Atmospheric Acid Gases in Tokushima, Japan, Monitored with Parallel Plate Wet Denuder Coupled Ion Chromatograph

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During the summer of 2011 and winter of 2012, we continuously measured trace acid gas concentrations in Tokushima, Japan, using a parallel plate wet denuder coupled ion chromatograph. The average concentrations of hydrochloric acid (HCl), nitrous acid (HONO), nitric acid (HNO₃), and sulfur dioxide (SO₂) were, respectively, 0.54, 1.20, 1.17, and 3.22 µg m⁻³ in the summer, and 0.09, 1.06, 0.46, and 5.11 µg m⁻³ in the winter. In the summer, concentrations of all the acid gases increased after sunrise and showed a strong diurnal pattern with daytime maxima and nighttime minima, but the time at which concentration levels began to increase and the pace of increase differed among the acid gases. The concentration of HONO increased sharply immediately after sunrise, while concentrations of the other three gases began increasing about one and half hours later. SO₂ showed the fastest rate of increase, followed by HNO₃ and HCl. These differences were likely attributable to the formation processes of gaseous substances.

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Introduction

Measurements of atmospheric acid gases have been taken in regions across the globe in order to study their impact on health and the environment.^{1,2} The anthropogenic sources of some acid gases include direct emissions from power plants, automobiles, and factories.³⁻⁵ Volcanic activity emits a significant amount of HCl and SO₂.^{6,7} The reaction of HNO₃ with sea-salt particles is also a major source of HCl.⁵ In the atmosphere, HNO₃ and HONO are formed as a by-product the photochemical reaction of nitrogen compounds.^{8,9} Conventional filter-based methods are widely used for the collection of water-soluble acid gases. These simple methods, however, expose the positive and negative artifacts during air sampling,¹⁰⁻¹² and cannot provide the sufficient time resolution needed to investigate the circadian variation of objective substances. Diffusion denuder techniques coupled with an analysis system such as ion chromatograph enable nearreal-time monitoring of multicomponent gases.¹³⁻¹⁶ We recently reported on a parallel plate wet denuder coupled ion chromatograph (PPWD-IC), which allows for highly sensitive and high time resolution monitoring of trace acid gases in an industrial cleanroom environment.¹⁷ With PPWD-IC, we continuously measured the concentrations of atmospheric HCl, HONO, HNO₃, and SO₂ in Tokushima, Japan. We discuss here the seasonal/circadian variations of acid gases using the high time resolution data.

Experimental

During August 18 – 31 in 2011 and February 6 – 19 in 2012, the ambient air was sampled from the fourth-floor north window (12 m above ground level) of a six-story building on the campus of the University of Tokushima, Tokushima, Japan (34°04'N, 134°30'E). The sampling site is surrounded by Mt. Bizan (277 m above sea level) to the south, and is located about 8 km west of the Kii Channel. To the north is a busy road, National Route 192 (average traffic volume per day, approximately 34704 cars on weekdays).

The PPWD-IC was used for the continuous measurement of HCl, HONO, HNO₃, and SO₂ with 15 min time resolution. Details of the PPWD-IC have been described previously.^{17,18} In short, the PPWD is composed of two textured Plexiglas plates and a Teflon spacer (each with a 6 × 42 cm active area, separated by 0.3 cm). The air sample is aspirated from the bottom of the PPWD at 5 dm³ min⁻¹. The denuder liquid (0.5 mmol dm⁻³ H₂O₂) is delivered to flow down the inner plates at 0.25 cm³ min⁻¹ plate⁻¹. This diluted H₂O₂ enables the detection of collected SO₂ as sulfate, with much less production of nitrite and nitrate from NO_x.¹⁹ The entire PPWD effluent is sent to one of two anion concentrators (TAC-2, Dionex) that are connected to a 10-port injection valve (Cheminert C2, Valco Instruments). After 15 min sample loading, the analyte is determined by means of a Dionex ICS 1500 ion chromatograph (AG20 2-mm guard column, AS20 2-mm separation column, ASRS300 2-mm electrochemical suppressor, CRD 2-mm carbon dioxide removal device, DS6 heated conductivity detector, Chromeleon 6.7 data system, and 15 mmol dm⁻³ KOH eluent).

The data for temperature, relative humidity, sunshine, sunrise and sunset in Tokushima were provided by the Tokushima Local

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Fig. 1 Temporal variations of atmospheric acid gas concentrations and sunshine during summer (left, August 18–31 in 2011) and winter (right, February 6–19 in 2012) in Tokushima, Japan. The x-axis indicates midnight of the date. The shaded regions are the nighttime hours (sunset to sunrise). Sunshine shows the percentage of sunshine per hour.

Meteorological Observatory, which was located about 3.5 km east from the sampling site.

