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**Parameterization of  
ion-induced  
nucleation rates**

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# Parameterization of ion-induced nucleation rates based on ambient observations

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## Abstract

Atmospheric ions participate in the formation of new atmospheric aerosol particles, yet their exact role in this process has remained unclear. Here we derive a new simple parameterization for ion-induced nucleation or, more precisely, for the formation rate of charged 2-nm particles. The parameterization is semi-empirical in the sense that it is based on comprehensive results of one-year-long atmospheric cluster and particle measurements in the size range  $\sim 1\text{--}42$  nm within the EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality interactions) project. Data from 12 field sites across Europe measured with different types of air ion and cluster mobility spectrometers were used in our analysis, with more in-depth analysis made using data from four stations with concomitant sulphuric acid measurements. The parameterization was given in two slightly different forms: a more accurate one that requires information on sulfuric acid and nucleating organic vapor concentrations, and a simpler one in which this information is replaced with the global radiation intensity. In principle, these new parameterizations are applicable to all large-scale atmospheric models containing size-resolved aerosol microphysics.

## 1 Introduction

Formation of new atmospheric aerosol particles by nucleation is a frequent and worldwide phenomenon (Kulmala et al., 2004; Kulmala and Kerminen, 2008). Nucleated particles have been observed to grow into cloud condensation nuclei (CCN) sizes (e.g. Laaksonen et al. 2005; Wiedensohler et al., 2009), and to participate in cloud droplet activation (Kerminen et al., 2005). Model investigations demonstrate that nucleation may contribute significantly to the number concentration of CCN, and thereby to indirect climate forcing, in the global atmosphere (e.g. Spracklen et al., 2008; Merikanto et al., 2009; Pierce and Adams, 2009).

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Although our understanding on atmospheric nucleation has increased substantially during last few years (e.g. Kerminen et al., 2010), quantifying the climatic and other effects of atmospheric nucleation is probably not possible without knowing the dominating nucleation pathways in different environments and under varying atmospheric conditions. One important source of uncertainty in this respect is the role of ions: while they are known to influence both nucleation and subsequent growth of nucleated particles (e.g. Nadykto and Yu, 2003; Winkler et al., 2008), the overall effect of ions on atmospheric aerosol formation has remained controversial (Enghoff and Svensmark, 2008; Kazil et al., 2008; Yu et al., 2008; Kulmala et al., 2010; Mirme et al., 2010).

Over the years, a few parameterizations to treat ion-induced nucleation in large-scale atmospheric models have been developed (Turco et al., 1998; Modgil et al., 2005; Kazil and Lovejoy, 2007; Yu, 2008a). All these parameterizations reproduce the underlying nucleation theory with good accuracy, making them both practical and appealing tools to investigate ion-induced nucleation in the global atmosphere. However, none of these parameterizations have been tested properly against atmospheric measurements due to the general lack of suitable field data for this purpose.

In this work, we will develop a new parameterization for ion-induced nucleation, or more precisely for the formation rate of charged 2-nm particles, based entirely on field measurements. The measurements data will be taken from the European Integrated Project on Aerosol Cloud Climate Air Quality Interactions (EUCAARI) project (Kulmala et al., 2009). In EUCAARI, different types of cluster mobility spectrometers were deployed simultaneously in 12 European sites, representing a variety of geographical and atmospheric conditions to quantify the spatial and temporal distribution of the particle formation events (Manninen et al., 2010). The new parameterization is very simple, and it will be provided in two different forms to facilitate its use in practically all current atmospheric models capable of simulating aerosol microphysics.

## 2 Materials and methods

### 2.1 Measurements

The Air Ion Spectrometers (AIS), Neutral cluster and Air Ion Spectrometers (NAIS) and Balanced Scanning Mobility Analyzers (BSMA) have been operating simultaneously in 12 field sites in Europe within the EUCAARI project (see map in Fig. 1). The measurements presented in this paper started in March 2008 and ended between February and May 2009 depending on the site (Manninen et al., 2010). The measurements sites were Pallas and Hyytiälä (Finland), Vavihill (Sweden), Mace Head (Ireland), Cabauw (The Netherlands), Melpitz and Hohenpeissenberg (Germany), K-Pusztá (Hungary), Jungfraujoch (Switzerland), Puy de Dôme (France), San Pietro Capofiume (Italy) and Finokalia (Greece). These sites represent a wide variety of environments, such as marine, coastal, remote continental, suburban, rural and mountain conditions, as well as altitudes from sea level to several thousand meters above sea level (a.s.l.).

