Interactive comment on “Characterization of ions at Alpine waterfalls” by P. Kolarž et al.

Anonymous Referee #1 - Received and published: 24 October 2011

The authors have studied the formation of waterfall-generated ions, or so called balloelectric ions, during three years of various field campaigns in the Austrian Alps. They have monitored the concentrations of waterfall-generated ions at five different waterfalls applying self-made Gerdien-type integral air ion counters and a modified GrimmSMPS aerosol spectrometer to cover the size range of 0.9–350 nm, from cluster ions up to large charged aerosol particles. The measurements showed high negative ion and moderate positive ion concentration gradients near the waterfalls, as expected of the generation of ions by balloelectric mechanism. The most important outcome of the study is the spatial distribution of the waterfall-generated ions, influenced by the local orography and meteorological conditions.

This work can be considered as one in the line of investigations of balloelectric ions started by Philipp Lenard (Lenard, 1982; 1915), continued by Chapman (1938a, b), Blanchard (1955), Gathman and Hoppel (1970), Levin (1971), Reiter (1994), Hõrrak et al. (2006), Hirsikko et al (2007), Laakso et al. (2006, 2007) and Tammet et al. (2009).

The subject of the paper is certainly relevant to the aerosol researchers’ community and also to the larger audience of the journal of Atmospheric Chemistry and Physics, giving an impulse to the further investigations of balloelectric ions. The authors have done a good and interesting job, which is worth to be published in the ACP. However, the present paper has also some shortages and can be accepted for the publication in the ACP if these problems are satisfyingly resolved. The authors are asked to consider the following general and specific comments, questions and recommendations.

General comments

We noted that the introductory part of the paper is quite short, the motivation and main objectives of the present work are missing. Also, too little attention is paid to the earlier investigations in this field. At least one important recent work on balloelectric ions by Tammet et al. (2009) is missing, but the contributions of some others, listed above, are also worth to be mentioned or introduced in some more detail. Thus, the authors are asked to consider giving their work a broader perspective with respect to other works in this field. Regarding an overview of atmospheric ions, we recommend including two recent review papers by Arnold (2008) and Hirsikko et al. (2011). The paper should also be structured in a more proper and reader-friendly way, concentrating passages of similar matters in appropriate sections, and inserting some additional tables for a better overview of the measurements and instrumentation. The authors are also asked to reduce the number of megabits in their 10.3 MB-long article by reducing the resolution of the photos.

A crucial problem is that the description of the self-invented and built Gerdien-type air ion counter, as well as the applied measuring method, is too short and some of its aspects are missing at all. Therefore, it is hard to understand how the size distribution of air ions was obtained from the integral ion counter measurements. So, we recommend adding a more detailed description of the measurement technique and measurement methods. We also recommend using a proper terminology of air ion classes (small or cluster ions, intermediate ions, large ions), introduced in page 25299, throughout the manuscript to avoid misunderstandings. Waterfall-generated ions cover the size range from about 1 nm up to 30 nm, from the cluster ion size range up to large aerosol ions; in some cases, the changes up to 350 nm in the size distribution can be seen. Therefore, the authors are asked to specify the ion group or size range of ions under discussion, instead of only using the term “WF ions”.

First of all we would like to thank the referee for the useful and constructive comments on the manuscript. We have accepted most of the comments and discussed each single point. The referee comments have been pasted below in italic (black) while our answers are colored in red and sections regarding the main text in italic (red).

Answer to General comments:

We appreciate the big effort of the reviewers to comment on our manuscript in detail. Reading of the comments and suggested literature improved our knowledge on this subject and hopefully made our article much better. We extended our introductory part, added 23 new references (listed below in section "New Added References"), added motivation and objectives. We amended the structure and inserted additional data. Air ion counter and measuring techniques are described in detail and adequate references have also been added. We unified air ion class terminology according to Hõrrak et al. (2000). Other improvements are listed in the section "Specific Comments".

Specific comments

Specific comments are given below in the order of the paper's sections (chapters).

Introduction

1.1 Air ions in the environment

Page 25298, lines 22-23. We cannot agree that the background concentration of air ions in the environment is about a few hundred per cubic centimeter. Probably the authors mean here only the cluster or small ion concentrations. For typical concentrations see Hirsikko et al. (2011).

We agree that it is not correct to define typical concentrations, that are varying on a very large scale. Measurements in Austrian alps (far from waterfalls at the reference sites) revealed daily ion concentrations of around 400 ions/cm^3 of each polarity, but during the evening and night measurements concentrations reached up to 2000 ions/cm^3 probably due to temperature inversion and trapping radon in near ground level. Therefore, we skipped that statement.

Page 25299, lines 1-5. The authors should specify the category of ions they are talking about - cluster or small ions.

We agree with the comment. We used size categorization provided by Hõrrak et al. (2000). Air ions are classified in: small cluster ions 0.36–0.85 nm (3.14–1.28 cm^{2}V^{-1}s^{-1}), big cluster ions 0.85–1.6 nm (1.28–0.5 cm^{2}V^{-1}s^{-1}), intermediate ions 1.6–7.4 nm (0.034–0.5 cm^{2}V^{-1}s^{-1}) and large ions 7.4–79 nm (0.034–0.00041 cm^{2}V^{-1}s^{-1}).

