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# Generation and Determination of Negative Air Ions

Hai-Feng Lin<sup>1</sup> · Jin-Ming Lin<sup>1</sup>

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**Abstract** This review intends to cover a range of brief description of the generation mechanisms, the determination of the concentration, and the identification of negative air ions (NAI). This is divided into two parts: (i) it pays attention to the generation of NAI, which contains natural and artificial methods. According to the variation of energy in the environment, different methods based on natural generation are introduced in detail. As for artificial generation of NAI, corona discharge is dominantly elaborated due to its preponderance in convenient to control of the concentration of ions. (ii) it tends to introduce the determination of NAI, containing quantitative and qualitative detection, by using ion counting device and mass spectrometer, respectively.

**Keywords** Negative air ions · Generation · Determination · Ion counting device · Mass spectrometer

## Introduction

Negative air ions (NAI), arousing considerable interest in the application of air ionizers to purify air condition, are known as “air vitamin”, which plays a significant criterion when it comes to air quality evaluation [1, 2]. Abundant negative air ions, which are clusters of molecules, exist in natural environments such as forests, waterfalls, and rainstorms, in a range of approximately  $0.5 \times 10^3$ – $10 \times 10^3$  ions/cm<sup>3</sup> [3].

Comparing with natural generation of NAI, devices that produce air ions artificially are available for obtaining high concentration of NAI by providing sufficient energy via ionizing radiation or high-voltage potential which results in the loss or gain of an electron to form an ion [4].

In 1889, Elster and Gertel independently found the existence of NAI [5]. Promptly thereafter, a lot of papers reported their experimental findings to demonstrate a variety of physiological and biochemical responses in human and other organisms. For example, NAI play a positive role in altering the concentration of serotonin and cyclic nucleotides in the cerebral cortex of rats [6]. After that, various researchers demonstrated that NAI inhibit the growth of microorganism [7, 8].

In recent years, researches on NAI mostly focused on correlation, qualitative, and quantitative aspects. Correlation researches pay close attention to the relationship between the concentration of NAI and temperature, humidity, environmental pollution, and the wind effect index. Quantitative researches keep a watchful eye on the determination of the concentration of NAI and the controlling of the concentration of ion generation while qualitative researches concern the identity of NAI. Many electric appliances have negative-ion functions [9]. There is a great potential for utilization of NAI generators in preventing decay of fruits and vegetables [10], reducing the ambient air microbial load [11] and hospital-acquired infections in clinics [12, 13] as well as preventing the spread of diseases in animal houses [14].

## The Generation of NAI

The generation of NAI can be divided into two types: natural generation and artificial production.

✉ Jin-Ming Lin  
jmlin@mail.tsinghua.edu.cn

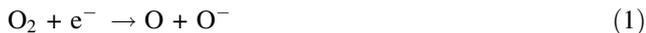
<sup>1</sup> Beijing Key Laboratory of Microanalytical Methods and Instrumentation, Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

## Natural Generation of NAI

The energy required to ionize atmospheric molecules, such as cosmic ray and ultraviolet radiation, electrostatic force, photoemission, photosynthesis, lighting excitation, directly results in initial ionization of the neutral gas molecules. The air is dominantly composed of nitrogen and oxygen, whose ionization energy is of the order 14.5 eV (1400 kJ/mol) and 13.5 eV (1300 kJ/mol), respectively. Therefore, the energy can extract an electron from atmospheric gases when it is more than 1400 kJ/mol. Generally speaking, there are six classifications of naturally-occurred NAI from the source of energy required for gas ionization, including cosmic ray, ultraviolet radiation and photoelectric emission, ray released by radioactive elements in rock and soil, waterfalls impact and friction, lighting excitation and storm, photosynthesis, the mechanisms of which is introduced as follows:

**The source from cosmic ray** With tremendous power, cosmic ray was absorbed by Earth's atmosphere mainly contributing to the initial ionization of atmospheric gases. After the ionization event, if the free electrons initially produced have sufficient energy (>360 kJ/mol), then oxygen radicals can be produced by the dissociative attachment process, as shown in Fig. 1.

