THE UNIVERSITY OF KITAKYUSHU
GRADUATE SCHOOL OF ENVIRONMENTAL ENGINEERING

Assessment on the sampling artifact related to HNO_3 in the filter pack method

NGUYEN KHANH LINH

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Declaration

I hereby declare that this dissertation has been composed solely by myself and the data provided herein is my original work except where due reference has been properly cited in the text. This dissertation has not been previously submitted, in whole or in part, for a degree, diploma or other qualifications.

Kitakyushu, Japan
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Nguyen Khanh Linh

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Abstract

The term air pollution refers to any changes that modifies the natural state of ambient air. Air pollution started with the discovery of fire and has become a global issue since the Industrial Revolution. It’s claimed as the culprit of more than four million deaths per year due to its adverse on health effects, namely, respiratory disease, heart disease and lung cancer. Obviously, air pollution is required to be precisely determined and assessed for appropriate countermeasures.

Nitric acid gas (HNO_3) is an active and common secondary pollutant that participates in many important chemical processes in the atmosphere including the removal of atmospheric nitrogen. To precisely determine the ambient HNO_3 provides the better understanding and evaluation on the characteristic of the atmosphere. Filter pack is a common and useful method in the sampling of HNO_3. However, this device suffers from the sampling artifacts, which is a typical drawback of filter-based method. This research aims to fix the disadvantage of this method on the sampling HNO_3 by using only the filter pack method itself to assess the sampling artifacts.

In ***Chapter 1. Introduction***, the history of air pollution and sampling method for ambient air will be briefly summarized. Nitric acid gas, its important role and its sampling methods as well as the advantages and drawbacks of each method including sampling artifacts are also introduced.

Chapter 2. Assessment of HNO_3 concentration under the effect of sampling artifact and chlorine loss reaction provides step-by-step approach, a new validation method on HNO_3 concentration determined by a common four-stage filter pack method by using the filter-pack itself. Started with the distinctive seasonal pattern of HNO_3 recorded at the survey site where is highly affected by marine aerosol with high concentration of sea salt, this chapter aimed to find the answer for a question that whether there is a relation or an effect of sea salt on the specific seasonal variation of HNO_3; furthermore, if the consideration is right, how is the influence and how to correct it.

In ***Chapter 3. Assessment of sampling artifact on HNO_3 using multi-stage filter pack systems and the reveal of ambient pre-neutralized H_2SO_4***, the sampling artifact is

considered with a different approach by the simultaneous implement of a four-stage and a five-stage filter pack. Despite the similar pattern in seasonal trend, the difference in the concentration of HNO_3 between the two filter pack systems was recorded. With the feature of coarse particle segregation in the five-stage filter pack, this experiment aimed to find the influence of sampling artifact on HNO_3 with the joint of coarse particulate matter, i.e., does the artifact actually exist? and how does it affect? or what is the mechanism of the influence? The answer will be revealed in this chapter.

The final ***Chapter 4. Summary and future prospects*** sums up and gives a conclusion on the effect of sampling artifact on HNO_3 related to sea salt, NH_4NO_3 and H_2SO_4. These findings suggest several future directions to complete the understanding about the sampling artifact on HNO_3 determined by filter pack method.

Chapter 1. Introduction

1.1 Overview of air pollution and the need of air sampling and measurement

Air pollution started with the discovery of fire when humans were exposed to and aware of the discomforts during biomass burnings (Fowler et al., 2020; Seigneur, 2019). Since the middle of the 19th century, the Industrial Revolution raised awareness of air pollution as a severe problem for human society. The first and foremost significant event was the "The Great London Smog" in 1952, which led to 12000 deaths in two months (Bell et al., 2004; Wilkins, 1954). The phenomenon was the result of extremely high SO_2 concentration due to coal burning. In 1943, photochemical smog, a result of automobile exhaust, was first recognized and documented (Haagen-Smit, 1952). During the 1970s, the average annual acidity was reported at about pH 4 in North America (Gorham, 1998; Likens and Bormann, 1974), which marked the first sign of acid deposition. In terms of Japan, in the 1960s, Yokkaichi asthma, a respiratory disease related to SO_2 emission was listed as one of the four biggest diseases related to pollution in Japan (Economics, 1991; Fuwa, 1994; Yoshida et al., 1964).

In 1988, Intergovernmental Panel on Climate Change (IPCC) was established with the aim to provide regular assessments on climate change, its impacts and future risks; and option for adaptation and mitigation as the alarming rise of greenhouse gases due to human activities (www.ipcc.ch).

Due to WHO, air pollution causes the death of more than four million people per year and around 90% of the world population live in a place where air quality exceeds WHO guideline limit (www.who.int). The adverse effect on the respiratory, the risk of heart disease, and lung cancer of air pollution were also reported (Du et al., 2016; Hayes et al., 2020; Kurt et al., 2017; Manisalidis et al., 2020; Yu et al., 2021; Zhang and Routledge, 2020). Hence, the precise sampling and measurement of air pollutants is required for appropriate countermeasures for air pollution control.

1.2 General about the sampling of the air component

Air pollution is defined as contamination of the indoor or outdoor environment by any chemical physical or biological agent that modifies the natural characteristics of the atmosphere (www.who.int), in other words, a species is considered as an air pollutant when its concentration is higher than that in the natural environment.

Air pollution measurement can be classified as direct and indirect sampling. In direct measurement, a target substance is collected directly and analyzed. On the other hand, in indirect measurement, a target substance itself is not collected and is determined or characterized by an indicator (ex. Light scattering) (Vallero, 2019, 2014)

The atmosphere is the mixture of gases and particles of solid and liquid. These two forms have different physical and chemical characteristics; hence, their sampling methods have several differences based on the target substances.

1.2.1 Sampling of particulate matter

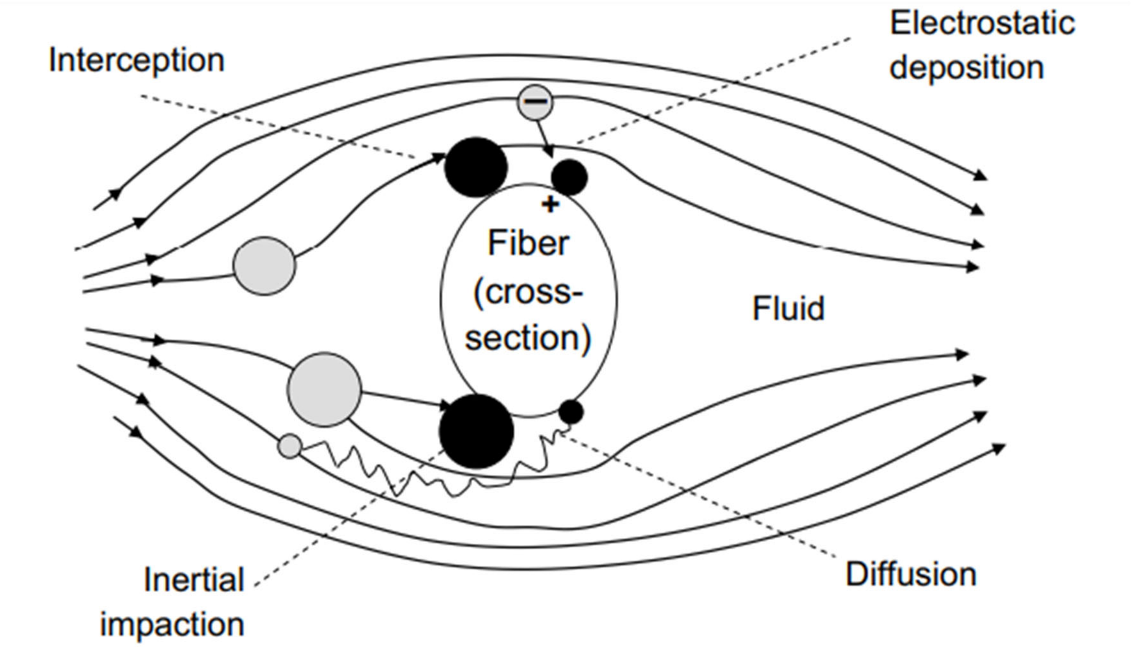


Fig. 1-1 Mechanical process involved in collecting particulate matter (Forbes., 2015)

Atmospheric particles or particulate matters (PM) include any airborne substances that are not in the gas phase. Particulate matter suspended in the atmosphere is called aerosols. Particulate matters are classified into several size ranges based on their effect on human health. The common classification is fine particles or $PM_{2.5}$ (particulate matters have aerodynamic diameter ≤2.5 µm) and coarse particles or $PM_{10-2.5}$ (particulate matters have an aerodynamic diameter in the range of 2.5-10 µm (Colls, 2002; Seinfeld and Pandis, 2016). In terms of air pollution, PM_{10} referring to particulate matter less than 10 µm in diameter is also commonly used as its risk to the respiratory system. Particulate matter can be measured directly or indirectly. The original approach is to collect the particles from a determined volume of air, weight and chemically analyze. Depending on its size range, particulate matters are collected in filter paper by four mechanisms: diffusion (≤0.1 µm diameter), interception (diameter between 0.1 and 1 µm), inertial impaction (diameter ≥1 µm), and electrostatics (occurs when a particle in the inlet stream is attracted by a charged filter media) (Fig. 1.1) (Lindsley, 2016; Vallero, 2014).

1.2.2 Sampling of gaseous components

Sampling of gases can be classified into two types: grab sampling and preconcentration.

Grab sampling/whole-air sampling: In this method, the air is collected in a sampling vessel for transport back to the analytical laboratory. There are several types of vessels are in use, namely evacuated bottles, syringes, bellows, and bags. In grab sampling, bags are filled by air using a pump or they are placed in an airtight container and the air is drawn into them when their inlet is opened. In the case of rigid container, the vessel is evacuated, and the air sucked in when opening the inlet. The advantage of this method is no power requirement. However, there is the risk of degradation or changing the characteristic of the air sample due to the chemical reactions during retention time (Colls, 2002; McQuaid, 1985).

Preconcentration: Based on the mechanism how the air is collected, preconcentration methods can be divided into three types: absorption, adsorption, and condensation trapping (Colls, 2002; McQuaid, 1985).

Absorption: is the most common method for air sampling. In this method, the target gas is retained in a liquid phase absorbent due to a chemical reaction. The following are several arrangements based on this mechanism:

Bubblers: The air stream is bubbled through a liquid phase adsorbent. This method is appropriate for sampling campaigns that do not require a large number of samples or frequent sampling.

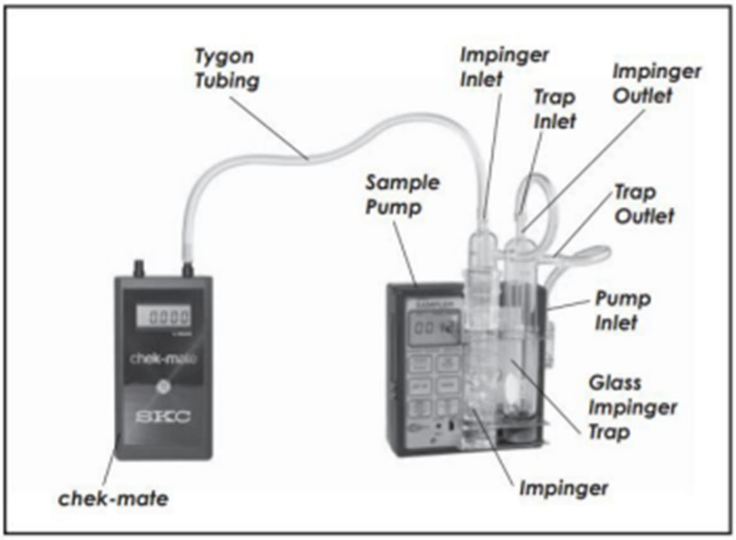


Fig. 1-2 Sampling system in bubbler method (www.skcltd.com)

Impregnated filter: The target substance is eliminated from the inlet gas stream and retained in the filter paper which is impregnated by an adsorbent for the selective gas. Usually, several filters are used. This is clearly showed in the employment of filter pack method, which is described in detail in 1.3.

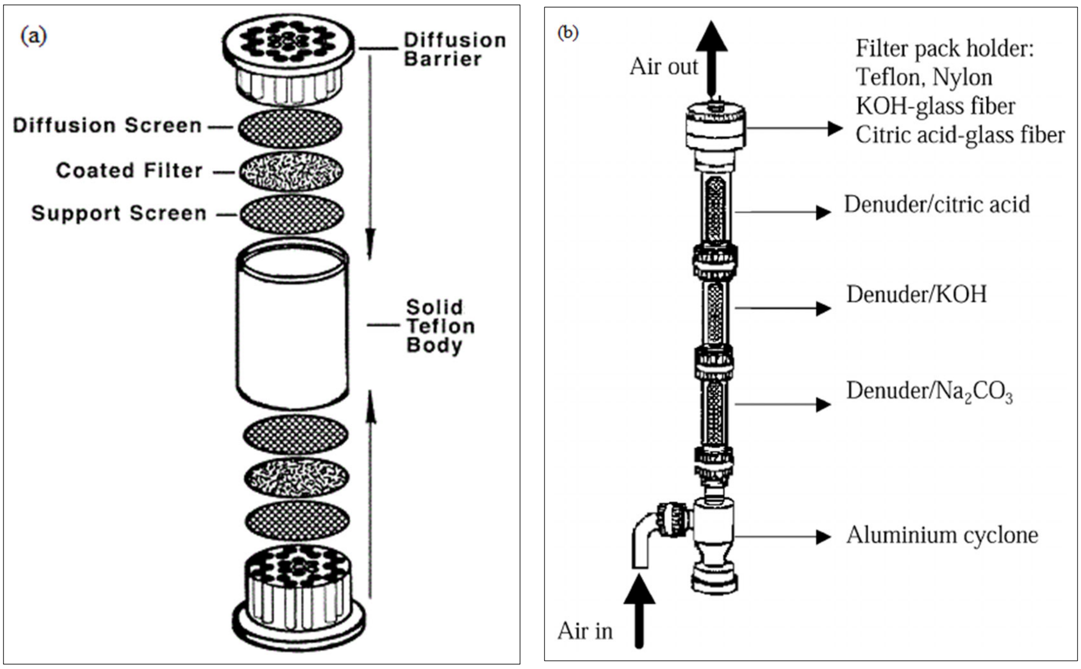


Fig. 1-3 Passive sampler (Krupa, S.V., 2000) (a) and annular denuder/filter system (Limon-Sanchez, M.T., 2002) (b)

Passive sampling or static sampling: Passive sampling system (Fig. 1-3 (a)) refers to those that do not have active air-moving component to pull the target substance to the collection medium. In other words, there is no pump or requirement of electricity, which is the outstanding advantage of this method. The air diffuses through a passive sampling tube from one end and the target substance is captured in the selective impregnated filter set up in the other end. As stated, this method is no power requirement, ease of handling, low cost and has no limitation on target substances. However, this method suffers from the collection ability in short sampling interval (e.g. hourly or daily sampling) (Aikawa et al., 2010; Colls, 2002; Forbes et al., 2015; Krupa and Legge, 2000; McQuaid, 1985; Vallero, 2014; Van Duy et al., 2020).

Denuder: Denuder is a hollow tube, inside of which is coated by an absorbent. In the denuder sampler, the air flow is kept laminar by modulating the flow rate to the tube diameter. The target air is eliminated from the air stream and absorbed by denuder wall, whilst other analyte substances including particulate matters are remained in the outlet stream. Annular denuder (Fig. 1-4) is the advance type of denuder including concentric tubes in which inner surface of outer tube and outer surface of inner tube are coated with an absorbent for a target gas. In this system, the air stream flows between these double coated walls which improves collection efficiency, shortens the tube length, shortens sampling time, and increases flow rate (Allegrini et al., 1987; Colls, 2002; Forbes et al.,

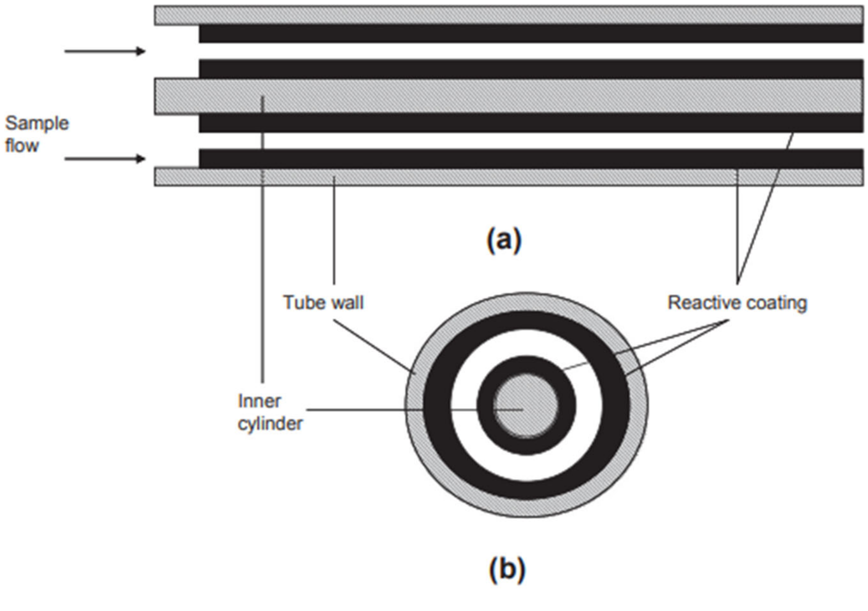


Fig. 1-4 Schematic diagram of an annular denuder (a) longitudinal view and (b) in cross-section (Forbes et al., 2015)

2015; Vallero, 2014). The use of denuders in air sampling is to primarily separate the gas phase in prior to particulate collection by filter-based method to avoid sampling errors caused by the retention of gases on filter and gas-to-particle reactions (Allegrini et al., 1987; Forbes et al., 2015). The drawback of this sampling method is that fine particle from the air stream can also be captured by the denuder as a consequence of sedimentation or Brownian diffusion (Forbes et al., 2015; Harrison and Kitto, 1990; Possanzini et al., 1983).

<u>Adsorption</u>: In adsorption, the target gas molecules are binding on the surface of a solid adsorbent due to intermolecular force. Then, they are stripped off by thermal desorption or solvent extraction for chemical analysis. The commonly used adsorbents are: activated carbon, silica gel and organic polymers (Colls, 2002; Dettmer and Engewald, 2002; McQuaid, 1985).

<u>Condensation trapping</u> is basically to change the target substance from gaseous to liquid phase when passing through a chamber cooled at the temperature of liquid oxygen (-183°C) by the mixtures of water, ice, salt, dry ice, liquid air, and liquid oxygen. The primary difficulty of this method is the condensation of water containing components (Colls, 2002; McQuaid, 1985).

1.3 Filter pack method

Fig. 1-5 A NILU four-stage filter holder and assembly in one stage (www.innovation.nilu.no)

There are several air pollution monitoring methods which have their own advantages and disadvantages, namely: automatic monitoring, filter pack, denuder, and passive sampler. Among them, the filter pack method is commonly used due to its feature of collecting both particulate matters and gases in one sampling operation.

1.3.1 Overview of filter pack method

A filter pack consists of several in-line filter papers set up in a filter holder, each of which has different roles and specifications. When an air stream pass through a filter pack, particulate matters are collected in the first filter, and gaseous compounds are collected in subsequence filters (Harrison and Kitto, 1990; SAC3, 2003; Sickles et al., 1999; Soares, 2013).

