Interactive comment on "Characterization of ions at Alpine waterfalls" by P. Kolarž et al.
Anonymous Referee #2
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General Comments

Manuscript presents inventive experiments and interesting ion data measured nearby waterfalls in the Austrian Alps. However, the authors could go more in detail with their data (i.e. temporal variation of ion concentrations and ratios), and add some more discussion related to motivation of their work, measurements and conclusions. After considering following comments, I recommend publishing this manuscript in the Atmospheric Chemistry and Physics.

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 coloured in red and sections regarding the main text in italic (red).

Specific Comments

Please discuss the motivation of your work, i.e. why did you characterise waterfall generated ions. I think it is good to indicate some of the main research aims already in the abstract (p. 25298) and continue more in detail in the introduction.

In an amended version of the manuscript we have highlighted the scientific motivation on several occasions. In Abstract:

Here, we present spatial, time and size distributions of waterfall generated ions under the influence of surrounding topography.

In Introduction

The motivation of this study was to investigate the spatial and mobility distributions of WF-generated ions which are influenced by location - specific WF physics and orogenic structures in the region of the Austrian Alps. The physical characterization of WF-generated ions was part of a clinical field study, which focused on the influence of these ions and WF generated aerosols on human physiology. Within this study we analysed five WFs to investigate the different properties of ions originating from each WF.

Currently introduction discusses air ions in general (p. 25298-25299) and possible information pathways of waterfall generated ions (p.25299-25300). I recommend compressing the first part to give only relevant background information, and extending the discussion of the later topic, which is more essential for this manuscript.

We significantly extended the discussion section but according to comments of the other reviewers, we also extended the introduction part.

3. Throughout the manuscript, please pay attention that you are consistent with names of charged particles (i.e. waterfall generated/natural small ions (< 2 nm in diameter) and charged particles (> 2 nm in diameter)) and size ranges (i.e. smaller than 2 nm or narrow size range around 2 nm). In this manuscript detailed size classification is unnecessary and may be confusing (p. 25299, l. 10-14).

According to the comments given by all three referees, we rearranged names of size classes to the 4 most important for this work. It is essential to distinguish size range of background small cluster ions generated by radioactive decay and cosmic rays from big cluster ions and intermediate ions. Also, concentration peak of WF generated ions is in intermediate size range.

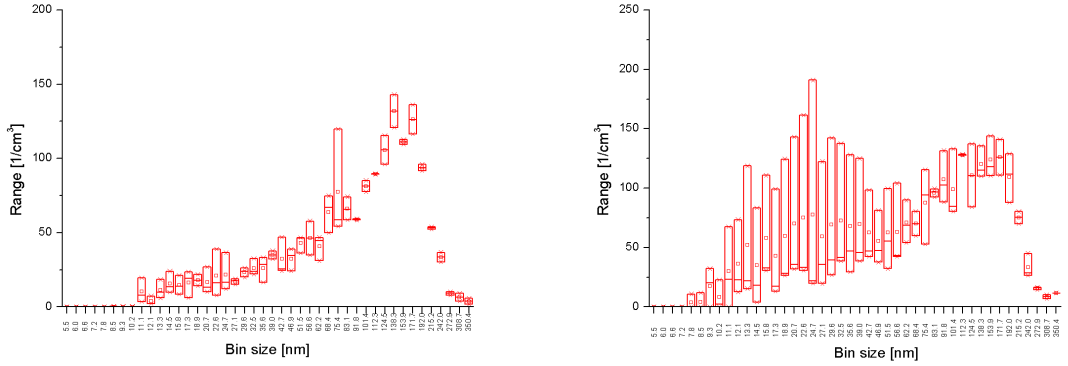
Concerning the distribution of measured small and intermediate ions versus mobilities, we defined ions with limiting mobilities: 0.3, 0.55 and 1.18 $cm^2V^{-1}s^{-1}$, which corresponds to the boundary mass diameters of 0.9, 1.5 and 2 nm (Tammer, 1995). Since measured values are the integral, the following ion size classes are obtained after subtraction: 0.36-0.9 nm, 0.9-1.5 nm and 1.5-2 nm.