The more detailed data set used in this study was collected from four of the above mentioned stations: Hyytiälä, Melpitz, Hohenpeissenberg and San Pietro Capofiume (Paasonen et al., 2010). Also these four sites differ significantly in terms of anthropogenic influence, geographical latitude and altitude, ranging from close to sea level in San Pietro Capofiume to 985 m a.s.l. in Hohenpeissenberg. At these four sites Chemical Ionization Mass Spectrometer (CIMS) was used to measure ambient sulphuric acid concentrations.

The Air Ion Spectrometer (AIS, Mirme et al., 2007) measures mobility distributions of both negative and positive air ions simultaneously in the range between 3.2 and  $0.0013 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which corresponds to a mobility diameter range of 0.8–42 nm. We apply the mobility diameter i.e. Millikan diameter when converting the measured mobility to the particle diameter (see Mäkelä et al., 1996). The AIS consist of two parallel cylindrical Differential Mobility Analyzers (DMAs); one DMA classifies negative ions and the other positive ions. The ions are simultaneously classified, according to their electrical mobility, and collected to electrically isolated sections. Each section has its

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own electrometer to measure the currents carried by the ions. The NAIS (Kulmala et al., 2007) measures in addition the concentration of neutral atmospheric clusters by charging them with a unipolar corona charger prior to analyzing their mobility. In this study, we use only data gathered with the ion mode of the NAISs, and thus it is similar to the AIS data. The Balanced Scanning Mobility Analyzer (BSMA, Tammet, 2006) measures mobility distributions of small air ions and naturally charged aerosol particles of both negative and positive polarity, the mobility distribution is measured by scanning through the corresponding mobility range within 10 seconds. The mobility range of the BSMA is  $3.2\text{--}0.032\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ , corresponding to the mobility diameter range of 0.8–8.0 nm. The BSMA consists of two plate capacitors, one for each polarity, and a common electrical amplifier connected to a balanced bridge circuit. A more detailed description of the measurements during the EUCAARI and the data set gathered is given in Manninen et al. (2010).

The sulphuric acid concentrations were measured with Chemical Ionization Mass Spectrometers (CIMS). The measurements in Hohenpeissenberg, Melpitz and San Pietro Capofiume were performed with the CIMS operated by the Deutscher Wetterdienst DWD (Berresheim et al., 2000), whereas in Hyytiälä the CIMS of the University of Helsinki was used (Petäjä et al., 2009). We also utilize global radiation data that includes both direct and diffuse solar radiation.

## 2.2 Particle formation rates

The growth rate of the newly formed aerosol population can be determined from the measured number size distributions using the method presented in Hirsikko et al. (2005). A normal distribution function was fitted into the time series of the particle concentrations in every size bin. After determining the moment corresponding to the maximum concentration in each of the size bins, the growth rates (GR) were obtained by a linear least-square fit through the data points in the selected size classes. Both negative and positive polarities were analyzed separately. The average charged particle growth rates were obtained for three diameter classes (1.5–3 nm, 3–7 nm and

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7–20 nm) from the AIS data, and in case of BSMA measurements, for the two first size classes, and only during the event time, when there was high enough concentrations of ions. The growth rate estimate with this method (Hirsikko et al., 2005) can deviate from the real one by up to a factor two because of observational uncertainties.

The charged particle formation rates were calculated from the ion concentrations measured in the size range 2–3 nm by taking into account particle losses due to coagulation scavenging and growth of particles out of the considered size range. Also losses due to ion-ion recombination and sources due to charging of 2–3 nm neutral particles were taken into account (see Kulmala et al., 2007, supporting information). The formation rate of charged 2-nm charged particles is thereby obtained from the following equation:

$$J_2^\pm = \frac{dN_{2-3}^\pm}{dt} + \text{CoagS}_2 \times N_{2-3}^\pm + \frac{1}{1\text{nm}} \text{GR}_3 N_{2-3}^\pm + \alpha N_{2-3}^\pm N_3^\mp - \beta N_{2-3} N_2^\pm. \quad (1)$$

Here the superscript  $\pm$  refers to positively and negatively charged particles,  $N_{2-3}^\pm$ ,  $N_{<2}^\pm$  and  $N_{<3}^\pm$  are the concentrations of ions and charged particles in the size range 2–3 nm, below 2 nm and below 3 nm, respectively, and  $\text{GR}_3$  is the particle growth rate at 3 nm. The ion-ion recombination coefficient,  $\alpha$ , and the ion-neutral attachment coefficient,  $\beta$ , are assumed to be equal to  $1.6 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  and  $0.01 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ , respectively (e.g. Tammet and Kulmala, 2005). The ion concentrations were obtained from the charged particle number size distributions measured with AIS and BSMA. Due to uncertainties both in the measurements and data analysis, the formation rate values estimated here could be higher or lower by approximately a factor of two (Manninen et al., 2009).