Table 1-1 The specifications of each stage in filter pack method (SAC3, 2003)

Stage	Specification	Collection mechanism	Collective species
First (F_0)	Teflon (PTFE) filter	Filtration	Aerosol
Second (F_1)	Nylon (Polyamide) filter	Adsorption	HNO_3, partial SO_2 and HCl
		Neutralization by collected acid gases	Partial NH_3
Third (F_2)	K_2CO_3-impregnated cellulose filter	Neutralization	SO_2 and HCl
Fourth (F_3)	H_3PO_4-impregnated cellulose filter	Neutralization	NH_3

The most common assembly of a filter pack is the four-stage filter pack. The first filter being Teflon filter paper is in charge of collecting aerosol including NO_3^-, Cl^-, SO_4^{2-}, NH_4^+ and other cations (Na^+, K^+, Mg^{2+}, Ca^{2+}). The second stage is set up with a nylon filter (polyamide filter) to collect HNO_3 and partial SO_2, HCl, and NH_3. The third stage, being alkali-impregnated cellulose filter paper is to collect the remaining SO_2 and HCl.

An acid-impregnated cellulose filter paper set up in the last stage is responsible for NH_3 collection. The detailed specification and role of each stage are described in Table 2-1.

After sampling, filter papers are extracted and chemically analyzed.

The foremost merit of the filter pack method is to collect both particulate matters and gaseous compounds in one sampling cycle. In addition, this method shows its flexibility in that its arrangement can be modified by addition or simplifying based on the sampling purposes.

Shimohara et al. (2001) employed multistage filter packs including a one-stage, a three-stage, and a four-stage filter pack simultaneously to measure the concentration of gaseous and particulate matter in the southern area of Japan. In this study, the one-stage filter pack was set up with a nylon filter and the three-stage consisted of a PTFE filter, a K_2CO_3-impregnated cellulose filter, and a H_3PO_4-impregnated quartz filter paper.

Akata et al. (2016) introduced a nine-stage filter pack for a simultaneously sampling of particulate matter including (coarse and fine particles), inorganic and organic gaseous halogens (Cl, Br and I) in ambient air.

In addition, low operation cost and ease of handling are also the advantages of this method.

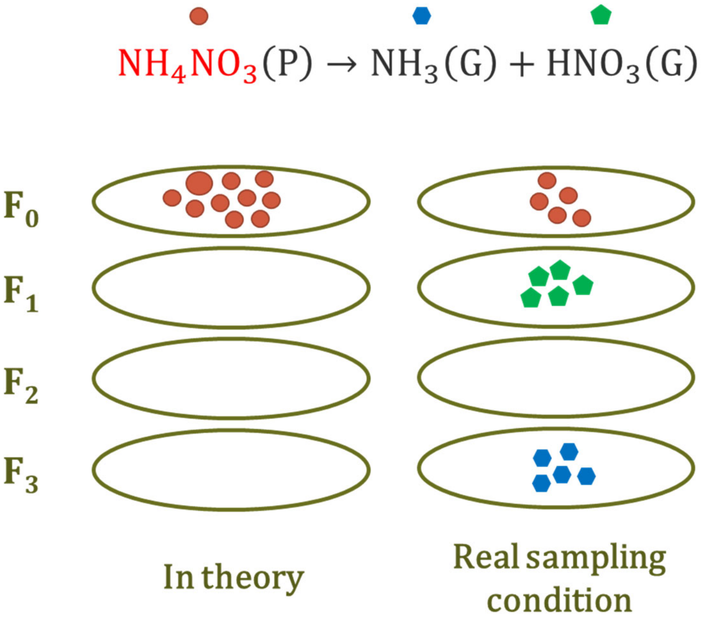
On the other hand, due to the operation principle, the filter pack suffers from the typical systematic error of the filter-based method, being sampling artifact, which is further described in the following section. Besides, the need of electric power is also a minus point when sampling at mountainous area.

1.3.2 Sampling artifacts in filter pack method

Sampling artifact, errors occurred during operation, is a common difficulty of filter-based method in air sampling. There are two principles for the presence of sampling artifact, which are:

(1) The volatilization or evaporation of particle from the filter media, which is referred to as “blowoff”. This phenomenon is the consequence of the change in equilibrium condition due to the disturbance of temperature or pressure during sampling process (Forbes et al., 2015; Harrison and Kitto, 1990; Shaw et al., 1982). The dissociation of NH_4NO_3 is an example for blowoff phenomenon (Fig. 1-6).

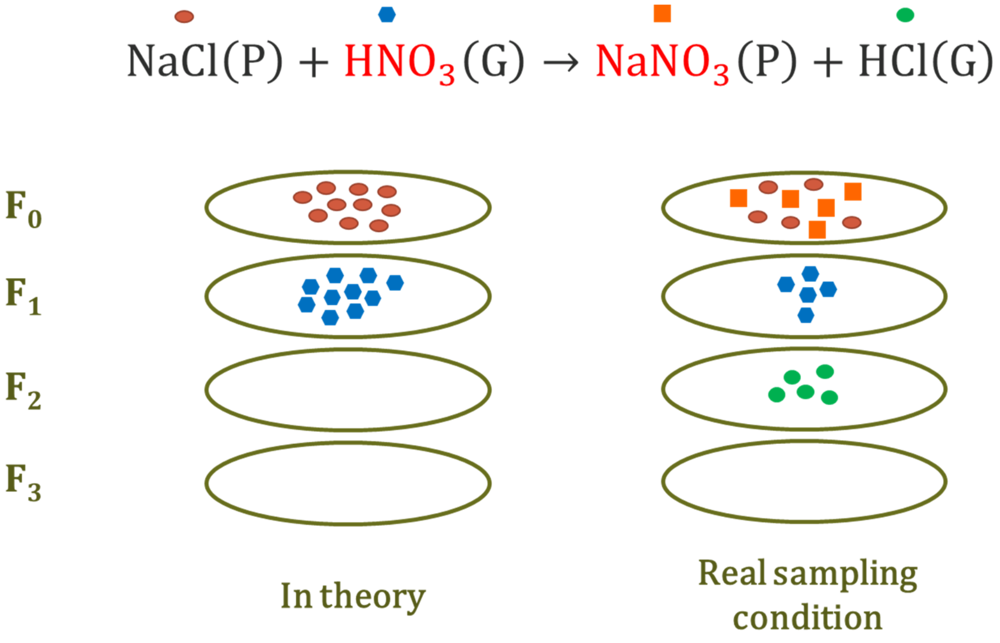
In this cases, HNO_3 and NH_3 gases as the product of the dissociation are then collected in the second and the fourth filter paper. As a consequence, the concentration of HNO_3 and NH_3 are enhanced in the final result.



$$NH_4NO_3(P) \rightarrow NH_3(G) + HNO_3(G)$$

Fig. 1-6 The dissociation of NH_4NO_3 as an example of blowoff phenomenon

(2) The possibility of gas-to-particle reactions on the filter surface. As the operation principle, particles are collected in the first filter, and gases subsequently, which



$$NaCl(P) + HNO_3(G) \rightarrow NaNO_3(P) + HCl(G)$$

Fig. 1-7 The reaction of sea salt NaCl and HNO_3 on filter surface during sampling means, the air stream including gaseous compounds pass through and come in contact with the particle collected on the first filter before reaching the designated filter to be originally collected. It leads to the possibility that gases react with the collected particle right on the Teflon filter and results in bias in the determined concentration (Forbes et al., 2015; Harrison and Kitto, 1990; Shaw et al., 1982). In addition, the reaction among particles collected in the filter paper due to retention time is potential for errors in quantification. Fig. 1-7 describes the reaction of sea salt NaCl and HNO_3 on the filter surface during sampling. In theory, sea salt and HNO_3 are captured in the first and second filters, respectively. However, in actual sampling, HNO_3 when passing through the particle collected filter – the first filter can react with sea salt particles and produce $NaNO_3$ and HCl. This results in the loss of HNO_3 and the increase in HCl concentration in the final result.

Matsumoto and Okita (1998) reported that nitrate species (HNO_3 and NO_3^-), ammonium-related species (NH_3 and NH_4^+), and chloride species (HCl and Cl^-) were the main chemical species influenced by artifacts. The chemical reactions which lead to sampling artifacts in filter pact are summarized as follows:

(1) Artifacts related to HNO_3

$$\mathrm{NH_4NO_3(P) \rightarrow NH_3(G) + HNO_3(G)}$$

$$\mathrm{NH_4NO_3(P) + H_2SO_4(P) \rightarrow NH_4HSO_4(P) + HNO_3(G)}$$

$$\mathrm{NaNO_3(P) + H_2SO_4(P) \rightarrow NaHSO_4(P) + HNO_3(G)}$$

$$\mathrm{NaCl(P) + HNO_3(G) \rightarrow NaNO_3(P) + HCl(G)}$$

(2) Artifacts related to NH_3

$$\mathrm{NH_4NO_3(P) \rightarrow NH_3(G) + HNO_3(G)}$$

$$\mathrm{NH_4Cl(P) \rightarrow NH_3(G) + HCl(G)}$$

$$\mathrm{H_2SO_4(P) + NH_3(G) \rightarrow NH_4HSO_4(P)}$$

$$\mathrm{NH_4HSO_4(P) + NH_3(G) \rightarrow (NH_4)_2SO_4(P)}$$

(3) Artifacts related to HCl

$$\mathrm{NaCl(P) + HNO_3(G) \rightarrow NaNO_3(P) + HCl(G)}$$

$$\mathrm{2NaCl(P) + H_2SO_4(P) \rightarrow Na_2SO_4(P) + 2HCl(G)}$$

$$\mathrm{NH_4Cl(P) \rightarrow NH_3(G) + HCl(G)}$$

Based on the target substances, a chemical reaction can be considered as a positive artifact (e.g., production reaction which enhances the concentration of a species) or a negative one (e.g., decomposition reaction which lessens the concentration of a species) (Shaw et al., 1982).

Consider the following reaction

$$\mathrm{NaCl(P) + HNO_3(G) \rightarrow NaNO_3(P) + HCl(G)}$$

The designated collected filter for collecting NaCl(P) is F_0, and HNO_3(G) being F_1. During operation, this reaction takes place, NO_3^- changes its form from gaseous to particle phase, whilst the opposite is seen in Cl^-. From the viewpoint of gaseous HNO_3 and particulate Cl^-, this is obviously a negative artifact due to the loss of their concentration. On the other hand, this reaction is considered as a positive artifact to particle NO_3^- and gaseous HCl.

1.4 Ambient nitric acid gas

1.4.1 Sources and fate of ambient nitric acid gas

The NO_x, which emitted from combustion process, comprises of NO and NO_2 due to their short lifetime. NO_y family refers to total active nitrogen including NO_x and their oxidation products namely nitric acid (HNO_3), peroxyacetyl nitrate (PAN), HONO, organic nitrates and particulate nitrates (Brown et al., 2004; Vallero, 2014).

Nitric acid is the secondary pollutant mainly originated from the photochemical of nitrogen oxides in daytime as the following reactions. (Akimoto Hajime, 2017; Seinfeld and Pandis, 2016; Warneck, 2000):

$$\mathrm{NO_2 + OH + M \rightarrow HNO_3 + M}$$

Another pathway of HNO_3 formation is from the reaction of N_2O_5 with liquid water on particle (Brown et al., 2006, 2004; Brown and Stutz, 2012; Fuhrer, 1985; Warneck, 2000). At night, when the photochemical oxidation is inactive, any NO rapidly reacts with O_3, as a result, almost NO_x at night is in the form of NO_2. Then, NO_2 reacts with O_3 to produce nitrate (NO_3) radical. At night, NO_3 radical reacts with NO_2 to form dinitrogen pentoxide N_2O_5, a precursor for the nighttime formation of HNO_3. The formation of N_2O_5 is reversable in which, N_2O_5 decompose into NO_2 and NO_3 radical as the rise of temperature.

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_2 + NO_3 \rightleftharpoons N_2O_5$$

As NO_3 radical is rapidly photolyzed, during the day, the sequence reaction to form N_2O_5 is interrupted. Then, the produced N_2O_5 is hydrolyzed to HNO_3.

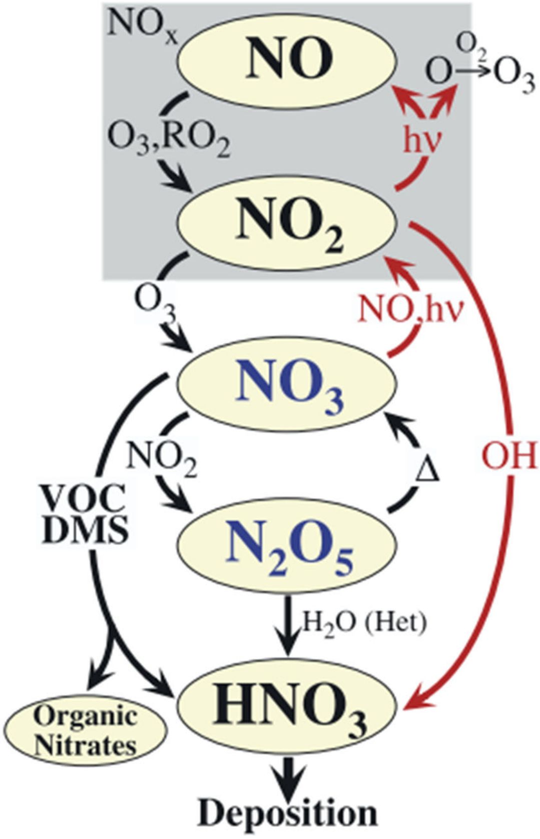


Fig. 1-8 Chemical cycling of nitrogen oxides. Red arrows indicate photochemical reactions.

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

In gas phase, the hydrolysis of N_2O_5 is very slow, however, it can be rapid on aerosol particles as a heterogeneous process.

In the atmosphere, HNO_3 is an active gas and can easily convert into particulate NO_3^- due to the reaction with sea salt or neutralization by NH_3.

$$\mathrm{NH_3 + HNO_3 \rightleftharpoons NH_4NO_3}$$

$$\mathrm{NaCl + HNO_3 \rightarrow NaNO_3 + HCl}$$

The reaction of sea salt with HNO_3 in ambient air is well known as chlorine loss reaction (Harrison and Pio, 1983a; Hitchcock et al., 1980; Pio and Lopes, 1998), which occurs in the area where maritime air masses is mixing with the continental air masses (Harrison and Pio, 1983; Pakkanen, 1996). Since the uptake coefficient of HNO_3 on sea salt is large, most of HNO_3 is converted to $NaNO_3$ in a few hours, hence, this reaction is considered as an important source of coarse particulate nitrate and gaseous HCl in the ambient atmosphere (Dasgupta et al., 2007; Pakkanen, 1996; Pio and Lopes, 1998). In addition, the deposition rate of HNO_3 is much larger than $NaNO_3$, which means the conversion of HNO_3 to NO_3^- provides the ability of long range transport of particulate nitrate (Akimoto Hajime, 2017).

As the former product of NO_x, the oxidation to HNO_3 is considered as the major removal of NO_x and HNO_3 being the sink of nitrogen oxides. HNO_3, then, is scavenged from the atmosphere through dry and wet deposition, which refers to as acid deposition. (Seinfeld and Pandis, 2016; Vallero, 2014; Warneck, 2000).

1.4.2 Sampling methods

Filter-based method is a common method for sampling of ambient HNO_3. Since gaseous HNO_3 and particulate NO_3^- is coexist in the ambient air, sampling of HNO_3 is potentially affected by the collection of both species. A common assembly is the use of a Teflon (PTFE) filter, backed up with a nylon filter. In this couple, the Teflon filter, which is immune to HNO_3 and nitrogen compounds, is responsible for nitrate aerosol collection, while the nylon filter is in charge of collecting HNO_3 in downstream. However, this assembly suffers from the possibility of overestimating of HNO_3 concentration in the nylon filter due to the dissociation of particulate NH_4NO_3. On the other hand, the loss of HNO_3 is possible due to the interaction of HNO_3 with collected sulfate aerosol in the Teflon filter.

Denuder method has been developed to overcome this difficulty of a conventional filter-based method. In sampling system, a denuder is set up in prior to a filter to separate HNO_3 from the air stream before aerosols are collected subsequently (Allegrini et al., 1987; Colls, 2002; Forbes et al., 2015; Possanzini et al., 1983). There are several options of coated chemical for dry denuder in HNO_3 sampling, namely Na_2CO_3 (Bai and Wen, 2000; Harrison and Kitto, 1990; Koutrakis et al., 1988), K_2CO_3 (Matsumoto and Okita, 1998). However, this method still has the potential of positive artifact, namely: collection of fine particles in denuder wall or HNO_3 and HNO_2 formation from nitrogen oxides in Na_2CO_3-coated denuder. Wet denuder method has also been used to sample HNO_3 (Acker et al., 2004; Dasgupta et al., 2007; Genfa et al., 2003).

1.5 Objectives

HNO_3 plays an important role in atmospheric chemistry and the removal of HNO_3 from the ambient air either by wet or dry deposition contributes to the acidification process of the environment. Obviously, HNO_3 concentration requires precise determination. At present, there is no commercial device for automated quantification of HNO_3 concentration. Filter-based method, namely, filter pack, is widely employed for the sampling of ambient HNO_3.

As stated, filter pack method suffers from the influence of sampling artifact, and the concentration of HNO_3 determined by this method is obviously affected through four chemical reactions as mentioned in 1.3.2.

To overcome this drawback, the most common approach is to combine with a denuder. In denuder/filter pack system, gas phase analytes from air stream are denuded/collected by corresponding denuders in prior to a filter pack in subsequence (Amoroso et al., 2008; Forbes et al., 2015; Harrison and Kitto, 1990; Kim et al., 2015; Matsumoto and Okita, 1998). Hence, by the use of this combination, the sampling artifacts are significantly minimized. In addition, the system also allows the determination of artifacts related to blowoff phenomenon which is addressed by the concentration in gases collection filters set up in filter pack.

Shaw et al. (1982) introduced "denuder difference method" to measure the concentration of nitric acid gas in which, two samplers run parallelly. One sampler was set up with a nylon filter to collect both particulate NO_3^- and gaseous HNO_3. The other consisted of a denuder to collect HNO_3 in prior to a nylon filter. The difference in the concentration of NO_3^- determined by the two samplers indicates nitric acid gas concentration.

Matsumoto and Okita (1998) conducted a one-year measurement using a three-line annular denuder filter system to evaluate the loss rate of particulate NO_3^-, Cl^- and NH_4^+ collected on filters.

Sickle et. al. (Sickles et al., 1999) evaluated the performance of the filter pack using an annular denuder as a reference and found a slight bias on HNO_3 concentration collected in filter pack system due to the conversion of retained HNO_2 on nylon filter to HNO_3 under the presence of O_3.

Hayami (Hayami, 2005) employed a denuder/filter-pack system in measuring the daily concentration of inorganic aerosols and gaseous substances in Fukue Island, Japan. The sampling device consisted of an impactor to collect coarse particles, followed by a single denuder to collect both alkaline (NH_3) and acidic (HCl and HNO_3) gases, and a three-stage filter pack to collect fine aerosol and gases from volatilization.

However, the denuder/filter pack does have disadvantages, namely: the hardware is complex, more expensive than filter pack and fragile, which provides difficulty in operation and handling (Sickles et al., 1999).

Shimohara et. al. (2001) proposed a different approach when employing multi-stage filter pack systems with different assemblies in parallel to investigate the characteristic of atmospheric air pollution. In this study, the concentration of ambient HNO_3 was quantitated based on the difference in NO_3^- concentration determined in a one-stage filter pack (which is the sum of particle NO_3^- and gaseous HNO_3) and NO_3^- concentration in a three-stage filter pack, being the concentration of atmospheric NO_3^-.

