Atmospheric Observations over Central Japan Using a Helicopter: Measurements of Hydrogen Peroxide and Formaldehyde

Koichi Watanabe*, Mei Jia Jin, Xiao Jing Song, Liu Yang, Kaede Genmoto, Yumeko Ichikawa, Yu Nagahori, Kanji Chimura, Haruka Nagamura

Toyama Prefectural University, Imizu, Toyama 939-0398, Japan

ABSTRACT

Hydroperoxide, formaldehyde (HCHO), ozone (O₃), sulfur dioxide (SO₂) concentrations, and number concentrations of aerosol particles were measured made over the coastal site of the Sea of Japan in central Japan during the cold and autumn seasons using a helicopter. During the cold months, the hydrogen peroxide (H₂O₂) concentrations were usually below 1 ppb, lower than the SO₂ concentrations—a condition known as "Oxidant Limitation". The concentrations of H₂O₂ were also lower than the concentrations of HCHO, suggesting that the formation of hydroxymethanesulfonate might have been more likely than that of sulfate in the liquid phase. The H₂O₂ concentrations were generally higher in autumn than in the cold season, and they were higher than the SO₂ concentrations in the high-altitude atmosphere. However, few measurements were taken in autumn, and future observations are required.

Keywords: Helicopter, Hydrogen peroxide, Formaldehyde, Sulfur dioxide, Ozone

1 INTRODUCTION

The authors have been conducting high-altitude atmospheric observations using a small helicopter over the Sea of Japan coast of central Japan, an area strongly affected by trans-boundary pollution originating from the Asian continent (Watanabe et al., 2016, 2018a, 2021). A helicopter, which does not require a runway and can hover, can quickly transport samples taken at high altitude to a university laboratory. Therefore, it is suitable for measuring chemical components that need to be analyzed immediately after sample collection, such as peroxides and aldehydes. A helicopter is also suitable for making localized observations and has been used to observe air pollution in the boundary layer and for bio-aerosol sampling at low altitudes (Crosman et al., 2017; Maki et al., 2017, 2023).

Using helicopter observations, the authors have mainly focused on measuring hydroperoxides (hydrogen peroxide (H₂O₂) and organic hydroperoxides, such as methyl hydroperoxide (MHP)), which are very important liquid-phase oxidants for sulfur dioxide (SO₂), and in addition to hydroperoxides, ozone (O₃), SO₂, and the number concentrations of aerosol particles have been measured (Watanabe et al., 2016, 2018a). In the summer, the concentrations of H₂O₂ were higher than several ppb, which were sufficiently higher than those of SO₂, and the potential oxidation ability of SO₂ may be sufficiently high over central Japan during the warm season (Watanabe et al., 2016). During the cold month (March), the H₂O₂ concentrations were lower than 1 ppb, and those were also lower than the SO₂ concentrations ([H₂O₂] < [SO₂]), which is a condition known as Oxidant Limitation (Kleinman and Daum, 1991); therefore, during the cold months, there is a shortage of oxidizing capacity for SO₂, and liquid-phase oxidation to sulfuric acid is thought to be suppressed (Watanabe et al., 2018a).

Formaldehyde (HCHO) is an important chemical species in situations where there is a shortage of H₂O₂, and hydroxymethanesulfonate (HMS) is produced by the liquid-phase reaction of SO₂ and...
HCHO (Seinfeld and Pandis, 1998; Moch et al., 2018). H$_2$O$_2$ and HCHO are also important reservoirs of HOx (OH, HO$_2$) (e.g., Seinfeld and Pandis, 1998). Therefore, measurements of H$_2$O$_2$ and HCHO as well as SO$_2$ in the high-altitude atmosphere are important. Simultaneous measurements of hydroperoxides and HCHO (but not SO$_2$) have been made over the United States and Europe (e.g., Snow et al., 2007; Klippel et al., 2011; Bozem et al., 2017). These observations have been conducted on a large scale by large fixed-wing aircraft. However, there are few examples of such measurements in East Asia, including Japan, which is located in the leeward region of large air pollution sources. Moreover, chartering a large fixed-wing aircraft is difficult in Japan, especially due to high costs.

