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PMF analysis of impacts of SO_2 from Miyakejima and Asian Continent on Precipitation Sulfate in Japan

Kyo Kitayama[a, *], Naoto Murao[b], Hiroshi Hara[a]

[a]*Tokyo University of Agriculture and Technology, 3-5-8 Saiwaicho, Fuchu, Tokyo, Japan*

[b]*Hokkaido University, Nishi 5, Kita 8, Kita-ku, Sapporo, Hokkaido, Japan*

Abstract

PMF and back-trajectory analyses successfully evaluated contributions of sulfur dioxide to precipitation chemistry in Japan in terms of two major emission sources, Miyakejima and the Asian Continent. Precipitation chemistry datasets of Japanese Acid Deposition Survey (JADS) were subjected to PMF analysis to obtain the calculated concentration with contributions of five factors. The major sources were discussed for four selected JADS sites: Tanzawa, Tsukuba, Echizen and Goto. The first two are located close to Miyakejima, a volcano starting to erupt in 2000, while the others are located close to the Asian Continent on a national scale. PMF analysis of the observations suggested five factors, Factors 1 to 5, which corresponded to different acids and salts: Factor 1; H_2SO_4, Factor 2; HNO_3 and NH_4NO_3, Factor 3; $(NH_4)_2SO_4$ and NH_4NO_3, Factor 4; $CaSO_4$ and $CaNO_3$, and Factor 5; NaCl and $MgCl_2$. Concentration changes associated with the eruption of Miyakejima and the seasonal airflow were discussed in term of Factors 1 to 5. At Tanzawa and Tsukuba, the monthly mean concentration of Factor 1 remarkably changed after the onset of the eruption, although the concentrations of the other factors remained unchanged. This change suggested the volcanic SO_2 would be responsible for the Factor 1 concentration. No particular seasonality was confirmed for these sites. On the other hand, the volcanic impact did not appear to extend to Echizen and Goto because no apparent increases were detected in association with the eruption. However, remarkably seasonal changes were clearly detected for these sites, where winter concentration of SO_4^{2-} was two to four times larger than summer ones. This seasonal change was attributable to the northwesterly monsoon in winter which will transport SO_2 and SO_4^{2-} from the continental sources and the sea salt SO_4^{2-} from East China Sea and Sea of Japan, which was supported by back-trajectory analysis.

Keywords: Positive Matrix Factorization, precipitation chemistry, sulfate, Miyakejima, Japan

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*Corresponding author. Tel.: +81-042-367-5818; fax:+81-042-367-5818.

E-mail address: 50009953007@st.tuat.ac.jp (K. Kitayama).

1. Introduction

Sulfur dioxide is the precursor of sulfuric acid and emitted from both natural and anthropogenic sources. Whelpdatea et al. estimated that anthropogenic sources accounted for 71 % of global SO_2 emission (Whelpdale *et al*., 1996). In Japan, SO_2 emitted from the Asian Continent is as important as domestic sulfur dioxides. Sulfur dioxide from the Asian Continent is transported to Japan and influences its precipitation chemistry. Chinese emission accounts for a large part of the continental emissions. Streets et al., (2003) reported that Chinese emission in 2000 was estimated at 20,385 Gg, whereas Japanese emission was estimated at 801 Gg. Natural sources include volcanoes and oceans. In Japan, volcanoes are the major natural source of sulfur dioxide. The total emission of the six major volcanoes in Japan was 0.6 Tg-S of sulfur dioxide per year, which was more than the domestic anthropogenic emission, 0.5 Tg-S y^{-1} (Fujita et al., 1990).

Miyakejima, the volcano 200 km south from Tokyo, began to erupt in July 2000 and emitted a large amount of SO_2. The daily emission was evaluated to be some ten thousands tons per day for the period from September 2000 to January 2001 (Kazahaya, 2001). The emission rate is ten times lager than that of Sakurajima (2000 ton day^{-1}) which had been the largest source of volcanic SO_2 before the Miyakejima eruption.

The intensive emission has impacted precipitation chemistry by increasing SO_4^{2-} concentration and decreasing pH. Measurements and modeling studies of precipitation chemistry have clarified the impact of Miyakejima for 2000 to 2001 (An et al., 2003; Kajino et al., 2004; Akata et al., 2004; Matsuda et al., 2004; Okuda et al., 2005). Kitayama et al., (2008) analyzed nation-wide measurements of precipitation chemistry to reveal the volcanic impacts on the SO_4^{2-} concentration and pH for the sites close to Miyakejima, Tanzawa and Tsukuba in particular, from 2000 to 2002, but such impacts did not appear at sites distant from the volcano, Echizen and Goto. Precipitation at these sites in western Japan, however, was expected to suffer from the influence of anthropogenic SO_2 emitted by the sources in the Asian Continent. Lin et al., (2008b) estimated contributions of Asian sources to deposition by Community Multiscale Air Quality model (CMAQ) and reported that Japanese emission and long-range transport of anthropogenic sulfur from Central China and Southeast China equally contributed to a large part of wet sulfur deposition in Japan. Katayama *et al*., (2008) estimated nss-SO_4^{2-} deposition in Japan by using CMAQ and concluded that the increasing SO_2 emission of China after 2000 influenced the increase of nss-SO_4^{2-} deposition in Japan.

Impacts of the volcanic and continental SO_2 emissions should be considered in discussing precipitation SO_4^{2-} in Japan. For the evaluation of the influences of these sources, PMF will work as a receptor model to estimate the contribution of sources to the concentration.

PMF is one of the multivariate receptor models and works better than customary models like factor analysis and principal component analysis in aerosol and precipitation chemistry. Juntto and Paatero, (1994) analyzed precipitation data of Finland with PMF. A good agreement between the PMF-calculated and observed concentrations was confirmed and also a good ion balance was obtained for the calculated source compositions. Anttila et al., (1995) studied Finnish data of monthly bulk deposition. The observations were classified into four source apportionments, and the source contributions had the reasonable seasonality and regional variation. These successful cases ensured that the PMF application to precipitation chemistry will clarify contributing sources to observed ionic concentrations.

More applications of PMF are available to aerosol chemistry. Zhou et al., (2004) used two back-trajectory-based statistical models with the source contribution values obtained by the PMF analysis of $PM_{2.5}$ data to demonstrate the source locations. Kim and Hopke, (2004) applied PMF to the chemistry of $PM_{2.5}$ with backward trajectories and surface wind direction, and identified sources and the regional influences.

Back-trajectory analysis is a common method to discuss the probable routes of pollutant transportations to a receptor site. The collaboration between trajectory analysis and PMF successfully clarified the potential source area and the contribution in previous studies (Polissar et al., 1999; Liu et al., 2003; Raman and Hopke, 2007; Bhanuprasad et al., 2008). Application of back-trajectory analysis to the dataset of precipitation chemistry in Japan will identify regions of responsible sources for the SO_4^{2-} concentration.

The present work is a statistical extension of the previous work (Kitayama et al., 2008) which is based on only the wet-only daily-basis measurement to assess the volcanic impact. Influences of the volcanic and continental sources were evaluated by using PMF and back-trajectory analyses with much attention focusing on SO_4^{2-} concentration at some selected sites in Japan. The datasets are applied to PMF in order to produce the estimates of the SO_4^{2-} concentration with specific contributions of potential source factors. Back-trajectory analysis was also conducted for each of the daily-basis estimates. In terms of these estimated quantities, concentrations and contributions of the source factors were explored and discussed with corresponding trajectories to evaluate the impact of the volcano and other potential major sources.