The aim of this research is to go insight into the artifact on HNO_3 by using filter pack itself for its features of low operation cost and ease of handling. The study provides an assessment on the artifact of nitric acid gas in two different approaches: using a four-stage filter pack itself and in the employment of multi-stage filter pack systems.

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Chapter 2. Assessment of HNO_3 concentration under the effect of sampling artifact and chlorine loss reaction

2.1 Introduction

A filter pack is a convenient and useful sampling device for collecting particulate matter and gaseous compounds in ambient air; therefore, it has been frequently used in monitoring networks such as European Measurement and Evaluation Programme (EMEP), National Atmospheric Deposition Program (NADP), and Acid Deposition Monitoring Network in East Asia (EANET), and big datasets have been accumulated in the world. The strongest advantage of the filter pack method is the ability to simultaneously collect both particulate matter and gaseous compounds in one sampling operation. The device basically includes four in-line filter papers—four stages, in which particulate matter is collected on the first stage and gaseous compounds are on subsequent stages (Sickles et al., 1999), meaning that gaseous compounds pass through and come in contact with the particulate matter collected on the first filter before reaching the designated filter to be originally collected. This mechanism leads to an unavoidable disadvantage of the filter pack, "artifact", i.e., the gas-to-particle conversion and/or chemical reactions between particulate matter and gaseous compounds on the surface of the filter paper (Matsumoto and Okita, 1998). Kaneyasu et al. (1995) collected aerosols using a quartz fiber filter installed in a low-volume air sampler, and the chlorine loss reaction (Harrison and Pio, 1983a; Hitchcock et al., 1980; Pio and Lopes, 1998) was reported to be responsible for the difference between the observed chloride and the sea-salt chlorine. Despite the result that chlorine loss from sea salt was witnessed in their study, the exact cause of the phenomenon was not elucidated.

With the purpose of evaluating the artifacts of the filter-based method, Matsumoto and Okita (1998) conducted a one-year measurement of atmospheric species by denuder coupled with a filter pack where the loss rates due to artifacts were shown; the average loss rate of Cl^- and NO_3^- due to the dissociation of semi-volatile particulate matter (NH_4Cl and NH_4NO_3) was reported to be 0.46 and 0.44, respectively. They showed that nitrate species (HNO_3 and NO_3^-), ammonium-related species (NH_3 and NH_4^+), and chloride species (HCl and Cl^-) were the main chemical species influenced by artifacts, and as for nitrate species, the chemical reactions below were mainly related with artifacts.

(R1) $NaCl(p) + HNO_3(g) \rightarrow NaNO_3(p) + HCl(g)$

(R2) $NH_4NO_3(p) \rightarrow NH_3(g) + HNO_3(g)$

(R3) $NH_4NO_3(p) + H_2SO_4(p) \rightarrow NH_4HSO_4(p) + HNO_3(g)$

(R4) $NaNO_3(p) + H_2SO_4(p) \rightarrow NaHSO_4(p) + HNO_3(g)$

Among those reactions, reaction (R1), occurring not only on the filter paper but also in ambient air, provides a negative artifact for $HNO_3(g)$ and is generally referred to as a chlorine loss reaction, while reactions (2)–(4) provide positive artifacts. The change of chemical form from $HNO_3(g)$ into $NaNO_3(p)$ accordingly influences its kinetic behavior and destination in the atmosphere through the change of its chemical reactivity and the retention time (Pakkanen, 1996). On the other hand, chloride also changes its chemical form from NaCl(p) to HCl(g) where NaCl(p) is inherently harmless whereas HCl(g) is harmful, indicating that a harmful substance originates from a harmless one. The anthropogenic emission of HCl(g) is strictly controlled by some laws and acts; however, due to reaction (1), HCl(g) is unintentionally produced as a result of chlorine loss in ambient air, which is impossible to control.

Ambient HNO_3 originates from NO_2 through a chemical reaction in the atmosphere, then deposits onto the surface through dry deposition process and/or is washed from the air by precipitation through wet deposition process, together resulting in acid deposition. The HNO_3 is an important chemical species in the atmosphere from the viewpoints of not only its role in atmospheric chemistry but also a scavenging of nitrogen from the atmosphere. Its concentration should, therefore, be precisely quantitated; on the other hand, as mentioned above, the reaction of HNO_3 with sea salt taking place not only in the ambient air but also on filter paper, namely, artifact prohibit us from the precise determination of the HNO_3 concentration in ambient air.

In this manuscript, we focused on HNO_3 and tried to quantitatively evaluate the chlorine loss in ambient air and the artifact during the sampling in the four-stage filter pack system. For better considerations and understanding, we adopted a daily (24-hour) sampling for a year-round survey. We introduced new concepts/parameters on nitrate species, studied temporal and seasonal variations, and proposed a new validation methodology on nitric acid concentration by simply using the four-stage filter pack system.

2.2 Methodology

2.2.1 Survey site

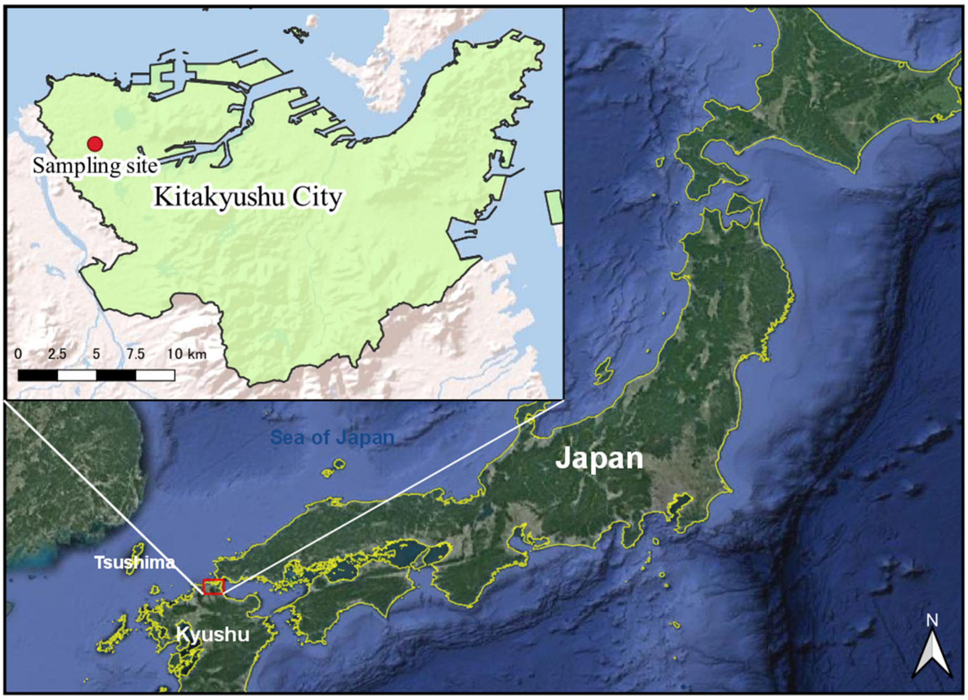

Fig. 2-1 Sampling site

Air sampling was conducted on the roof of the University of Kitakyushu (33.89° N, 130.71° E). The survey site is in Kitakyushu City, a major industrial city in Japan (Fig. 2-1), with a population density of 935,084 people/492 km^2. Since the 19th century, with the growth of key industries, the city has evolved as one of the four largest industrial zones in Japan. Kitakyushu City is located in the northmost part of Kyushu Island, northly facing the Sea of Japan through the Tsushima Straits; therefore, the city as well as the site is influenced by marine air masses, which is characterized by the high concentration of sea-salt aerosol. Our site is situated in suburban Kitakyushu City ca. 6 km from the sea. The surrounding residential area is still being developed, and an industrial area is located approximately 15 km to the east.

2.2.2 Sampling and chemical analysis

Air sampling was carried out on a daily basis (noon (12 pm) to noon, Japan Standard Time (JST)) year-round from December, 2016, to November, 2017. The ambient air was collected using a four-stage filter pack at a flow rate of 9–10 L/min. The filter pack used was comprised of four stages as follows: a PTFE filter to collect particulate matter (SO_4^{2-},

NO_3^-, Cl^-, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+}) without size classification; a nylon filter to collect HNO_3, partially SO_2, HCl, and NH_3; a K_2CO_3-impregnated cellulose filter to collect SO_2 and HCl; and a H_3PO_4-impregnated cellulose filter to collect NH_3. The methodology of the chemical procedures, such as the extraction of filters and the system constitution of the ion chromatograph, is described in detail in our previous literature (Aikawa et al., 2005; Aikawa and Hiraki, 2008b; Zhang et al., 2021).

2.2.3 Seasonal classification

In the analysis of seasonal variation, seasons are defined as follows: winter—December, January, and February; spring—March, April, and May; summer—June, July, and August; autumn—September, October, and November.

2.3 Results and discussion

2.3.1 Influencing factors to control nitrate species

Four chemical reactions; reactions (R1)–(R4) in the Introduction, relate to the artifacts on nitrate species in the sampling by a four-stage filter pack. Among those, the reaction of HNO_3(g) with NaCl(p) is the only reaction converting nitrate from gaseous species to particulate species ($NaNO_3$(p)) and takes place on the PTFE filter where particulate matter is collected, leading to the unexpected loss of HNO_3(g) and the gain of HCl(g).

The reaction also appears in ambient air, not only on the filter, when there is mixing of the maritime air mass with the continental one (Harrison and Pio, 1983a; Pakkanen, 1996). Our survey site is located near the sea (ca. 6 km), suggesting that the characteristics of the air around our site would be highly affected by marine aerosols. Therefore, the influence of the chlorine loss reaction would be notable and should be considered in our results.

2.3.2 Temporal changes and seasonal variations

2.3.2.1. HNO3 and HCl

In this manuscript we will comprehensively and conclusively consider and discuss the (R1) reaction from the following two viewpoints: (1) ambient HNO_3 loss, well known as chlorine loss in the atmosphere, and (2) sampling artifacts on PTFE filters; in both, the amount of HNO_3 loss corresponds to that of the NaCl loss, i.e., that of HCl production.

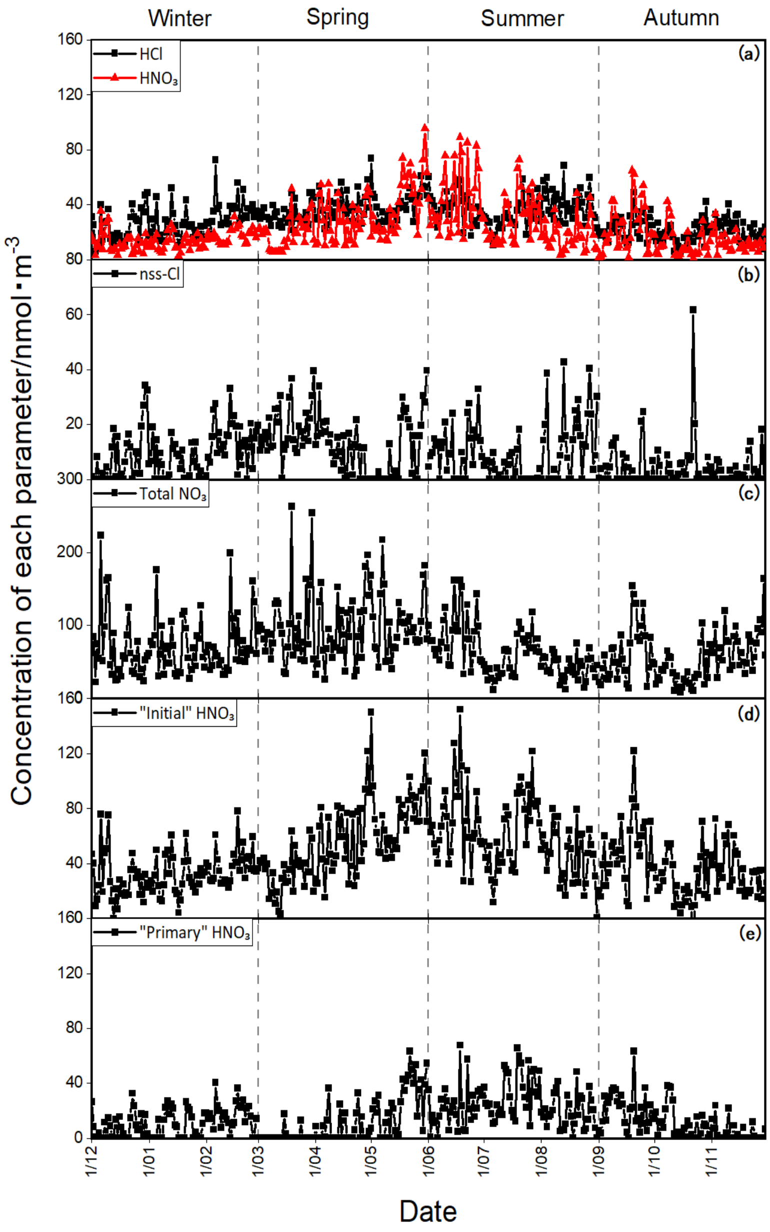

Fig. 2-2 Temporal change in concentration of HCl and HNO_3 (a), nss-Cl (b), Total NO_3 (c), "Initial" HNO_3 (d) and "Primary" HNO_3 (e)

Table 2-1 Mean concentrations in each season and their statistical differences among seasons

	Number of samples	HNO_3		HCl		nss-Cl		Total NO_3		"Initial" HNO_3		"Primary" HNO_3	
		nmol/m^3		nmol/m^3		nmol/m^3		nmol/m^3		nmol/m^3		nmol/m^3	
Spring	90	29.2	a[1]	36.9	a	13.3	a	97.70	a	52.8	a	10.40	b
Summer	92	30.0	a	36.7	a	9.4	b	61.20	bc	57.3	a	21.80	a
Autumn	92	15.9	b	21.2	c	4.4	c	56.30	c	32.7	b	8.80	b
Winter	91	13.8	b	27.1	b	9.1	b	69.20	b	31.8	b	10.50	b

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[1] Different letters indicate the significance in the difference based on ANOVA test at $p<0.001$, in which "a" refers to the highest, follow by "b" and "c". "bc" indicates the range between "b" and "c". There is a statistically significant difference among different letters, and "bc" means that there is a statistically significant difference between "bc" and "a"; there is, however, no statistically significant difference between "bc" and either "b" or "c".

In this manuscript we will comprehensively and conclusively consider and discuss the (R1) reaction from the following two viewpoints: (1) ambient HNO_3 loss, well known as chlorine loss in the atmosphere, and (2) sampling artifacts on PTFE filters; in both, the amount of HNO_3 loss corresponds to that of the NaCl loss, i.e., that of HCl production.

Fig. 2-2(a) shows the temporal change in daily HCl and HNO_3 concentrations from December 1, 2016, to November 30, 2017, where each point represents a daily concentration as determined by a four-stage filter pack system.

To understand the temporal changes of the species, seasonal variations were analyzed by the analysis of variance and summarized in Table 2-1, together with the seasonal mean and the statistical difference ($p<0.001$). The HNO_3 concentration was the highest in summer and lowest in winter, mainly due to the secondary production from the photochemical reaction of nitrogen oxides because of high temperature and strong solar radiation (Brown et al., 2006; Matsumoto and Tanaka, 1996; Pryor and Sørensen, 2000; Shimohara et al., 2001). A similar record was observed previously (Aikawa et al., 2008, 2005; Kaneyasu et al., 1995; Matsumoto and Okita, 1998; Zhang et al., 2021). On the other hand, it is noteworthy that the HNO_3 concentration in spring was equivalent to that in summer. This is discussed in detail later.

The HCl(g) exists in the ambient air via the following three processes: (1) anthropogenic emission as a primary pollutant from coal combustion (Lightowlers and Cape, 1988; Thimonier et al., 2008), refuse incineration (Thimonier et al., 2008), and municipal and industrial waste incineration (Kaneyasu et al., 1999) etc.; (2) natural emission as a primary pollutant, e.g., volcanic eruption (Hirabayashi et al., 1982; Iwasaka et al., 1988), and (3) chemical reaction of sea salt with acid substances in the atmosphere as a secondary production (Eldering et al., 1991; Pio and Lopes, 1998; Shimohara et al., 2001). Details on chloride species will be discussed in the next section. The HCl concentration also showed a temporal change, and it was basically similar to that of HNO_3 although strictly speaking, the statistical significance among the season was different (Table 2-1). A southern wind is generally dominant in Japan including our study site. On the other hand, the wind field during our study period was studied in detail, and the west-northwestern wind as well as the southern wind had a certain level of impact at this site in the study period (Zhang et al., 2021). The high concentration of HCl in this season is possibly due to the reaction of the marine aerosols with HNO_3 as the result of "chlorine loss" reaction. Further, the suppression of NH_4Cl formation in high temperatures (Pio and Harrison, 1987) is also attributable to its seasonal variation. The higher concentration in spring would be strongly related to the transboundary transportation from the Asian continent (Peng et al., 2021).

2.3.2.2. nss-Cl

Hydrochloric acid (HCl) is secondarily produced by the reaction (1) in ambient air; as shown above, this is frequently referred to as "chlorine loss" (Harrison and Pio, 1983a; Hitchcock et al., 1980; Pio and Lopes, 1998). HCl produced through this pathway should be absolutely distinguished from that produced by anthropogenic and/or natural emission sources. For this discrimination, non-sea-salt chloride (nss-Cl) was estimated.

In our present analysis, the next two points are noteworthy; first, the HCl emission from a volcanic eruption could also be classified into nss-Cl even though it is natural, not anthropogenic; second, Peng et al. (2021) clarified that there was little impact from the volcanic eruption around our survey site. Therefore, nss-Cl around our present site should be mostly due to anthropogenic emissions. Unlike anthropogenic HCl, HCl produced by the reaction (R1) originated from NaCl; therefore, it should be categorized as an inherently natural chloride that was originally sea-salt chloride (ss-Cl).

The nss-Cl is estimated by the next formula: $nss\text{-}Cl = T\text{-}Cl - ss\text{-}Cl$, in which T-Cl is the sum of particulate chloride (Cl^-) and gaseous hydrochloric acid (HCl) determined by the four-stage filter pack system. The ss-Cl is calculated based on the concentration of Na^+ ($ss\text{-}Cl = (535.1/455)*Na^+$), assuming that sea salt is the only source of Na^+ at the survey site. In this estimation, the negative nss-Cl was observed, which indicated that there is no source of HCl other than from chlorine loss reaction. The negative nss-Cl is modified to zero for the latter consideration. The temporal change and seasonal variation of the nss-Cl concentration are shown in Fig. 2-2(b) and Table 2-1, respectively, in the same manner as HNO_3 and HCl. The temporal change in the nss-Cl concentration was different from that of HCl (Fig. 2-2(a)), and there was seasonal variation in the order of Spring > Summer ≈ Winter > Autumn ($p<0.01$) (Table 2-1).

2.3.3 Evaluation of the loss of HNO_3

2.3.3.1. Total nitrate

In ambient air, nitrate exists as gaseous HNO_3 and particulate NO_3^- in the chemical forms of $NaNO_3$, NH_4NO_3, etc. Gaseous HNO_3 is in equilibrium with particulate NH_4NO_3, as below:

(R5) $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$

In addition, nitrate changes its phase between gas and liquid/solid by a chemical reaction in the atmosphere and on the PTFE filter. However, the sum of gaseous HNO_3 and particulate NO_3^- is definitely conserved as the total amount. We, therefore, introduce the concept of total NO_3, being expressed as the sum of the particulate and gas in the four-stage filter pack system. The total NO_3 concentration could be calculated by the sum of the NO_3^- and HNO_3 concentrations to be determined in the four-stage filter pack system.

$$Total\ NO_3 = NO_3^- + HNO_3$$

The temporal change and seasonal variation of the Total NO_3 concentration are shown in Fig. 2-2(c) and Table 2-1, respectively, and they were different from any other parameters mentioned in the previous sections.