4. As I understand, the authors have assumed that all air ions (natural and waterfall generated) are singly charged (p. 25299, l. 14-16). This assumption holds for ions small enough. However, with increasing size multiple charges should be included in the mobility diameter conversion. Unfortunately, the charge distribution as a function size for waterfall generated ions is unknown. This is especially a problem when analyzing and discussing SMPS size distribution data. This should be considered when finalizing the manuscript.

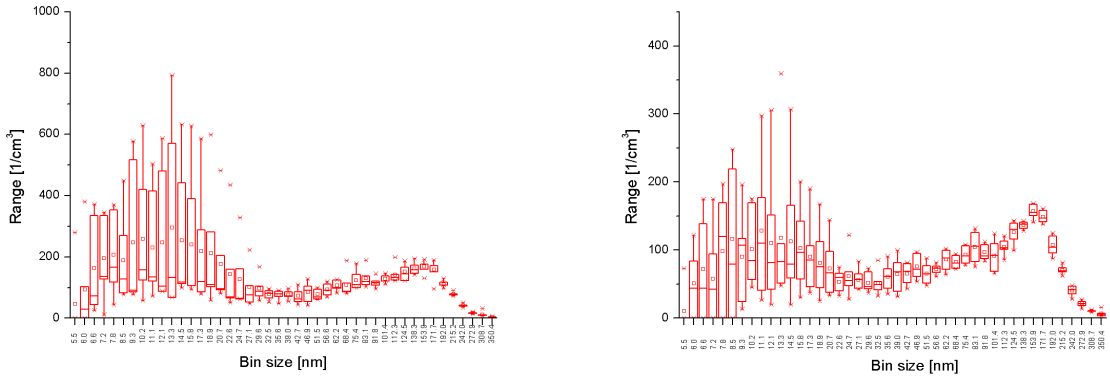
The issue of the multiple charges was of concern to all three referees. For better visibility the same answer was repeated in all three referee comments.

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.

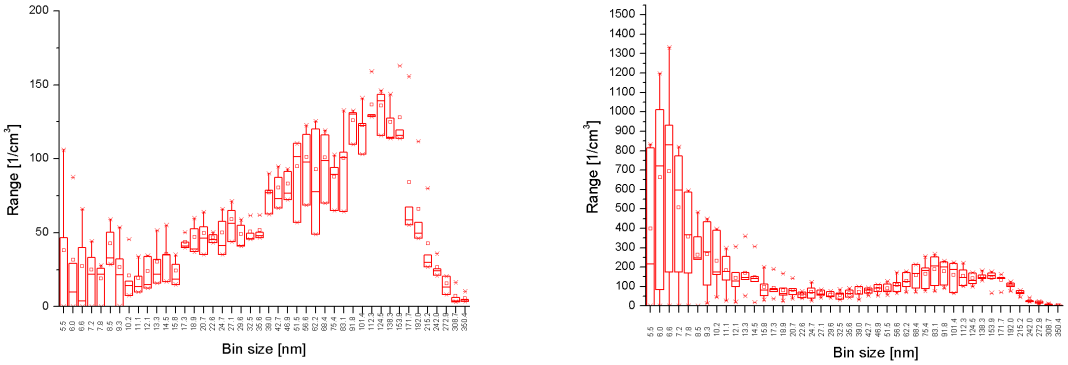
What does this mean for our field study? Since we operated our setup without the ^{241}Am neutralizer, it implies that the particles with multiple charges detected by the SMPS shift from the original size bin to one that corresponds to a net smaller size bin (due to the multiple charge loading, such a particle behaves like a smaller one); thus, the spectrum obtained with the SMPS in the larger size range (>50 nm) 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 100 nm 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.



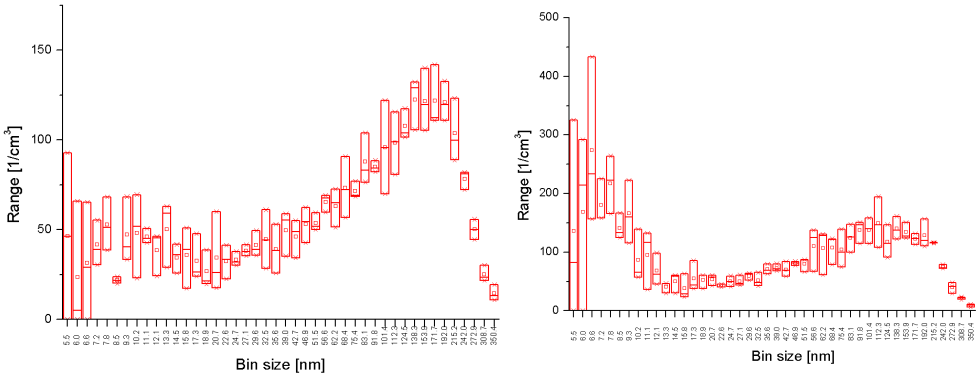
WP 73 Neulengbach Ref-Site - with ^{241}AM source (left) and w/o ^{241}AM source (right)