The process can also be demonstrated through chemical equation as follows:



The initial  $\text{O}^-$  can contribute to the formation of secondary ions, such as  $\text{CO}_3^-$  and  $\text{O}_3^-$ , by collision-aided electron attachment processes as follows:



The secondary ions in turn lead to the formation of tertiary ions. Through cyclic process, a large number of NAI were produced, called "avalanche effect". If the energy is high enough,  $\text{O}_3$  can be produced in relatively small concentrations.



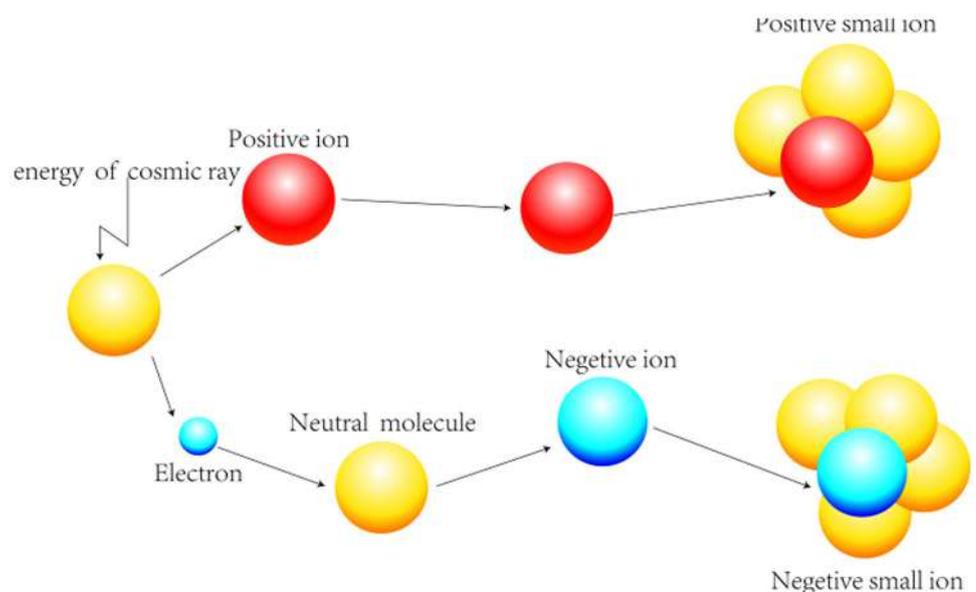
The resultant ions are pretty different due to the diverse supporting energy. Hence, the harmful neutral gas can be produced when the energy is enough, using the processes shown in the Eqs. (5)–(7), while the produce ions such as  $\text{O}_2^-$ ,  $\text{CO}_4^-$  are initially facilitated with the presence of water vapor in the atmosphere [15, 16].

In general, gas ionization reactions caused by cosmic ray always take place in middle troposphere which is at a 10–12 km distance from Earth's surface in mid-latitude. The basic scheme of negative air ions' transformation processes is shown in Fig. 2 [17]. The main routes for evolution of ions are marked by continues lines, while less important routes are marked by dashed lines [18].

The symbols X and Y stand for chemical fragment which may be absorbed on the ion cores in the process of clustering, such as  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ . Commonly, the evolution of NAI transformation begins with a mixture of primary  $\text{O}_2^-$  and  $\text{O}^-$  ions; then after the collision and clustering repeatedly, various compound ions are left.

