ATMOSPHERIC IONS

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ABSTRACT: The amount of publications about atmospheric ions has not increased in the last decade. During the review period of 1999-2002, the most popular topic was ion-induced nucleation. Considerable progress was achieved in the understanding of the chemical composition of atmospheric cluster ions, in the study of the mobility distribution of atmospheric ions, and in the development of measuring methods.

INTRODUCTION

The present review examines the statistics of papers and selected results about atmospheric ions published during 1999-2002. References have been found from databases using the keyword combination:

"atmospheric ions" OR "air ions" OR "ion-induced nucleation".

The amount of newspaper publications and Web resources on the biomedical applications of air ions is huge. GOOGLE provides about 1330 matches on the search term "air ions". A popular free source of scientific information WWW.SCIRUS.COM does not include publications in many important journals e.g. J. Geophys. Res., Geophys. Res. Lett., and Aerosol Sci. Technol. Thus the specific resources were used.

STATISTICS OF PUBLICATIONS

The number of publications concerning atmospheric ions has decreased during the last decade. The reference base for the present review consists of 90 journal papers dating from 1999-2002. Distribution of these papers according to the main subject is shown in Table 1.

Table 1

Distribution of papers in scientific journals according to the main subject matter

Main subject	Papers
Biomedical effect and applications	20
Ion-induced nucleation	17
Measuring methods and instruments	13
Chemistry and physics	12
The middle and upper atmosphere	6
Measurements in the lower atmosphere	5
Role in particle deposition	5
Role in climatology	5

Four years ago, the most popular journal was J. Aerosol Sci. The situation has changed and in 1999-2002 the most popular journals were J. Atmos. Solar. Terr. Phys. (6), Atmos. Res. (5), J. Geophys. Res. (4), Rev. Sci. Instr. (4), and J. Electrostatics (4). The numbers indicate the amount of published papers about atmospheric ions. The single monographic paper about atmospheric ions in the review period is the PhD thesis by Hõrrak [2001].

ATMOSPHERIC IONS OR AIR IONS?

Different authors prefer different terms. Some of the terms used are "air ions", "gaseous ions", "ions", "chemiions". The main alternative for "atmospheric ions" is "air ions". When considering the above mentioned 90 journal papers, "atmospheric ions" was preferred 20 times and "air ions" 40 times. 17 of the latter papers discuss biomedical applications where the ions are not of natural origin but created in the air using air ionizers. When considering only atmospheric applications then "atmospheric ions" was preferred 19 times and "air ions" 23 times. Thus the term "air ions" seems to be slightly more popular even in atmospheric research.

The meanings of these two terms are not exactly identical: "atmospheric ions" is seldom used when speaking about artificially generated ions. The concepts of "gaseous ions", "air ions" and "atmospheric ions" can be presented with three ellipses as in Figure 1.

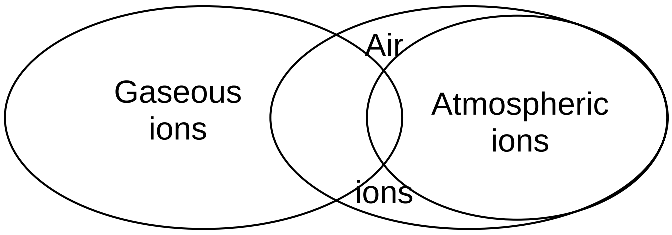

Figure 1. Relations between the three concepts.

All atmospheric ions are the air ions but not all of them are the gaseous ions. Large ions are not called ions in physics and chemistry where they are considered as charged macroscopic particles.

PROGRESS IN THE CHEMISTRY OF ATMOSPHERIC IONS

Beig and Brasseur [2000] developed a complex model of atmospheric ion composition including the existing theoretical knowledge and results of known measurements. The presence of charged nanometer particles is considered in the model. The model contains several new families of atmospheric ions. Neutral compounds, that are responsible for the formation of positive cluster ions in the troposphere, include ammonia, pyridine, picoline, lutidine, acetone, etc. Model results for positive small ions show that pyridinated cluster ions are most abundant up to about 5 km altitude. Above 7 km, ions having acetone as parent neutral species are in majority. Ammonia and methyl cyanide cluster ions are found to be less abundant. Above 13 km the relative abundance of methyl cyanide cluster ions is rapidly increasing. The concentration of pyridinated compounds is variable from one location to another and the relative abundance of ammonia cluster ions could be high in some remote environments. The model shows that $NO_3^- \times HNO_3 \times (H_2O)_n$, HSO_4^-, and NO_3^- families of ions are the most abundant negative small ions in the troposphere during nighttime. The first family dominates below 6 km, whereas the second type dominates between 6 and 10 km. NO_3^- core ions are the most abundant ions above 10 km. Some observational data suggest a dramatic increase in the concentration of sulfuric acid, malonic acid, and methane sulfonic acid during daytime with a related change in the negative ion composition. The model by Beig and Brasseur suggests that under these conditions HSO_4^--core ions can be the dominant ions below 10 km altitude.