2. Method

2.1 Data

From a nation-wide monitoring network of Japanese Acid Deposition Survey, four sites were selected for the present analysis: Tanzawa, Tsukuba, Echizen and Goto. Tanzawa and Tsukuba are situated on the Pacific Ocean side and are 100-200 km from the volcano, Miyakejima. Meanwhile, Echizen and Goto are located on the other side of Japan distant from the volcano in Fig. 1 which also includes the locations of major volcanoes (Japan Ministry of the Environment, 2001; Kitayama *et al*., 2008; Japan Meteorological Agency, 2008). Goto is close to Sakurajima, the second largest active volcano in Japan. The precipitation was collected on a daily basis with wet-only samplers from April 1997 to May 2003 whereas Tanzawa site was closed in April 2003. The data quality was assured in terms of ionic balance and conductivity check assessment (Japan Ministry of the Environment, 2001).

2.2 PMF

PMF is a statistical model which utilizes error estimates and produces non-negative results (Paatero and Tapper, 1994). The calculation of PMF provides factors representing acids and salts contributing to the concentration. In this work, the two-dimensional PMF program, PMF2 ver. 4.2 (Paatero, 2007), was utilized. The PMF modeling is written as follows

$$X = GF + E. \tag{1}$$

X is $n \times m$ matrix of the observed concentrations, where n is the number of the samples and m is the number of the ionic species of interest. G and F are the unknown matrices which represent $n \times p$ matrix of the factor contributions and $p \times m$ matrix of the factor compositions, respectively, where p is the number of the factors. E represents the residual matrix of dimensions $n \times m$. In the component form of ith sample and jth species, the above matrix equation can be rewritten as follows

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}, \tag{2}$$

where x_{ij} is the observed concentration of jth species in the ith sample, g_{ik} is the concentration of kth factor contributing to the ith sample, f_{kj} is the jth species fraction in kth factor and e_{ij} is the residual of the jth species concentration in ith sample. The task of PMF is to minimize the function Q defined as

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij} / s_{ij})^2, \tag{3}$$

where s_{ij} is the uncertainty of observed concentrations. For quantitative discussions, some measures were defined: F_k is the ionic composition of *k*th factor, GF_j is the total *j*th ionic concentration, and G_kF_{kj} is the *j*th ionic concentration of *k*th factor.

To determine the optimal number of factors, it is necessary to test different numbers of factors and evaluate the calculation of PMF. The details of the several trials for determining the number were described in Section 3.1.

2.3 Trajectory analysis

Isentropic backward trajectories were calculated for all daily precipitation events by using National Oceanic Atmospheric Administration (NOAA) HYSPLIT 4 model (Draxler and Rolph, 2004) with National Centers of Environmental Prediction (NCEP) meteorological data. Each 72-h trajectory started at 0300 UTC from the four sites and the altitude of the start is 1500 m.

3. Results and discussion

3.1 Determination of the number of factors

The number of factors was determined by calculation of a dataset with different *p's*. The outputs were evaluated in terms of three indicators, the value of Q, the calculated concentrations GF_j and the balance of the ionic fractions F_{kj} to assess the reproducibility of the concentrations and the chemical characteristics of the factor compositions.

The value of Q is an appropriate indicator of the validity of the PMF calculation. The variation of the Q-value with p's from 3 to 7 is shown in Fig. 2. The Q-value decreased with increasing p for all sites. This indicated that the calculated concentration GF_j became fitted to the observation. The same tendency of the Q-value was reported in the PMF applications to Finnish precipitation and particulate matter (Juntto and Paatero, 1994; Lee et al., 1999; Yakovleva and Hopke, 1999). The Q-value showed that the PMF outputs with $p \geq 5$ fit better than $p \leq 4$, but the physical meaning of the output must be assessed by other verification methods.

The calculated concentration should agree with the observation to evaluate precipitation chemistry in terms of the PMF output for further discussion. The calculated concentrations were directly compared with the observed concentrations, and the correlation coefficients were calculated for different *p's* (Fig. 3). The correlation coefficients of the concentrations were almost unity for $p \geq 5$. In the cases of $p = 3$ and $p = 4$, the correlation coefficients were far lower. The agreement between the concentrations supported the view that appropriate p was 5, 6 and 7.

Physical meaning of PMF output was also evaluated with the ionic balance between cations and anions of the ionic composition of the factors. The balances were estimated with R_1 defined as $R_1 = (C - A) / (C + A) \times 100$, where C and A are the sums of cations and anions, respectively (Japan Ministry of the Environment, 2001). Factors with R_1 equal or close to zero have balanced ionic composition which will represent reasonably ionic compounds. Therefore, if R_1 is far from zero, the factor has poor chemical meanings. R_1 was calculated for varying p's from 3 to 7 (Fig. 4). For all sites, R_1's for p = 3, 4 and 5 were close to zero whereas those for p = 6 and 7 were far from zero. The evaluation of the balance suggested that the cases of p = 6 and 7 were unsuitable.

Eventually, these evaluations of the PMF outputs concluded that the optimal p is 5. Further estimations were conducted based on this p value.

3.2 Confirmation of PMF results

3.2.1 Compositions of factors

The PMF factors with the optimal p of 5 were only statistically calculated. These factors will be further chemically classified as Factors 1 to 5 which are common for the sites by the ionic composition (F_k) (Fig. 5).

Factor 1 was composed of a large amount of H^+ and SO_4^{2-}, and will represent H_2SO_4 contributing to the observed concentrations. This factor also included a small fraction of Cl^- which would be originated from volcanic HCl. The Cl^- fraction was significant for Tanzawa, Tsukuba and Goto which are close to volcanoes, Miyakejima or Sakurajima (Fig. 1). Factor 2 had NO_3^- which are dominant over the anions for all sites. Major cations of factor 2 were H^+, NH_4^+ and Na^+ whereas the fractions of the cations differed between the sites. The quantitative composition of Factor 2 would represent HNO_3 or nitrate salts produced by neutralization between HNO_3 and bases. Factor 3 included NH_4^+ and SO_4^{2-} for all sites, and also contained NO_3^- for Tanzawa and Echizen. This factor would represent the ammonium species, $(NH_4)_2SO_4$ or NH_4NO_3, which are produced by neutralization between ammonia and the corresponding acids. Factor 4 was constituted of SO_4^{2-}, NO_3^-, Ca^{2+} and Mg^{2+} for Tanzawa, Tsukuba and Echizen, but NO_3^- was not included for Goto. The composition of Factor 4 would represent soil particles like $CaCO_3$ and $MgCO_3$ which neutralize H_2SO_4 or HNO_3. Factor 5 was composed of sea salt ions like Cl^-, Na^+, Mg^{2+} and SO_4^{2-}. The composition closely agreed with the ionic fraction of sea salt (Table 2) (National Astronomical Observatory, 2007).

In this work, SO_4^{2-} was the target for evaluation of the influences of SO_2 from the volcano and the Asian Continent. To focus SO_4^{2-}, Factors 1 to 5 were regarded to be the acids and salts contributing to the SO_4^{2-} concentration: Factor 1; H_2SO_4, Factor 2; no SO_4^{2-}, Factor 3; $(NH_4)_2SO_4$, Factor 4;

$CaSO_4$, Factor 5; sea-salt SO_4^{2-}. The calculated SO_4^{2-} concentrations of these factors are effective for evaluating the influence of the sources.