**The source from radioactive elements in rock and soil** With alpha, beta, gamma emissions, radioactive sources

**Fig. 1** The cosmic ray-induced production of negative air ions



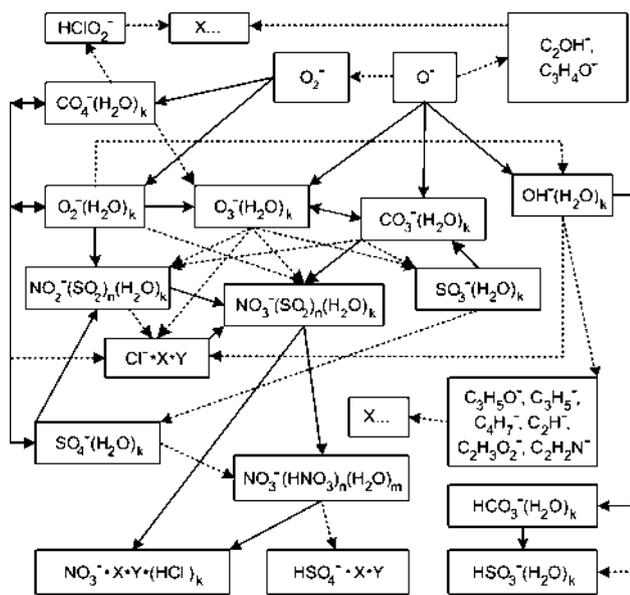


Fig. 2 The basic scheme of the negative air ions transformation processes

such as tourmaline and pumice displace an electron from neutral molecule of atmosphere gases by supporting the required energy for ionization, leaving positive-charged molecules. Surrounded by  $2.7 \times 10^{19}$  molecules per cubic centimeter air, the displaced electrons are promptly captured by gaseous molecules such as  $O_2$  and  $CO_2$  to form the negative-charged ions with  $10^9$  Hz frequency. In nature, water molecules form aggregates ranging from 1 to 8 around the charged molecules within  $2 \times 10^{-7}$  s. It is obvious that the concentration of charged ions will finally reach a balance for the continuous process of evolution and disappearance.

*The source from ultraviolet radiation and photoemission* Normally, with strong energy, short-wavelength ultraviolet can simply aggravate the rate of collision between ions and surrounding molecules, which result in the charge transfer, producing air ions with high concentration, especially when the reaction is exposed to the ultraviolet ray.

*The source from the waterfalls impact and friction* Water-generated negative ions, created by the ionization of water through shearing of water droplets, called “the Lenard effect” [19], naturally occur around waterfalls. When water is broken up into small droplets, electrons are arranged on the surface of small water droplets in dipolar fashion. The active molecules such as oxygen and carbon dioxide, acting as the electron acceptors, combine with these electrons which are abundant in the natural air. It was reported that oxygen combines with up to 20–30 water molecules to form negative-ion cluster:  $O_2(H_2O)_n$  [20].

### Artificial Generation of NAI

There are several ways to generate air artificial ions, including corona discharges, thermionic electron emission from hot metal electrodes or photo-electrodes, radiation from radioisotopes, ultraviolet, and ejection of high-pressure water. However, exposing to ultraviolet with short wavelengths, to displace electrons from metal materials or dust particles nearby and attach to gas molecules performs inefficiency in producing large concentrations of NAI. In addition, it inhibits the application in the domain of utility for the generation of noxious gas such as ozone and nitric oxide. Thermionic and photo-induced electron emission, affected by the material attribution, the environment temperature, and humidity, only generates a small part of small air ions which is beneficial to human physical and psychological health; on the contrary, positive air ions act on activities such as excitation of nerves and sympathetic nerves which have a harmful impact on human health. Different from the above-mentioned two methods, corona discharges and radioisotopes are generally preferred for producing high negative air ion concentrations.

The radioactive materials such as tritium and polonium contained materials commonly impregnated into titanium, zirconium or stainless steel foils [1]. When voltage about 500 V is applied to the radioactive surfaces, NAI are produced through the emission high-energy particles which depend on the value of voltage.

Comparing with polonium that has a half-life of 0.4 years and large  $\beta$ -energy of 0.02 MeV, tritium, with a half-life of 12.3 years and large  $\beta$ -energy of 5.3 MeV, exhibits larger potential in the application with generation rates of  $10^9$  ions per second. In their basic form, such ion sources can cause problems when used for biological studies due to the unhealthy radioactive effect on human.

Apart from direct exposure to radioactive emission, acting as most common method of air ion generation, the corona discharge produces NAI when high voltages are applied to wires or pin electrodes. The relationship between the electric field at the tip of a pin electrode and other environmental parameters is as follows:

$$E \cong \frac{2V}{a} \log_e(4x/a), \tag{8}$$

where  $a$  is curvature radius of the electrode tip,  $x$  is the distance to the nearest earth plane,  $V$  is electrode voltage and  $E$  is strength of electric field. Electric field in excess of  $-10^8$  V/m at electrode tips, which greatly exceed the normal breakdown voltage ( $-3 \times 10^6$  V/m) for air, is readily attainable. With complete electrical breakdown of air, a large number of energetic electrons are released at an electrode tip while those gas molecules nearest the tip become ionized since the field at an electrode tip rapidly

diverges. When the electrode is at a negative voltage, the negative ions produced are accelerated away from the electrode. On the contrary, the positive ones are accelerated toward the electrode where they become neutralized by electrons “leaking” from ground potential. The pin electrodes of the corona discharge, commonly made of tungsten, stainless steel or carbon fiber which is the most popular material with great commercial potential, are essential to the quality of NAI generation. Using the 40,000 carbon fibers as electrode, the generation rates greater than  $10^{11}$  ions per second are readily achievable. Besides, this type of electrode has less possibility of being involved in dirt accumulation and bluntness of the electrode tip.