In this study, trace gases H$_2$O$_2$, HCHO, O$_3$, and SO$_2$ as well as the number concentrations of size-separated particles, were measured over the Sea of Japan coast in central Japan using a small helicopter—which is relatively cheap to operate, especially during seasons when the atmosphere is highly affected by air pollution from the Asian continent—to understand the concentrations and vertical profiles of each trace gas over a local site in central Japan. Then the capacity to produce sulfate and HMS was evaluated.

2 METHODS

Atmospheric observations over Imizu City, Toyama Prefecture, on the coastal region of central Japan (Fig. 1) were made using an R44 light helicopter by Advanced Air Co., Ltd. (Watanabe et al., 2016, 2018a, 2021). The observation site is located approximately 50 km west (windward side) of Mt. Tateyama. Therefore, observations in the high-altitude atmosphere are important for cloud chemistry, aerosol production, and ecosystem impact assessment in a mountain region (Watanabe et al., 2016, 2018a; Kume et al., 2020). In this study, observations were made in the early afternoon.
during cold months (17 March 2017, 28 March 2018, 25 December 2019, and 17 March 2021) and in the autumn (15 October 2015 and 23 September 2021). High-altitude atmospheric measurements were made at two altitudes, 1,200 m (4,000 ft) and 2,400 m (8,000 ft). Observations at the ground level were made at Toyama Prefectural University (Fig. 1).

In this study, a helicopter was used to perform sampling and measurements using the same methods as in the papers by Watanabe et al. (2016, 2018a, 2021). Atmospheric hydroperoxides (H₂O₂ and MHP) and HCHO samples were collected in a mist chamber (Hatakeyama et al., 1993; Watanabe et al., 2016) for 10 minutes during horizontal flights at altitudes of 2,400 m and 1,200 m. The collection efficiencies of H₂O₂ and HCHO are almost 100% and 70%, respectively. There was no influence of exhaust gases from the helicopter during the sampling (Watanabe et al., 2016, 2018a). After collecting samples at each altitude, the helicopter immediately descended to the campus of Toyama Prefectural University and dropped the sampled collection solution stored in polyethylene bottles at an extremely low altitude (approximately 5 m altitude). The helicopter then ascended to the next altitude and took samples again, and also immediately descended after the sampling to the campus to transport the sample. The sampled solution was immediately transported to the laboratory and analyzed using two high-performance liquid chromatography (HPLC) systems (JASCO CO., LC-2000 Plus). Analytical errors were within 5%. The detailed HPLC analytical methods are presented in the papers of Iwama et al. (2011) and Watanabe et al. (2016). Using these methods, the samples collected in the high-altitude atmosphere could be analyzed for H₂O₂ and HCHO within about 15 minutes.

Measurements of SO₂ and O₃ were made by a SO₂ analyzer (KIMOTO ELECTRIC CO., LTD., SA-633) and an O₃ analyzer (KIMOTO ELECTRIC CO., LTD., OA-683), respectively. The number concentrations of size-separated particles were measured by an optical particle counter (RION CO., LTD., KC-01E). The measuring instruments were inspected and calibrated by each manufacturer before the observations. To measure the meteorological condition, a temperature and humidity data logger was attached to the helicopter bottom. Detailed observation methods are presented by Watanabe et al. (2016, 2018a).

3 RESULTS AND DISCUSSION

3.1 Helicopter Observations During Cold Seasons

The surface weather charts (JST 09H) on the observation days and the results of the 3-day backward trajectory analysis ending at altitudes of 1,200 m and 2,400 m over Imizu City, Toyama Prefecture, are shown in Figs. 2 and 3, respectively. The trajectories were calculated by the HYSPLIT model, NOAA Air Resources Laboratory (Stein et al., 2015). During the observation periods, central Japan was under the influence of high-pressure systems originating from the Asian continent, and it is thought that it was susceptible to the effects of materials from the continent. The weather was clear on all observation days.