2.3.3.2. "Initial" nitric acid gas

Atmospheric HNO_3 mostly originated from the photochemical reaction of NO_2 in the atmosphere. "Actual" HNO_3 exists in the ambient air after both experiencing the reaction of chlorine loss in the atmosphere, not on the PTFE filter, and the equilibrium with NH_4NO_3 particle (reaction (5)).

Here, we introduce the parameter of "Initial" HNO_3, being estimated as follows:

$$\text{“Initial” } HNO_3 = HCl - \text{nss-}Cl + HNO_3,$$

in which HCl and HNO_3 are the concentrations determined by the four-stage filter pack method, and the nss-Cl concentration is estimated as in previous section. This estimation is based on the assumption that particulate nitrate captured on the PTFE filter is not involved in the production/reduction of HNO_3 after being captured once. In the estimation above, the former part (HCl – nss-Cl) indicates the amount of HNO_3 reacted with NaCl, i.e., the amount of HNO_3 loss due to the reaction with NaCl. In other word, “Initial” HNO_3 indicates the concentration of HNO_3 before experiencing both the “chlorine loss” reaction in the ambient air and the artifact caused by the same reaction on PTFE filter paper. The concept of “Initial” HNO_3 focuses on the chlorine loss in the atmosphere and the artifact on the PTFE filter on only HNO_3. The temporal change and seasonal variation of “Initial” HNO_3 concentration are described in Fig. 2-2(d) and Table 2-1, respectively, and they showed similarity to those of the HNO_3 concentrations determined by the four-stage filter pack system, despite the different concepts of these two parameters. Actually, the correlation coefficient between determined HNO_3 and “Initial” HNO_3 concentrations was $r=0.93$ ($p<0.001$).

2.3.3.3. “Primary” nitric acid gas

As shown and discussed above, under the comprehensive influences of chemical reactions, not only in the atmosphere but also on the PTFE filter, it is difficult to precisely determine the actual concentration of chemical species in ambient air by the four-stage filter pack system. HNO_3 is not an exception. Ammonium nitrate, NH_4NO_3, is semi-volatile compound in normal atmospheric conditions and is under the equilibrium of $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$, which shows that the HNO_3 concentration is driven by the dissociation reaction of NH_4NO_3 beside the reaction with sea salt. Its reversible equilibrium is sensitive to ambient temperature and relative humidity (Harrison and Pio, 1983b; Mozurkewich, 1993; Stelson et al., 1979; Stelson and Seinfeld, 1982) and the chemical composition of aerosols and gases (Matsumoto and Tanaka, 1996). Matsumoto and Okita (1998) evaluated the loss rate (α) of NO_3^- in the dissociation of NH_4NO_3 on a monthly basis. The dissociation of NH_4NO_3 is unavoidable in our analysis as well; therefore, the estimated "Initial" HNO_3 was also under the influence of the production of HNO_3 due to the equilibrium above. In other words, "Initial" HNO_3 was overestimated by the HNO_3 produced from the dissociation of NH_4NO_3. As for this equilibrium, the amount of HNO_3 produced corresponds to that of the NO_3^- lost as NH_4NO_3. Taking account of the chemical stoichiometry in the equilibrium of $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$ and a study by Matsumoto and Okita (1998), we introduced a new parameter of "Primary" HNO_3, representing the actual amount of HNO_3, accompanied by the influence neither from the reaction of HNO_3 with sea salt nor the dissociation of NH_4NO_3.

"Primary" HNO_3 was estimated as follows:

$$"Primary"HNO_3 = "Initial"HNO_3 - \frac{\alpha}{1-\alpha}NO_3^-$$

where "Initial" HNO_3 is calculated as above, and the NO_3^- concentration is determined by the four-stage filter pack system. The latter part represented the amount of HNO_3

produced by the dissociation of NH_4NO_3 after taking account of the chemical stoichiometry in the equilibrium of $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$ and a study by Matsumoto and Okita (1998). In this estimation, seasonally averaged α was calculated based on the monthly α by Matsumoto and Okita (1998). The estimated seasonal α was 0.48, 0.54, 0.42, and 0.31 for spring, summer, autumn, and winter, respectively. As can be seen from the calculated α, $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$ has the highest impact in summer and the lowest in winter.

The temporal variation and seasonal variation of the “Primary” HNO_3 concentrations are shown in Fig. 2-2(e) and Table 2-1, respectively, where the negative value of “Primary” HNO_3 was replaced with zero in the estimation of “Primary” HNO_3. The estimated “Primary” HNO_3 showed the highest concentration in summer, as was generally expected. The statistically same seasonal mean concentrations were estimated in the other three seasons. The negative “Primary” HNO_3 concentration was, however, mainly observed in spring; the rate of days when the “Primary” HNO_3 concentration was negative was 0.57, 0.05, 0.27, and 0.28 in spring, summer, autumn, and winter, respectively. As for the month, negative cases most frequently appeared in March, followed by April, January, November, and December; the others were insignificant (less than 5 samples/month).

The seasonal variation of “Primary” HNO_3, being higher in warmer season, was basically the same as those of HNO_3 and "Initial” HNO_3, except for spring, and was consistent with previous studies (Aikawa et al., 2008a, 2005; Chiwa, 2010; Kaneyasu et al., 1995; Matsumoto and Okita, 1998; Osada et al., 2018). “Primary” HNO_3, referring to the concentration of HNO_3 regardless of the chlorine loss reaction in ambient air, the influence of the artifacts, and the dissociation of NH_4NO_3, showed the highest concentration in summer. In contrast, the most significant difference in seasonal variation among HNO_3, "Initial" HNO_3, and "Primary" HNO_3 was observed in spring. As shown in Table 2-1, unlike HNO_3 and "Initial" HNO_3, which are higher in spring, the "Primary" HNO_3 concentration in spring was distinctly lower than that in summer. This could be attributable to the combined consequences of the following two effects: (1) loss rate α and (2) the transboundary transportation of air pollutants. First, the loss rate of α (0.48) in spring used for the estimation was the second largest, next to that in summer, which leads to no small impact due to the dissociation of NH_4NO_3 in spring. Secondly, our study site, located on the eastern edge of the Asian region, is strongly influenced by the transboundary transportation of air pollution from the Asian Continent (Aikawa et al., 2017; Kaneyasu et al., 2014; Pan et al., 2018; Takahashi et al., 2010; Zhang et al., 2021), and the concentration of PM2.5 including NH_4NO_3 actually becomes high in spring (Coulibaly et al., 2015; Pan et al., 2018; Zhang et al., 2021). Zhang et al. (2021) found that secondary nitrate, namely NH_4NO_3, was transported by west-northwestern and northwestern winds to the sampling site and had a high contribution to PM2.5 concentration. This conclusively and comprehensively results in the distinct differences between "Primary" HNO_3 and HNO_3 and "Initial" HNO_3 in this season.

It's obviously seen that under the unavoidable influence of chlorine loss reaction and sampling artifacts, the concentration of HNO_3 determined by four-stage filter pack as well as the information it reflects (i.e., seasonal pattern) was significantly affected due to seasonal characteristic of the comprehensive impact. Through the step-by-step calculation of “Initial HNO_3” and “Primary HNO_3”, the behavior of HNO_3 in ambient air and during sampling was revealed. Since the estimation of these two parameters was basically based on the dataset obtained from a four-stage filter pack with a typical arrangement, this approach allowed applying to not only newly obtained dataset but also accumulated datasets for novel information as a validation methodology.

2.4 Conclusions

The loss of ambient nitric acid gas related to sea-salt chloride was studied and evaluated based on the one-year dataset by four-stage filter pack observation on a daily basis. The reaction of NaCl with HNO_3 was considered from the viewpoint that the HNO_3 loss corresponds to the chlorine loss from sea salt. The “Initial” HNO_3, which referred to the concentration of HNO_3 before being affected by either chlorine loss reaction in the ambient air or artifact related to sea salt on filter paper, showed a similar seasonal trend in the concentration of HNO_3 determined by filter pack itself. On the other hand, the concentration of “Primary” HNO_3, representing the concentration of HNO_3 before receiving comprehensive impact, i.e., the HNO_3 loss due to the reaction with NaCl (not only the chlorine loss in ambient air but also the artifacts on the filter paper) and the HNO_3 production because of the dissociation of NH_4NO_3 on the filter, showed different seasonal patterns. The most significant comprehensive impact on HNO_3 loss was observed in spring. The filter pack method is quite useful and convenient for measuring both aerosol and gas all together; however, the method suffers from the unavoidable disadvantage of artifact. The proposed step-by-step approach via “Initial HNO_3” and “Primary HNO_3” can give an insight on the HNO_3 behavior in ambient air and during sampling as well as provide a new validation methodology for precise estimation of HNO_3 concentration observed by four-stage filter pack method.

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Chapter 3. Assessment of sampling artifact on HNO_3 using multi-stage filter pack systems and the reveal of ambient pre-neutralized H_2SO_4

3.1 Introduction

Ambient sulfate (SO_4^{2-}) is one of the major components of PM2.5) (Akimoto 2016; Huang et al. 2014; Ma et al. 2015; Zhang et al. 2021), and most SO_4^{2-} in ambient air exists as chemical forms of $(NH_4)_2SO_4/NH_4HSO_4$, i.e., as a chemical composition after neutralization and/or partial neutralization by NH_3 in ambient air (Akimoto 2016). Ambient H_2SO_4 originates from the oxidation of SO_2 by hydroxyl radicals, followed by the reaction of produced SO_3 with water vapor (Akimoto 2016; Lovejoy et al. 1996; Stockwell and Calvert 1983). As low vapor pressure, the generated gaseous H_2SO_4 condenses and yields particulate H_2SO_4 (Akimoto 2016; Seinfeld 2014). Ambient H_2SO_4 is an important species as a precursor for new particle formation and in subsequent particle growth (Boy et al. 2005; Fiedler et al. 2005; Kulmala 2003; Stolzenburg et al. 2020). In the troposphere, under the presence of gaseous NH_3, particulate H_2SO_4 is neutralized immediately and produces ammonium sulfate aerosols (Akimoto 2016). Hence, ambient SO_4^{2-} is rarely observed in the chemical form of H_2SO_4 (Charlson et al. 1978; Warneck 2000).

A filter pack is a frequently employed sampling instrument in some monitoring networks such as the European Measurement and Evaluation Programme (EMEP), the National Atmospheric Deposition Program (NADP), and the Acid Deposition Monitoring Network in East Asia (EANET) for its useful and convenient features, including the ability to collect both particulate matter and gaseous compounds simultaneously. The typical and most common assembly is a four-stage filter pack, in which particulate matter is captured in the first filter paper, and gaseous compounds are collected in the subsequent layers (Sickles et al. 1999). During operation, gaseous compounds pass through the first filter, which captures particles before they reach their designated filter; this leads to the most concerning disadvantage of the device: the presence of artifacts (Allegrini et al. 1987; Harrison and Kitto 1990; Matsumoto and Okita 1998; Sickles et al. 1990).

An artifact is defined as an error caused by unintended gas-to-particle conversion that occurs during sampling. The presence of artifacts in the filter pack is widely recognized for nitrate, chloride, and ammonium species (Matsumoto and Okita, 1998). SO_4^{2-} does not convert to gas (SO_2) by the artifact; therefore, the presence of artifacts for SO_4^{2-} and SO_2 themselves is not identified. However, it is possible that H_2SO_4 is related to the artifact of other species. The example of artifact on HNO_3 with the presence of H_2SO_4 can be shown as follows (Matsumoto and Okita, 1998):

$\mathrm{NaCl(P) + HNO_3(G) \rightarrow NaNO_3(P) + HCl(G)}$ (1)

$\mathrm{NaNO_3(P) + H_2SO_4(P) \rightarrow NaHSO_4(P) + HNO_3(G)}$ (2)

$\mathrm{NH_4NO_3(P) + H_2SO_4(P) \longrightarrow NaHSO_4(P) + HNO_3(G)}$ (3)

$\mathrm{NH_4NO_3(P) \rightarrow NH_3(G) + HNO_3(G)}$ (4)

In these reactions, H_2SO_4 is associated with reactions (2) and (3), and both lead to a biased HNO_3 concentration being the positive artifact. Therefore, the presence of ambient H_2SO_4 hinders the precise determination of the HNO_3 concentration in the filter pack system.

On the other hand, ambient SO_4^{2-} is rarely observed in the chemical form of H_2SO_4. However, if H_2SO_4 exists in ambient air, it has some impacts on the determination by filter pack. In this study, we tried to validate the existence of ambient H_2SO_4 by the paralleled installation of four-stage and five-stage filter packs.

3.2 Experimental

3.2.1 Sampling site

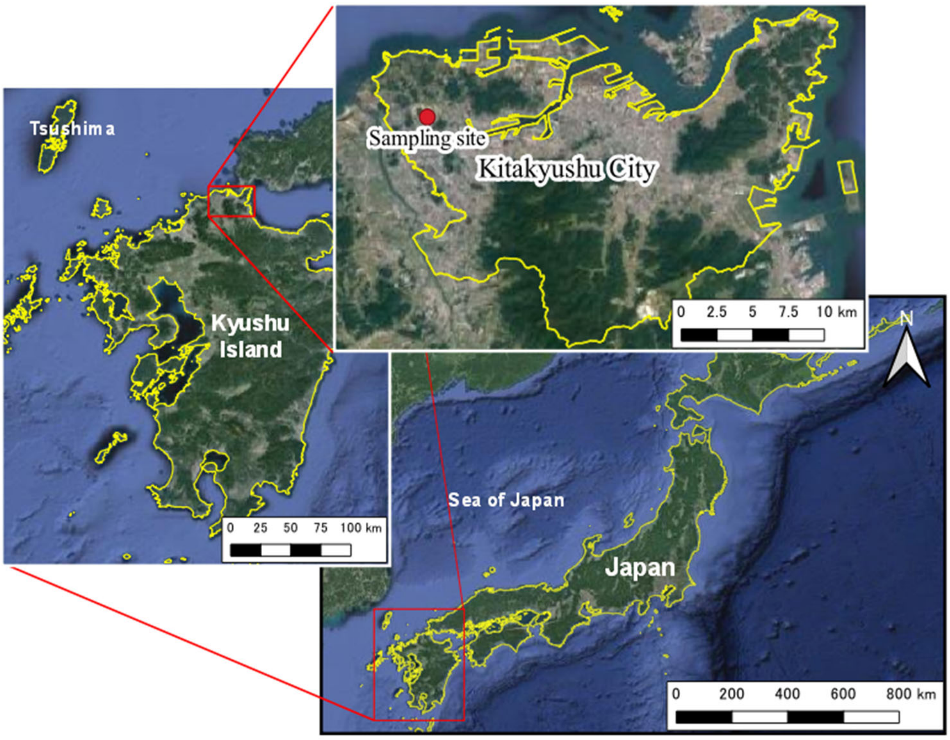

Fig. 3-1 Location of sampling site

The sampling of ambient air was conducted on the roof of the University of Kitakyushu (33.89° N, 130.71° E) (Fig. 3-1). The site is in Kitakyushu City, a major industrial city in Japan. Located in the suburb in the northmost part of Kyushu Island, approximately 6 km from the sea, the survey site is characterized by the mixing of continental and maritime air masses.

3.2.2 Sampling method and chemical analysis

Air sampling was carried out in four periods from August 2018 to May 2019. Each period lasted for one month and represents one season: August 2018—summer, October 2018—autumn, January 2019—winter, May 2019—spring.

Particulate matter (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) and gaseous compounds (HCl, HNO_3, SO_2, and NH_3) were collected on a daily basis from noon (12 pm) to noon (Japan Standard Time (JST)) by four-stage and five-stage filter pack systems in parallel on the same schedule.

The four-stage filter pack (Type A) had the typical assembly, including a PTFE filter paper, a polyamide filter paper, a 6% K_2CO_3–2% glycerin-impregnated cellulose filter paper, and a 5% H_3PO_4–2% glycerin-impregnated cellulose filter paper. All of the filters were set up in an open-face Norwegian Institute for Air Research (NILU) filter holder.

The five-stage filter pack (Type B) consists of an impactor stage, set up with a torus-shaped quartz filter paper, mounted on top of a basic four-stage filter pack to separate coarse particles which have the aerodynamic diameter larger than 2.5 μm.

The specifications of each filter in Type A and Type B are summarized in Table 3-1.

Table 3-1 Specifications of filters in Type A and Type B

Stage	Specifications of filters	Collected species	
		Type A	Type B
F_I	Torus-shaped quartz filter	-	Coarse particles
F_0	PTFE filter	Total particles	Fine particles
F_1	Polyamide filter	HNO_3; Partial SO_2, HCl	
F_2	6% K_2CO_3–2% glycerin-impregnated cellulose filter	SO_2, HCl	
F_3	5% H_3PO_4–2% glycerin-impregnated cellulose filter	NH_3	

The flowrates during air sampling were around 1.5 and 2.0 $L.min^{-1}$ for four-stage and five-stage filter packs, respectively.

The material collected by each filter was determined by ion chromatograph (Thermo Scientific^{TM} Dionex^{TM} Integrion Thermo Fisher Scientific Inc., Waltham, MA, USA) for eight water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) after the extraction. The details is the same as our previous studies and described in our manuscript (Aikawa et al., 2016, 2013, 2008, 2005). On the other hand, in addition to our previous methodology, pH value was also measured for the extracted solution of PTFE filters in both types to determine H^+ concentration in our current study.

3.3 Result and discussion

3.3.1 Concept of artifact on HNO_3 on four-stage and five-stage filter packs

As mentioned in the Introduction, before reaching the designated filter paper, HNO_3 experiences four artifacts (reactions (1) to (4)); hence, the concentration of HNO_3 determined by the four-stage filter pack is under the combined effect of those reactions. Among them, in reactions (1) and (2), the combination of coarse particle (NaCl) and gaseous HNO_3 (reaction (1)) and the combination of coarse particle ($NaNO_3$) and fine particle (H_2SO_4) (reaction (2)) are involved in the artifact on HNO_3. From that point, if the coarse particle can be separated from the inlet stream, these two reactions can be avoided, and their impact, then, is eliminated. This is accomplished by the use of a five-stage filter pack with a top-mounted impactor. Due to its inertial force, this impactor stage is responsible for separating and collecting coarse particles; hence, the rest of the airstream—including fine particle and gaseous species—can reach the subsequent filters without being in contact with the coarse particles collected.

From this viewpoint, the artifact on HNO_3 caused by reactions (1) and (2) can be detected and assessed by considering the difference between the concentration determined by the four-stage (Type A) and the five-stage (Type B) filter packs. In addition, from the viewpoint of HNO_3, reaction (1) is inclined to decrease the concentration of HNO_3, while reaction (2) has the opposite propensity. Thus, comparing the HNO_3 concentration in the two systems would reveal the contribution of each reaction to the combined impact of artifacts.