Investigation towards the concentration gradient of NAI in various humidity and distance have been carried out while detailed relationship between them was shown in Fig. 3.

Figure 3 indicates that there were four slope trends at different space locations. The divisions of space locations into four trends were at 10–30 cm, 70–360 cm, 420–450 cm, and 560–900 cm from the discharge electrode by the diverse variation trends of the concentration of NAI when the relative humidity increased, which are slight increase, greatly decrease, light decrease, and great increase, respectively [23].

Figure 4 shows the average NAI concentration versus the distance starting from the discharge electrode and at different levels of relative humidity. It demonstrates a logarithmic linear tendency of the concentration of NAI within a log-linear distance.

By ejecting water with high pressure, a great many water-generated negative ions were released into air where

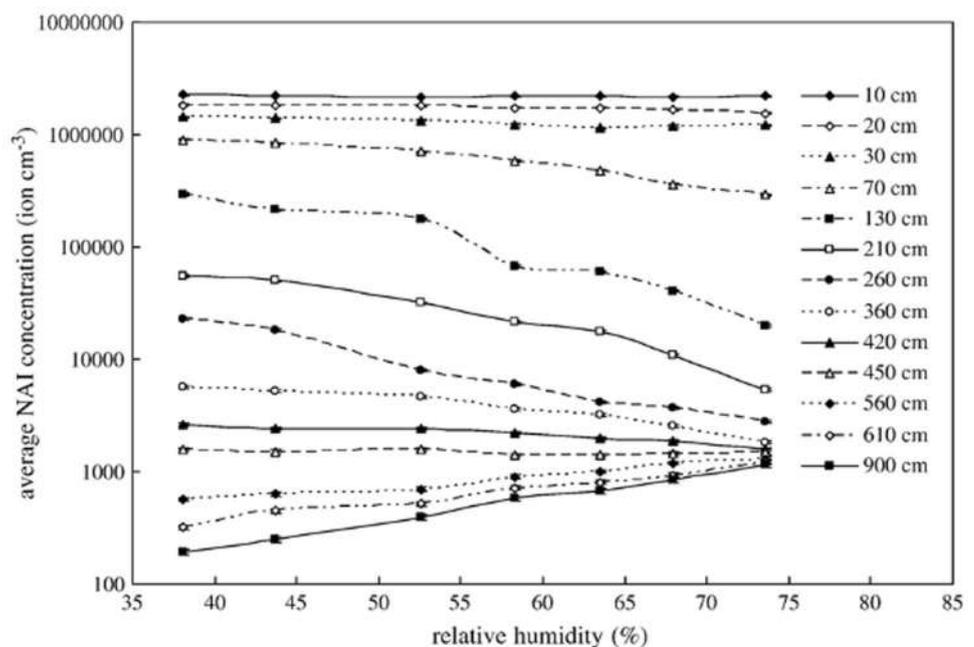
the mechanism is similar to waterfall. The lifetime of these negative ions were several minutes and they have positive effects on human body.