3.2.2 Confirmation of the calculated concentration

The calculated concentrations of SO_4^{2-} based on the factors (GF_{SO42-}) were plotted against the observed SO_4^{2-} concentrations to confirm the validity of the calculations (Fig. 6). For all the sites, these concentrations fell on the one-to-one line. The correlation coefficients were almost unity ranging from 0.93 to 0.99. The successful agreement ensures further discussion with the calculated concentration because the factors will give insights of the potential sources and its ionic compositions. The calculated concentration was divided into the contributions of each factor described as the equation, $[SO_4^{2-}]_{calc} = g_{i1} \times f_{1SO42-} + g_{i2} \times f_{2SO42-} + g_{i3} \times f_{3SO42-} + g_{i4} \times f_{4SO42-} + g_{i5} \times f_{5SO42-}$. The contributions of the factors to the concentrations were utilized to evaluate the impacts of sources on the SO_4^{2-} concentration.

3.3 Monthly concentration of PMF calculation

The monthly variation of the calculated concentration from April 1997 to March 2003 was focused to evaluate the influences of the volcanic source and the continental source (Fig. 7). At Tanzawa and Tsukuba, the sites close to Miyakejima, the concentration of Factor 1 drastically increased immediately after the onset of eruption, June 2000, whereas the contributions of the other factors remained unchanged. These facts supported the view that Factor 1 reflected the volcanic influence. The Factor 1 concentration before the onset would be derived from SO_2 emitted by other sources. The three-year averaged Factor 1 concentrations were estimated before and after the onset, and the difference was discussed to evaluate the contribution of Miyakejima (Table 3). The differences accounted for 49 % and 33 % of the SO_4^{2-} concentration of 2000 to 2002 for Tanzawa and Tsukuba, respectively. At these sites, the SO_4^{2-} concentrations were strongly influenced by SO_2 from Miyakejima.

However, the concentration of Factor 1 at the sites distant from Miyakejima, Echizen and Goto, did not increase after the onset. The result indicates that precipitation of Echizen and Goto did not receive the volcanic influence. The difference between the three-year averaged concentration of Factor 1 before and after the onset occupied 5 % and 3 % of the SO_4^{2-} concentration in 2000-2002 for Echizen and Goto, respectively. The influence of the volcanic SO_2 would not be noticeable on the SO_4^{2-} concentrations at these sites. However, the concentrations of SO_4^{2-} changed seasonally. In winter, these concentrations were higher than those in the other seasons. This seasonality would be involved with the northwesterly monsoon in this season, which will be discussed with the seasonal concentration.

3.4 Seasonally SO_4^{2-} concentration before and after the onset of the eruption

The concentrations of SO_4^{2-} were seasonally averaged over the two periods, three years before and after the onset, where the winter is defined as the months from December through February and the other seasons are accordingly defined (Fig. 8). At Tanzawa and Tsukuba, the concentration of Factor 1 after the onset was much larger than those before the onset. The seasonal change was much smaller than the change before and after the onset. The volcanic influence was significant on the SO_4^{2-} concentrations at the two sites.

At Echizen and Goto, changes due to the volcanic eruption were not recognized, but the concentration in winter was two to four times larger than that in summer. Especially, the concentrations of Factors 1, 4 and 5 in winter were much lager than in the other seasons. This seasonality would be caused by the northwesterly monsoon in winter where the airflow would transport SO_2 from the continental sources over the sea and capture sea-salt SO_4^{2-} on the way. The increase of Factor 4 concentration would be influenced by $CaSO_4$ derived from $CaCO_3$ and H_2SO_4. Calcium carbonate included in Asian dust will react with H_2SO_4 to compose $CaSO_4$. Cao et al., (2008) revealed that Asian dust contains pollutants including SO_4^{2-} in downwind regions of the desert. The seasonal difference of the transport route will be discussed in terms of the trajectory analysis.

3.5 Seasonal trajectory analysis

All trajectories of precipitation events were divided into four groups based on the seasons (Fig. 9). Most winter trajectories came from the Asian Continent. In contrast, the summer group included far less trajectories originating from the Asian Continent than the winter trajectories. This is attributable definitively to the northwesterly monsoon in winter which transports SO_2 from the area and sea salt SO_4^{2-} from East China Sea and Sea of Japan to the site. Because of the winter trajectories, the high SO_4^{2-} concentrations were observed in this season for Echizen and Goto.

Lin et al., (2008a) estimated that the SO_2 concentration in eastern China in winter reached more than 15 ppb, which was much higher than in the other area in East Asia (Fig. 10). Sulfur dioxide from this high SO_2 concentration area in eastern China would be transported by the northwesterly monsoon and influence precipitation in Japan. To evaluate the influence of this high concentration area, all trajectories were classified into two according to passing through the high SO_2

concentration areas or not and the percentage of the trajectories through the area is discussed. For Echizen and Goto, the trajectories through the high concentration area accounted for 60 % and 70 % in winter, respectively, whereas the percentages in summer decreased to 28 % and 36 %, respectively (Table 4). The percentages in winter confirmed that long-range transported SO_2 from this area and sea salt SO_4^{2-} largely influenced the SO_4^{2-} concentration at Echizen and Goto. In autumn and spring, the percentages of the trajectories were between the winter and summer percentages, and these varying percentages were corroborated by the seasonality of the SO_4^{2-} concentration discussed above.

6. Conclusion

PMF analysis expanded the previous work of the volcanic impacts to assess the volcanic contribution to precipitation SO_4^{2-}. The PMF results further exposed impacts of the Asian Continent. The PMF application accurately reproduced the concentration by five factors representing chemical compounds.

The calculation of PMF was tested for three points: Q-value, the reproducibility of observations, and chemical meanings of ionic compositions of factors. The factors were identified by the chemical components as Factors 1 to 5: Factor 1; H_2SO_4, Factor 2; HNO_3 and NH_4NO_3, Factor 3; $(NH_4)_2SO_4$ and NH_4NO_3, Factor 4; $CaSO_4$ and $CaNO_3$, and Factor 5; sea salt. Precipitation SO_4^{2-} was discussed with the calculated concentration in terms of Factors 1 to 5.

At Tanzawa and Tsukuba, the volcanic influence was recognized by the increase of the SO_4^{2-} concentration immediately after the onset of the eruption, and the dominant increase of Factor 1 indicated that Factor 1 was related to the volcanic impact. At these sites, no remarkable seasonal changes of the SO_4^{2-} concentration were noted.

At Echizen and Goto, the SO_4^{2-} concentration did not change at all after the onset of the eruption. The winter SO_4^{2-} concentration, however, was two to four times lager than the summer one. The increase was due to Factors 1, 4 and 5. This increase would be attributable to the northwesterly monsoon which transports SO_2 and alkaline calcium compounds from the Asian continent as well as sea salt from Sea of Japan. This view was supported by a large number of back-trajectories from the Asian Continent to the sites in winter.

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4.2. We also thank NOAA Air Resources Laboratory for HYSPLIT model.

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Table Captions

Table 1 Ratios of major ions of Factor 5 for the four sites and sea water to Na^+ (eq / eq)

*National Astronomical Observatory, 2007

Table 2 Three-year averaged SO_4^{2-} concentration of Factor 1 and Factors 1to 5 before and after the onset of the eruption (μeq L^{-1})

Table 3 Number of the trajectories passing through the high SO_2 concentration areas for different seasons

n: Number of the trajectories passing through the high SO_2 concentration areas,

N: Number of the total trajectories.

Figure Captions

Fig. 1 Locations of the selected JADS sites (○） and major volcanoes (△）.

Fig. 2 *Q*-value for different number of factors.

○ : Tanzawa, □ : Tsukuba, ◇ : Echizen, △ : Goto.

Fig. 3 Coefficient of determination between observed and calculated concentrations for different number of factors.

○ : Tanzawa, □ : Tsukuba, ◇ : Echizen, △ : Goto.

Fig. 4 R_1 for each factor for different number of factors.

Fig. 5a Ionic compositions (*F*) for Factors 1 to 5 for Tanzawa (above) and Tsukuba (below).