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### 3 Parameterizations

#### 3.1 Parameterization based on sulphuric acid and nucleating organic vapors

In order to derive a new semi-empirical parameterization for ion-induced nucleation, we investigated how the formation rate of charged 2-nm particles depends on the concentrations of cluster ions, sulphuric acid and nucleating organic vapors in our measurement sites. While the involvement of cluster ions and sulphuric acid is quite clear based on earlier studies on ion-induced nucleation (e.g. Kazil and Lovejoy, 2007; Yu, 2010), we decided to include also organic vapors in the parameterization because of their plausible participation in atmospheric nucleation processes (see e.g. Paasonen et al., 2009; Metzger et al., 2010). We assumed that the formation rate of charged 2 nm particles has the following functional form:

$$J_2^\pm = C^\pm \cdot F(N_{\text{clus}}^\pm, [\text{H}_2\text{SO}_4], [\text{Org}]) \quad (2)$$

Here  $C^\pm$  is the empirical fitting parameter determined by a linear least-squares fit to the measurement data,  $N_{\text{clus}}^\pm$  is the concentration of cluster ions in the diameter range 0.80–1.25 nm and  $[\text{H}_2\text{SO}_4]$  is the sulphuric acid concentration. The concentration  $[\text{Org}]$  is the growth-equivalent organic vapor concentration, i.e. the concentration needed to explain the observed particle growth rate from 2 to 4 nm in addition to calculated growth rate related to sulphuric acid condensation. The time dependent concentration of  $[\text{Org}]$  is derived by scaling the calculated concentration during the growth rate determination (Hirsikko et al., 2005) by global radiation and condensation sink (Kulmala et al., 2001). The calculation of  $[\text{Org}]$  is explained in more detail by Paasonen et al. (2010) and will not be repeated here. Since atmospheric nucleation rates have consistently been found to be proportional to the power of 1–2 of the precursor vapor concentrations (Riipinen et al., 2007; Kuang et al., 2008; Paasonen et al., 2010), function  $F$  in Eq. (2) is assumed to be a polynomial containing the terms  $N_{\text{clus}}^\pm$ ,  $[\text{H}_2\text{SO}_4]$  and  $[\text{Org}]$  raised to the power of 0–2 (Paasonen et al., 2010). We chose the upper size limit of the cluster ions in Eq. (2) to be 1.25 nm, since it is seen from the data that during nucleation events

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the concentration of cluster ions smaller than this limit is typically diminished while the concentration of larger ions is increasing. This can be regarded as evidence of cluster ions smaller than about 1.25 nm participating in the nucleation processes, probably via an activation mechanism (Kulmala et al., 2006).

By fitting Eq. (2) to the data obtained from the four sites with parallel ion and sulphuric acid measurements and varying the function  $F$ , we ended up with the following equation:

$$J_2^\pm = C^\pm \times N_{\text{clus}}^\pm ([\text{H}_2\text{SO}_4] + [\text{Org}])^2. \quad (3)$$

Considering the individual terms Eq. (3), they actually represent three different pathways for nucleation: collision between cluster ion and either two molecules of sulphuric acid or condensable organic vapor or one of both. Figure 2 shows how the observed and parameterized formation rates of charged 2-nm particles correlate with each other for the whole data set from the four sites. The correlation coefficients were equal to 0.60 and 0.62 for negative and positive ions, respectively. The values determined for the fitting coefficients  $C^\pm$  of Eq. (4) are given in Table 1. It is notable that by multiplying the vapour concentration term in Eq. (3) by the ion cluster concentration the correlations were clearly better than if it was ignored. This suggests that the cluster ions are really taking part in the ion-induced nucleation process. We also tested Eq. (3) without the organic concentration, i.e. parameterization based only on the product of cluster ion concentration and sulphuric acid concentration squared. As can be seen from Fig. 2c and d this leads to clearly worse results than the parameterization including the organic concentration. The fitting coefficient in this case is also given in Table 1, although it is not recommended to use Eq. (3) without the organics concentration.