Page 25299, lines 5-7. The meaning of the sentence is hard to understand and it should be rewritten. We cannot understand how the lower mean mobility of positive cluster ions causes their lower concentration in the atmosphere. Due to the atmospheric electric electrode effect the concentration of positive cluster ions near the ground should be higher compared to the negative one. This is a generally known fact.
The lower mean mobility of positive ions plays a secondary role here, it only results in lower attachment rates of positive ions to the surfaces (aerosols, ground surface, vegetation canopy, etc) compared to the negative ones. Also, the beta-coefficient is called an effective attachment coefficient, which is an integral over the size distribution of aerosol particles (see Laakso et al., 2004; Hõrrak et al., 2008).

During our measurements in aerosol enriched or highly polluted air, we noticed that the unipolarity coefficient is rising along with the number of aerosols (especially in indoor environments). We relate this to the attachment coefficient but it can also be attributed to some other neutralization processes such as electrostatic deposition. Thus, we changed the sentence according to the comment:

The atmospheric electric electrode effect in near ground layer induces an imbalance between positive and negative small air ion concentrations and results in a ratio of n^+/n^- = 1.12 (Hoppel et al., 1986; Hõrrak, 2001).

Page 25299, line 10. The reader is referred to the original work by Hõrrak (2001). In addition to this PhD thesis it would be very advisable to refer to some more widely distributed journal article, e.g. Hõrrak et al., (2000).

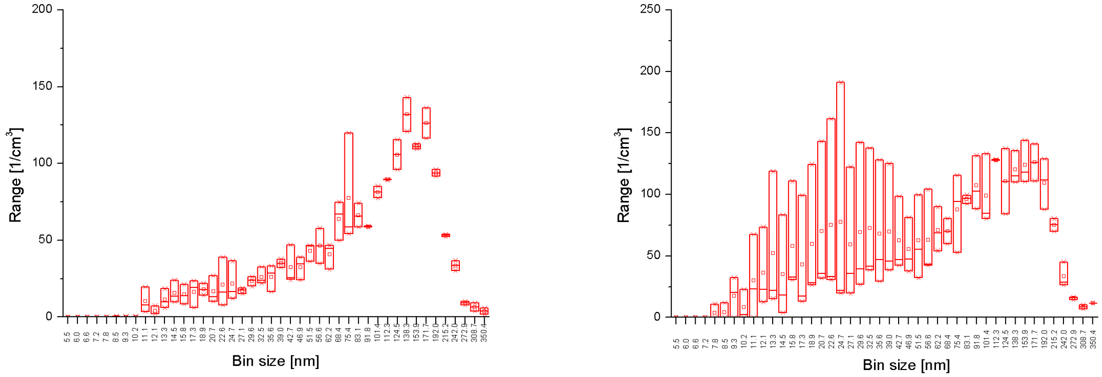
We added reference: Hõrrak et al. (2000).

Page 25299, lines 14-15. Only the cluster ions are supposed to carry one elementary charge, but not all the aerosol ions. Thus, the concretization is needed. The charging probability for multiple charges on atmospheric aerosol particles is still low up to about 40 nm.

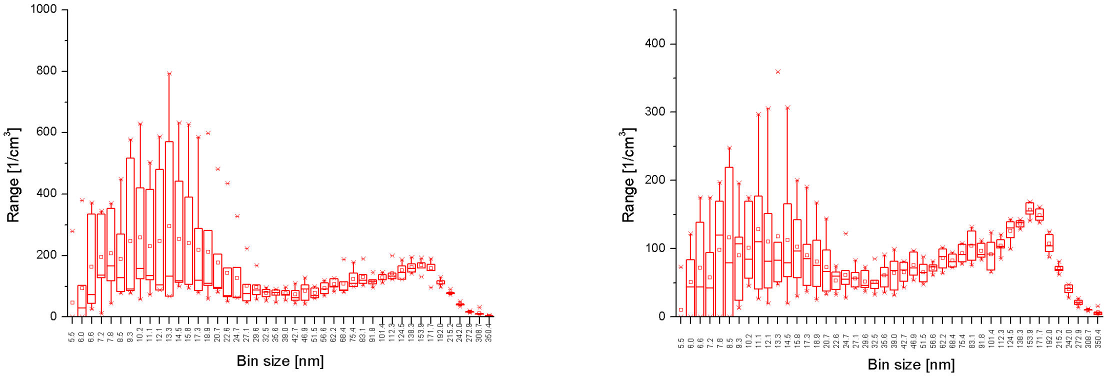
Thank you for this very important comment.

In our experimental setup we assumed that each aerosol size class is dotted with one single negative charge - even though we are all well aware of that larger diameters can easily occupy multiple charges. The use of a single SMPS device does not allow us to determine the exact amount of charge residing on particles of a given size class. The only way to determine the true value would be to use two SMPS' in series; within such a tandem design, the first DMA would be set to a given aerosol size class while the second DMA would screen the real quantity and along with the CPC also the corresponding diameter. By pooling the data of all 44 individually screened size classes into one graph containing all size classes one obtains the charge-diameter relationship for the entire spectrum between 5.5-350 nm. As such a design is rather inappropriate for field measurements, it should be done in the lab - as long as a 2nd DMA with a controller unit is available.