3.3.2 Comparison of the concentrations of nitrate species observed in the two systems

3.3.2.1. Seasonal variation in the concentration of nitrate species in the two systems

Fig. 3-2 shows the concentrations of HNO_3, nitrate particles (P-NO_3^-), and total nitrates ($T\text{-}NO_3^- = HNO_3 + P\text{-}NO_3^-$), where P-$NO_3^-$ in Type A is determined by the PTFE filter, and P-NO_3^- in Type B is expressed as the sum of the PTFE (fine particle) and torus-shaped quartz filter paper (coarse particle). The concentration of nitrate species had a similar trend in the two systems; the HNO_3 concentration generally showed a high concentration in summer, and this was confirmed in previous studies (Aikawa et al. 2005, 2008; Matsumoto and Okita 1998; Zhang et al. 2021). In contrast, in concurrence with summer, the highest HNO_3 concentration was observed in spring as well, which does not coincide with reported documents. This unexpected high HNO_3 concentration was shown and discussed in detail in another of our manuscripts (Nguyen and Aikawa 2022), and this phenomenon was attributed to the comprehensive impact of the reaction of sea salt with HNO_3 and the dissociation of NH_4NO_3. The highest concentration of P-NO_3^- was observed in winter, followed by spring, autumn, and summer. In winter, the temperature-dependent equilibrium $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$ toward the particle phase largely contributes to the highest P-NO_3^- concentration (Harrison and Pio 1983; Mozurkewich 1993; Seinfeld and Pandis 2016; Stelson and Seinfeld 1982), while the long-range transport of air masses from the Asian continent is strongly responsible for the high concentration in spring (Aikawa et al. 2017; Inomata et al. 2016; Zhang et al. 2021).

3.3.2.2. Difference in the nitrate species concentration in the two systems

Despite the similar trend in concentration (Fig. 3-2), there were differences in the concentration of nitrate species of the two systems. Those differences would be caused by differences in the devices themselves (the use of four-stage and five-stage) and/or by sampling artifact. For T-NO_3^-, Type A generally showed a higher concentration than Type B. The same difference was reported by Sasaki et al. (2022), and they attributed the higher concentration in the four-stage system to the unintentional collection of rain drops and ambient particles in conditions of strong winds. Therefore, when the difference in the two systems is compared and discussed, this unintentional difference due to sampling condition should be taken into account.

Table 3-2 shows the median ratio between the concentration determined in Type A and Type B (concentration in Type A/concentration in Type B). All nitrate species showed higher concentrations in Type A, which is qualitatively similar to the result of Sasaki et al. (2022). The difference in P-NO_3^- and T-NO_3^- is statistically insignificant ($p>0.05$) with biases toward Type A of around 4–10% and 8–15%, respectively. On the other hand, a higher concentration in Type A was observed for HNO_3, and its ratio varied by season, with $p<0.05$ in summer, autumn, and spring; this strongly suggests that the HNO_3 concentration is affected by sampling artifacts.

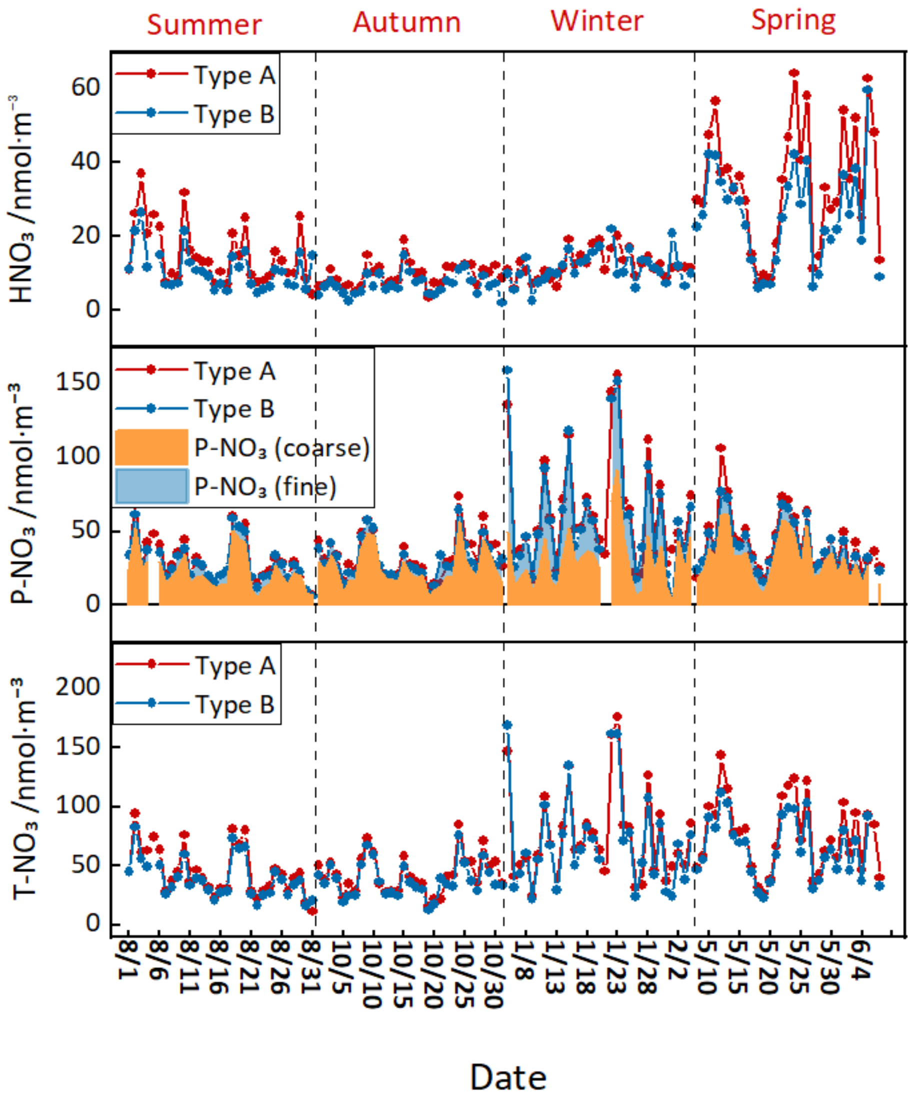

Fig. 3-2 Concentration of nitrate species (HNO_3, $P\text{-}NO_3^-$ and total nitrate ($T\text{-}NO_3^- = HNO_3 + P\text{-}NO_3^-$) determined in four-stage (Type A) and five-stage (Type B) filter pack systems. Here, $P\text{-}NO_3^-$ in Type A is determined by PTFE filter and $P\text{-}NO_3^-$ in Type B is expressed as the sum of PTFE (fine particle) and torus-shape quartz filter paper (course particle).

Table 3-2 Median ratio of nitrate species between Type A and Type B (Type A/Type B)

	HNO_3	$P\text{-}NO_3$	$T\text{-}NO_3$
Summer	1.41	1.04	1.12
Autumn	1.33	1.10	1.13
Winter	1.12	1.07	1.08
Spring	1.35	1.07	1.15

To determine which reaction caused that variance, Δ is introduced and calculated as follows:

$$\Delta = \Delta HNO_3 - \Delta T\text{-}NO_3^-,$$

in which ΔHNO_3 and $\Delta T\text{-}NO_3^-$ are the difference in the concentration of HNO_3 and T-NO_3^- between Type A and Type B (Type A – Type B), respectively. Here, the second term ($-\ \Delta T\text{-}NO_3^-$) is a term to correct the unintentional difference due to sampling conditions between Type A and Type B. If the difference in the devices themselves caused the dissimilarity, $\Delta T\text{-}NO_3^-$ should be larger than or equal to ΔHNO_3. If not, the sampling artifact is a contributor to the difference in the HNO_3 concentration (ΔHNO_3) between the two systems. Furthermore, if a negative Δ is observed, it means that reaction (1) has a larger contribution and/or the differences in the devices largely contribute; on the other hand, if a positive Δ is observed, it means that reaction (2) should have a large contribution to the determination of the HNO_3 concentration. The positive Δ was actually and frequently observed; and the number of positive Δ varied by season, with the most frequent cases in summer, followed by spring, autumn, and winter. This suggests that the sampling artifact on HNO_3 did exist and had seasonal characteristics. This will be discussed in detail in later sections (3.3 and 3.4). The observed positive Δ makes the point that reaction (2) with the participation of H_2SO_4 would have a significant/larger contribution to the HNO_3 concentration. This finding also reveals the existence of pre-neutralized H_2SO_4 particles, which is unusual based upon common knowledge about the existence of atmospheric H_2SO_4.

3.3.3 Acidity in the PTFE filter

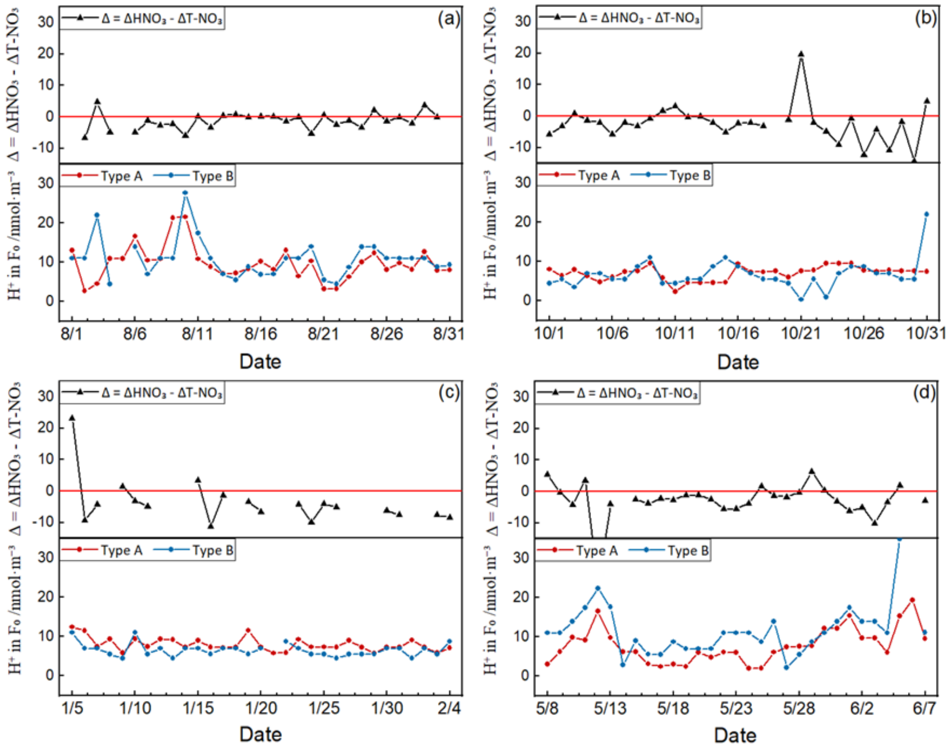

Fig. 3-3 Δ and H^+ concentration in the PTFE filter determined in Type A and Type B in summer (a), autumn (b), winter (c) and spring (d).

The PTFE filter in Type A (the common four-stage filter pack) collects particles. In Type B, due to the presence of an impactor stage, the PTFE collects only fine particles, including H_2SO_4. The H^+ that arises from H_2SO_4 collected in the PTFE filter refers to the acidity measured as the pH of the extraction from the PTFE filter. Theoretically, in Type B, the two reactions ((1) and (2)) can be avoided due to the impactor stage; hence, if there is a decrease in the H^+ concentration in Type A, it is supposed to be caused by reaction (2) invited by $NaNO_3$ produced by reaction (1) on the PTFE filter in Type A and/or $NaNO_3$ originally/directly collected from ambient air. The concentration of H^+

in the PTFE filters in Type A and Type B in each season is demonstrated in Fig. 3-3, together with the corresponding.

In summer, the positive Δ was observed on 11 of 30 days; here, 30 days is the total number of sampling days in summer. In contrast, in winter, the positive Δ was observed on just 3 of 30 days, and on 5 of 31 days and 6 of 30 days in autumn and spring, respectively, corresponding to the middle season between summer and winter. In response to Δ, the number of days that showed higher H^+ concentrations in Type B varied seasonally. Of 30 days in summer and winter, a higher H^+ concentration in Type B was observed 19 and 3, respectively. This is consistent with the seasonal variation in Δ. Here, the number of days showing a higher H^+ concentration in Type B was 11 of 31 days in autumn, which is not inconsistent with the seasonal variation shown above. In contrast, in spring, 26 of 30 days showed a higher H^+ concentration, meaning that the rate in Type B in spring was exceptionally higher than those in other seasons. This special situation in spring will be discussed in the next section (3.3.4).

3.3.4 Especially high H^+ concentration in Type B in spring

As has been discussed, the higher H^+ concentration in Type B is dependent on reaction (2) on the PTFE filter in Type A; namely, H_2SO_4 consumed in reaction (2) on the PTFE filter in Type A leads to a lower H^+ concentration in Type A, i.e., a relatively higher H^+ concentration in Type B. Japan generally experiences a strong impact of the transboundary transportation of particulate matter in spring (Itahashi et al. 2010; Kaneyasu et al. 2014; Takahashi et al. 2010), and our study site also suffers from a greater impact due to the outflow from the Asian continent (Nguyen and Aikawa 2022; Peng et al. 2021; Zhang et al. 2021), including PM2.5 and Kosa events (Itahashi et al. 2010; Iwasaka et al. 1988; Pan et al. 2015). Here, we focus on the derivation of $NaNO_3$ in reaction (2) by dividing it into two occasions, as follows:

occasion (i): in the case in which $NaNO_3$ is provided by reaction (1) on the PTFE filter in Type A; and occasion (ii): in the case in which $NaNO_3$ is originally/directly collected as particles from ambient air by sampling. In occasion (i), NO_3^- in $NaNO_3$ originates when HNO_3 passes through and comes in contact with collected NaCl on the PTFE filter in Type A (reaction (1)), and then, if H_2SO_4 exists in a subsequent air flow, NO_3^- is returned to HNO_3 due to reaction (2). This means that in occasion (i), there should be no difference in the HNO_3 concentration determined in Type A and Type B if H_2SO_4 sufficient to return NO_3^- to HNO_3 is provided; in this case, there should be no difference in Δ if there is adequate H_2SO_4 to return NO_3^- to HNO_3. Even though H_2SO_4 sufficient to return NO_3^- to HNO_3 is not supplied, the value of Δ should be negative. In contrast, in occasion (ii), HNO_3 produced by reaction (2) on the PTFE filter in Type A should provide a net additional increment of HNO_3 in Type A, meaning that, in occasion (ii), it is expected that Δ should have a positive value. Practically, as shown in 3.3, only 6 of 30 days in spring had a positive Δ; thereby, occasion (i) was indicated. As a consequence, in spring, the combination of reaction (2) with the production of $NaNO_3$ on the PTFE filter in Type A, as well as the direct collection of $NaNO_3$, plays an important role in the determination of the HNO_3 concentration in the filter pack.

3.3.5 Source appointment of ambient H_2SO_4 at the survey site

To gain insight into how H_2SO_4 exists, 72-hour backward trajectories were plotted using TrajStat software (Wang et al. 2009) (Fig. 3-4). The trajectory started at 0:00 JST (15:00 UTC) at a height of 1500 m.

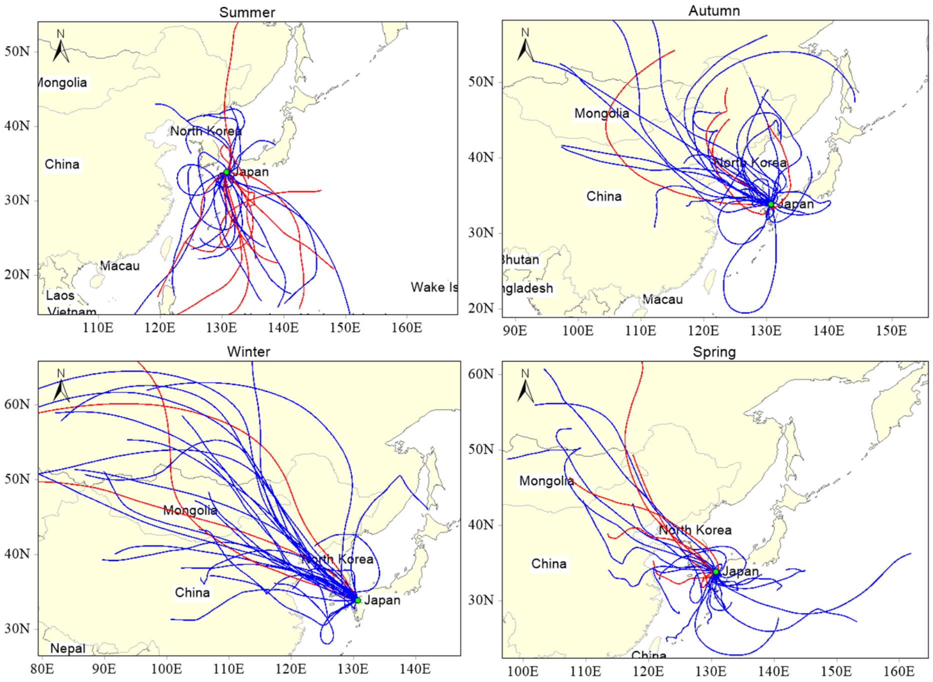

Fig. 3-4 72-hour backward trajectories calculated at 1500-meter heigh in each season, in which trajectories in red color indicate the day with positive Δ.

During the summer, southern air masses from the ocean passed through Japan inland and arrived at the sampling site. These air masses covered almost every day that positive Δ was detected. Volcanic activity of Sakurajima, one of the most active volcanoes in the south of Kyushu Island, was recorded in August 2018 (www.ds.data.jma.go.jp) and coincided with the observation period. Therefore, SO_2 emitted from the Sakurajima volcano would impact on the positive Δ, high acidity, and unneutralized H_2SO_4 in our results.

In autumn and winter, the northwestern air mass from the Asian continent became dominant. In spring, the survey site experienced air masses from both northwest and south/southeast directions. As for three seasons (autumn, winter, and spring), on days on which positive Δ was observed, the trajectories started from the northwest, i.e., the Asian continent.

3.4 Conclusions

We successfully detected pre-neutralized sulfuric acid (particulate H_2SO_4) based on daily sampling by four-stage and five-stage filter packs conducted in parallel. Thanks to the installation of an impactor in the five-stage filter pack, the chemical reactions between coarse particles and gaseous species/fine particles, which cause sampling artifacts, are avoided. The presence of particulate H_2SO_4 was confirmed by the difference in the HNO_3 concentration between the four-stage and five-stage filter packs. The pre-neutralized particulate H_2SO_4 was more dominantly observed in summer than in other seasons, and its existence was deeply related to the volcanic explosion and the subsequent transportation of ejecta.

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Chapter 4. Summary and future prospects

4.1 Summary

Nitric acid gas (HNO_3) is an important gas in terms of atmospheric chemistry. Ambient HNO_3 mainly generates from the photochemical reaction of NO_x, which is the exhausted product from the use of fossil fuel, hence, it is considered as the sink of nitrogen oxides. Ambient HNO_3 can be scavenged from the atmosphere due to dry and wet deposition and result in acid deposition, which has a direct impact on human health and the biosphere. Therefore, the monitoring of atmospheric HNO_3 needs to be focused and to be precise. In terms of sampling method for ambient HNO_3, the filter pack stands out as its features of collecting both gases and particulate matter in one operation. Although this method suffers from the typical difficulty of filter-based method, being sampling artifacts, it can't be denied that the filter pack is still an effective and commonly used method for HNO_3 sampling. This research provides an assessment on the sampling artifact of HNO_3 on the filter pack method. The assessment is described under two approaches: in the four-stage filter pack itself and in the simultaneous employment of multi-stage filter pack method.

The study has successfully introduced three new parameters to describe and assess HNO_3 concentration under the impact of sampling artifacts related to the reaction with sea salt, the dissociation of NH_4NO_3 and the reaction with the participation of unneutralized H_2SO_4. The newly developed parameters and their scientific meaning are summarized in Table 4.1.