In addition to the fittings described in Eq. (3), we tested performance of the following fittings into the same data set:

$$J_2^\pm = C^\pm (N_{\text{clus}}^\pm)^{p_1} [\text{H}_2\text{SO}_4]^{p_2} [\text{Org}]^{p_3}, \quad (4)$$

where the exponents  $p_i$  can be 0, 1 or 2. All the different combinations of  $p_i$  led to weaker correlations than achieved with Eq. (3). Especially, the correlation coefficients

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resulting from  $p_3=0$ , i.e. the fittings made with sulfuric acid and ion cluster concentrations alone, did not exceed  $R=0.38$ . By visual inspection of the fittings made without taking [Org] into account, we can conclude that these parameterizations are even less reliable than the correlation coefficients would suggest. Furthermore, by changing the vapor concentrations to the power of 1 or by raising  $N_{\text{clus}}$  to the power of 2 in Eq. (4) the results were worsened.

### 3.2 Parameterization based on solar radiation

Since the concentrations of sulphuric acid and/or organics are not necessarily available in modeling frameworks or when analysing measurement data, we derived an even simpler form of the parameterization that relies on the intensity of global radiation instead of sulphuric acid and growth-equivalent organic vapour concentration. While very rough, this approach can be justified by considering that (i) the production rate of sulphuric acid, and to large extent also of low-volatile organic vapors, are driven by OH radicals, (ii) the OH radical concentration usually follows the UV-B light intensity (Rohrer and Berresheim, 2006), and (iii) the UV-B and global radiation intensity tend to correlate strongly with each other. It has been shown that the sulphuric acid concentration can be parameterized quite well with the help of the solar radiation intensity (Petäjä et al., 2009).

Figure 3 shows how the formation rate of charged 2-nm particles depends on the product of cluster ion concentration and global radiation. The data points in the top-left corners of these plots represent cases when a relatively high charged particle formation rate takes place at low global radiation levels, typically below about  $50 \text{ W m}^{-2}$ . These data points correspond to evening and night periods, and are not related to traditional new-particle formation and growth events. This kind of night-time cluster ion growth events have been reported, for example, by Junninen et al. (2008) in measurements conducted at Hyytiälä. If the data points corresponding to evening and night-time ion events are excluded, the correlation between the observed formation rate of charged 2-nm particles and the product of cluster ion concentration and global radiation becomes much clearer.

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We considered following types of fittings as candidates for the parameterization based on global radiation:

$$J_2^\pm = C_{\text{rad}}^\pm \cdot (N_{\text{clus}}^\pm)^m \cdot \text{GlobRad}^n. \quad (5)$$

As in case of (Eqs. 2 and 3),  $C_{\text{rad}}^\pm$  is the semi-empirical fitting parameter determined by a linear least-squares fit between the observed and parameterized formation rate of charged 2-nm particles. GlobRad (in  $\text{W m}^{-2}$ ) is the intensity of global radiation, and the exponents  $m$  and  $n$  are constrained to values 1 or 2. For both negative and positive ions, the best correlation between the observed and parameterized formation rate was obtained with  $m=1$  and  $n=2$ , the correlation coefficients being equal to 0.44 and 0.41, respectively. The values of the corresponding fitting coefficients  $C_{\text{rad}}^\pm$  are given in Table 1. Figure 4 shows the relation between the measured and parameterized values of  $J_2^\pm$  for all the 12 EUCAARI measurement sites. As one might expect, the parameterization utilizing global radiation is not as good as the one based on the concentrations of sulphuric acid and nucleating organic vapors.

When examining the sites individually, there was roughly an order of magnitude variation in the values of the fitting coefficients  $C_{\text{rad}}^\pm$ . The smallest values were obtained for Puy de Dome,  $1.9 \times 10^{-10}$  for negative and  $1.6 \times 10^{-10}$  for positive ions. The highest value for negative ions was found in Hyytiälä ( $1.9 \times 10^{-9}$ ), and for positive ions in Cabauw ( $2.7 \times 10^{-9}$ ). The correlation coefficients between the observed and parameterized values of  $J_2^\pm$  varied from 0.3 in Hyytiälä and Pallas to roughly 0.6 in Hohenpeissenberg and Melpitz.