Fig. 5b Ionic compositions (*F*) for Factors 1 to 5 for for Echizen (above) and Goto (below).

Fig. 6 PMF calculated concentrations against observed concentrations.

Fig. 7 Monthly averages of calculated SO_4^{2-} concentration in terms of Factors 1 to 5.

■ : Factor 1, ▩ : Factor 2, ▨ : Factor 3, ░ : Factor 4, □ : Factor 5.

Fig. 8 Seasonal averages of calculated SO_4^{2-} concentration in terms of Factors 1 to 5.

■ : Factor 1, ▩ : Factor 2, ▨ : Factor 3, ░ : Factor 4, □ : Factor 5.

Fig. 9a Back-trajectories in seasons at Echizen. Each trajectory started at 0300 UTC for daily precipitation events and persisted for 72 hours.

Fig. 9b Back-trajectories in the seasons at Goto. Each trajectory started at 0300 UTC for daily precipitation events and persisted for 72 hours.

Fig. 10 High SO_2 concentration areas in Asia estimated by Lin et al. (2008a).

Table
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Table 1 Ratios of major ions of Factor 5 for the four sites and sea water to Na^+ (eq / eq)

	Cl^-	Mg^{2+}	SO_4^{2-}	Ca^{2+}	K^+
Tanzawa	1.23	0.18	0.06	0.01	0.05
Tsukuba	1.15	0.21	0.10	0.05	0.03
Echizen	1.12	0.22	0.09	0.03	0.02
Goto	1.13	0.21	0.10	< 0.001	0.02
sea salt*	1.16	0.23	0.12	0.04	0.02

*National Astronomical Observatory, 2007

Table 2 Three-year averaged SO_4^{2-} concentration of Factor 1 and Factors 1to 5 before and after the onset of the eruption (μeq L^{-1})

		SO_4^{2-} concentration (μeq L^{-1})	
		Factor 1	Factors 1 to 5
Tanzawa	1997-1999	5.8	10.6
	2000-2002	17.1	23.3
Tsukuba	1997-1999	7.8	24.0
	2000-2002	20.2	37.4
Echizen	1997-1999	17.2	50.3
	2000-2002	20.5	61.9
Goto	1997-1999	10.9	33.1
	2000-2002	12.2	38.5

Table 3 Number of the trajectories passing through the high SO_2 concentration areas for different seasons

		n	N	n／N (%)
Echizen	winter	190	317	60
	spring	58	198	29
	autumn	26	176	15
	summer	60	213	28
Goto	winter	90	99	70
	spring	50	208	31
	autumn	19	180	11
	summer	53	183	36

n: Number of the trajectories passing through the high SO_2 concentration areas,

N: Number of the total trajectories.

Figure

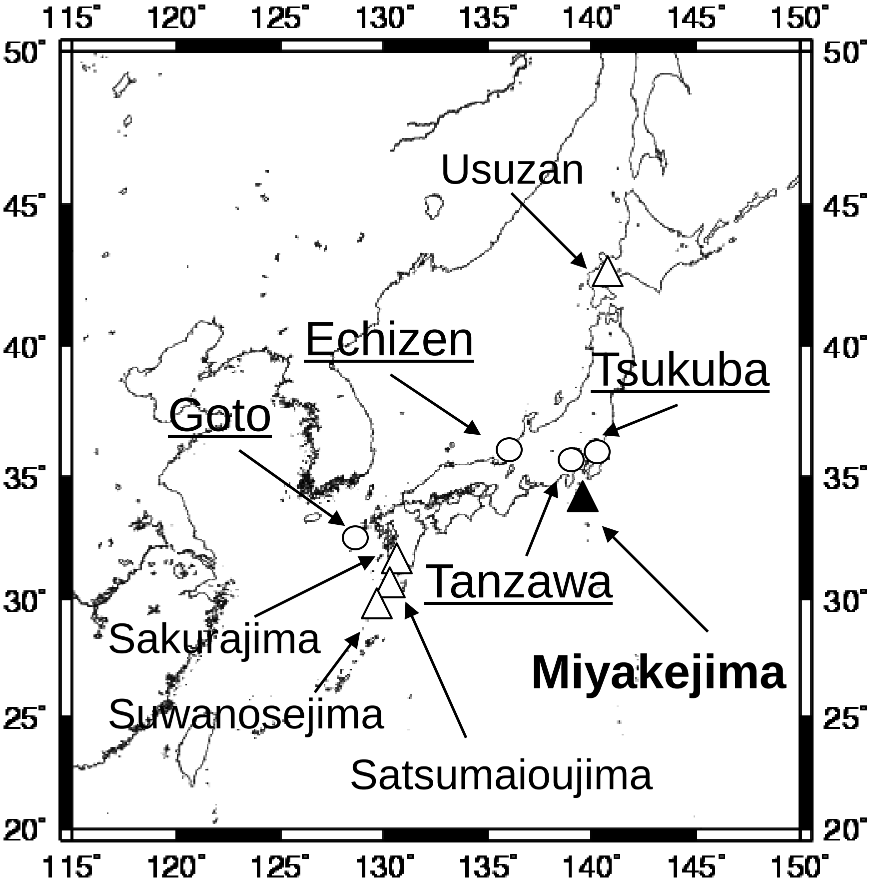


Fig. 1 Locations of the selected JADS sites (○) and major volcanoes (△).

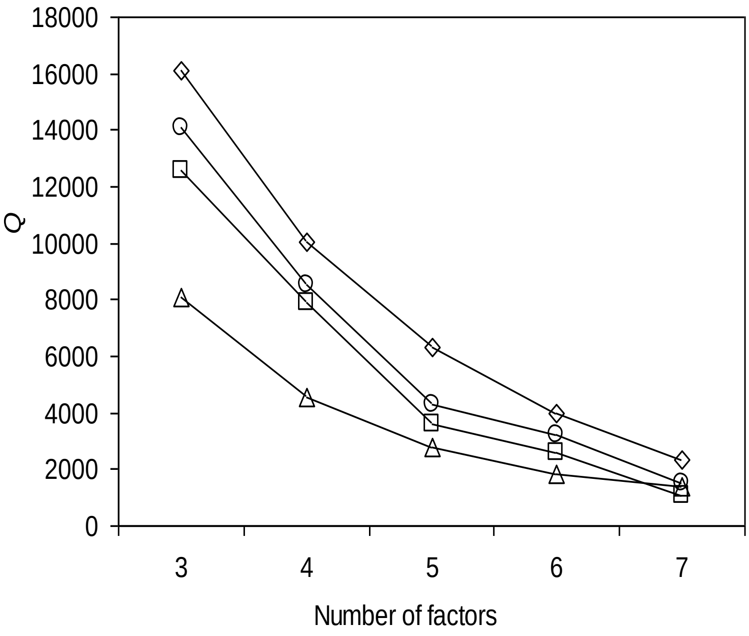


Fig. 2 *Q*-value for different number of factors.

○ : Tanzawa, □ : Tsukuba, ◇ : Echizen, △ : Goto.