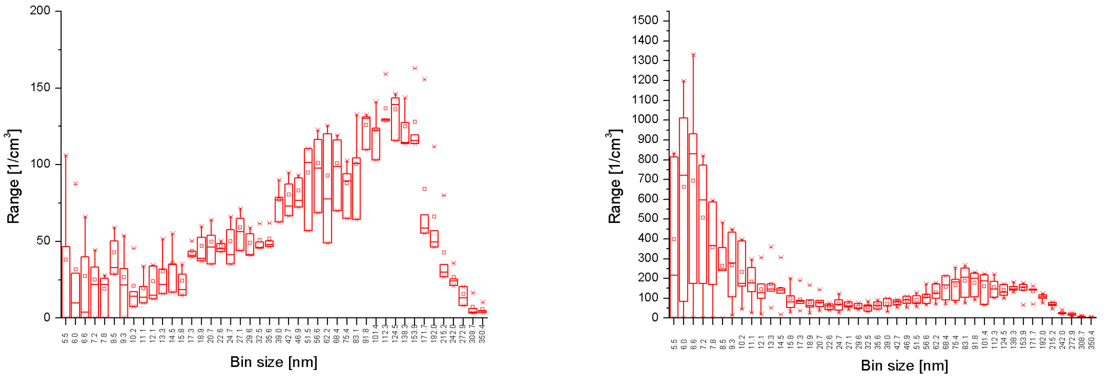
What does this mean for our field study? Since we operated our setup without the ^{241}Am neutralizer, it implies that the particles with multiple charges detected by the SMPS shift from the original size bin to one that corresponds to a net smaller size bin (due to the multiple charge loading, such a particle behaves like a smaller one); thus, the spectrum obtained with the SMPS in the larger size range (>50nm) is smaller in amplitude than it really is. The graphs below depict the sampled inventory belonging to a given site that was probed with (left plots) and without (right plots) the ^{241}Am radiation source (the neutralizer causes the aerosol to be discharged according to the Boltzmann distribution pattern). In both scans the 100nm fraction is well represented, whereas the 10nm range is completely stripped off the spectra when the ^{241}Am-source was attached to the DMA. This indicates that in comparison, the size distribution is present in principle, yet the actual number concentration of the raw aerosol (not using the ^{241}Am radiation source) can not accurately be determined with the setup we used.



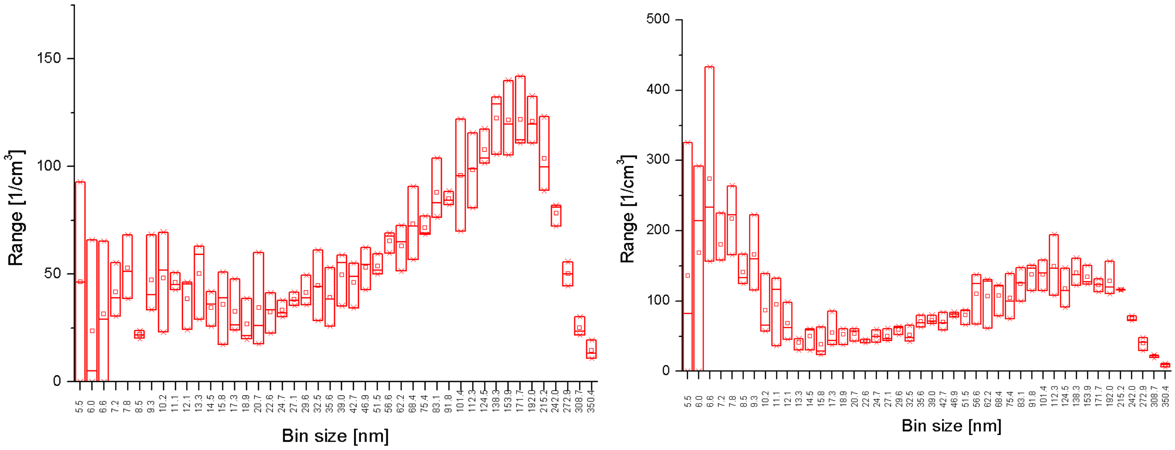
WP 73 Neulengbach Ref-Site - with ^{241}AM source (left) and w/o ^{241}AM source (right)



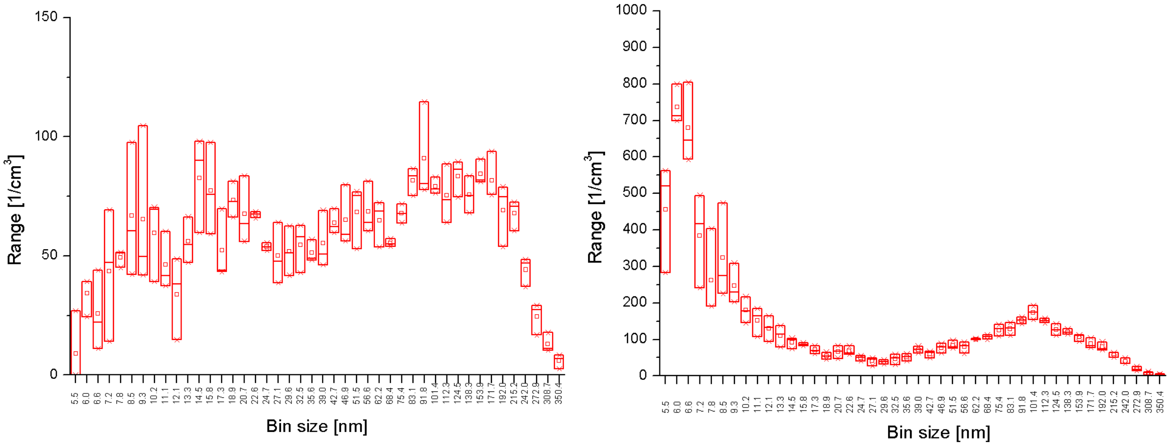
WP 74 Falkenstein Ref-Site - with ^{241}AM source (left) and w/o ^{241}AM source (right)