Finally, we tested the parameterization based on global radiation Eq. (5) for the data set obtained on the four stations Hyytiälä, Melpitz, Hohenpeissenberg and San Pietro Capofiume, from where sulphuric acid data were available. Figure 5 shows the comparison between parameterizations given by (Eqs. 3 and 5) for this data set. It can be seen that for both negative and positive ions, the parameterization based on the vapor concentrations tends to predict somewhat higher  $J_2$  values than the parameterization based on global radiation at times when the observed  $J_2$  is highest. As during these

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times also the global radiation is highest, this might be due to the strong dependence of particularly organic vapor concentrations on other factors than solar radiation, for example temperature. However, no clear correlation between the fitting coefficients  $C$  and temperature was found.

### 5 3.3 Determining the cluster ion concentration

Very few atmospheric models trace cluster ion concentrations needed to apply (Eqs. 3 and 5). The balance equation for the cluster ion concentration may be written as (see e.g. Laakso et al., 2004):

$$\frac{dN^{\pm}}{dt} = Q - \text{CoagS}_{\text{ion}} \cdot N^{\pm} - \alpha \cdot N^{-} \cdot N^{+}. \quad (6)$$

10 The first term on the right hand side of Eq. (6) is the ion production rate, the second term represents the scavenging of cluster ions with larger pre-existing particles by coagulation, and the third term accounts for the ion-ion recombination. By assuming a pseudo-steady state, i.e.  $dN^{\pm}/dt = 0$ , and that the concentrations of negative and positive cluster ions are equal to each other, Eq. (6) can be solved analytically:

$$15 N^{\pm} = \frac{\sqrt{\text{CoagS}_{\text{ion}}^2 - 4 \cdot \alpha \cdot Q} - \text{CoagS}_{\text{ion}}}{2\alpha}. \quad (7)$$

Here, the ion-ion recombination coefficient  $\alpha$  is again about  $1.6 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  (Tammet and Kulmala, 2005), and the coagulation sink for cluster ions,  $\text{CoagS}_{\text{ion}}$ , can be calculated from the pre-existing particle number size distribution according to Kulmala et al. (2001) by approximating that the diameter of cluster ions is about 1 nm. The ion production rate,  $Q$  (ions  $\text{cm}^{-3} \text{ s}^{-1}$ ) depends on the flux of cosmic rays and, close to the Earth's surface, also on the natural radioactivity related to radon emissions and direct gamma radiation from the soil (Harrison and Carslaw, 2003). The contribution of cosmic rays to  $Q$  can be evaluated quite accurately with help of available models (see Bazilevskaya et al., 2008, and references therein).

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## 4 Discussion and conclusions

The main purpose of this paper was to derive a simple, semi-empirical parameterization for ion-induced nucleation to be used in large-scale modeling frameworks. We found that the parameterization having the best predictive power requires knowing the concentrations of cluster ions, sulphuric acid and nucleating organic vapors (see also Paasonen et al., 2010). Since both sulphuric acid and nucleating organic vapor concentrations are not available in most current atmospheric models, we derived an additional and even simpler parameterization based on the global radiation intensity and cluster ion concentration. It should be noted that the parameterizations relying on global radiation result in indubitably better approximation for ion induced nucleation rate than those, in which sulphuric acid is considered but the organic vapor concentration not. Finally, a means to calculate the cluster ion concentration, a quantity not usually traced in large-scale atmospheric models, was provided.

Compared with existing ion-induced nucleation parameterizations (Mogdil et al., 2005; Kazil and Lovejoy, 2007; Yu, 2010), the two parameterizations derived here have both their strengths and weaknesses. Clear strengths in this respect are (i) the simplicity of the new parameterizations, (ii) their applicability to practically all atmospheric models containing size-resolved aerosol microphysics, (iii) the practicality of getting the charged particle formation rate at a fixed particle diameter of 2 nm, and (iv) the fact that the new parameterizations rely on field observations at multiple sites, not only on highly uncertain nucleation theories. The apparent drawback in our empirical approach is that it lacks plenty of the physics involved in the ion-induced nucleation process. As a result, our parameterizations cannot capture the influence of temperature and humidity in the nucleation process (Yu, 2010), nor the role played by ions of different chemical identity. The data set used to derive the new parameterizations did not include observations from marine areas or upper troposphere, so their performance in these regions is unclear at the moment.