## The Determination of NAI

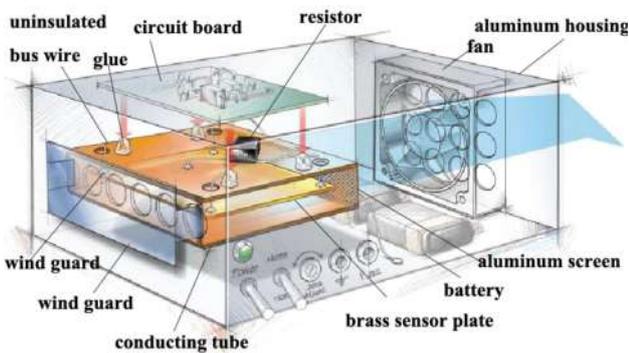
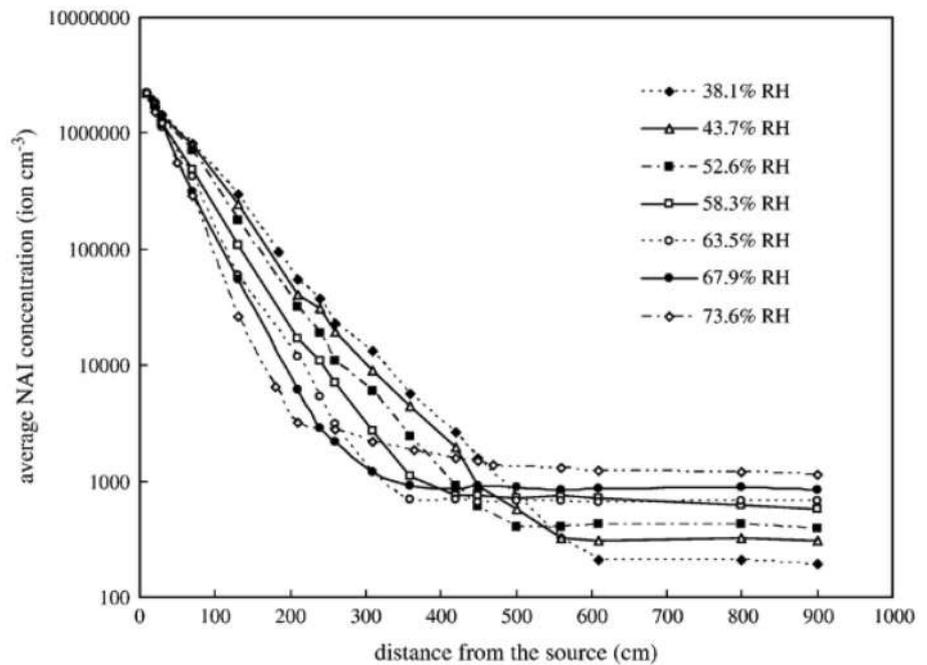
The determination of NAI can be divided into two parts: the measurement of NAI concentrations and the identification of NAI. The measurement of NAI concentrations can be achieved by measuring the variation of electrical conductivity of the atmosphere when NAI go through a conducting tube. Figure 5 shows the outline of ion counting instrument, which contains a fan, circuit board, brass sensor plate, etc.. The fan was used to draw air through a conducting tube. Inside the tube, the brass sensor plate charged with  $-5$  V voltage drives negatively charged ions. It also serves as NAI receptor which creates a proportional voltage drop so that a simple circuit can be amplified for measurement [21, 22]. However, such measurements must be made with care to ensure that there is no external disturbance at the air velocity driven by the fan so that it cannot be well quantitated when measuring the concentration of the NAI flow. Besides, NAI with large particle size maybe go through without adhering to the brass plate, resulting in the deviation of the measurements.

To identify ions produced by corona sources, mass spectrometry, measuring the characteristics of individual molecules efficiently, has been applied to measure NAI, by which a variety of negative ion species have been identified, including  $O^-$ ,  $O_2^-$ ,  $O_3^-$ ,  $CO_3^-$ ,  $CO_4^-$ ,  $HCO_3^-$ ,  $NO_2^-$  and  $NO_3^-$  ions. [23, 24].

**Fig. 3** Average NAI concentration at different relative humidities and distances from the electric discharge electrode (temperature  $25.2 \pm 1.4$  °C; standard deviation of NAI concentration 1.1–5.2%)



**Fig. 4** The average NAI concentration versus the distance from the discharge electrode at different relative humidities (Standard deviation of negative ions was 5.2%)



**Fig. 5** The outline of ion counting instrument

**Conclusion**

The generation and determination of negative air ions are described in this paper, as an aid to further studies on NAI; besides, it may be helpful while purchasing negative air ion generators or designing a device to determine the NAI.

The qualitative and quantitative researches are the main aspects of the NAI study. Besides, the application research concerns on the effect of NAI on human body are arousing high interests. With the mass spectrum technology development, NAI can be qualitatively and quantitatively detected which aids in understanding more clearly the mechanism of the generation of NAI and makes a more successful NAI generator.

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