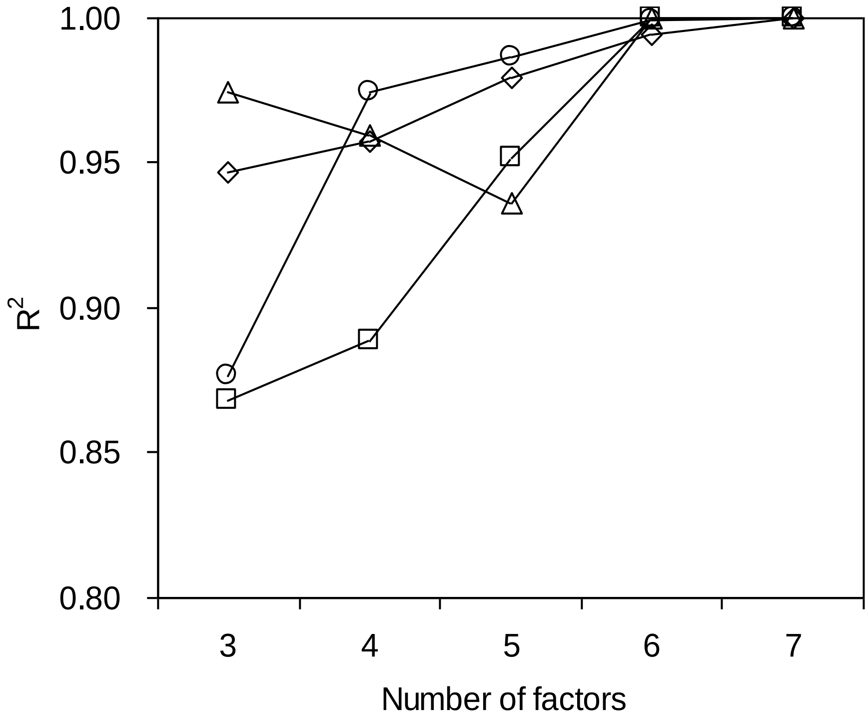


Fig. 3 Coefficient of determination between observed and calculated concentrations for different number of factors.

○ : Tanzawa, □ : Tsukuba, ◇ : Echizen, △ : Goto.

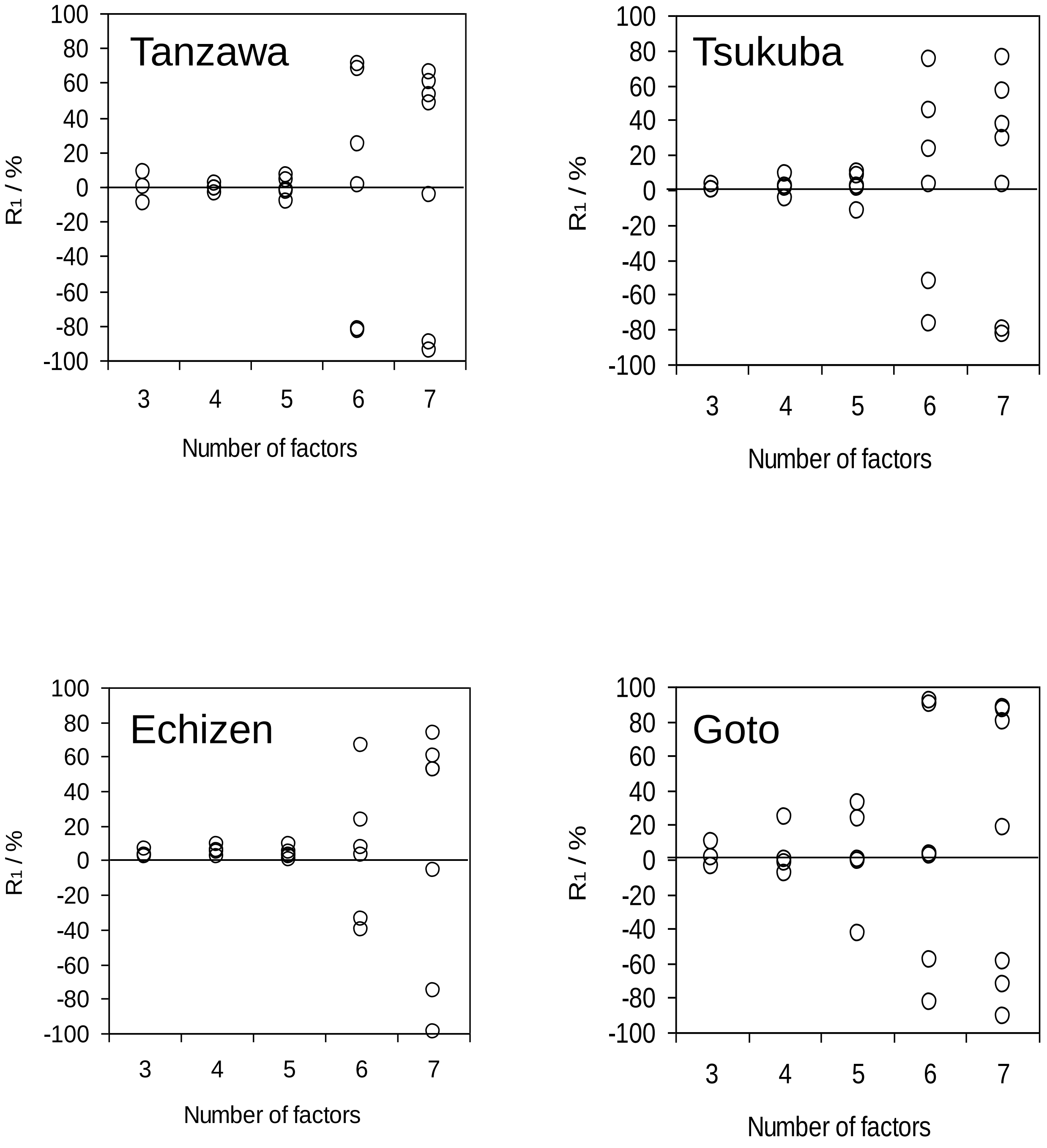


Fig. 4 R_1 for each factor for different number of factors.