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Large-scale atmospheric models provide, at the end, the only tool to address the role of ion-induced nucleation in the global aerosol production. With this in mind, it would be extremely important to investigate how the different ion-induced nucleation parameterizations compare with each other in the global atmosphere, and how they perform in the growing list of field sites with direct measurement data on charged particle formation rates (e.g. Manninen et al., 2010). New measurement data on the formation rates of charged and neutral particles in the middle and upper troposphere over both continental region and marine atmosphere would be extremely useful in this regard.

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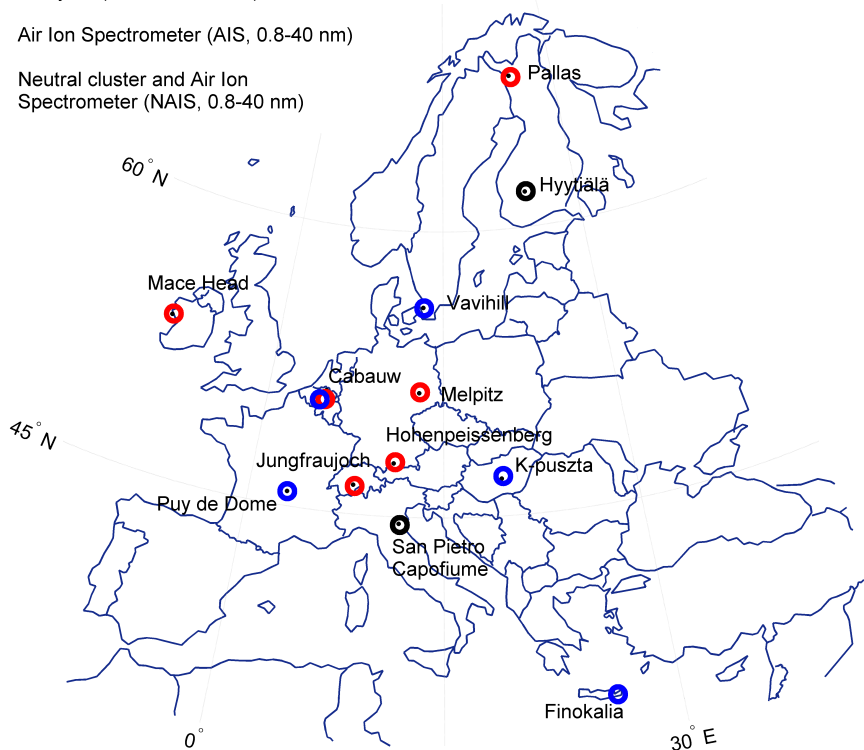
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**Table 1.** Values of the fitting coefficients  $C$  and correlation coefficients for the parameterizations of (Eqs. 4 and 6). When using the parameterizations, the cluster ion and vapor concentrations are given in units molecules/cm<sup>3</sup>, and global radiation in W/m<sup>2</sup>.

	Fitting parameter $C$		Correlation coefficient	
	Neg	Pos	Neg	Pos
$J_2^\pm = C \cdot N_{\text{clust}}^\pm \cdot (\text{H}_2\text{SO}_4 + \text{Org})^2$	$1.55 \times 10^{-19}$	$1.55 \times 10^{-19}$	0.61	0.64
$J_2^\pm = C \cdot N_{\text{clust}}^\pm \cdot (\text{H}_2\text{SO}_4)^2$	$6.7 \times 10^{-18}$	$6.5 \times 10^{-18}$	0.19	0.30
$J_2^\pm = C \cdot N_{\text{clust}}^\pm \cdot \text{GlobRad}^2$	$7.86 \times 10^{-10}$	$7.95 \times 10^{-10}$	0.44	0.41

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- Balanced Scanning Mobility Analyzer (BSMA, 0.8-7 nm)
- Air Ion Spectrometer (AIS, 0.8-40 nm)
- Neutral cluster and Air Ion Spectrometer (NAIS, 0.8-40 nm)



**Fig. 1.** Locations of the 12 field sites from where data has been used in the parameterizations. The type of ion spectrometer used at each site is indicated by the color of the circle around the station.