WP 55+72 Krimml WF - with ^{241}AM source (left) and w/o ^{241}AM source (right)



WP 101 Gartl WF - with ^{241}AM source (left) and w/o ^{241}AM source (right)



WP 104 Gartl WF - with ^{241}AM source (left) and w/o ^{241}AM source (right)

Since we assumed that multiple charges on water aerosols contribute in the distortion of the spectra towards the smaller size bins – a fact that can hardly be deduced from the above scans – the evidence presented so far shall be enough to say that multiple charges on few larger particles do not heavily interfere with the bulk of smaller particles. This assumption attains more weight if you look at the reference-site measurements presented above – they look pretty similar with and without the neutralizer (although Neulengbach looks a bit more nosier – but this could be the input of radon decay products).
We added three sentences, one in the Introduction and another two in the Discussion, respectively:

> *The effect of multiple charges is assumed to be significant in the case of heavy large particles >50 nm (Hõrrak, 2001) which is considered as artefact.*
>
> *By operating the SMPS with and without the ^{241}Am neutralizer, it was possible to uncover the differences in the spectra. Besides the sharp increase in sub-20 nm size range when the SMPS was operated without the neutralizer, the remainder of the spectra (20-350 nm) still reveal similar trends – regardless whether the neutralization source was attached or not.*

2 Methods

2.1 Instrumentation and measurements

Page 25300, section "Instrumentation and measurements". As mentioned above, more information is needed about measurement methods to understand and properly interpret the Gerdien counter (CDI-06) measurements. If we understood it correctly, the measurements have been performed at certain limiting mobilities, which correspond to the limiting diameters (or critical diameters) of 0.9, 1.5, 2 nm. The direct measurement data contain some information about the mobility distribution of air ions, but this information cannot be extracted without mathematical data processing. If any mathematical procedures have been used to derive ion mobility or size distribution form direct measurements of three different CDI-06s, these should be outlined in this section. As a comment we can say that the derivation of the ion mobility distribution from the integral counter measurements is a complicated task. The second order derivatives of the voltampere characteristic curve of the ion counter measurements should be found (see overview paper by Hirsikko et al. (2011)).

Gerdien condenser i.e. integral ion counters are used for the determination of ion mobilities in many previous measurements such as: Dhanorkar et al. (1991, 1992), Misaki (1961), Hõrrak et al. (2008), etc. They are not as accurate and narrowbanded as for e.g. a DMA (differential mobility analyzer) but their reasonable production price, portability and robustness compensate these disadvantages and allow measurement on nearly impassable terrains. In order to obtain a more precise mobility distribution from the integral ion counter, we applied the analysis as proposed by Flagan (1998), Horrak et al. (2008), and Tammet (1970). Current to voltage characteristics were recorded on several places near WFs where ion fluctuation was moderate and concentration of WF generated ions in abundance. After applying the second derivative of current to voltage (I toV) characteristic (using Origin) i.e. d^2I/dV^2 and V values, we calculated the contribution of ions larger than the polarizing voltage using formulation by Flagan (1998). Similar results were obtained using the method described by Horrak et al. (2008) when using the I to U curve tangent interception. The averaged excess signal generated by ions beyond the limiting mobility was estimated and incorporated into the measuring signal; that is: it was incorporated into the air ion concentration conversion factor (thereby reducing the multiplication factor). It was done for each instrument separately. This procedure is applied for the reason that on most of near WF measuring points recording of I-U curve makes no sense due to large fluctuations of ion concentrations and limited time for measurements caused by wetting. Specially knowing that quality of the 2nd derivative is depending on the number of recorded points, which requires long term measurements. That is why we used 3 detectors with fixed critical polarization voltages instead of changing the voltage or air-flow. On the other hand, three detectors enables measurement of only three ion mobility size classes, and therefore are not sufficient to precisely determine the dependence of the ion concentration on the reciprocal of the limiting mobility (or current-voltage characteristic curve).

We added following sentences to the section 2.1.

> *Correction of ion concentration for each mobility class was obtained using second derivation of current to voltage characteristics (Horrak et al., 2008, Flagan,1998) measured at the place where a sufficiently high concentrations of WF generated ions were present, while corresponding fluctuations due to gusts were moderate. The estimated correction was incorporated into the measuring signal to air ion concentration conversion factor. Further derivation of ions with critical mobilities of 0.55 and 1.18 $cm^2V^{-1}s^{-1}$ from integral values was obtained using the subtraction method as proposed by Dhanorkar et al. (1992); gaining ions in size windows of 0.36-0.9 nm, 0.9-1.5 nm and 1.5-2 nm.*

> *Although the determination of ion mobilities using integral Gerdien counters is not as accurate and narrowbanded as for e.g. a DMA (differential mobility analyzer), portability and robustness compensate these disadvantages and allow measurement on nearly impassable terrains.*

Regarding instruments installation, nothing is said about the electrical grounding (earthing) of spectrometers, which is also important in field measurements.

