (in March) and 104 $cm^{-3} s^{-1}$ (in May) in the early morning (04:00). The minimum values were recorded at noon (12:00), 2.8 and 2.7 $cm^{-3} s^{-1}$, respectively. A significant diurnal variation and height profile from the ground was reported also by Prasad et al. [2005] and Ragini et al. [2008] according to measurements at Mysore, India. The ionization rate via radon decay is highly sensitive to the elevation from the ground.

Laakso et al. [2004] studied the ionization rate in a boreal forest by using two different methods: small air ion and aerosol particle concentration measurements, and external radiation and radon concentration measurements. They obtained the average ion production rate of 2.6 ion pairs $cm^{-3} s^{-1}$ from particle measurements, which underestimates the parameter especially during the day, whereas the average ionization rate based on external radiation and radon measurements was 4.5 ion pairs $cm^{-3} s^{-1}$ in average.

Few other studies have estimated the ionization rate from the small air ion and aerosol particle measurements using small ion balance equation [e.g., Hõrrak et al. 2008; Komppula et al. 2007, Schobesberger et al. 2009]. Hõrrak et al. [2008] estimated the average values of the ionization rate and small ion sink on aerosols during nucleation event days 0.005 s^{-1} and during non-event days 0.01 s^{-1} in a boreal forest. The average ionization rate at a height of about 2 m above the ground during early spring was about 6 ion pairs $cm^{-3} s^{-1}$. Hirsikko et al. [2007] estimated the total ion production rate to be in the range of 4.2–17.6 ion pairs $cm^{-3} s^{-1}$ based on direct measurements of ionizing radiation in a boreal forest, and the fraction of radon contribution in the ion production was about 11% in average. The monthly averaged ion production rates obtained from the measurements of radon (^{222}Rn) and gamma radiation spectra in Hyytiälä in 2008 reported by Franchin [2009] varied in the range of 5.9–10.9 ion pairs $cm^{-3} s^{-1}$, resulting in the mean ionization rate of 9.4 ± 1.7 ion pairs $cm^{-3} s^{-1}$. The estimates of the monthly variations and the mean value of the ionization rate for the same period based on the calculations from small air ion balance equation were considerably smaller: 2.2–4.9 ion pairs $cm^{-3} s^{-1}$ and 3.3 ion pairs $cm^{-3} s^{-1}$, respectively [Schobesberger et al. 2009]. The discrepancy was explained by the incomplete knowledge of the ionization process, and by underestimating the sinks of small ions and mutual recombination. Tammet et al. [2006] have considered the forest sink of clusters ions (about 20% from total sink), as well as humidity correction of the measured dry aerosol particle size distribution in the improved balance model and estimated the average ionization rate for Hyytiälä at the height of 2 m from the ground to be 5.6 ± 0.8 ion pairs $cm^{-3} s^{-1}$ and at the height of 14 m 3.9 ± 0.2 ion pairs $cm^{-3} s^{-1}$.

Hensen and van der Hage [1994] give a review of a variation in the ionization rate from 1.4 to 2.8 $cm^{-3} s^{-1}$ within different latitudes in the marine atmosphere, where galactic cosmic rays are the primary ionization source and determine the minimal ionization rate close to the Earth surface.

Disagreements between the results of different studies have been considerable. Thus, the progress in

the study of atmospheric aerosol formation requires an adjustment of the air ionization characteristics and development of new measurement methods.

THE METHOD

We propose a new experimental method, which relies on the theory of balance and dynamics of small ions and incorporates both the time-dependent and steady state equations (1) and (2). It does make no attempt to specify the sources of either ionization rate I or ion sink S_{ion}. Therefore, provided the equations (1) and (2) completely characterizes the processes, the proposed method should yield the correct values of both I and S_{ion}, notwithstanding of the detailed nature of these parameters. A specification of concrete sources of these parameters is important, but is outside of the scope of the present study.

Small air ions are the finest charged nanoparticles and their sink S_{ion} caused by ion attachment to aerosol particles can be expressed also as the coagulation integral calculated over all negative, zero, and positive values of electric charges. The coagulation coefficients of small ions with aerosol particles are usually called the attachment coefficients and can be estimated according to approximation formulas, e.g., given by Tammet and Kulmala [2012]. This enables to get additional estimate of the ion sink obtained by different and more direct method for testing of theoretical models and measuring techniques when comparing the results.