Vertical profiles of temperature, dew point temperature and relative humidity over the observation site during the observation days are presented in Fig. 4. On 28 March 2018, the temperature was high for March, exceeding 20°C on the ground. Based on the surface weather map (Fig. 2), this is thought to be due to the moving high-pressure systems. On 17 March 2021, the temperature lapse rate was low at altitudes of 1,200 m to 2,400 m, and the atmospheric condition was extremely stable. Also, the relative humidity and dew point temperature were relatively high. On other observation days, the dew point temperature in the upper atmosphere was low, and it is thought that the higher atmosphere was dry.

Fig. 5 shows the vertical profiles of the number concentrations of the fine particles (> 0.3 μm) and the coarse particles (> 2 μm). Unfortunately, the particle number concentrations could not be measured on 25 December 2019. It has been reported that the concentrations of the fine particles increase when affected by anthropogenic pollutants, and the coarse particles increase during Asian dust phenomena (Watanabe et al., 2018a, 2022). On 28 March 2018, the number concentrations of the fine particles were extremely high at altitudes below 1,200 m, and it is thought that the atmosphere was greatly affected by the anthropogenic air pollution derived from the Asian continent. However, the fine particles were low at an altitude of 2,400 m. On the
Fig. 2. Surface weather charts (JST 09H) on the observation days.

On the other hand, the impact of anthropogenic pollution might have been relatively low for both observation dates in March 2017 and 2021.

The number concentrations of the coarse particles were significantly high at altitudes below 1200 m on 17 March 2021 (Fig. 5). On the observation day, Asian dust events were observed in central Japan (JMA, 2021), and the high coarse particles are thought to be mainly Asian dust particles whose origin was not local. Although it may be repetitive, it is well known that coarse particles increase in Japan during the Asian dust phenomena (e.g., Watanabe et al., 2005, 2018a, 2022). As mentioned above, the number concentrations of the fine particles were relatively low on 17 March 2021, and it is thought that the Asian dust particles were transported without being contaminated by anthropogenic pollution from the Asian continent. Furthermore, the concentrations of coarse particles were very low at an altitude of 2,400 m (Fig. 5), suggesting that the influence of the Asian dust particles did not extend to higher altitudes. On 17 March 2017, the number concentrations of the coarse particles were low, and it is thought that there was almost no influence from Asian dust particles.

Vertical profiles of the concentrations of the trace gases (H₂O₂, HCHO, SO₂, and O₃) over Imizu City, Toyama Prefecture, during the cold months are shown in Fig. 6. The concentrations of SO₂ were relatively high (> 1 ppb), except for the case of March 2021, and it is thought that the cases were affected by the trans-boundary pollution. In particular, in the case of March 2018, when the fine particles were extremely high at altitudes below 1,200 m, high SO₂ exceeding 3 ppb was observed. On 25 December 2019, high SO₂ (> 2 ppb) was also detected at an altitude of 2,400 m (Fig. 6). On both days, the trajectories originated from industrial areas along the coast of the Yellow Sea (Fig. 3), and it is thought that air pollutants were easily transported. The relatively high concentrations of SO₂, which have sometimes been observed in the high-altitude atmosphere...
Fig. 3. Results of the 3-day backward trajectory analysis ending over Imizu City, Toyama Prefecture, Japan.

during cold months, are considered to be one of the characteristic of the atmospheric environment over the Sea of Japan coast in central Japan.

$O_3$ concentrations were normally around 40 to 50 ppb, but on 28 March 2018, when the temperature was high (Fig. 4), $O_3$ concentrations as high as 80 ppb were observed (Fig. 6). HCHO and $H_2O_2$ concentrations also were relatively high on this day. Fig. 7 shows the relationships between temperature and the concentrations of $H_2O_2$, HCHO, and $O_3$. Positive correlations were found between temperature and HCHO and between temperature and $O_3$. In particular, the correlation between temperature and HCHO was significant, suggesting that secondary formation might have been active under conditions of high temperature. On the other hand, there was no correlation between temperature and $H_2O_2$, which may be because $H_2O_2$ was usually lowest on the ground (Fig. 6). Although not shown in the figure, no correlation was observed between the trace gases and dew point temperature or relative humidity.