The collecting electrode is at virtual ground potential; the measuring system, including the polarization circuit, is galvanically separated from the power supply and the PC communications port (USB). Of course, each detector has its own power supply and one additional for the heaters if necessary. One more reference describing the ion detector in detail is added: Kolarž et al. (2011).

The radon activity-concentration counters RAD-7 and the Gamma Scout counter, as well as all the meteorological devices should also be described in this section. Radon counters are first introduced only in Page 25307.

The following sentence is added to section 2.1. Instrumentation and measurements.

> *Radon concentration in the air was measured with a continuous radon gas monitor RAD7 Durridge Co, USA (http://www.durridge.com). Natural radioactivity in the air was measured using a Gamma Scout counter based on Geiger-Müller principle (http://www.gamma-scout.com).*

Page 25300, line 19. The discrete sizes of 0.9, 1.5, 2 nm are given here, but the meaning of these discrete sizes remains unclear for the reader. It should be mentioned that ion concentrations were measured at certain limiting (or critical) diameters of 0.9,1.5, 2 nm. In addition to limiting diameters also the values of the corresponding limiting mobilities should be given. The limiting mobility is a characteristic of the ion counter and it enables a better comparison with other data than the diameter, which depends on the used mobility-size conversion algorithm and particle charge. We recommend presenting all the technical parameters of ion counters (voltage applied to the mobilityanalyzer, air flow rate, etc) operated under different regimes in a separate table.

We fully agree with the referee comment, we added limiting mobilities and belonging boundary mass diameters defined by Tammet, 1995.

The following sentences are added concerning measured ion mobilities and description of mobility analyser, although it is described in detail in new reference added Kolarž et al. (2011):

> *Integral aspiration counter also known as Gerdien condenser is the most commonly used tool for atmospheric conductivity measurements (Gerdien, 1905). Its operation is based on the polarizing voltage that is applied between two aspirated coaxial electrodes. Ions of the same polarity as polarising voltage are deflected toward the central electrode depositing charge ($q=1.62\cdot10^{-19}$ C) and generating current (I):*
>
> $I=n\cdot q\cdot Q$ *(2)*
>
> *where Q is air-flow through the electrodes.*
>
> *The critical mobility of the aspiration condenser (μc), determines the ion mobility above which all ions should be collected on the central electrode, and is defined as a combination of polarizing voltage (U) and air flow:*
>
> (equation 2 in Discussion manuscript) *(3)*
>
> *where R_2 and R_1 are the radii of the polarizing and collecting electrode; L is the collecting electrode length and V_S is the air velocity through the electrodes (Applin, 2005).*
>
> *Concentrations of small and intermediate ions with mobilities smaller than 0.3 $cm^2V^{-1}s^{-1}$ were measured using three identical Gerdien condenser detectors (CDI-06), made at the Institute of Physics, Belgrade. Using the dynamic property of ionic motion in an electric field, the polarizing voltage and air flow on three identical CDI-06 detectors was set to measure small cluster, big cluster and intermediate ions with the following critical mobilities: 1.18, 0.55 and 0.3 $cm^2V^{-1}s^{-1}$, which corresponds to the boundary mass diameters of 0.9, 1.5 and 2 nm (Eq.3). Ion mobility (measured by*

> *CDI–06) to mass diameter conversion was based on the formulation given by Tammet (1995). Selected critical mobilities correspond to characteristic ion-sizes originating from WFs, which is around 2 nm (Laakso et al., 2007) and by background ionisation sources as nuclear decay as well as cosmic rays - with the latter up to 0.9 nm (small cluster ions).*
>
> *The relatively large electrode cross–section (R_1=0.028 m, R_2=0.005 m) along with the central electrode length (L=0.4 m) provides a relatively high air flow (0.0048 m^3s^{-1}) and sufficiently intense signal to use a relatively small measuring resistor (R_M=1 GΩ) thus resulting in a reduced measuring uncertainty. The collecting electrode is at virtual ground potential; with the measuring system, including the polarization circuit, is galvanically separated from the power supply and the PC communications port (USB). Each of the three detectors has its own power supply, temperature, pressure and relative humidity sensor, and also features a sophisticated such as dynamic zeroing (eliminates zero offset drifts during measurements), live data acquisition, with programmable data averaging, sampling and polarity change options (Kolarž et al., 2011).*
>
> *According to Eq.2, the detector amplifier (i.e. A/D converter) output signal to air ion concentration conversion factor was calibrated prior each measurement using a Keithley Picoampere 261 source. The limiting mobility was calculated using Eq.3. Correction due to ion repulsion of small ions at the inlet of the detector (Anderson et al., 1991; Misaki, 1961) on detector measuring ions with lower mobilities (0.3 $cm^2 \cdot V^{-1} \cdot s^{-1}$), i.e. with highest polarizing voltage, was experimentally obtained and incorporated into measuring signal to air ion concentration conversion factor.*

Page 25300, lines 24-25, regarding the fragment of the sentence “The critical mobility (μc), i.e. the smallest ion mobility to be measured (maximum size), is defined as. . .”. This sentence is not correct. It is known that the Gerdien-type integral ion counter has a relatively flat transfer function, where the limiting (or critical) mobility determines its breaking point (Tammet, 1970; Flagan, 1998). Accordingly, the ions with mobilities above this limit are measured in the "saturation regime", while ions with mobilities below this limit are measured in the "conductivity regime" in proportion to their electrical mobility. Therefore, the “smallest ion mobility” is, in principle, equal to zero (or infinite particle size).