We accept the assumption of symmetric charging of aerosol particles by small ions and weak polarity symmetry, which states that the attachment rates (sinks) of small ions to neutral aerosol particles are equal: $\beta_o^+ c^+ = \beta_o^- c^-$ and use symbols $\beta_o = (\beta_o^+ + \beta_o^-)/2$ and $c = (c^+ + c^-)/2$, where the terms with upper indexes " $+$ " and " $-$ " mean that the corresponding terms are measured or calculated for a particular polarity. The dependence of the recombination coefficient α on the properties of recombining small ions is ill known, its empiric value is considered more reliable than theoretical estimates. The published empiric values vary in the range of 1.4–1.6×10^{-6} cm^3 s^{-1} and we use the estimate of $\alpha = 1.5 \times 10^{-6}$ cm^3 s^{-1} [Israël 1970; Hoppel and Frick 1986]. However, the recombination sink is a minor component in Equations (1) and (2), considering typical atmospheric conditions, and the uncertainty in the value of recombination coefficient has no considerable effect on the results.

We employ a new measurement method using a long metal tube measurement technique with a controlled electrostatic gate of air ions at the inlet and an air ion spectrometer at the outlet of the tube (Fig. 1). The voltage of the closed gate is chosen so that the rest passage of small ions through the gate is reduced to the noise level of ion spectrometer. Therefore, in the case of closed gate we can apply the Equation (1), where $c(t)$ at $t = 0$ is equal to the average noise level and $c(t)$ at $t = $ T is equal to the concentration measured at the outlet of the tube. T is equal to the time of the passage of air along the long metal tube. When the gate is open (the voltage of the gate is zero) and $t > $ T after the switching zero potential on, the spectrometer records the concentration of ambient ions. We assume the steady state concentration of ambient ions and, therefore, in the case of open gate we can apply the Equation (2).

General equation of small ion dynamics (1) was analytically solved by Israël [1970, see p. 167]. However, a numerical integration is usually more convenient method: choose a small value of the differential dt (about 0.1 s or less), determine initial value of c at time $t = 0$ and repeat T/dt times a recalculation $c := c + (I - \alpha c^2 - S_{ion} c)\,dt$ until $t = $ T. Solution of the Equation (1) can be interpreted as a special function $c = f(c_0, I, S_{ion}, t)$. As a result, we have two unknown parameters I and S_{ion}, two different

measured concentrations of small ions $c(T)$ and c_∞, and a system of equations:

$$\begin{cases} c = f(c_0, I, S_{ion}, t) \\ \\ I = \alpha\, c_{nat}^2 + S_{ion} c_{nat} \end{cases} \tag{3}$$

Here we assume also that the steady state concentration of small ions equals to that of measured in ambient air in the case of open electrostatic gate ($c_\infty = c_{nat}$). Therefore, we can apply the measured concentrations, solve the system of equations (3) and obtain the searched values of I and S_{ion}. In this work, the system of equations (3) is solved numerically by iteration. Let's start from initial values $I = 5$ cm^{-3} s^{-1} and $S_{ion} = 0.1$ s^{-1}. An iteration step begins with the numerical integration of the first equation by sequence $c := c + (I - \alpha c^2 - S_{ion}\, c)\, dt$ from time $t = 0$ to $t = T = 10$ s, which yields a value of small ion concentration c. This value is compared with the measured value $c(T)$. If c is equal to $c(T)$ within expected accuracy, the iteration ends, otherwise the algorithm either decreases or increases the value of I. On the bases of the new value of I and second equation of system (3) the algorithm computes the new value of $S_{ion} = I / c_{nat} - \alpha c_{nat}$ and enters the next iteration step.

In experiments we used a galvanized steel sheet metal tube with the length of 5 m and the cross sectional area of 0.0625 m^2 (Fig. 1). The time T of the passage of air along the tube is equal to 10 seconds. The measurements have been performed in series where the gate was closed for 5 minutes and open for subsequent 5 minutes; the ion spectrometer recorded the corresponding average ion concentrations $c(T)$ and c_∞, respectively. For preliminary testing of the experimental system, it was installed not in outdoor but indoor conditions at the attic room of the building of Institute of Physics at Tähe 4, Tartu.
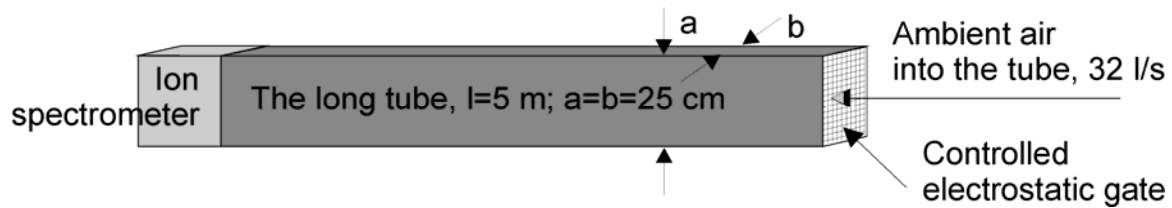