Results and Discussion

Acidic gas concentrations in summer and winter

Figure 1 shows the temporal variations of HCl, HONO, HNO₃, and SO₂ concentrations along with sunshine data. The average

acid gas concentration during the summer and winter were, respectively, 0.54 ± 0.65 and 0.09 ± 0.12 $\mu\text{g m}^{-3}$ for HCl, 1.20 ± 0.92 and 1.06 ± 0.90 $\mu\text{g m}^{-3}$ for HONO, 1.17 ± 0.93 and 0.46 ± 0.41 $\mu\text{g m}^{-3}$ for HNO₃, and 3.22 ± 3.72 and 5.11 ± 3.18 $\mu\text{g m}^{-3}$ for SO₂. The HCl and HNO₃ concentrations were higher during the summer than winter, the summer/winter concentration ratio (S/W) being 6.0 and 2.5, respectively. Our sampling site was located near the ocean. Therefore, it is possible that the reaction of HNO₃ with NaCl in sea-salt particles increased, and resulted in higher HCl concentrations during the summer.²⁰ The formation of NH₄Cl particles is strongly suppressed by high temperatures.^{21,22} This might be another reason that the HCl concentration was higher during the summer than winter. The HNO₃ is produced as a by-product of the photochemical reaction of the OH radical and nitrogen compounds such as NO₂ contained in vehicular exhaust,⁸ thereby the HNO₃ concentration is strongly influenced by traffic volume. Horng and Cheng²³ reported that the HNO₃ concentrations at a site near an expressway were several times higher than at a site some distance from an expressway during the daytime. As a densely trafficked road abutted on our sampling site, there was not much difference between traffic volumes during summer and winter. Hence, the OH radicals produced by higher solar radiation intensity may have accelerated HNO₃ formation in the summer. Contrary to the seasonal trends for HCl and HNO₃, the SO₂ concentration was lower during summer than winter (S/W, 0.6), and the HONO concentration during summer was comparable with winter (S/W, 1.1). The primary source of atmospheric SO₂ is the combustion of fossil fuels,⁴ thus the S/W of SO₂ might reflect the amount of fuel used during each sampling period. Moreover, higher temperatures and relative humidity might enhance the conversion of SO₂ to particulate SO₄²⁻ during summer.²⁰

In summer, concentrations of all the acid gases showed a strong diurnal pattern with daytime maxima and nighttime minima as shown in Fig. 1. Meanwhile in winter, acid gas concentrations did not show a distinct shift as in summer. Worth noting is that the variation of HCl in summer is quite similar to that of HNO₃. This point will be examined later again. Another interesting finding was that the SO₂ concentration in summer reached near-zero values during the nighttime, while the SO₂ concentration in winter did not decrease as in summer. The heating fuel used in winter was likely the reason for relatively high residual levels of SO₂ throughout the day.

Circadian variations of acid gases during summer season

Next, we examine the variation of acid gases during the summer in more detail. Figure 2a shows the circadian variation of acid gas concentrations during the summer. Each plot in Fig. 2a shows the average level of two weeks of data. In order to easily compare the variations of gas concentrations, the relative concentration ratio, *RCR*, was calculated by Eq. (1) and the circadian variation of *RCR* is shown in Fig. 2b.

$$RCR = (C - C_{\min}) / (C_{\max} - C_{\min}) \times 100\% \quad (1)$$

where *C* is the acid gas concentration, *C*_{min} and *C*_{max} are the minimum and maximum acid gas concentration measurements in summer (0.15 and 1.43 $\mu\text{g m}^{-3}$ for HCl, 0.30 and 2.04 $\mu\text{g m}^{-3}$ for HONO, 0.47 and 2.67 $\mu\text{g m}^{-3}$ for HNO₃, 0.79 and 8.82 $\mu\text{g m}^{-3}$ for SO₂, respectively). Although all the acid gases showed higher levels of *RCR* during daytime, the *RCR* for HONO increased sharply immediately after sunrise. The levels of HONO *RCR* peaked around 9:00 and remained constant until 14:00, then decreased gradually through midnight but remained

Fig. 2 Circadian variations of average a) atmospheric acid gas concentration and b) relative concentration ratio during summer (August 18–31 in 2011) in Tokushima, Japan. The temperature (solid line) and relative humidity (dashed line) are also shown as references in the upper part in Fig. 2a. The relative concentration ratio was calculated by Eq. (1). (a) Solid circle, HCl; triangle, HONO; solid square, HNO₃; diamond, SO₂. (b) Solid line, HCl; dashed-dotted line, HONO; dashed line, HNO₃; dotted line, SO₂.

relatively high compared to other acid gases. This circadian variation of HONO was different from the diurnal pattern with daytime minima and nighttime maxima published in some other studies.^{24,25} Recently, Kleffmann⁹ proposed three new photochemical daytime sources of HONO: formation on surfaces treated with HNO₃, reduction of NO₂ on organic surfaces, and gas phase photolysis of *ortho*-substituted nitroaromatics. Although the daytime HONO source is not fully explored, it is possible that the above reactions might have resulted in higher concentration levels during daytime. The increase in RCR for SO₂, HNO₃ and HCl began around 7:00, with that for SO₂ showing the fastest rate of increase, followed by HNO₃ and HCl. The SO₂ RCR increase might be due to increasing direct emissions from anthropogenic sources in the morning. In Fig. 2a, the HCl variation appears to be the corresponding pattern to the HNO₃. However, by examining the RCR in Fig. 2b, a time lag in the rates of increasing RCR

between them was revealed. These results suggest that HNO₃ is first formed by the homogeneous reaction of NO₂ with $\cdot\text{OH}$, and then HCl is formed by the reaction of the produced HNO₃ with particulate NaCl, as expressed below,

In the summer, a strong correlation ($r = 0.874$) was obtained between the concentrations of HCl and HNO₃. In addition, the correlations between the temperature and the concentrations of HCl and HNO₃ in summer were relatively high ($r = 0.737$ for HCl and $r = 0.698$ for HNO₃). These results support that the reactions of Eqs. (2) and (3) were dominant for the HCl and HNO₃ by-product formations during the summer season.

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