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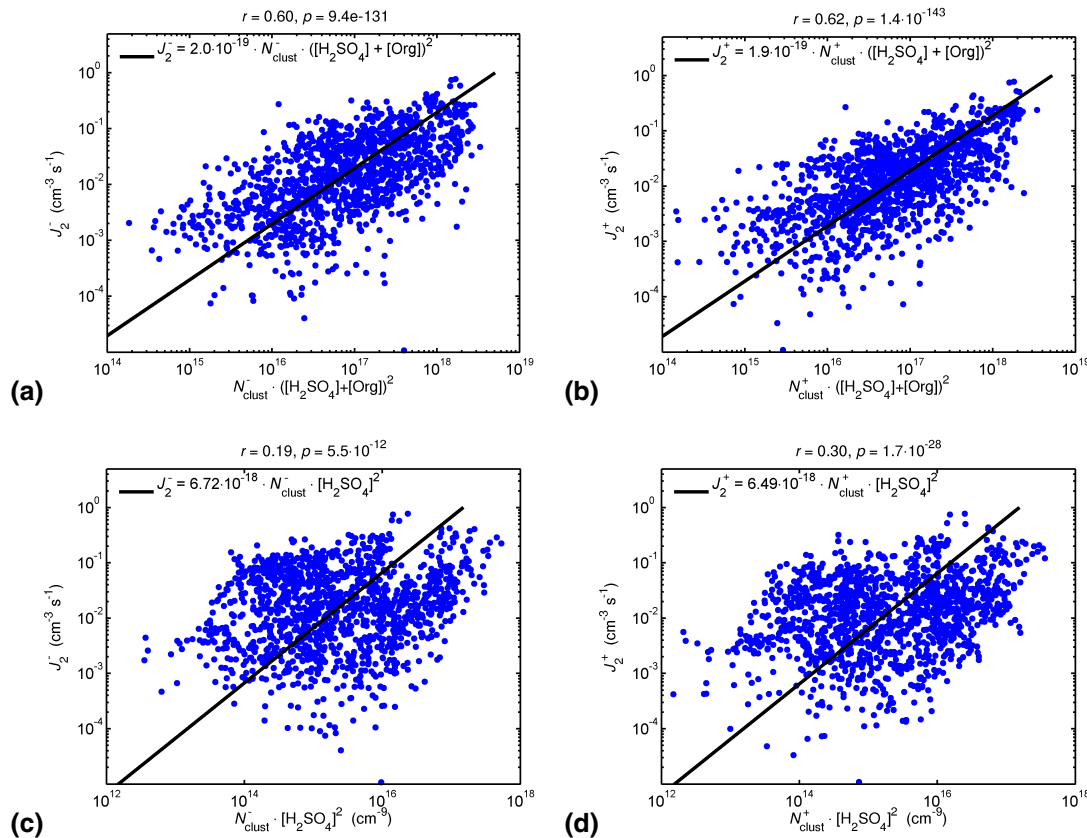
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**Fig. 2.** Ion-induced nucleation rates of **(a)** negative and **(b)** positive ions at 2 nm, as a function of cluster ion concentration multiplied with the squared sum of sulphuric acid and growth equivalent organic vapour concentrations. The data is measured in Hyytiälä (May 2007), Hohenpeissenberg (from July 2007 to July 2008), Melpitz (May 2008) and San Pietro Capofiume (July 2009). Panels **(c)** and **(d)** show the same  $J_2$  values when leaving out the organic concentration from the parameterizations.