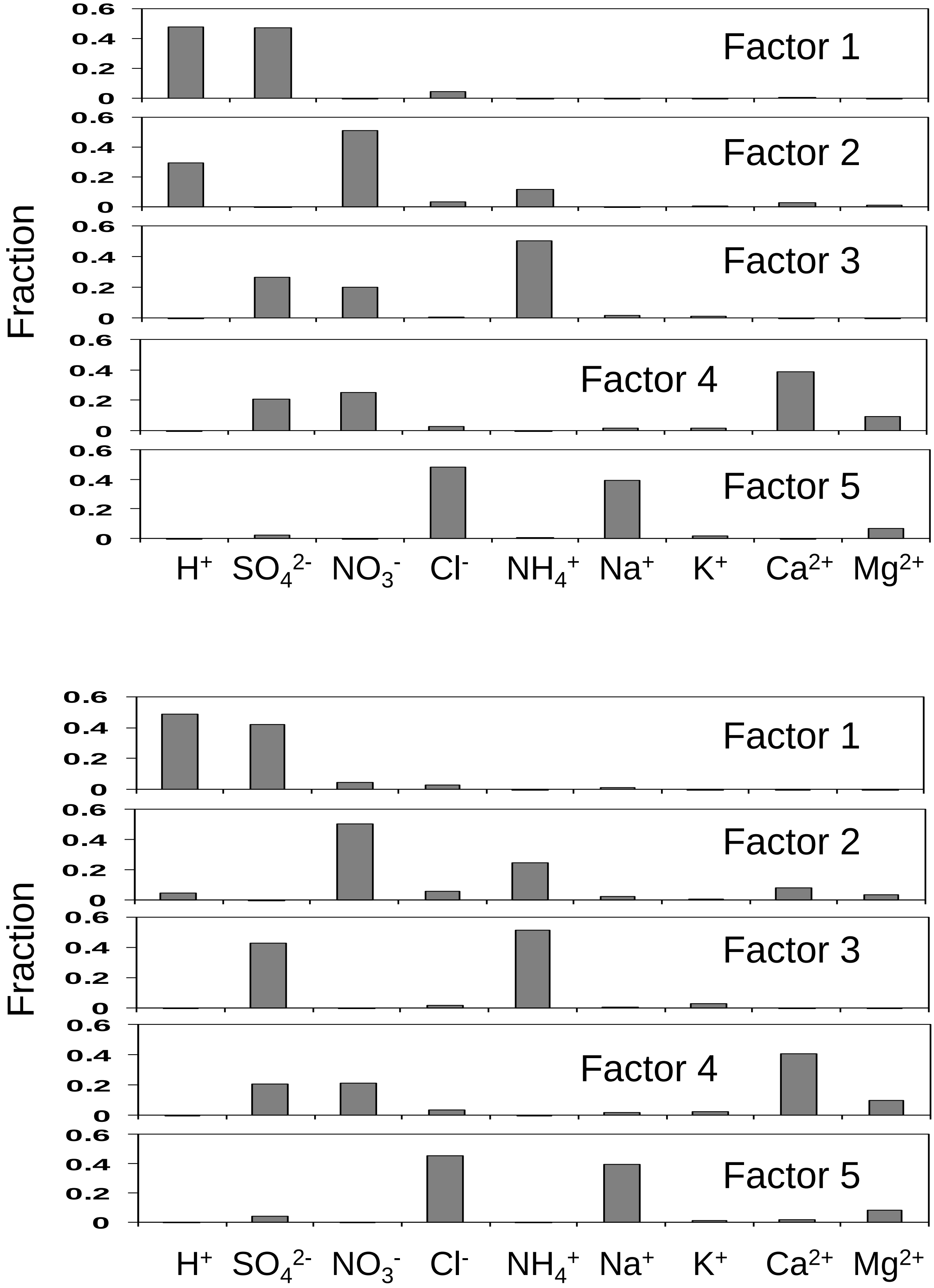


Fig. 5a Ionic compositions (*F*) for Factors 1 to 5 for Tanzawa (above) and Tsukuba (below).

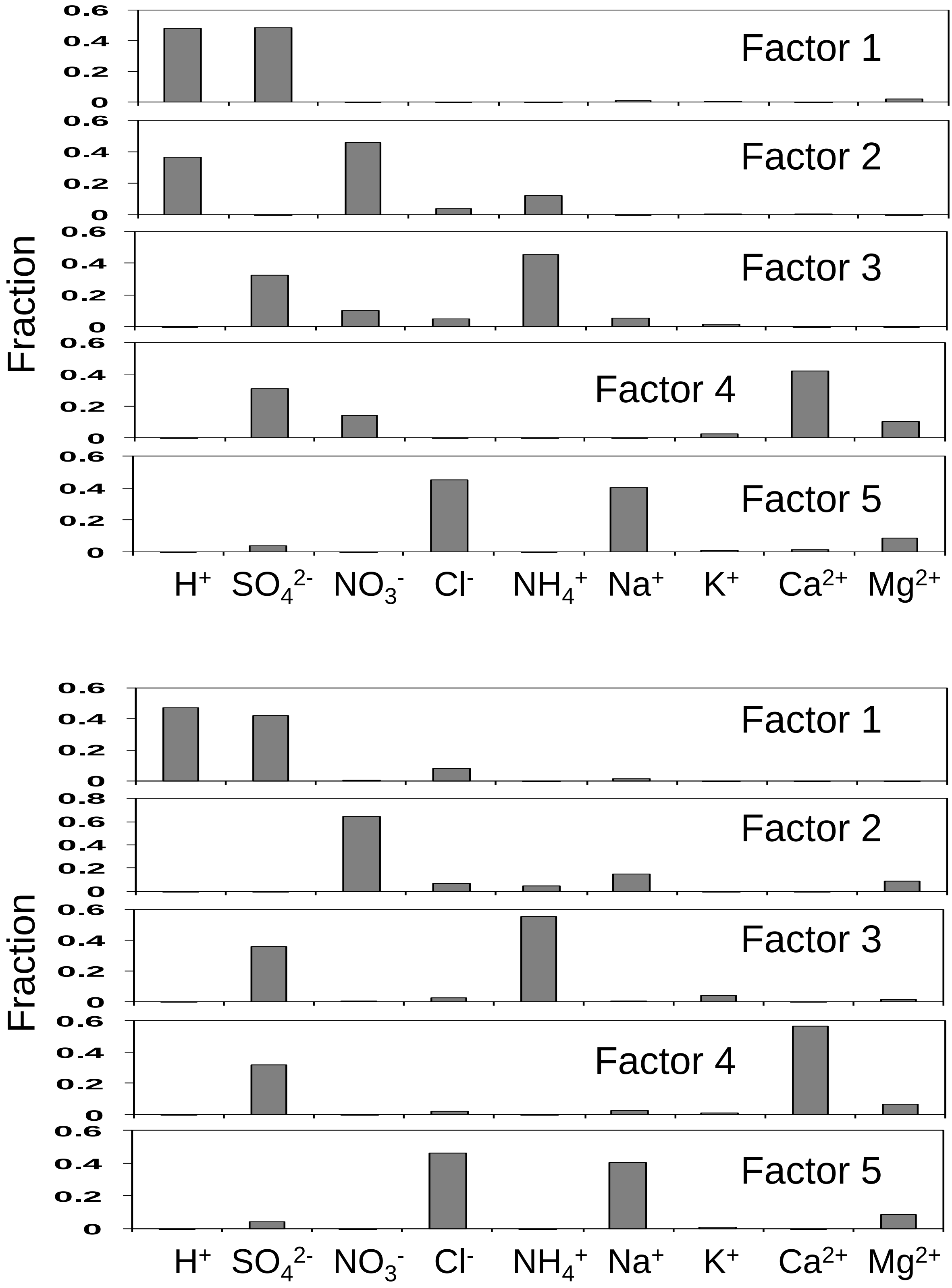


Fig. 5b Ionic compositions (*F*) for Factors 1 to 5 for for Echizen (above) and Goto (below).