We agree, sentence is changed according to the comment.

Page 25301, lines 8-10. It is not obvious what the authors mean with the end of this sentence. Perhaps they mean “approximately equal air ion concentrations”?

We tried to explain that by using a better wording:

> *Away from the WF, in conditions where mostly small cluster ions prevail (except in cases of nucleation bursts of intermediate ions), two detectors that are measuring ions with lower mobilities should measure equal or slightly higher ion concentrations as one that is measuring small ions (Laakso et al., 2007). As stated above, similar applies to the ratio of positive and negative background ion concentrations on the reference sites where n^+/n^- should be about 1.12.*

3. Measurements and discussion

3.1. Study of 5 different WFs

Page 25302, regarding the section “3.1. Study of 5 different WFs”. Overview of the various measurement campaigns carried out during a three-year period at five different waterfalls is missing. It is recommended to add one table, which contains data about the time and duration of the campaigns, used instrumentation (CDI-06, SMPS, etc), number of measurements obtained etc. This table can, in principle, be companied also with Table 1.

Here is the overview of measuring campaign and the table, which has also been placed into the main text:

Section 3.

The study of WF-related aerosol inventory lasted for three years, from 2008 till 2010. At the very beginning measurements on several different WFs have been conducted - as shown in section 3.1. After locating the WF in Krimml as the most promising and convenient, spatial measurements at this WF have been done during June and September 2009 - shown in section 3.2. In section 3.3 measurements of ion *size distribution are presented in detail.*

Table 1 lists the height, average and maximal water flow of each WF, while positive and negative air ion averages and maximal number concentrations of ions are given in Table 2.

Table 1. WF height (approximate), average and maximal water flow.

WF name	*Height (m)*	*Average water flow* (m^3/s)	*Maximal water flow* (m^3/s)
Krimml	*140 x 100 x* ***140***	*5.1*	*17.5*
Stuiben	*150 x* ***150***	*1.6*	*2*
Bad Gastein	*310 (measured cascade* ***50****)*	*1.83*	*6.8*
Gartl	*100 (50 x* ***50****)*	*0.6*	*0.9*
Artificial (river Möll)	***5***	*1.33*	*4.66*

We added a whole new set of measurements that we carried out at Krimml WF during the project named „Immediate effects of waterfall ions on physiological parameters (during July and September of the year 2009). WF generated ion measurements were carried out simultaneously with exposure of every proband. Our intention is to describe short and long time ion concentration change and relation with seasonal water airflow. Measuring details are added to Section 3.2. as listed below:

A series of 7-day measurements of ions ≤2 nm have been performed and included two separate field campaigns: 10-26th of July as well as 09-23rd of September, 2009. Measurements were carried two times a day, and regards a sampling session during the morning hours (around noon) and one in the afternoon (around 16 h) for 1h each. This was done simultaneously along with the medical survey to monitor immediate responses of exposed individuals. According to the data provided by the authorities of the local hydro power plant, which is just 700 m downstream from the fall, the average water flow in June was 14.4 m^3s^{-1} *whereas in September it was 5.5* m^3s^{-1}*. The former is 2.6 times larger than the latter and directly correlates with the period of intensive glacier melting during summer. Daily variations of negative WF ion concentrations were within the 8% range. However, the average ion concentration in July (10944 ions·cm*$^{-3}$*) was 1.5 times higher than in September (7502 ions·cm*$^{-3}$*) of that year. While daily differences in ion concentrations are the consequence of local meteorological parameters, the significant difference between July and September are related to the reduced water masses during September. In any case, the drastic reduction in the amount of water flow affects negative ion generation and sinking ratio to a much greater extent than the suppressed generation in ion concentrations.*

Page 25303, lines 11-14. In order to draw this conclusion, the data in Table 1 should be complemented by additional data. It is recommended to include data about the characteristics of waterfalls (height, number of cascades, amount of water flow, surrounding topography), as well as data about ion background measurements in the vicinity of waterfalls.

This information can be found only for some waterfalls in the text, but for the comparison, it is better to concentrate it into one table.

We added table 1, as stated above and more topographic data in the text.

Page 25303, lines 23-26. The authors have pointed out that "one of the processes that contribute to WF ion generation is charge separation via aerodynamic break-up of micrometer-sized water droplets into nano-sized aerosols (Zilch et al., 2008)." A similar statement or assumption can be found in Page 25304, lines 5-8. We doubt that purely mechanical aerodynamic break-up or fragmentation by bubble bursting can generate nanometer size particles from large water drops. The microphysical mechanism behind this phenomenon is still unknown (see Tammet et al., 2009). Do the authors know any mechanical methods to generate nanometer size particles?

It's true in the subsequent publication "The formation of coherence domains for aerosolized water molecules at alpine waterfalls" (Madl et al., 2011 in revision), we indeed propose a quantum electrodynamic formation principle of the excessive negative charge that is based on the Josephson effect (Preparata, 1995).

3.2 Ion inventory at the Krimml WF

Page 25304, lines 15-16. Regarding the sentence "The height of the last WF cascade provides maximal velocity to water droplets as the flow reaches 53 ms−1". The reader may think and ask also about the speed of falling water droplets of different size. For example, the terminal velocity of about 6-millimeter raindrop in the atmosphere was found to be approximately 10 m/s.
Sentence is unnecessary and deleted.