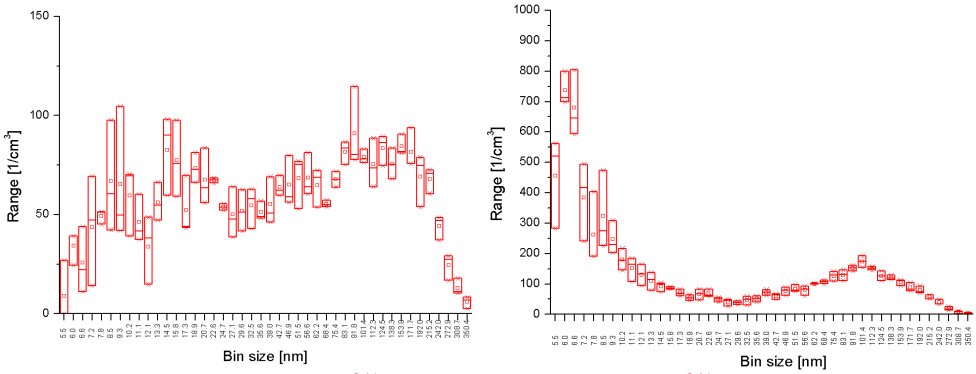
WP 74 Falkenstein Ref-Site - with ^{241}AM source (left) and w/o ^{241}AM source (right)



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 noiser – 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:

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.

5. p. 25300, l. 17. To make manuscript more fluent, please describe more in detail all measurement sites and measurement periods at each site.
6. p. 25303, l. 5-9: If possible show some more detailed analysis based on your data.
We agree with both comments. Accordingly, in Section 3. we added an overview of the measurement times:

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.

In Section 3.1 measurement site is described in detail:

However, the topography of the Austrian Alps often implies glaciers that feed their liquid phase into creeks. Runoffs often make their way downhill in turbulent conditions through the valleys. The collecting torrent form little cascades that also generate WF ions leading to variable ion distribution spectra in their embedded areas. Measurements at every WF have been carried out during midday along existing footpaths. Measurements were performed using a CDI-06 setting that has been configured to measure ions with mobilities up to 1.18 $cm^2 \cdot V^{-1} \cdot s^{-1}$ (e.g. for 2 nm ions). 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. An important feature of the artificial WF at the river Möll regards the manner water makes its way downhill - there it pours straight past a manmade barrier into the bottom pond, so that no water splashing on rocks does take place. At all sites ion concentrations were measured at places of maximal ionization and moderate wetting of the instruments. The highest average concentration increase of negative ions up to 2 nm in comparison to control point concentration was found to be 80–fold. Evidently, alpine WF ion concentrations fluctuate depending on the WF sampled. Ion averages at the examined sites typically depend on the amount of water flowing, which is subject to seasonal variations and oscillate with the melting of the glaciers. In contrast, the origin and structure of the ions generated at reference sites arise mostly from natural radioactivity, which is subject to diurnal changes and related to the fluctuation in concentrations of radon, thorium and their progenies..

In Section 3.2. we have added whole set of measurements and analysis concerning temporal variations of ion concentrations:

During the 2009 field campaign, 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.

7. The conclusions should be extended to show the importance of the results (p. 25309): I would appreciate if discussion of connection between results and research aims would be included.

We extended the conclusion and relate it with motivation.

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.

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.

Important result of this study relates to the impact of ions and aerosols generated by waterfall on human health. Spatial and size distribution, polarity ratio, ion lifetime and size are crucial for defining charged particles that are penetrating human lungs. Article concerning this subject is submitted.

References used in the comments section:

Tammet, H.: Size and mobility of atmospheric particles, clusters and ions, J. Aerosol. Sci., 26, 459–475, 1995.