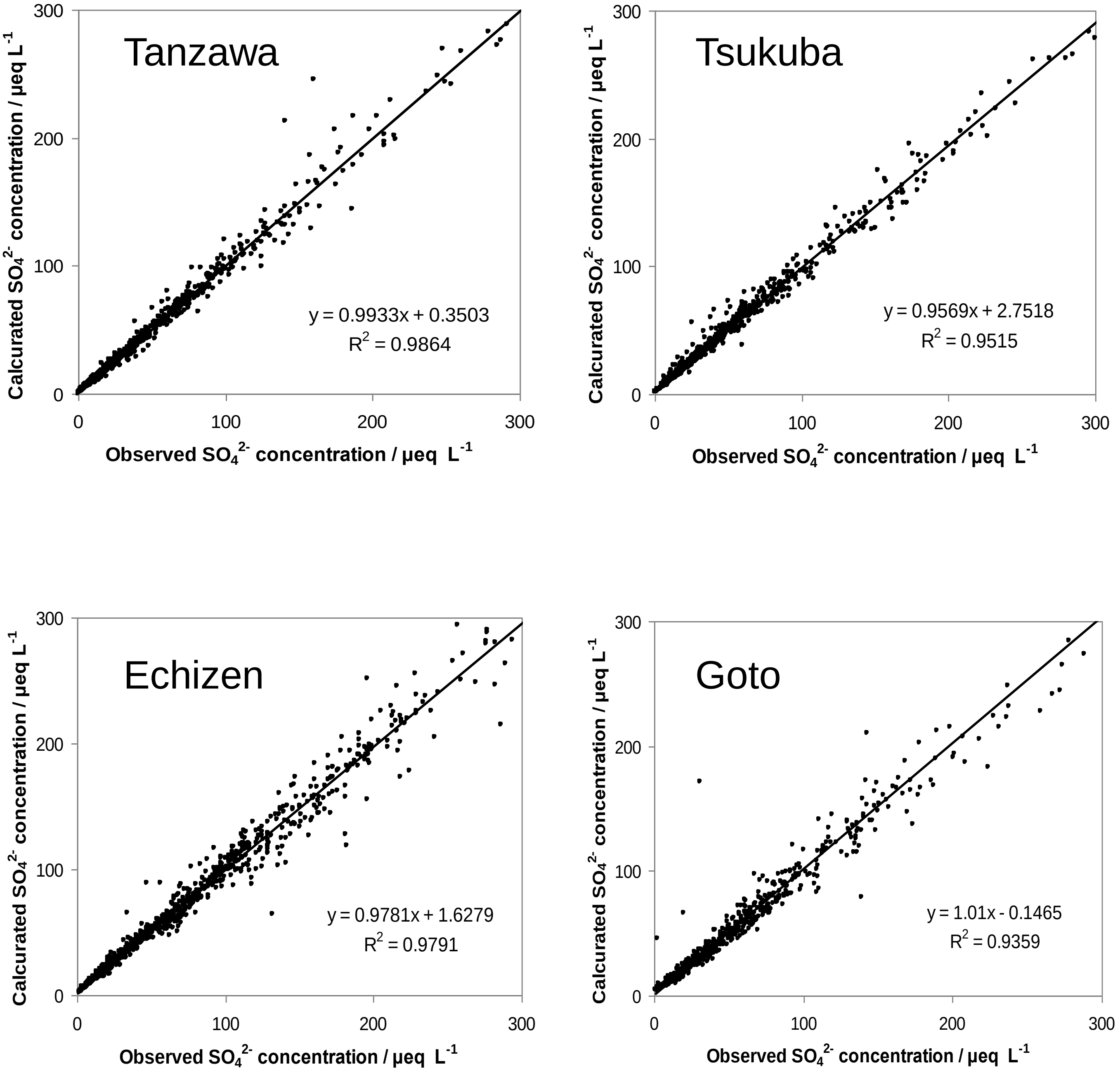


Fig. 6 Calculated concentrations against observed concentrations.

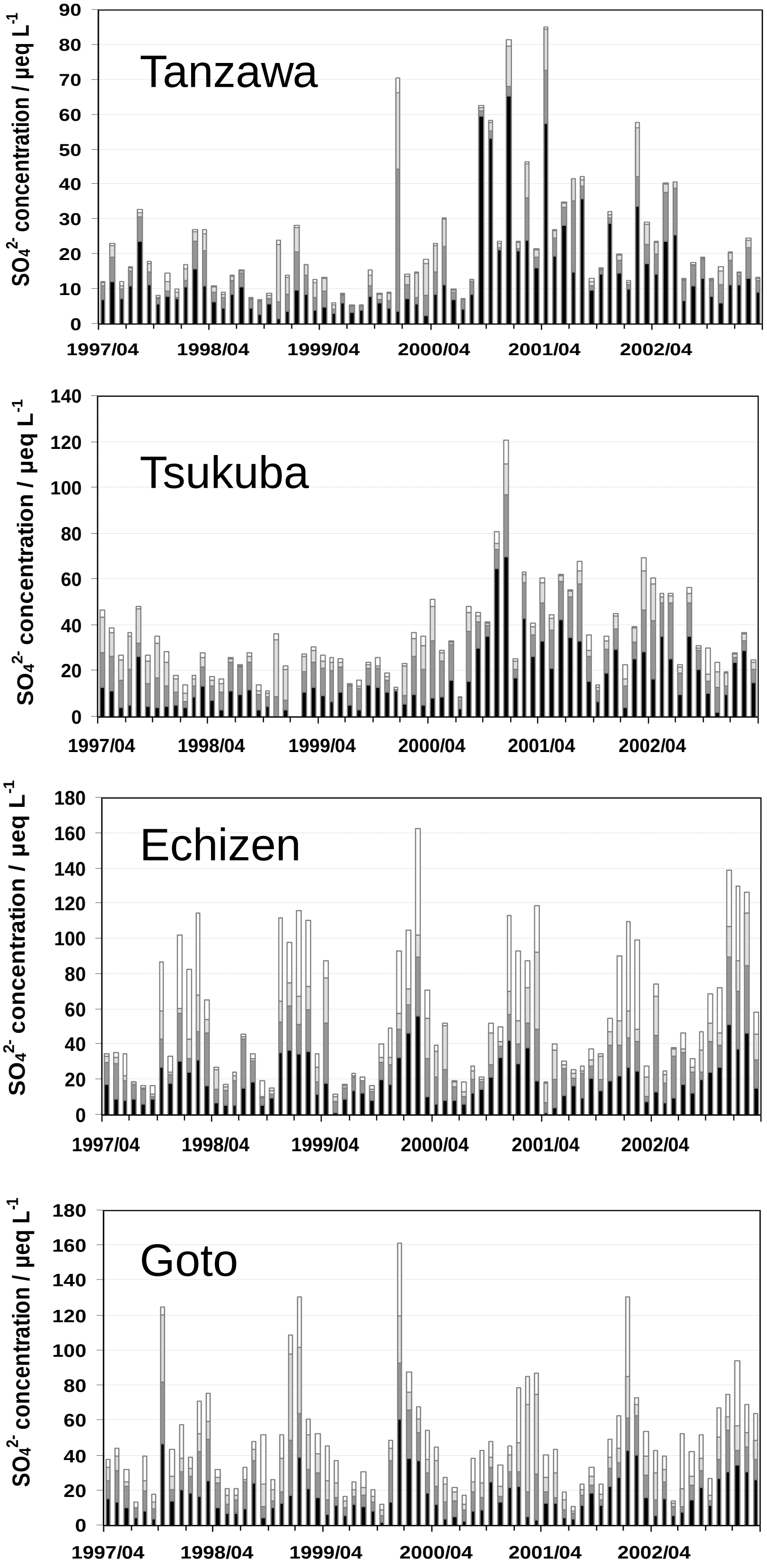


Fig. 7 Monthly averages of calculated SO$_4^{2-}$ concentration in terms of Factors 1 to 5.

■ : Factor 1, ▩ : Factor 2, ▨ : Factor 3, ░ : Factor 4, □ : Factor 5.