The concentrations of $H_2O_2$ were usually lower than 1 ppb (Fig. 6), which are much lower than the concentrations in summer over Imizu City (several ppb or more) (Watanabe et al., 2016). It is thought that the atmosphere’s oxidizing ability is insufficient during cold months when the photochemical formation of $H_2O_2$ seems to be significantly suppressed. Atmospheric $H_2O_2$ levels
Fig. 4. Vertical profiles of relative humidity (RH), temperature (Temp), and dew point temperature (DP) over Imizu City, Toyama Prefecture, Japan.

Fig. 5. Vertical profiles of the number concentrations of the fine particles (> 0.3 µm) (right panel) and the coarse particles (> 2 µm) (left panel) over Imizu City, Toyama Prefecture, Japan.

are high in the summer and low in the winter (e.g., Sakugawa and Kaplan, 1989; Watanabe et al., 2018b). The helicopter observations conducted from March 2014 to 2016 showed similarly low H₂O₂ concentrations, less than 1 ppb (Watanabe et al., 2018a). In particular, the H₂O₂ concentrations on 25 December 2019, when the observation was conducted during the minimum solar radiation period, were significantly low (Fig. 6). However, on 28 March 2018, the concentrations of H₂O₂ exceeded 1 ppb at an altitude of 1,200 m (the O₃ concentration was also high), and it is thought that the conditions were relatively active to generate photochemical oxidants. The concentration of H₂O₂ at the ground surface on 17 March 2021 was extremely low. Perhaps, it was affected by decomposition on the surface of the Asian dust particles due to heterogeneous reactions of H₂O₂ (Zhao et al., 2013).
Throughout the observation days, the H$_2$O$_2$ concentrations were lower than the SO$_2$ concentration ([H$_2$O$_2$] < [SO$_2$]) \textit{(Oxidant Limitation)}, and sulfate formation due to the liquid-phase oxidation of SO$_2$ might have been suppressed. In addition, the H$_2$O$_2$ was lower than the HCHO ([H$_2$O$_2$] < [HCHO]) even in the higher atmosphere (Fig. 6). The condition of [H$_2$O$_2$] < ([HCHO], [SO$_2$]) seems to be characteristic over central Japan during the cold season. Perhaps, the formation of HMS by the reaction between SO$_2$ and HCHO was more likely than the formation of sulfate. Further detailed investigation, such as HMS measurement in clouds and aerosols at Mt. Tateyama, is required.

### 3.2 Helicopter Observations in Autumn

The surface weather charts (JST 09H) on 15 October 2015, and 23 September 2021, and the results of the 3-day backward trajectory analysis during the observation days are presented in Figs. 8 and 9, respectively. The atmosphere over the observation site on both days is also considered to have been susceptible to the Asian continent’s influence. On 23 September 2021, the trajectories originated from industrial regions along the coast of the Yellow Sea. The weather was clear on both days. Vertical profiles of the meteorological condition on both days are shown in Fig. 10. The temperature on 15 October 2015, was similar to 28 March 2018, which was relatively high for March (Fig. 4), and the temperature on 23 September 2021, was higher than that on the observation days in March and December (Fig. 4). The relative humidity and dew point temperature on 15 October 2015, were relatively low (Fig. 10), and the air was dry.

Fig. 11 shows the vertical profiles of the size-separated number concentrations of the particles on the two days. The number concentration of the small particles (> 0.3 µm) on 23 September 2021, was relatively high (even at the higher altitude) and is thought to have been influenced by anthropogenic pollutants from the Asian continent. The number concentrations of the coarse particles were not high, and the influence of Asian dust particles was low. On 15 October 2015, the particle number concentrations were low for all particle sizes, and the air seemed to be clean.

Vertical profiles of the trace gases (H$_2$O$_2$, MHP, HCHO, SO$_2$, and O$_3$) over Imizu City, Toyama Prefecture, on 15 October 2015, and 23 September 2021, are presented in Fig. 12. Unfortunately, the HCHO could not be measured on 15 October 2015. MHP concentrations were also measured.
Fig. 7. Relationships between temperature and the concentrations of H$_2$O$_2$ (upper panel), HCHO (middle panel), and O$_3$ (lower panel) over Imizu City, Toyama Prefecture, Japan.