Table 4-1 Formular and scientific meaning of the newly introduced parameters

Parameter	Formula	Scientific meaning
"Initial" HNO_3	$HCl - nss\text{-}Cl + HNO_3$	HNO_3 concentration regardless the influence of the reaction with sea salt both in the atmosphere (chlorine loss reaction) and on the PTFE filter surface (sampling artifact)
"Primary" HNO_3	$\text{"Initial"}HNO_3 - \frac{\alpha}{1-\alpha}NO_3^-$	HNO_3 concentration regardless the comprehensive impact (including the impact of the reaction with sea salt and the dissociation of NH_4NO_3 on the PTFE filter surface)
Δ	$\Delta HNO_3 - \Delta T\text{-}NO_3^-$	A detector for sampling artifact related to HNO_3. If positive Δ is observed, sampling artifact on HNO_3 is detected.

In chapter 2, ambient HNO_3 concentration is considered under the influence of chlorine loss reaction in the ambient air and the sampling artifact including the reaction of HNO_3 with collected sea salt and the dissociation of NH_4NO_3 in Teflon/PTFE filter. The assessment is based on one-year sampling on a daily basis using a four-stage filter pack method. The assessment was conducted at a survey site which is highly affected by marine aerosol, i.e., high concentration of sea salt. The result determined by the four-stage filter pack showed a higher HNO_3 concentration in warmer seasons with a similar mean value in spring and summer, which is a specific phenomenon and inconsistent with the previous report about ambient HNO_3. Three parameters are introduced including *Total* NO_3, "*Initial*" HNO_3, and "*Primary*" HNO_3. *Total* NO_3 is simply the sum of particle NO_3^- and HNO_3 determined by the four-stage filter pack. "*Initial*" HNO_3, refers to HNO_3 concentration regardless the effect of $NaCl(p) + HNO_3(g) \rightarrow NaNO_3(p) + HCl(g)$ in either ambient air or in Teflon filter paper, is calculated as *"Initial" HNO_3 = HCl – nss-Cl + HNO_3* from the viewpoint that the loss of HNO_3 is corresponding to the produced HCl. "Initial" HNO_3 showed the similar seasonal variation with the HNO_3 concentration directly determined by the four-stage filter pack, hence, this factor, i.e., the reaction of HNO_3 with sea salt does influence of the concentration of HNO_3 but it is definitely not the factor to impact on the specific seasonal pattern of HNO_3 concentration in this survey site. Lastly, imply from the loss rate α of NO_3 due to the dissociation of NH_4NO_3 which is previously reported by Matsumoto and Okita (1998), *"Primary" HNO_3 = "Initial" HNO_3 – $(\alpha/(1-\alpha))$ NO_3* is introduced, represents for the concentration of HNO_3 before receiving the comprehensive impact from both sampling artifacts and chlorine loss reaction from the atmosphere. "Primary" HNO_3 showed the highest concentration in summer, which is in agreement with previous reports for ambient HNO_3 concentration. The distinguished seasonal pattern of "*Primary*" HNO_3 in comparison to that of "*Initial*" HNO_3 and HNO_3 determined directly from the four-stage filter pack indicates the strongest impact of this comprehensive impact in spring. The phenomenon in spring can be explained by (1) the relatively high value of α in spring, which indicated the high influence of the dissociation of NH_4NO_3 in this season, and (2) the transboundary transportation of Asian air masses at the sampling site. This approach successfully proposes a step-by-step validation method for not only the present data but also for the accumulated HNO_3 concentration determined by the common four-stage filter pack method in the past.

Chapter 3 describes the influence of sampling artifacts on HNO_3 concentration in the employment of a four-stage and a five-stage filter pack method in parallel. A five-stage filter-pack, which is a modified version of a common four-stage filter pack with an impactor filter mounted on top to firstly capture/eliminate coarse particles ($AD \geq 2.5\mu$), promised some hints on sampling artifacts. A one-year sampling including the daily samples obtained in a month for each season was taken into consideration. As expected, a disparity in HNO_3 concentration was observed with a distinctive bias toward the four-stage filter pack in summer, autumn and spring which suggests the possible influence from sampling artifacts. As the relatively higher concentration in Type A was observed in all nitrate species including T-NO_3, NO_3^- and HNO_3, a new parameter Δ was introduced as a detector for the presence of sampling artifact. Δ was calculated as the difference ΔHNO_3 - $\Delta T\text{-}NO_3$. Since T-NO_3 is the sum of NO_3^- and HNO_3, any differences in HNO_3 between Type A and Type B should be covered by the difference in T-NO_3, i.e., ΔHNO_3 should be less than/equal to $\Delta T\text{-}NO_3$, and sampling condition is the only factor to cause the disparity. Other than that ($\Delta HNO_3 > \Delta T\text{-}NO_3$, i.e., positive Δ), sampling exists and is the second reason for the disparity in HNO_3 concentration. By the use of a five-stage filter pack, the following artifacts are avoided

$$\mathrm{NaCl(P) + HNO_3(G) \rightarrow NaNO_3(P) + HCl(G)}$$

$$\mathrm{NaNO_3(P) + H_2SO_4(P) \rightarrow NaHSO_4(P) + HNO_3(G)}$$

The HNO_3 concentration collected in the four-stage filter pack is under the combined impact of these two reactions. Positive Δ was observed, which indicated that the sampling artifact did affect the concentration of HNO_3 in the four-stage filter pack. Furthermore, a bias toward Type A in HNO_3 concentration supported that the reaction of $NaNO_3$ and H_2SO_4 in Teflon/PTFE filter has a larger contribution to this phenomenon. As a consequence, the existence of ambient H_2SO_4 at the sampling site is revealed. The presence of ambient H_2SO_4 is frequently observed in summer (August) than in winter (January). The acidity of PTFE filter paper is referred by the concentration of H^+ derived from H_2SO_4 in PTFE filter. If H_2SO_4 reacts with $NaNO_3$ as an artifact the relatively higher acidity in Type B is observed, as a result. In spring, the highest number of cases to have a higher acidity in Type B was observed while the corresponding Δ was only 6. This distinctive phenomenon in spring was attributed to $NaNO_3$ produced from the reaction of HNO_3 with sea salt in PTFE filter as well as $NaNO_3$ directly collected from the atmosphere. To investigate the source of suspected H_2SO_4, 72-hour backward trajectories was analyzed. The results indicated that SO_2 released from a domestic volcano was responsible for the ambient H_2SO_4 in summer, while in the other seasons except for summer, SO_2 was carried to the survey site by northwestern air masses.

4.2 Future prospects

In Chapter 2, the concept of a step-by-step approach to validate the HNO_3 concentration under the comprehensive impact of the reaction with sea salt and the dissociation of NH_4NO_3 was successfully introduced and applied under the flow rate of 10L/min. In the next step, an assessment on the system with a different flow rate i.e., 2 L/min will be taken into consideration to answer these questions: Is the method applicable to different flow rates? Does the change in flow rate has any impact on the calculation?

In this research, the influences of the reactions that occurred during operation related to sea salt, NH_4NO_3 and H_2SO_4 on HNO_3 concentration has been considered separately and showed a significant impact. However, the combined impact of these factors has not been clarified yet. On the other hand, a five-stage filter pack showed its advance in segregating the coarse particle as well as eliminating the impact from coarse particles. Therefore, in the future, the combined impact will be considered by the employment of a five-stage filter pack.

List of publication

1. **Nguyen, K. L.**, & Aikawa, M. (2022). A novel step-by-step assessment methodology for the correction of sampling artifact and chlorine loss reaction on HNO3 in ambient air. *Water, Air, & Soil Pollution 233, 110*. https://doi.org/doi.org/10.1007/s11270-022-05570-4
2. **Nguyen, K. L.**, & Aikawa, M. (2022). Record of pre-neutralized H_2SO_4 implied in the results of four-stage and five-stage paralleled filter pack observations on the western edge of Japan. *Water, Air, & Soil Pollution* **233,** 319. https://doi.org/10.1007/s11270-022-05823-2

Appendix

In the following, the collected data and corresponding calculated parameter are presented. Some of those showed negative value. These negative values were set to 0 in statistical analysis and in figure plotting.

Appendix 1 Concentration of each parameter in the four-stage filter pack under the flow rate of 10 L.min^{-1} in winter 2016 (December 2016, January, February 2017)

(Unit: nmol/m^3)

Date	T-NO_3	HNO_3	NO_3^-	HCl	T-Cl	nss-Cl	"Initial" HNO_3	"Primary" HNO_3
12/1/2016	62.6	17.0	45.6	31.00	81.7	1.1	46.8	26.36
12/2/2016	84.4	13.3	71.1	25.40	87.8	-1.7	40.4	8.44
12/3/2016	22.1	3.1	19.0	5.82	28.7	-0.3	9.3	0.72
12/4/2016	74.2	11.2	63.0	10.98	35.9	8.3	13.9	-14.39
12/5/2016	54.6	9.1	45.5	12.02	47.3	-3.0	24.0	3.59
12/6/2016	223.2	35.3	187.9	39.85	120.3	-0.7	75.8	-8.57
12/7/2016	51.6	7.1	44.4	14.51	82.3	2.3	19.4	-0.58
12/8/2016	98.1	18.0	80.1	27.22	87.1	-2.3	47.5	11.51
12/9/2016	162.0	27.5	134.6	27.59	69.2	4.4	50.7	-9.81
12/10/2016	165.2	29.9	135.4	36.63	140.8	-8.9	75.4	14.57
12/11/2016	46.1	7.2	38.9	15.15	83.9	-4.3	26.6	9.10
12/12/2016	32.5	6.2	26.3	18.03	79.7	11.8	12.5	0.68

12/13/2016	89.0	7.8	81.2	10.43	51.7	18.5	-0.2	-36.73
12/14/2016	24.6	7.4	17.2	15.11	89.4	1.1	21.4	13.74
12/15/2016	26.0	3.3	22.7	19.16	42.3	15.6	6.8	-3.40
12/16/2016	39.5	11.4	28.1	17.00	108.5	0.2	28.2	15.60
12/17/2016	29.7	8.0	21.7	11.68	65.8	1.9	17.8	8.04
12/18/2016	57.9	9.4	48.6	12.68	43.5	-2.8	24.9	3.06
12/19/2016	54.6	10.0	44.6	12.83	38.1	6.3	16.5	-3.57
12/20/2016	86.3	15.1	71.1	16.59	47.3	13.1	18.7	-13.29
12/21/2016	124.8	15.2	109.6	18.32	41.8	16.5	17.1	-32.14
12/22/2016	61.6	16.2	45.4	30.87	80.8	11.8	35.3	14.93
12/23/2016	37.3	4.0	33.3	40.27	214.2	-3.3	47.5	32.58
12/24/2016	33.4	6.7	26.7	30.95	143.3	2.3	35.4	23.44
12/25/2016	54.5	10.0	44.5	29.49	98.1	10.1	29.4	9.45
12/26/2016	77.9	15.3	62.6	28.23	84.0	9.5	34.0	5.91
12/27/2016	29.7	5.9	23.8	13.41	86.2	2.1	17.2	6.47
12/28/2016	39.8	12.0	27.7	37.45	161.6	19.4	30.0	17.58
12/29/2016	24.2	4.3	19.9	34.50	101.8	27.0	11.8	2.85
12/30/2016	52.2	19.2	33.0	47.05	124.6	34.3	31.9	17.06
12/31/2016	58.0	9.1	48.9	48.84	94.2	32.5	25.4	3.40
1/1/2017	61.6	11.6	49.9	16.74	41.8	5.5	22.9	0.42
1/2/2017	77.8	13.6	64.3	20.25	49.0	6.7	27.1	-1.75
1/3/2017	73.6	9.3	64.2	29.56	57.6	19.1	19.7	-9.11
1/4/2017	85.7	14.1	71.5	16.74	66.7	-0.7	31.6	-0.54
1/5/2017	176.7	18.4	158.4	45.89	96.0	14.4	49.8	-21.32
1/6/2017	30.0	7.5	22.5	15.37	116.7	-0.8	23.7	13.59
1/7/2017	59.7	6.1	53.7	17.59	88.4	9.6	14.1	-10.02
1/8/2017	99.1	5.1	94.0	13.22	70.6	5.4	12.9	-29.30

1/9/2017	33.0	8.0	25.0	13.92	59.9	-2.7	24.6	13.35
1/10/2017	67.0	12.8	54.3	29.09	89.6	-4.7	46.5	22.14
1/11/2017	71.2	21.6	49.7	27.30	95.1	-0.7	49.6	27.26
1/12/2017	48.2	14.3	33.9	20.12	95.2	1.7	32.7	17.44
1/13/2017	104.9	25.4	79.6	52.08	150.9	17.0	60.4	24.70
1/14/2017	71.7	21.9	49.8	33.47	153.8	11.2	44.2	21.82
1/15/2017	33.4	8.4	25.0	24.90	141.2	12.8	20.5	9.31
1/16/2017	30.8	8.4	22.4	19.06	105.9	9.3	18.2	8.12
1/17/2017	35.9	2.6	33.4	10.11	77.4	8.5	4.2	-10.82
1/18/2017	34.9	4.9	30.0	12.27	68.5	3.9	13.3	-0.22
1/19/2017	114.5	10.6	103.9	24.97	100.5	10.5	25.1	-21.62
1/20/2017	119.8	15.1	104.7	26.93	128.7	0.5	41.5	-5.57
1/21/2017	95.8	17.9	77.9	43.31	172.2	-0.4	61.6	26.61
1/22/2017	55.1	12.2	42.9	25.26	106.0	-4.3	41.8	22.50
1/23/2017	27.2	6.9	20.3	23.90	144.7	1.2	29.6	20.50
1/24/2017	39.0	14.3	24.7	25.33	125.0	13.4	26.3	15.18
1/25/2017	68.8	13.6	55.3	16.01	39.2	6.5	23.1	-1.76
1/26/2017	44.1	11.4	32.7	21.19	72.5	13.5	19.1	4.44
1/27/2017	85.6	19.1	66.5	16.71	41.3	4.4	31.4	1.51
1/28/2017	81.2	7.7	73.6	18.42	127.4	1.0	25.1	-7.93
1/29/2017	127.7	15.0	112.7	23.94	68.4	3.0	35.9	-14.74
1/30/2017	56.2	10.3	45.9	16.40	66.8	-4.5	31.2	10.59
1/31/2017	42.8	8.3	34.5	24.41	168.8	-0.9	33.7	18.16
2/1/2017	62.9	14.6	48.2	26.87	108.8	1.4	40.1	18.46
2/2/2017	71.8	19.2	52.6	26.60	102.7	7.9	38.0	14.34
2/3/2017	38.6	16.1	22.5	18.12	104.7	6.1	28.1	17.96
2/4/2017	44.3	15.2	29.2	27.61	65.3	15.5	27.3	14.15

2/5/2017	69.7	19.2	50.4	35.01	65.9	25.3	28.9	6.24
2/6/2017	61.3	15.8	45.5	72.78	181.5	27.6	61.0	40.51
2/7/2017	57.5	15.3	42.2	37.11	153.1	9.6	42.8	23.84
2/8/2017	45.3	12.5	32.9	39.13	154.8	17.0	34.6	19.86
2/9/2017	51.7	11.2	40.6	25.49	97.0	10.9	25.7	7.53
2/10/2017	32.4	11.2	21.2	26.77	163.1	12.6	25.4	15.90
2/11/2017	32.4	10.8	21.6	26.35	147.9	8.9	28.2	18.50
2/12/2017	41.2	12.7	28.6	30.10	108.7	16.1	26.6	13.80
2/13/2017	38.4	12.6	25.8	25.77	79.5	15.8	22.5	10.92
2/14/2017	199.6	21.5	178.0	39.02	111.1	33.1	27.4	-52.60
2/15/2017	84.8	21.4	63.4	36.96	66.7	20.3	38.1	9.64
2/16/2017	109.3	31.2	78.1	38.54	61.1	23.3	46.4	11.34
2/17/2017	52.8	22.5	30.2	37.71	71.2	19.4	40.8	27.22
2/18/2017	117.8	24.1	93.7	55.91	194.4	1.7	78.3	36.23
2/19/2017	50.9	25.5	25.4	28.49	143.4	19.2	34.8	23.35
2/20/2017	62.1	17.7	44.5	30.09	118.3	5.2	42.5	22.57
2/21/2017	78.8	16.6	62.2	50.89	224.7	11.9	55.5	27.60
2/22/2017	50.1	11.5	38.6	32.00	185.6	14.2	29.3	11.97
2/23/2017	60.1	12.0	48.0	30.54	115.3	-0.8	43.4	21.82
2/24/2017	67.3	19.3	48.0	37.21	120.6	11.8	44.8	23.20
2/25/2017	65.3	20.5	44.8	35.81	82.5	20.4	36.0	15.84
2/26/2017	160.8	23.6	137.2	39.83	125.0	3.8	59.7	-1.97
2/27/2017	132.8	18.9	113.9	31.07	70.8	15.1	34.9	-16.30
2/28/2017	60.8	16.3	44.4	35.43	81.3	17.5	34.3	14.36

Appendix 2 Concentration of each parameter in the four-stage filter pack under the flow rate of 10 L.min^{-1} in spring 2017 (March, April and May)

(Unit: nmol/m^3)

Date	T-NO_3	HNO_3	NO_3^-	HCl	T-Cl	nss-Cl	"Initial" HNO_3	"Primary" HNO_3
3/1/2017	92.1	21.7	70.4	34.39	62.7	19.7	36.4	-29.43
3/2/2017	100.2	22.8	77.4	29.76	87.9	10.7	41.9	-30.47
3/3/2017	94.1	18.5	75.6	34.65	89.2	12.5	40.6	-30.09
3/4/2017	80.9	21.5	59.4	37.37	69.1	15.2	43.7	-11.84
3/5/2017	64.3	22.1	42.2	30.89	41.3	16.9	36.1	-3.39
3/6/2017	90.2	19.5	70.7	30.78	72.4	10.5	39.8	-26.30
3/7/2017	87.8	7.4	80.4	29.30	153.2	22.4	14.2	-61.01
3/8/2017	53.2	5.9	47.2	24.53	137.8	11.8	18.7	-25.44
3/9/2017	75.1	5.6	69.5	39.64	166.9	12.2	33.0	-31.97
3/10/2017	129.9	5.4	124.4	31.27	185.7	25.7	11.0	-105.36
3/11/2017	133.3	5.5	127.8	34.59	103.4	20.9	19.2	-100.33
3/12/2017	130.2	6.3	123.9	24.67	68.8	25.9	5.1	-110.79
3/13/2017	99.7	6.1	93.6	27.59	62.5	30.4	3.3	-84.24
3/14/2017	88.6	5.8	82.8	23.63	138.6	0.3	29.1	-48.38
3/15/2017	36.2	13.2	22.9	36.73	139.9	10.8	39.2	17.72
3/16/2017	33.8	9.3	24.5	29.71	159.1	12.7	26.2	3.29
3/17/2017	69.9	15.0	54.9	26.86	72.4	14.8	27.1	-24.24
3/18/2017	101.8	31.2	70.5	34.02	43.0	29.9	35.4	-30.62
3/19/2017	262.6	51.6	211.1	48.54	74.5	36.8	63.4	-134.10