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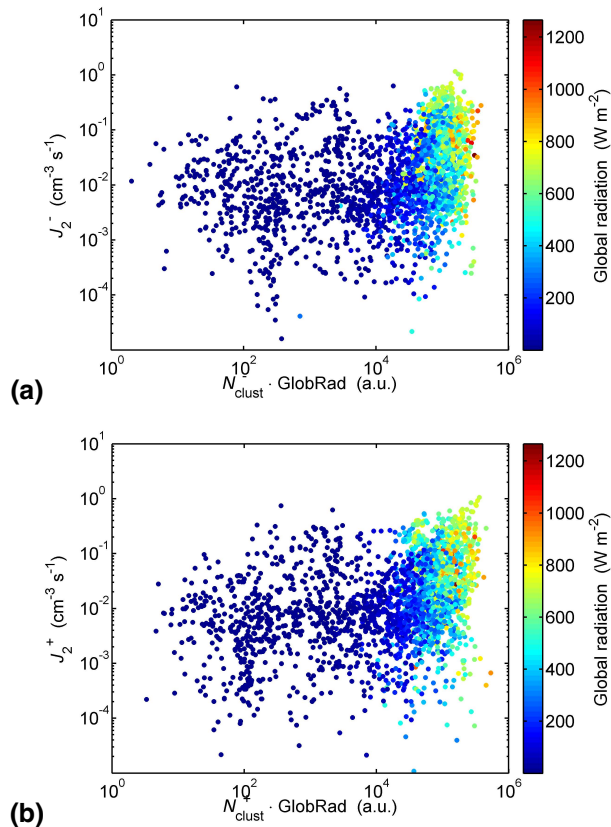
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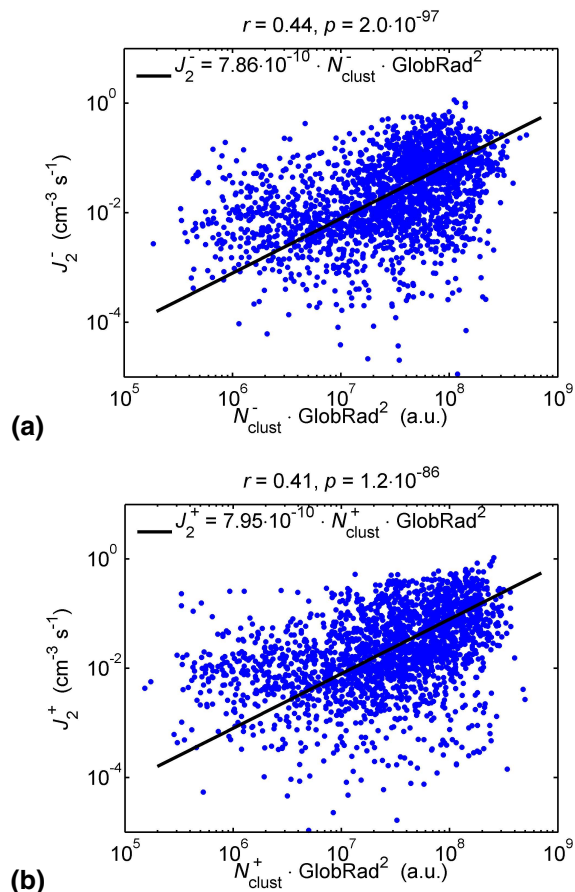




**Fig. 3.** Ion-induced nucleation rate of **(a)** negative and **(b)** positive ions at 2 nm as a function of the product of cluster ion concentration and global radiation. The data includes all the 12 EUCAARI measurement sites. The color of the data points indicates the intensity of global radiation.

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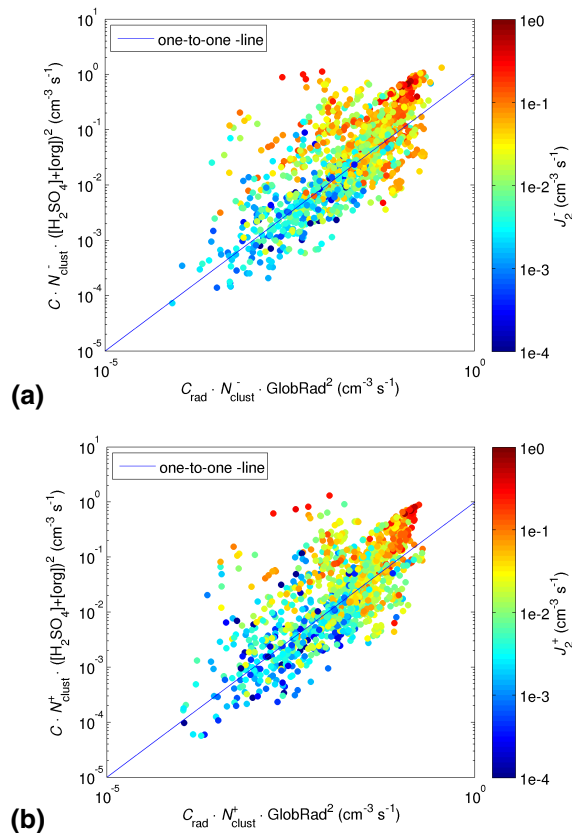


**Fig. 4.** Formation rates of (a) negative and (b) positive 2 nm ions as a function of product of cluster ion concentration and square of global radiation. The blue points mark data from the 12 EUCAARI sites data sets, and the black lines are linear least-squares fits to these data points. The data includes all times when global radiation intensity is above  $50 \text{ W m}^{-2}$ .

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**Fig. 5.** Comparison of the ion-induced nucleation rate parameterizations of (Eqs. 4 and 6) for (a) negative and (b) positive ions based on the data set from Hohenpeissenberg, Melpitz and San Pietro Capofiume. The color of the data points indicates the observed  $J_2$  value. The values for the fitting coefficients are  $C$  are those given in Table 1.

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