Page 25304, lines 25-28 and page 25305, lines 1-5. This paragraph belongs to the section "Instrumentation and measurements".
Page 25306, lines 1-14. This paragraph mainly belongs to the section "Instrumentation and measurements".
We agree and therefore rearranged the paragraphs accordingly.

3.3 Ion measurements at the Krimml WF

Page 25306, line 15. The fragment of the sentence "Gradients of 0.9, 1.5 and 2 nm size positive and negative integral ion concentrations" considering specific discrete sizes and "integral ion concentrations" cannot be understood by the reader.
In Fig.7 integral ion concentrations are shown (*0.36-0.9 nm, 0.36-1.5 nm and 0.36-2 nm)*, meaning that no derivation of measured concentrations by mobilities was done. This is due to clarity of the graphs, otherwise lines are intersecting and graphs are confusing. Size limit corrections are added on Figures 7 & 11 and part of the sentence is changed to:

> *Integral values of ions with boundary size limits of 0.36-0.9 nm, 0.36-1.5 nm and 0.36-2 nm on orographic right side of Krimml WF are...*

Page 25306, lines 23-24. Taking into account the uncertainty of the measurements, there is no need for changing the values of alpha- and beta-coefficients to explain the qualitative difference between positive and negative WF-generated ion concentrations.
We cannot agree with this, as the Gerdien condenser is an integral instrument it is not the perfect instrument to distinguish narrow banded mobilities. However, it is accurate enough for integral concentrations that are sufficient for this kind of assumption.
However, this effect is not visible on other WFs. Our explanation is related to the overall dimensions of the Krimml WF that causes very untypical air motions in time and space scale – both are the consequence of the combined effects of all 3 cascades. Motion of gusts that carries aerosolized water causes high fluctuations in ion concentration. Somewhere in that vortex of parameters positive ions are neutralized. It is important to say that we have no doubts in the quality of our results since both statistics and repeatability (on large sets of data) of the measuring results are consistent.

Page 25306, lines 25-26. A short lifetime of WF ions, not allowing propagation to larger distances, could also be a reason for "Equalization of the smallest positive and negative air ion concentrations".
We consider that ion lifetime is determined by neutralization events occurring later on.

Page 25307, line 9. The radon dose rates are given in units of mSvh−1, but for comparison with the RAD-7 data it is recommended to present the data also in the activityconcentration units (Bqm−3) if possible.
Sievert is the unit for absorbed biological dose while Becquerel represents the radioactive decay per second. These should not be mixed.

Page 25307, line 12. It is not obvious which one of the "air ion concentration peak at the reference point (547 m)" is mentioned. Please indicate the corresponding peak size in Figure 9.

Figure numbers are added.

Page 25307, line 15 and line 28. The discrete size of ions (0.9 nm) is not understandable for the reader here. Please consider recommendations given for the section "Instrumentation and measurements".

It is redefined as: ions with boundary diameter of 0.9 nm. Definition of measuring ranges is added in section "Instrumentation and measurements", as discussed earlier.

Page 25307, line 26. We did not understand the part of the sentence "clustering took place into a size window at around 120 nm". What does "clustering" mean here?

Clustering in this sense represents agglomeration of smaller particles to larger ones. This results in a decrease of the smaller size ranges and at the same time into a GMD (Geometric mean diameter) shift away from the smaller to the larger diameters – this hold only if no freshly made smaller ones are fed into the system. A continuous production of smaller particles yields a dynamic equilibrium that seems stationary, yet only a geographical shift away from the WF reveals the obvious shift in GMD.

3.4 Ion measurements at the Gartl WF

Page 25308, line 20. The sentence "Figure 13 depicts the negative ion concentrations vs. aerosol size" sounds a bit strange – "ions" versus "aerosol". Actually, the authors mean the ion concentration distribution by their size, assuming that ions carry one elementary charge.

We agree, sentence is partially changed according to the comment. Also figure captions 9 and 13 are changed according to comment.

4 Conclusion

Page 25309, lines 5-6. Regarding the statement that "ion size distribution was found to be almost identical". The statement is incorrect. It follows from Figures 9 and 13 that the size distributions have a similar shape, but the concentrations are significantly different.

We agree, sentence is partially changed according to comment:

> *…. ion size distribution was found to be similar in shape and in very good agreement ….*

Page 25309, line 7. A lower limit of the size range of 0.2–25 nm is probably a mistake.
It was not mentioned anywhere in the text before. Also, it is difficult to understand how this lower limit was found from the integral ion counter measurements. An explanation is needed.

The 0.2 nm ions are a mistake. The actual limit is 0.36 nm, which is the smallest ion diameter according to Hõrrak et al. (2000).

Page 25309, lines 10-11. Ions with discrete mobility-sizes (0.9, 1.5 and 2.0 nm) should be appropriately designated.

We agree, sentence is partially changed according to the comment:

> *The generation of ions within the range of 0.9-1.5 nm was less dominant than those at 0.36-0.9 and 1.5-2.0 nm.*

Page 25309, lines 10-11. The statement "The generation of 1.5 nm ions was less dominant than those at 0.9 and 2.0 nm" should be clarified. This statement is based on the size distribution data in Figures 9 and 13, but it seems to be inconsistent with the data in Figures 7 and 11. In both cases, the ion concentration data have been given.