3/20/2017	59.1	12.7	46.4	21.41	67.1	14.5	19.6	-23.78
3/21/2017	95.8	19.7	76.1	44.36	146.0	11.2	52.9	-18.34
3/22/2017	68.7	19.0	49.7	29.89	75.5	9.8	39.1	-7.41
3/23/2017	113.1	30.8	82.3	30.50	59.0	19.5	41.9	-35.11
3/24/2017	52.8	26.4	26.4	28.62	62.1	17.3	37.7	12.97
3/25/2017	76.6	23.2	53.4	29.50	55.6	12.2	40.5	-9.48
3/26/2017	51.3	12.8	38.6	25.30	66.2	14.8	23.2	-12.84
3/27/2017	163.8	30.3	133.5	34.26	47.7	24.2	40.4	-84.53
3/28/2017	73.8	22.0	51.7	25.47	56.5	13.9	33.6	-14.81
3/29/2017	155.6	37.4	118.2	48.63	78.6	22.1	64.0	-46.63
3/30/2017	254.0	40.3	213.7	48.72	90.5	30.5	58.5	-141.45
3/31/2017	53.5	14.2	39.3	45.24	75.4	39.5	19.9	-16.81
4/1/2017	32.3	10.8	21.5	30.58	114.9	12.7	28.8	8.67
4/2/2017	46.9	12.0	34.9	29.18	84.1	15.7	25.5	-7.14
4/3/2017	132.4	47.7	84.8	53.35	82.2	34.0	67.0	-12.29
4/4/2017	158.6	54.5	104.2	43.11	58.2	16.8	80.8	-16.64
4/5/2017	65.2	28.3	36.9	35.79	60.5	20.8	43.3	8.80
4/6/2017	25.7	10.3	15.3	22.37	30.7	17.3	15.4	1.09
4/7/2017	67.9	37.4	30.5	25.08	36.7	21.0	41.5	12.98
4/8/2017	94.9	55.2	39.7	31.71	40.2	13.4	73.5	36.34
4/9/2017	81.2	20.9	60.3	42.17	100.3	16.3	46.8	-9.67
4/10/2017	55.6	14.0	41.6	30.34	76.0	9.7	34.6	-4.26
4/11/2017	75.0	10.9	64.1	34.44	178.1	5.5	39.8	-20.13
4/12/2017	69.2	12.8	56.4	41.23	150.4	8.4	45.6	-7.21
4/13/2017	152.9	48.4	104.5	48.54	81.5	15.3	81.6	-16.20
4/14/2017	65.4	28.2	37.2	41.06	68.9	9.9	59.3	24.54
4/15/2017	120.7	27.3	93.4	56.30	92.4	3.4	80.2	-7.11

4/16/2017	87.0	37.2	49.9	38.04	54.7	15.8	59.4	12.72
4/17/2017	37.3	10.5	26.8	33.31	115.2	0.3	43.5	18.38
4/18/2017	116.9	27.8	89.2	50.26	159.3	1.2	76.8	-6.63
4/19/2017	84.2	13.7	70.5	27.93	115.3	16.8	24.8	-41.12
4/20/2017	121.8	14.2	107.6	35.60	58.7	11.7	38.1	-62.57
4/21/2017	133.8	39.3	94.5	38.09	71.3	1.7	75.7	-12.73
4/22/2017	29.8	11.0	18.9	25.45	60.7	12.6	23.8	6.15
4/23/2017	38.3	24.8	13.6	27.80	41.3	21.6	30.9	18.26
4/24/2017	84.2	36.2	48.0	53.08	83.1	11.7	77.6	32.69
4/25/2017	118.7	21.9	96.8	41.08	146.2	-16.9	79.8	-10.72
4/26/2017	55.8	27.5	28.3	26.23	33.3	11.5	42.1	15.63
4/27/2017	120.4	33.0	87.4	32.93	51.4	11.5	54.4	-27.33
4/28/2017	180.7	46.6	134.1	45.49	67.3	-1.9	94.0	-31.44
4/29/2017	196.7	52.4	144.3	58.30	74.8	-11.1	121.8	-13.17
4/30/2017	141.5	49.0	92.5	37.83	62.1	-4.7	91.6	5.01
5/1/2017	168.9	16.5	152.4	73.65	215.9	-59.8	149.9	7.35
5/2/2017	111.6	31.5	80.0	47.50	85.6	-17.2	96.2	21.30
5/3/2017	69.9	21.9	48.0	45.19	99.0	-4.9	72.0	27.08
5/4/2017	67.6	20.6	47.0	38.28	60.9	-3.6	62.5	18.60
5/5/2017	42.2	23.8	18.5	27.22	30.8	2.7	48.3	31.01
5/6/2017	143.8	14.2	129.6	21.66	63.0	-12.0	47.8	-73.42
5/7/2017	217.4	20.2	197.3	34.62	85.9	-20.2	75.0	-109.58
5/8/2017	156.4	21.2	135.2	27.34	62.5	-15.6	64.2	-62.23
5/9/2017	49.9	14.8	35.1	27.78	61.0	-1.3	43.9	11.03
5/10/2017	51.6	14.1	37.5	33.03	61.1	-6.4	53.6	18.47
5/11/2017	104.4	36.8	67.6	34.52	49.4	12.8	58.5	-4.70
5/12/2017	40.7	20.8	19.8	24.10	32.9	0.8	44.1	25.58

5/13/2017	70.3	32.6	37.7	22.73	29.5	-1.4	56.7	21.47
5/14/2017	68.8	19.3	49.5	35.37	92.1	3.0	51.6	5.31
5/15/2017	83.2	23.7	59.5	28.83	58.5	1.7	50.9	-4.77
5/16/2017	131.6	41.9	89.7	37.32	49.0	-7.3	86.5	2.54
5/17/2017	104.2	53.9	50.3	42.05	48.4	22.4	73.5	26.47
5/18/2017	116.7	74.2	42.6	38.32	40.9	30.0	82.5	42.66
5/19/2017	103.1	59.8	43.2	39.59	43.9	24.5	74.9	34.45
5/20/2017	77.7	53.6	24.1	36.36	39.4	25.9	64.1	41.61
5/21/2017	105.3	62.0	43.3	45.83	51.6	21.8	86.0	45.52
5/22/2017	112.4	69.7	42.7	52.35	59.0	19.1	103.0	63.06
5/23/2017	90.1	47.7	42.4	43.89	49.5	2.2	89.4	49.72
5/24/2017	96.3	61.1	35.2	27.49	30.0	15.9	72.7	39.77
5/25/2017	79.5	41.9	37.6	42.90	162.5	-3.5	88.3	53.14
5/26/2017	76.4	18.0	58.4	46.86	107.2	-5.7	70.5	15.88
5/27/2017	78.9	40.9	37.9	45.73	61.7	15.8	70.9	35.39
5/28/2017	104.8	51.3	53.5	60.79	77.2	19.6	92.5	42.49
5/29/2017	169.2	72.7	96.5	53.31	62.6	30.4	95.6	5.28
5/30/2017	182.5	95.6	86.9	52.90	58.8	28.2	120.3	39.08
5/31/2017	80.5	63.5	17.0	46.63	47.9	39.7	70.5	54.58

Appendix 3 Concentration of each parameter in the four-stage filter pack under the flow rate of 10 L.min^{-1} in summer 2017 (Jun, July and August)

(Unit: nmol/m^3)

Date	T-NO_3	HNO_3	NO_3^-	HCl	T-Cl	nss-Cl	"Initial" HNO_3	"Primary" HNO_3
6/1/2017	100.0	44.2	55.8	60.21	126.2	4.6	99.8	35.20
6/2/2017	78.6	25.1	53.4	46.00	87.4	8.5	62.6	0.73
6/3/2017	78.7	34.6	44.1	42.87	67.5	9.7	67.8	16.71
6/4/2017	67.1	30.3	36.9	38.63	63.8	14.8	54.1	11.37
6/5/2017	58.9	27.9	30.9	32.69	62.4	12.4	48.2	12.34
6/6/2017	67.1	30.6	36.5	23.39	43.2	13.6	40.4	-1.94
6/7/2017	52.6	17.3	35.3	31.64	79.7	-7.9	56.8	15.95
6/8/2017	76.1	42.5	33.5	35.73	41.0	11.3	67.0	28.16
6/9/2017	106.9	55.6	51.2	39.30	45.6	13.6	81.3	21.96
6/10/2017	124.7	75.6	49.1	38.06	43.4	20.9	92.7	35.84
6/11/2017	68.5	27.9	40.6	49.59	118.3	3.3	74.1	27.14
6/12/2017	45.6	16.4	29.2	32.51	67.8	9.4	39.5	5.63
6/13/2017	44.4	19.3	25.2	38.09	78.7	9.2	48.2	18.99
6/14/2017	92.8	52.5	40.4	40.97	45.8	24.0	69.5	22.74
6/15/2017	162.3	75.5	86.8	44.91	55.0	-7.1	127.5	26.97
6/16/2017	99.8	29.3	70.6	56.81	140.4	-12.7	98.7	17.01
6/17/2017	91.9	19.7	72.2	54.33	141.8	-14.7	88.7	5.00
6/18/2017	161.9	89.0	72.9	57.81	62.0	-5.2	152.0	67.61
6/19/2017	153.7	78.1	75.6	42.65	53.9	9.9	110.9	23.39

6/20/2017	33.2	14.8	18.5	19.58	76.4	6.9	27.4	6.01
6/21/2017	81.2	24.6	56.6	41.96	71.2	-4.3	70.9	5.30
6/22/2017	128.8	85.4	43.4	46.58	49.8	24.3	107.7	57.39
6/23/2017	80.9	48.3	32.6	38.26	43.6	27.7	58.8	21.07
6/24/2017	36.0	24.4	11.6	17.40	20.6	15.0	26.8	13.37
6/25/2017	60.5	37.5	23.1	25.81	28.6	5.3	58.0	31.26
6/26/2017	91.4	51.6	39.8	28.05	32.0	17.9	61.7	15.65
6/27/2017	143.8	83.0	60.8	24.49	27.6	15.3	92.2	21.69
6/28/2017	98.9	66.3	32.6	38.35	41.9	33.0	71.7	33.86
6/29/2017	52.7	34.7	18.0	35.20	64.3	14.0	55.9	35.02
6/30/2017	50.5	30.3	20.2	32.18	46.7	8.3	54.2	30.85
7/1/2017	46.0	29.7	16.3	31.07	38.2	5.1	55.7	36.83
7/2/2017	36.9	20.6	16.2	30.14	48.3	6.6	44.2	25.40
7/3/2017	24.5	14.4	10.1	27.89	52.3	6.9	35.4	23.70
7/4/2017	40.6	16.2	24.4	26.82	47.1	-9.8	52.8	24.55
7/5/2017	27.3	18.5	8.8	15.79	18.5	6.3	28.0	17.79
7/6/2017	11.7	10.8	0.9	10.69	11.9	9.6	11.9	10.80
7/7/2017	23.9	11.8	12.1	17.84	34.3	3.6	26.0	12.03
7/8/2017	41.8	14.7	27.1	29.32	64.2	-11.5	55.5	24.20
7/9/2017	28.2	13.3	14.9	22.73	41.4	1.5	34.6	17.31
7/10/2017	33.5	11.1	22.4	25.08	97.7	-10.2	46.4	20.50
7/11/2017	34.3	14.0	20.4	23.04	34.8	-3.8	40.8	17.24
7/12/2017	65.6	48.3	17.3	30.37	31.6	6.2	72.5	52.53
7/13/2017	66.5	39.7	26.8	33.62	36.5	-7.8	81.1	50.05
7/14/2017	64.8	40.9	23.9	39.75	44.7	5.4	75.2	47.52
7/15/2017	41.2	26.0	15.2	30.09	35.9	8.5	47.6	30.05
7/16/2017	29.9	17.1	12.9	27.39	35.8	9.7	34.7	19.82

7/17/2017	33.6	12.3	21.3	26.56	57.8	-1.1	39.9	15.19
7/18/2017	28.9	10.8	18.1	25.43	66.4	2.7	33.5	12.47
7/19/2017	87.9	66.2	21.7	35.60	37.9	11.0	90.9	65.73
7/20/2017	103.8	72.7	31.1	41.37	44.4	18.3	95.7	59.68
7/21/2017	94.6	52.9	41.8	40.73	46.1	-9.2	102.7	54.37
7/22/2017	80.7	33.5	47.2	58.39	73.3	0.2	91.7	37.06
7/23/2017	75.8	33.0	42.7	33.95	43.3	-12.2	79.2	29.67
7/24/2017	61.6	35.0	26.7	18.06	20.6	-0.4	53.4	22.52
7/25/2017	85.4	50.5	34.9	35.35	66.9	-11.2	97.1	56.61
7/26/2017	68.4	14.6	53.8	47.42	120.5	-9.3	71.2	8.87
7/27/2017	118.8	55.4	63.3	35.28	48.1	-31.1	121.8	48.42
7/28/2017	69.0	39.8	29.2	30.14	33.7	-13.7	83.6	49.77
7/29/2017	63.8	22.1	41.7	37.99	67.7	-21.8	81.9	33.64
7/30/2017	81.2	34.1	47.1	51.45	70.6	0.4	85.1	30.54
7/31/2017	63.4	45.5	17.9	27.97	31.3	3.9	69.6	48.91
8/1/2017	43.6	16.4	27.2	32.89	55.1	-1.1	50.3	18.80
8/2/2017	56.9	17.8	39.1	57.29	84.6	14.3	60.8	15.49
8/3/2017	55.9	28.6	27.4	44.32	56.9	20.0	52.9	21.18
8/4/2017	36.6	13.6	23.0	59.93	91.4	38.6	35.0	8.34
8/5/2017	37.9	9.9	28.0	35.97	95.1	-2.4	48.3	15.78
8/6/2017	34.9	8.6	26.3	33.60	144.3	-5.2	47.3	16.89
8/7/2017	66.9	15.2	51.7	51.05	98.9	-13.8	80.1	20.26
8/8/2017	62.3	36.7	25.6	29.34	32.6	3.6	62.4	32.68
8/9/2017	52.7	20.4	32.3	47.29	65.8	-6.4	74.1	36.67
8/10/2017	53.2	24.8	28.4	43.65	107.5	-5.9	74.3	41.39
8/11/2017	17.8	3.1	14.7	27.67	146.4	8.7	22.1	5.05
8/12/2017	23.4	3.8	19.6	39.56	134.6	14.7	28.6	5.92

8/13/2017	30.4	7.1	23.2	68.46	117.2	42.8	32.8	5.88
8/14/2017	12.2	6.6	5.6	26.11	36.1	15.9	16.8	10.32
8/15/2017	37.8	19.5	18.3	40.60	48.9	7.8	52.3	31.02
8/16/2017	53.5	19.4	34.1	35.26	47.3	-9.4	64.0	24.49
8/17/2017	43.6	13.3	30.3	37.22	77.8	-0.3	50.8	15.72
8/18/2017	35.4	10.3	25.1	29.78	46.8	14.3	25.7	-3.40
8/19/2017	32.9	14.6	18.3	42.14	55.7	25.1	31.7	10.43
8/20/2017	75.0	48.4	26.6	49.59	55.4	18.8	79.2	48.41
8/21/2017	25.1	17.0	8.2	38.18	44.4	29.0	26.2	16.76
8/22/2017	50.2	24.4	25.9	52.27	78.9	15.8	60.8	30.84
8/23/2017	44.0	15.8	28.2	41.71	88.7	-4.0	61.6	28.93
8/24/2017	14.5	5.0	9.5	24.34	49.1	12.7	16.6	5.55
8/25/2017	22.6	6.7	16.0	30.55	62.5	11.9	25.3	6.86
8/26/2017	53.4	24.2	29.2	47.20	56.2	23.9	47.5	13.67
8/27/2017	68.8	45.2	23.6	59.92	64.7	40.3	64.7	37.38
8/28/2017	54.8	32.3	22.6	45.25	52.0	23.8	53.7	27.56
8/29/2017	40.0	17.7	22.2	32.51	56.5	3.7	46.6	20.81
8/30/2017	28.7	8.6	20.0	30.74	82.1	8.7	30.7	7.44
8/31/2017	45.2	7.6	37.6	22.91	114.2	30.2	0.3	-43.22

Appendix 4 Concentration of each parameter in the four-stage filter pack under the flow rate of 10 L.min^{-1} in autumn 2017 (September, October and November)

(Unit: nmol/m^3)

Date	T-NO_3	HNO_3	NO_3^-	HCl	T-Cl	nss-Cl	"Initial" HNO_3	"Primary" HNO_3
9/1/2017	22.3	1.8	20.5	18.90	199.0	0.5	20.2	5.40
9/2/2017	18.6	1.9	16.7	17.87	197.6	3.9	15.9	3.82
9/3/2017	40.7	3.8	37.0	20.26	128.8	-14.8	38.9	12.08
9/4/2017	59.0	18.4	40.6	19.96	38.4	-21.7	60.0	30.60
9/5/2017	27.2	12.2	15.0	16.18	25.1	4.7	23.7	12.86
9/6/2017	25.4	15.2	10.2	13.19	22.3	-4.6	33.0	25.67
9/7/2017	32.4	19.2	13.2	24.59	28.6	4.5	39.3	29.77
9/8/2017	67.8	42.9	24.9	22.02	26.0	12.4	52.5	34.43
9/9/2017	69.3	42.7	26.6	26.11	31.2	13.2	55.6	36.32
9/10/2017	48.9	31.9	17.0	30.94	36.4	15.1	47.7	35.41
9/11/2017	25.8	8.3	17.5	19.74	70.5	-11.4	39.4	26.73
9/12/2017	46.5	10.3	36.1	28.21	59.4	-11.1	49.7	23.49
9/13/2017	86.3	26.9	59.4	30.46	62.0	-16.8	74.1	31.07
9/14/2017	53.4	27.6	25.9	24.89	38.9	9.2	43.3	24.57
9/15/2017	37.9	13.0	25.0	15.39	48.9	-0.9	29.3	11.17
9/16/2017	19.7	8.4	11.3	11.89	45.1	7.8	12.5	4.31
9/17/2017	13.9	1.4	12.6	12.18	266.2	4.3	9.2	0.13
9/18/2017	75.2	15.5	59.7	31.80	60.5	-16.9	64.2	20.98
9/19/2017	154.2	64.9	89.3	25.37	32.4	3.2	87.1	22.46

9/20/2017	143.1	62.1	81.0	48.90	66.4	-11.2	122.2	63.48
9/21/2017	130.6	36.0	94.6	26.69	55.5	-18.3	81.0	12.48
9/22/2017	83.5	28.8	54.8	19.45	27.7	-5.5	53.7	14.01
9/23/2017	78.3	21.4	56.9	15.55	24.4	-8.4	45.4	4.20
9/24/2017	99.1	46.8	52.3	34.54	41.3	21.1	60.3	22.40
9/25/2017	130.5	54.2	76.3	36.18	42.2	24.6	65.8	10.56
9/26/2017	84.9	38.5	46.4	27.86	58.6	-3.8	70.2	36.66
9/27/2017	16.1	4.0	12.0	11.98	141.5	1.9	14.1	5.42
9/28/2017	41.9	4.6	37.2	30.77	179.4	-2.9	38.3	11.34
9/29/2017	83.3	19.2	64.1	36.32	72.6	-14.9	70.4	23.95
9/30/2017	49.3	18.3	31.0	25.01	36.8	6.8	36.5	14.04
10/1/2017	46.9	17.8	29.1	16.26	34.2	-3.2	37.3	16.21
10/2/2017	19.6	5.3	14.2	13.64	99.8	-10.4	29.4	19.06
10/3/2017	28.8	3.9	24.9	26.70	233.2	10.7	19.9	1.92
10/4/2017	25.2	9.3	15.9	18.51	103.8	5.0	22.8	11.29
10/5/2017	39.5	9.7	29.7	13.94	47.1	-9.7	33.4	11.85
10/6/2017	37.8	10.4	27.4	13.25	25.9	-3.8	27.5	7.68
10/7/2017	44.3	16.6	27.7	19.26	31.4	-5.5	41.4	21.33
10/8/2017	64.9	42.5	22.4	20.83	24.3	8.9	54.5	38.21
10/9/2017	56.7	37.2	19.5	20.19	22.0	5.4	51.9	37.82
10/10/2017	55.3	31.8	23.5	24.67	30.3	2.3	54.2	37.11
10/11/2017	35.1	19.2	15.9	16.20	26.9	-3.7	39.1	27.63
10/12/2017	10.5	3.0	7.5	6.01	55.9	0.3	8.7	3.23
10/13/2017	30.7	3.3	27.5	13.50	142.3	-7.2	24.0	4.14
10/14/2017	15.2	2.6	12.6	9.42	80.3	1.9	10.1	1.03
10/15/2017	8.8	4.1	4.7	5.40	16.5	5.6	3.9	0.50
10/16/2017	15.1	7.5	7.7	8.43	16.5	6.1	9.8	4.27