Fig. 8. Surface weather charts (JST 09H) on 15 October 2015 and 23 September 2021.
Fig. 9. Results of the 3-day backward trajectory analysis ending over Imizu City, Toyama Prefecture, Japan.

Fig. 10. Vertical profiles of relative humidity (RH), temperature (Temp), and dew point temperature (DP) over Imizu City, Toyama Prefecture, Japan on 15 October 2015 (left panel), and 23 September 2021(right panel).

Fig. 11. Vertical profiles of the size-separated number concentrations of the particles over Imizu City, Toyama Prefecture, Japan on 15 October 2015 (left panel), and 23 September 2021 (right panel).
Fig. 12. Vertical profiles of the trace gases (H$_2$O$_2$, MHP, HCHO, SO$_2$, and O$_3$) over Imizu City, Toyama Prefecture, Japan on 15 October 2015 (left panel), and 23 September 2021(right panel). On both days. On 23 September 2021, which is thought to have been affected by anthropogenic air pollution, the O$_3$ concentrations were relatively high at approximately 60 ppb, but the SO$_2$ concentrations were low. It is thought that most of the SO$_2$ originating from the Asian continent seemed to be oxidized to sulfate during long-range transport. The SO$_2$ concentrations on 15 October 2015, were also low at less than 1 ppb.

The H$_2$O$_2$ concentrations in the higher atmosphere on the two days were also lower than those in the summer (Watanabe et al., 2016) but higher than the concentrations during the cold months (except on 28 March 2018) (Fig. 6). This suggests that the potential oxidation capacity of SO$_2$ might have been relatively high. On 23 September 2021, the H$_2$O$_2$ was higher than the SO$_2$ at the three altitudes. On 15 October 2015, the concentrations of H$_2$O$_2$ and SO$_2$ were about the same at an altitude of 1,200 m (or H$_2$O$_2$ was slightly lower than SO$_2$, but, there was a condition of ([H$_2$O$_2$] + [MHP]) > [SO$_2$]), which also seems to be an important indicator of SO$_2$ oxidation capacity), and at an altitude of 2,400 m, the H$_2$O$_2$ was higher than the SO$_2$ (Fig. 12). However, there are few measurements of H$_2$O$_2$ over central Japan (or East Asia), especially in the autumn, and future observations are needed.

4 CONCLUSIONS

Hydroperoxide and HCHO concentrations, as well as O$_3$ and SO$_2$ concentrations, and number concentrations of aerosol particles were measured over Imizu City, Toyama Prefecture, located on the Sea of Japan coast in central Japan, during cold months (17 March 2017, 28 March 2018, 25 December 2019, and 17 March 2021) and in the autumn (15 October 2015, and 23 September 2021) using a helicopter. The observations were conducted in the early afternoon on clear days. H$_2$O$_2$ concentrations during the cold months were usually below 1 ppb and lower than SO$_2$ concentrations (Oxidant Limitation). In particular, the H$_2$O$_2$ measured on 25 December 2019, which is the period of minimum solar radiation, was extremely low. Even in the high-altitude atmosphere, H$_2$O$_2$ was lower than HCHO, and it is thought that the conditions might have been such that hydroxymethanesulfonate formation progressed more than sulfate formation. Further detailed investigations, such as HMS measurements in clouds and aerosols, are required.

On 28 March 2018, the observation site was significantly affected by trans-boundary air pollution at altitudes below 1,200 m, with high concentrations of O$_3$ and SO$_2$ and a relatively high temperature. H$_2$O$_2$ concentrations were also relatively high, but lower than concentrations of SO$_2$ and HCHO. On 17 March 2021, Asian dust particles were observed at altitudes below 1200 m, and it is possible that H$_2$O$_2$ was decomposed on the surface of the dust particles.

The concentrations of H$_2$O$_2$ in the autumn were usually higher than those during the cold season and higher than those of SO$_2$ in the high-altitude atmosphere, suggesting that the potential oxidation capacity of SO$_2$ might have been relatively high. However, there are significantly few measurements of H$_2$O$_2$ and HCHO over Asian countries especially in the autumn, and future observations are needed.
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DISCLAIMER

The authors declare that they have no competing interests.

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