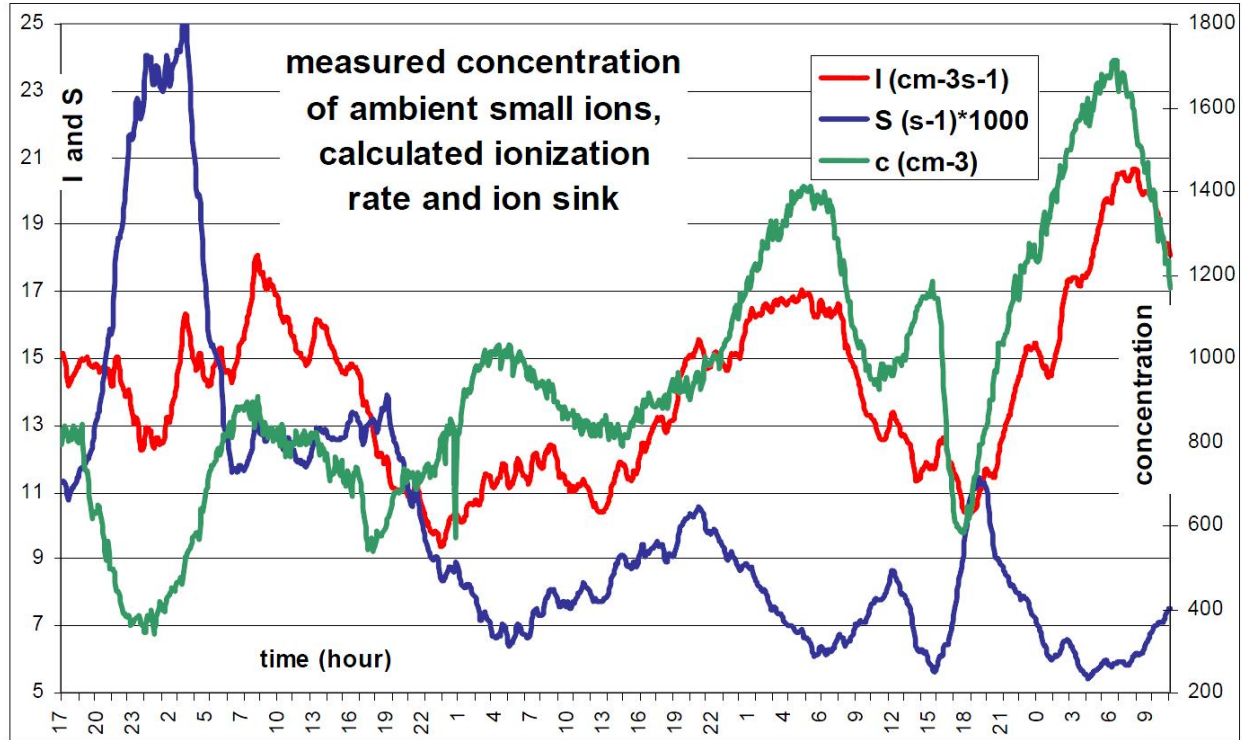Figure 1. The main elements of experimental setup.

Figure 2. The measured concentrations of ambient small ions (*c*) and the corresponding ionization rates (*I*) and sinks (*S*), calculated by the proposed new method.

RESULTS AND CONCLUSIONS

We designed an appropriate long metal tube with controlled electrostatic gate and recorded the corresponding indoor air ion concentrations by the ion spectrometer SIGMA [Tammet 2011]. The concentrations of small air ions, recorded during a measurement series, and the corresponding values of the ion sink and the ionization rate are depicted in Fig. 2. Both the corresponding ionization rates and small ion sinks have been calculated as described above. The results demonstrate substantial variations in the measured ambient concentrations of small ions, ranging for about 400 cm^{-3} up to 1700 cm^{-3}. Such a variation, which has a clear diurnal cycle with elevated concentrations recorded at nighttime, is known to us from earlier lab experiments and is caused by the accumulation of the radon in the building during decreased air ventilation. The ionization rates varied between about 9 cm^{-3} s^{-1} and 21 cm^{-3} s^{-1}. Such a large variation within few days is not a surprise, if to consider the effect of radon. The values itself are rational, because similar values have been obtained also elsewhere [e.g., Israël 1970; Hirsikko et al. 2007; Hõrrak et al. 2008]. The calculated sinks varied between about 0.005 s^{-1} and 0.025 s^{-1}; such values are reasonable as well [Tammet et al. 2006; Hõrrak et al. 2008]. The measured ambient small air ion concentrations in Fig. 2 correlate with the calculated ionization rates and anti-correlate with the calculated small ion sinks. Consequently, we have demonstrated that the described new method can be used to obtain both the ionization rate and the small ion sink in the ambient air.

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