10/17/2017	26.4	7.8	18.6	15.72	40.8	2.8	20.8	7.35
10/18/2017	22.6	7.0	15.7	7.04	15.6	1.7	12.3	0.98
10/19/2017	35.9	20.3	15.6	11.89	15.5	8.6	23.6	12.22
10/20/2017	20.7	7.7	13.0	18.04	116.4	7.1	18.6	9.22
10/21/2017	12.5	3.9	8.5	12.83	103.1	8.2	8.6	2.43
10/22/2017	11.0	0.7	10.3	12.98	618.9	61.7	-48.0	-55.44
10/23/2017	28.4	4.6	23.8	25.09	416.9	20.2	9.5	-7.77
10/24/2017	32.2	4.1	28.1	27.05	174.8	-4.8	36.0	15.64
10/25/2017	32.1	4.9	27.2	17.03	53.8	2.0	20.0	0.24
10/26/2017	75.9	18.6	57.2	21.94	43.1	-4.3	44.8	3.37
10/27/2017	103.3	28.4	74.9	31.77	69.5	-10.4	70.6	16.41
10/28/2017	18.9	8.4	10.5	8.74	44.0	-0.4	17.5	9.90
10/29/2017	62.8	8.9	53.9	42.44	300.2	3.4	47.9	8.86
10/30/2017	28.0	3.2	24.8	19.82	200.9	8.1	15.0	-2.98
10/31/2017	73.8	13.5	60.3	24.44	60.6	-8.2	46.1	2.41
11/1/2017	66.4	24.8	41.6	23.53	34.2	4.4	44.0	13.90
11/2/2017	62.6	18.6	43.9	22.22	43.7	1.9	38.9	7.12
11/3/2017	101.0	33.7	67.4	32.93	117.5	-6.1	72.7	23.88
11/4/2017	27.8	3.1	24.8	23.68	225.1	7.0	19.7	1.80
11/5/2017	55.1	10.7	44.4	27.88	76.7	6.1	32.5	0.29
11/6/2017	68.5	16.6	51.9	24.52	40.8	3.2	37.9	0.34
11/7/2017	51.7	11.1	40.6	17.68	35.2	-1.0	29.9	0.47
11/8/2017	120.6	18.3	102.3	30.43	100.8	-11.1	59.9	-14.22
11/9/2017	78.9	8.9	70.0	26.37	90.7	-18.9	54.2	3.51
11/10/2017	76.9	12.9	63.9	40.68	174.2	-14.6	68.2	21.88
11/11/2017	38.6	6.4	32.2	20.45	141.5	3.4	23.4	0.10
11/12/2017	44.8	7.0	37.8	20.99	84.8	0.3	27.7	0.37

11/13/2017	84.7	14.1	70.6	26.64	122.8	-19.6	60.3	9.14
11/14/2017	98.7	21.8	76.9	32.06	130.9	4.7	49.1	-6.57
11/15/2017	77.3	16.0	61.4	32.74	136.1	1.9	46.8	2.40
11/16/2017	45.3	7.8	37.5	12.85	53.9	0.6	20.0	-7.14
11/17/2017	62.1	9.6	52.5	10.58	51.8	0.1	20.0	-18.06
11/18/2017	49.6	10.4	39.1	27.23	209.6	1.6	36.1	7.74
11/19/2017	33.9	5.4	28.5	10.91	116.3	0.2	16.2	-4.44
11/20/2017	47.8	9.9	37.9	14.83	53.4	4.3	20.4	-7.09
11/21/2017	86.1	14.1	72.0	14.86	50.0	10.5	18.5	-33.63
11/22/2017	77.8	11.0	66.8	23.28	110.2	13.8	20.5	-27.86
11/23/2017	38.3	7.7	30.6	18.79	136.5	-7.5	34.1	11.91
11/24/2017	56.2	11.5	44.7	25.85	185.8	3.5	33.9	1.51
11/25/2017	75.3	10.5	64.8	16.66	69.3	-7.4	34.5	-12.44
11/26/2017	95.1	5.9	89.2	12.62	61.9	2.8	15.7	-48.88
11/27/2017	107.4	13.3	94.2	17.55	45.8	-4.3	35.1	-33.11
11/28/2017	90.3	11.5	78.8	20.82	51.7	18.1	14.2	-42.88
11/29/2017	164.7	8.5	156.1	7.45	55.2	-4.5	20.5	-92.56
11/30/2017	58.8	19.4	39.4	23.47	166.6	7.6	35.3	6.70

Appendix 5 Concentration nitrate species, H^+ and Δ in Type A and Type B in summer (August 2018)

(Unit: $nmol/m^3$)

Date	Type A (4-Stage)				Type B (5-Stage)				Δ
	NO_3^-	HNO_3	T-NO_3	H^+	NO_3^-	HNO_3	T-NO_3	H^+	ΔHNO_3 - ΔT-NO_3
8/1/2018	33.73	10.85	44.58	13.03	33.67	11.14	44.81	11.00	-
8/2/2018	67.95	26.24	94.19	2.69	61.37	21.40	82.77	11.00	-6.59
8/3/2018	24.33	36.92	61.25	4.48	29.01	26.43	55.44	21.94	4.68
8/4/2018	42.31	20.79	63.09	10.92	37.43	11.66	49.09	4.38	-4.88
8/5/2018	48.31	25.88	74.19	10.94	-	-	-	-	-
8/6/2018	40.59	22.58	63.17	16.58	35.58	15.02	50.61	13.84	-5.01
8/7/2018	20.55	7.60	28.15	10.48	19.28	6.86	26.14	6.94	-1.27
8/8/2018	27.13	9.96	37.09	10.82	24.49	6.76	31.24	11.00	-2.64
8/9/2018	35.66	9.18	44.84	21.28	33.47	7.18	40.66	11.00	-2.19
8/10/2018	44.25	31.86	76.12	21.50	38.22	21.46	59.68	27.64	-6.03
8/11/2018	20.14	16.25	36.39	10.82	20.37	12.91	33.28	17.44	0.23
8/12/2018	32.14	14.26	46.40	8.78	28.85	10.71	39.57	11.00	-3.29
8/13/2018	26.31	13.07	39.37	7.01	26.74	10.42	37.15	6.93	0.43
8/14/2018	18.99	12.99	31.98	7.26	19.78	9.22	29.00	5.52	0.79
8/15/2018	15.46	7.03	22.49	8.32	15.47	5.35	20.82	8.74	0.02
8/16/2018	20.15	10.36	30.51	10.25	20.21	7.14	27.36	6.92	0.07
8/17/2018	23.22	7.14	30.35	8.19	23.43	5.10	28.53	6.96	0.21
8/18/2018	60.40	20.77	81.17	12.97	59.00	14.48	73.48	11.00	-1.40

8/19/2018	53.11	14.91	68.02	6.40	52.96	11.74	64.70	10.99	-0.15
8/20/2018	54.77	25.07	79.83	10.30	49.48	15.82	65.30	13.93	-5.29
8/21/2018	18.67	9.53	28.20	3.23	19.20	7.15	26.35	5.51	0.53
8/22/2018	14.24	7.54	21.78	3.16	11.79	4.50	16.29	4.38	-2.45
8/23/2018	20.27	7.88	28.14	6.28	19.18	5.57	24.75	8.74	-1.09
8/24/2018	23.40	9.30	32.70	10.07	20.02	6.41	26.43	13.85	-3.38
8/25/2018	31.42	15.93	47.35	12.33	33.56	10.91	44.46	13.82	2.13
8/26/2018	28.88	13.40	42.28	8.14	27.46	10.35	37.80	10.99	-1.42
8/27/2018	18.25	10.03	28.28	9.79	18.12	7.04	25.16	11.00	-0.13
8/28/2018	29.23	10.02	39.26	8.10	27.28	6.47	33.75	10.98	-1.96
8/29/2018	18.54	25.45	43.99	12.61	22.12	15.62	37.73	10.99	3.58
8/30/2018	10.24	8.58	18.82	7.94	10.24	5.54	15.78	8.76	0.00
8/31/2018	6.74	4.32	11.06	8.00	6.08	14.72	20.81	9.32	-

Appendix 6 Concentration nitrate species, H^+ and Δ in Type A and Type B in autumn (October 2018)

(Unit: nmol/m^3)

Date	Type A (4-Stage)				Type B (5-Stage)				Δ
	NO_3^-	HNO_3	T-NO_3	H^+	NO_3^-	HNO_3	T-NO_3	H^+	ΔHNO_3 - ΔT-NO_3
10/1/2018	43.62	6.31	49.92	7.98	37.93	4.11	42.04	4.39	-5.69
10/2/2018	31.39	6.62	38.01	6.29	28.14	6.44	34.58	5.51	-3.25
10/3/2018	41.46	11.12	52.58	7.90	42.24	7.77	50.01	3.48	0.78
10/4/2018	34.09	8.24	42.33	6.28	32.76	6.39	39.15	6.94	-1.34
10/5/2018	16.36	6.17	22.53	4.76	14.32	4.61	18.93	6.94	-2.03
10/6/2018	27.81	6.85	34.66	5.96	21.95	2.45	24.40	5.51	-5.86
10/7/2018	23.04	4.85	27.89	7.42	20.93	4.36	25.29	5.51	-2.11
10/8/2018	48.97	6.53	55.50	7.55	45.90	4.91	50.81	8.74	-3.07
10/9/2018	58.12	14.96	73.07	9.50	57.36	9.89	67.25	11.00	-0.76
10/10/2018	50.92	10.40	61.31	5.85	52.49	6.45	58.94	4.38	1.57
10/11/2018	23.48	11.54	35.03	2.26	26.62	9.82	36.44	4.38	3.14
10/12/2018	20.89	6.88	27.77	4.59	20.60	5.63	26.22	5.51	-0.29
10/13/2018	20.78	7.89	28.67	4.54	20.70	6.75	27.45	5.51	-0.08
10/14/2018	20.64	8.13	28.77	4.62	18.65	5.76	24.41	8.74	-1.99
10/15/2018	39.40	18.92	58.32	4.68	34.33	14.71	49.04	11.00	-5.07
10/16/2018	28.11	12.82	40.92	9.40	25.81	10.45	36.25	8.73	-2.30
10/17/2018	26.50	9.77	36.27	7.31	24.34	7.55	31.89	6.94	-2.16
10/18/2018	24.87	10.12	34.98	7.31	21.66	8.26	29.92	5.51	-3.20
10/19/2018	12.26	3.30	15.56	7.56	7.75	4.43	12.18	5.51	-

10/20/2018	14.37	7.45	21.82	5.96	13.10	4.06	17.16	4.38	-1.26
10/21/2018	14.42	7.04	21.45	7.58	33.97	5.47	39.44	0.28	19.55
10/22/2018	28.40	11.83	40.23	7.69	26.24	7.97	34.21	5.51	-2.16
10/23/2018	30.55	11.52	42.07	9.47	25.67	7.21	32.88	0.87	-4.88
10/24/2018	73.85	11.00	84.84	9.49	64.82	10.93	75.75	6.96	-9.03
10/25/2018	41.60	12.24	53.84	9.53	40.88	11.93	52.80	8.70	-0.73
10/26/2018	41.29	12.37	53.66	7.70	28.92	7.94	36.85	8.73	-12.37
10/27/2018	28.61	6.61	35.22	7.50	24.43	4.36	28.79	6.94	-4.18
10/28/2018	60.03	10.85	70.88	7.72	49.13	9.34	58.46	6.94	-10.91
10/29/2018	39.70	10.15	49.85	7.61	37.95	6.24	44.19	5.51	-1.75
10/30/2018	41.12	12.12	53.24	7.51	26.89	7.17	34.06	5.51	-14.23
10/31/2018	26.34	8.79	35.13	7.38	31.12	1.95	33.08	21.94	4.79

Appendix 7 Concentration nitrate species, H^+ and Δ in Type A and Type B in winter (January 2019)

(Unit: nmol/m^3)

Date	Type A (4-Stage)				Type B (5-Stage)				Δ
	NO_3^-	HNO_3	T-NO_3	H^+	NO_3^-	HNO_3	T-NO_3	H^+	$\Delta HNO_3 - \Delta T\text{-}NO_3$
1/5/2019	136.16	11.01	147.17	12.40	159.27	9.82	169.08	10.99	23.10
1/6/2019	35.18	5.87	41.06	11.43	25.99	5.47	31.46	6.94	-9.19
1/7/2019	37.70	13.08	50.78	7.43	33.43	9.68	43.10	6.94	-4.28
1/8/2019	46.35	10.58	56.93	9.30	46.42	14.28	60.70	5.51	-
1/9/2019	17.30	7.12	24.42	5.78	18.76	2.55	21.31	4.38	1.46
1/10/2019	50.87	8.13	59.00	9.32	47.79	7.41	55.21	11.00	-3.08
1/11/2019	97.95	10.54	108.49	7.40	93.04	8.51	101.55	5.51	-4.92
1/12/2019	59.26	8.34	67.60	9.37	57.22	10.22	67.44	6.94	-
1/13/2019	23.25	6.25	29.50	9.14	19.62	9.94	29.57	4.38	-
1/14/2019	71.90	11.24	83.15	7.30	64.59	12.18	76.77	6.94	-
1/15/2019	115.11	19.16	134.27	8.96	118.43	16.55	134.97	6.94	3.32
1/16/2019	51.27	12.45	63.71	7.23	40.11	9.97	50.08	5.51	-11.16
1/17/2019	52.20	14.72	66.92	7.08	50.84	12.85	63.69	6.94	-1.36
1/18/2019	72.85	12.79	85.64	7.25	68.96	13.70	82.66	6.94	
1/19/2019	60.55	17.93	78.49	11.52	57.17	15.69	72.86	5.51	-3.38
1/20/2019	44.41	18.95	63.37	7.32	37.86	17.26	55.12	6.94	-6.55
1/21/2019	34.38	10.96	45.34	5.74	-	-	-	-	-
1/22/2019	144.72	16.72	161.44	5.81	139.79	22.05	161.84	8.73	-
1/23/2019	156.30	20.01	176.31	9.22	151.96	9.74	161.70	6.94	-4.34

1/24/2019	70.63	13.53	84.16	7.31	60.60	10.21	70.81	5.51	-10.03
1/25/2019	65.16	17.13	82.29	7.29	61.15	16.50	77.65	5.51	-4.01
1/26/2019	22.58	9.29	31.87	7.22	17.52	6.03	23.54	4.38	-5.07
1/27/2019	21.43	12.58	34.01	9.00	39.05	13.60	52.65	5.51	-
1/28/2019	112.00	14.56	126.56	7.24	94.43	12.94	107.37	5.51	-17.57
1/29/2019	34.78	11.14	45.91	5.71	31.04	11.44	42.48	5.51	-
1/30/2019	81.18	12.52	93.69	7.24	74.92	10.30	85.22	6.94	-6.26
1/31/2019	28.14	8.94	37.07	7.28	20.57	7.27	27.84	6.94	-7.57
2/1/2019	37.87	11.41	49.28	9.08	3.12	20.68	23.80	4.38	-
2/2/2019	48.78	11.44	60.21	7.18	56.52	11.89	68.41	6.94	-
2/3/2019	39.13	11.64	50.77	5.81	31.53	6.52	38.05	5.51	-7.59
2/4/2019	74.51	11.47	85.98	7.01	66.20	9.92	76.13	8.74	-8.30

Appendix 8 Concentration nitrate species, H^+ and Δ in Type A and Type B in spring (May 2019)

(Unit: nmol/m^3)

Date	Type A (4-Stage)				Type B (5-Stage)				Δ
	NO_3^-	HNO_3	T-NO_3	H^+	NO_3^-	HNO_3	T-NO_3	H^+	ΔHNO_3 - ΔT-NO_3
5/8/2019	18.45	29.87	48.32	3.06	23.91	22.49	46.40	10.99	5.46
5/9/2019	29.68	28.81	58.48	6.12	29.34	25.80	55.14	10.97	-0.33
5/10/2019	52.87	47.58	100.45	9.82	48.64	42.36	90.99	13.88	-4.23
5/11/2019	36.66	56.64	93.31	9.16	40.08	41.87	81.95	17.40	3.42
5/12/2019	106.35	37.37	143.72	16.55	77.10	34.67	111.77	22.34	-29.25
5/13/2019	76.66	38.49	115.15	9.74	72.73	30.05	102.78	17.50	-3.93
5/14/2019	45.97	32.40	78.37	6.13	42.75	33.15	75.90	2.83	-
5/15/2019	42.34	36.35	78.69	6.12	39.78	29.58	69.36	8.95	-2.56
5/16/2019	51.09	29.64	80.72	3.08	47.17	22.99	70.15	5.54	-3.92
5/17/2019	33.65	15.22	48.87	2.42	31.46	13.55	45.01	5.51	-2.19
5/18/2019	23.90	7.50	31.39	3.02	21.22	5.89	27.11	8.74	-2.68
5/19/2019	16.99	9.60	26.60	2.42	15.83	6.94	22.77	6.94	-1.16
5/20/2019	30.17	8.69	38.86	5.99	28.87	6.88	35.76	6.93	-1.29
5/21/2019	48.23	17.87	66.10	4.82	45.62	13.35	58.97	6.94	-2.61
5/22/2019	73.54	35.44	108.98	6.07	68.00	25.06	93.06	10.99	-5.54
5/23/2019	71.11	46.86	117.97	5.94	65.46	33.50	98.96	11.00	-5.65
5/24/2019	59.60	64.26	123.87	1.92	55.85	42.17	98.02	10.99	-3.75
5/25/2019	31.08	40.65	71.73	1.91	32.65	28.72	61.37	8.73	1.57
5/26/2019	63.47	58.22	121.68	6.05	62.14	40.59	102.73	13.85	-1.33

5/27/2019	25.77	11.21	36.98	7.35	24.00	6.24	30.24	2.19	-1.77
5/28/2019	28.19	14.63	42.82	7.55	27.87	9.63	37.50	5.51	-0.32
5/29/2019	29.50	33.30	62.80	7.63	35.69	21.38	57.06	8.73	6.18
5/30/2019	44.39	27.33	71.73	12.14	44.76	18.97	63.72	11.00	0.36
5/31/2019	28.15	29.27	57.42	12.07	25.07	21.95	47.01	13.84	-3.08
6/1/2019	49.44	54.31	103.76	15.34	43.18	36.72	79.90	17.43	-6.26
6/2/2019	25.03	35.55	60.59	9.66	20.02	25.91	45.92	13.84	-5.02
6/3/2019	42.85	52.15	95.00	9.64	32.73	38.38	71.11	13.84	-10.12
6/4/2019	21.18	25.06	46.25	5.96	17.79	18.90	36.69	10.99	-3.39
6/5/2019	30.28	62.86	93.14	15.27	32.12	59.71	91.82	34.90	1.83
6/6/2019	36.63	48.22	84.85	19.31	-	-	-	-	-
6/7/2019	26.26	13.55	39.80	9.54	23.41	8.94	32.34	11.06	-2.85

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