PROGRESS IN THE MEASUREMENT OF MOBILITY DISTRIBUTION

Hõrrak [2001] published the summary of the ground level atmospheric ion measurements carried out at Tahkuse, Estonia, during 1993-1994. The mobility distribution of two polarities was continuously recorded as 20+20 fraction concentrations in the mobility range of 0.00041-3.2 $cm^2V^{-1}s^{-1}$. Regularities in the variation of the mobility distribution were found and discussed. It was shown that the atmospheric ions of different mobility classes vary relatively independently and the boundaries of these classes make up the natural classification of atmospheric ions that could replace the common formal classification. The boundaries of natural mobility classes were determined using the methods of mathematical statistics. The resulting classification is presented in Table 2.

Table 2

Natural classification of atmospheric ions according to Hõrrak et al [2000].

Class of air ions		Mobility $cm^2 V^{-1} s^{-1}$	Diameter nm
Cluster ions	Small cluster ions	1.3–3.2	0.36–0.85
	Big cluster ions	0.5–1.3	0.85–1.6
Aerosol ions	Intermediate ions	0.034–0.5	1.6–7.4
	Light large ions	0.0042–0.034	7.4–22
	Heavy large ions	0.00041–0.0042	22–79

PROGRESS IN THE STUDY OF ION-INDUCED NUCLEATION

The ion-induced nucleation is considered as a mechanism explaining the climate effect of cosmic ray and Solar wind variations. Mechanisms of the climate change have been in the focus of awareness and the ion-induced nucleation has deserved special attention during the review period.

Yu and Turco [2001] studied the role of background ionization in the generation and evolution of nanometer particles in the marine boundary layer. They built a mathematical model that includes the entire course of particle evolution from the initial neutral and charged molecular clusters through their growth into stable nanoparticles. The model is based on a kinetic mechanism that treats the interactions between vapors, clusters, and particles of all sizes. The model calculations show that atmospheric ions could play a central role in the formation of new nanometer particles. The nucleation of aerosols under atmospheric conditions involves a series of competing processes, including molecular aggregation, evaporation, and scavenging by preexisting particles. In this highly sensitive nonlinear system, electrically charged embryos have a competitive advantage over similar neutral embryos. The charged clusters experience enhanced growth and stability as a consequence of electrostatic interactions. The key parameters of the model are the concentrations of precursor vapors and the surface area of preexisting particles, as well as the background ionization rate. It was shown that systematic variations in ionization levels due to the modulation of galactic cosmic radiation by the solar cycle are sufficient to cause a notable variation in aerosol production. This effect is the greatest when the ambient nucleation rate is limited by the availability of ions. Hence the greatest influence of such ionization is expected in clean air e.g. over the oceans and in the Arctic.

Laakso et al. [2002] created an alternative model for ion-induced nucleation and charged aerosol dynamics largely based on the thermodynamic approach. It was found that ion-induced nucleation is able to produce a considerable amount of new particles if the preexisting particle concentration is sufficiently low. Also, when only positive or negative ions nucleate a large amount of particles in observable sizes can be produced. It was also found that continuous nucleation can occur in the particle sizes below the detection limit of most commonly used aerosol instruments at low temperatures and high preexisting particle concentrations. In some simulated conditions, a fair agreement with the observed particle formation events in the boreal forest environment was achieved. According to the results, in certain situations ion-induced nucleation changes the charge distribution of the particles, which may allow the observation of ion-induced nucleation in the atmospheric conditions.

PROGRESS IN MEASURING METHODS AND INSTRUMENTATION

The two bottlenecks in the detailed analysis of atmospheric cluster ion mobility distribution are the Brownian broadening of the transfer function and the electrometric noise that limits the sensitivity of the instruments and the real mobility resolution. Innovative work has been done at Yale University. Fernandez de la Mora [2002] thoroughly analyzed the diffusion-limited resolution of aspiration mobility analyzers, regarding the air flow character that depends on the convergence of the flow channel. He showed that the converging geometry offers much better resolution than the traditional cylindrical geometry due to the possibility to work in a regime of high Reynolds number without losing the laminar character of the air flow. Camero-Castano and Fernandez de la Mora [2000] developed a condensation nucleus counter, which is able to detect the cluster ions. The counting of individual small ions offers a dramatic improvement of the sensitivity of mobility analyzers.

The progress in electronics allows to improve the performance of instrumentation. The integrated programmable atmospheric ion mobility spectrometer by Aplin and Harrison [2001] is a good example here. The electronic switching system permits the selection of different mobilities. Mobility spectrum information is extracted by varying the deflecting voltage under full computer control. The measurement error has been brought down to 1%, and the minimum mobility is of 0.1 $cm^2\,V^{-1}\,s^{-1}$.

Considerable technological progress has been achieved in Ion Mobility Spectrometry (IMS). IMS [see Eiceman and Karpas, 1994] is a method of analytical chemistry and it does not belong to atmospheric electricity. However, the knowledge and experience in IMS can be used in the study of atmospheric cluster ions. IMS instrumentation is produced commercially. International Journal of Ion Mobility Spectrometry was founded in 1998. The 12th International Conference on IMS will be held in Sweden on July 27 – August 1, 2003. Information can be found on the Web page of International Society for IMS, http://ims.isas-dortmund.de. It can be expected that the progress in IMS could provide useful information for the scientists, who are developing the methods and instruments for the analysis of mobility distribution of atmospheric ions. An instrument developed by Nagato [2001] provides a good example of usage the IMS techniques in atmospheric ion research.

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