In Figures 7 and 11, integral concentrations of ions are given. Otherwise, those graphs are unclear because lines are intercepting.

Page 25309, lines 12-14. Considering the explanation of the variation of positive ion concentration generated by different waterfalls. The statement that these variations can be ascribed to the increase in *the small ion recombination coefficient is rather strong. This is not sufficiently explained for being stated in the conclusions. We also have some doubts about the correctness of the statement itself.*

We agree that we have no sufficient data for this type of conclusion. Unfortunately SMPS could only be used to measure negative ion concentrations. Further research shall include devices that cover the intermediate region between 2 and 5.5 nm and to extend positive ion characterization.

Page 25309, lines 14-16. In the conclusion, the authors have listed numerous parameters that could affect the concentration of waterfall-generated ions, but many of them remained mainly without proof in this paper. The authors should show that these parameters can really be considered as factors, or list in the conclusion only those, whose effect is proven.

We agree, therefore we added a whole new set of measurements (can be found in answer to comment: Page 25302, regarding the section “3.1. Study of 5 different WFs” and data with analysis. Also, unproven parameters are deleted as follows:

> *Although the daily as well as seasonal variations of WF-related water masses (maxima versus minima differ by one to two orders of magnitude) is reflected in the fluctuating ion concentrations, concentration maxima of generated ions are more related to the geological structure of the WF than on the amount of water pouring down. Nonetheless, the combined mix of parameters such as topographic configuration (height and shape of the WFs and surrounding rock topography), quantity of water and local meteorological conditions are reflected in the detected ion concentrations of the fall. These parameters also determine the quantity of water aerosols dispersed in the air, which in turn, can increase the ion sink rate.*

Page 25309, lines 17-18. Regarding the sentence “These parameters determine the quantity of aerosolised water in the form of the ion neutralization coefficient”. It is hard for the reader to understand the meaning of the end of the sentence “aerosolised water in the form of the ion neutralization coefficient”.

We agree, the sentence is partially changed according to the comment using expression: water aerosols dispersed in the air.

Page 25309, lines 18-21. Hopefully the authors mean "bubble break-up on aqueous surfaces” and “splashing of water on solid surfaces". Please consider a revision. We did not find much discussion in the paper about the contribution of different mechanisms (bubble break-up on aqueous surfaces, splashing of water on solid surfaces, aerodynamic break-up of droplets) to the generation of “waterfall ions” to allow concluding that the first two are more important than the third one. If possible, please consider it in the revised manuscript.

We agree, sentence is partially modified according to the comment as follows:

> *Compared with the measurements from the artificial WF, we can conclude that bubble break-up on aqueous surfaces along with splashing of water on solid surfaces and the aerodynamic break-up of larger water droplets are three major sources of WF-related ions.*

Page 25309, Conclusion. Unfortunately, we did not find any conclusions about the spatial distribution of the concentration or its gradients of waterfall-generated ions measured by the CDI-6, as well as the unipolarity coefficients of ions in the Conclusion.

We agree, following sentences are added:

> *Spatial distribution of aerosolised ions of alpine WFs is attributed to air flow trajectories, which typically follow the course of the river bed. In the case of the Krimml WF, generated ions reached distances up to 500 m which implies maximal WF-related ion lifetime of approximately 120 s.*
>
> *Average negative ion concentrations have been found to be 11 to 80 times higher in the vicinity of the WFs than at their control points. Positive ions are also generated by WFs, but their near WF to control place concentration-ratio never exceeded a value of three.*

Figures

Page 25318, Figure 6, Page 25319, Figure 7 and Page 25323, Figure 11. Reading the figure captions, one can understand that there are "ion concentration gradients" given in these figures, but really there are ion concentrations.

Figure captions is changed to:

> *Integral ion concentration distribution by ion boundary diameter and polarity versus distance, measured..*

Also measured integral values (0.36-0.9 nm, 0.36-1.5 nm and 0.36-2 nm) are added on the graphs due to clarity.

Page 25321, Figure 9 and Page 25325, Figure 13. It remains unclear for the referee, as well as for the reader, how the data-points of the size distribution below 5 nm were determined from the integral ion counter measurements.

Data between 2 and 5 nm are interpolated by cubic B–spline. Derivation of ions with sizes 0.36-0.9 nm, 0.9-1.5 nm and 1.5-2 nm from integral values was obtained as described in the answer to previous comment starting: *Page 25300, section "Instrumentation and measurements".*

Ion mobility (measured by CDI–06) to mass diameter conversion was based on the formulation given by Tammet (1995).

Page 25324, Figure 11. It is interesting to know, why the measurements were limited up to the distance of 120 m from the Gartl waterfall, while at the Krimml waterfall the measurements were made up to about 550 m (see Figures 7 and 11). Taking into account the initially higher concentration of ions at the Gartl waterfall, it is expected that their influence can be found also at longer distances. Is there any orographical reason for stopping the measurements at 120 m and believing that the situation does not change farther off? The first coinciding data point of positive and negative ion concentrations shown in Figure 11 at 120 m may be occasional.

Unlike the Krimml WF where the terrain past the WF is flat, the terrain at Gartl WF is going a steep downhill track with cliff projecting into the valley even after 120 m.

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