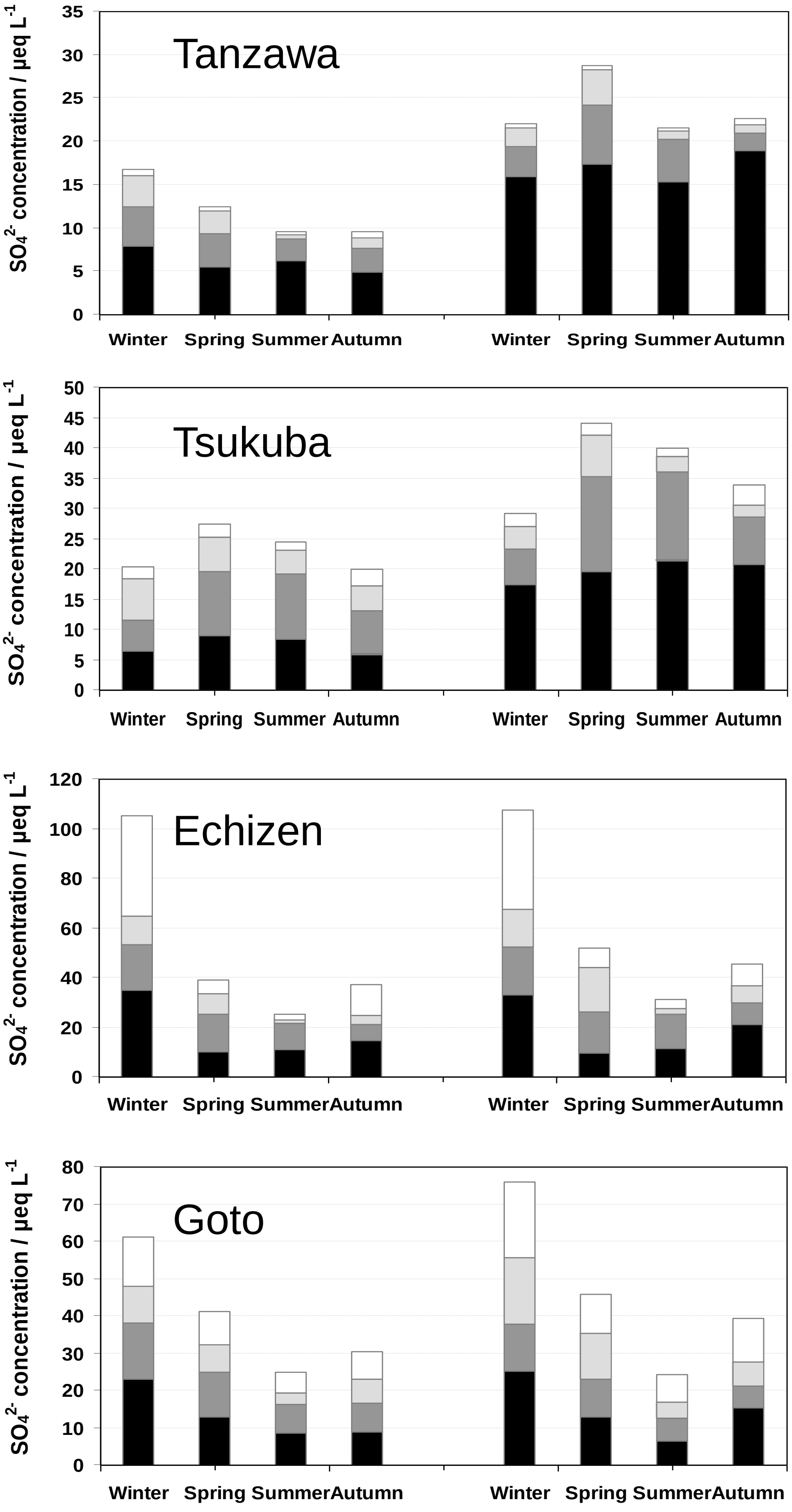
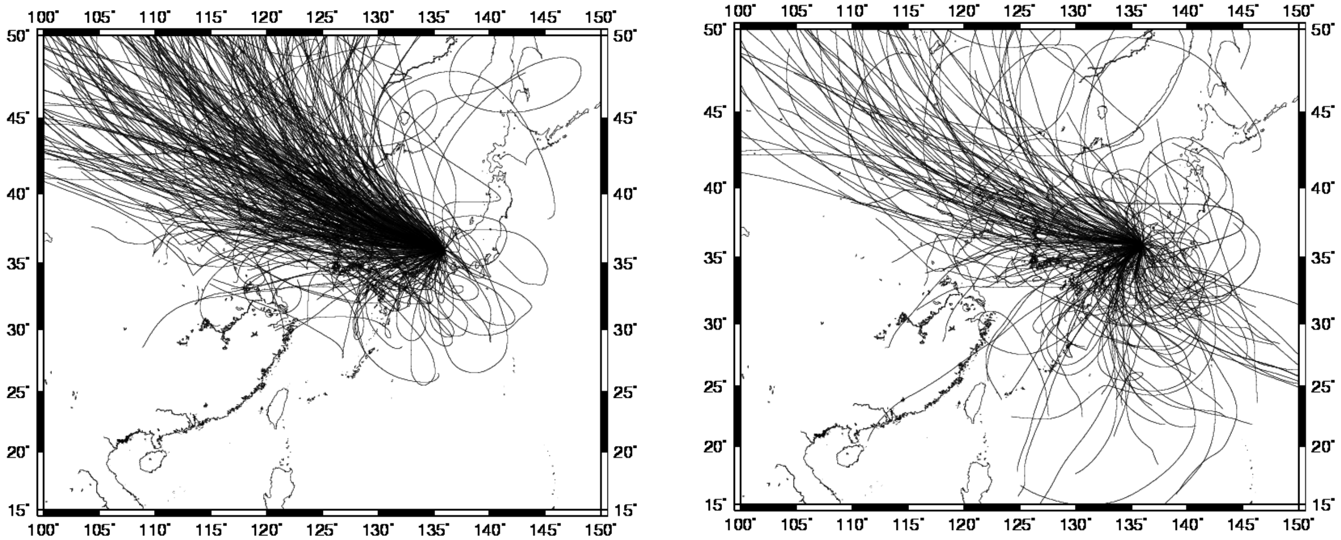
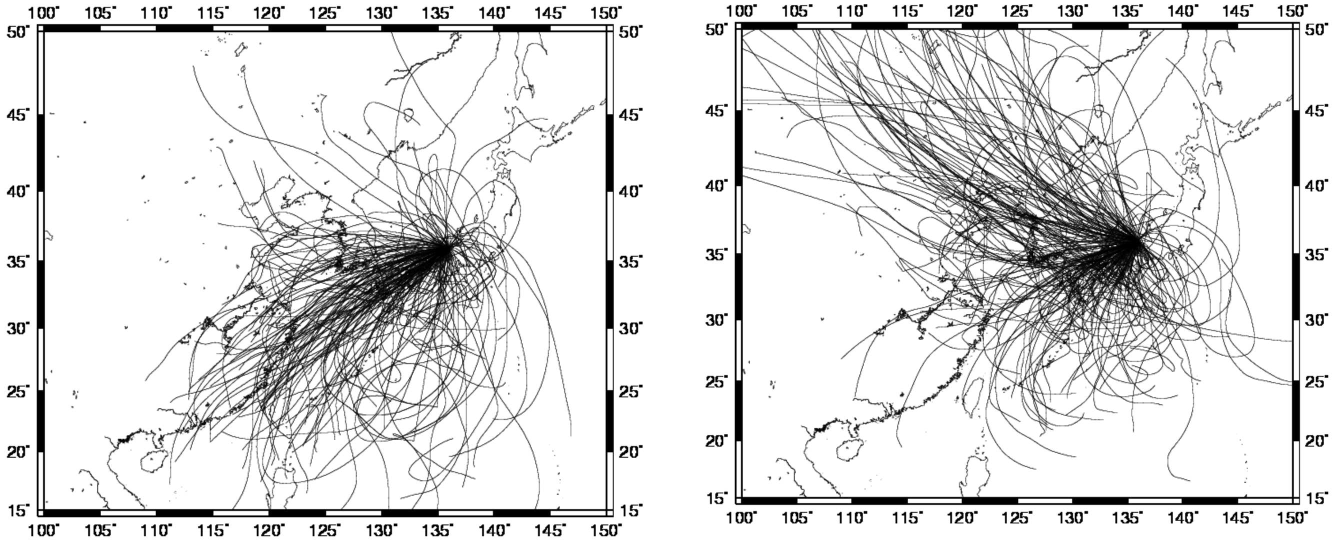


Fig. 8 Seasonal averages of calculated SO_4^{2-} concentration in terms of Factors 1 to 5.

■ : Factor 1, ■ : Factor 2, ▩ : Factor 3, ▨ : Factor 4, □ : Factor 5.

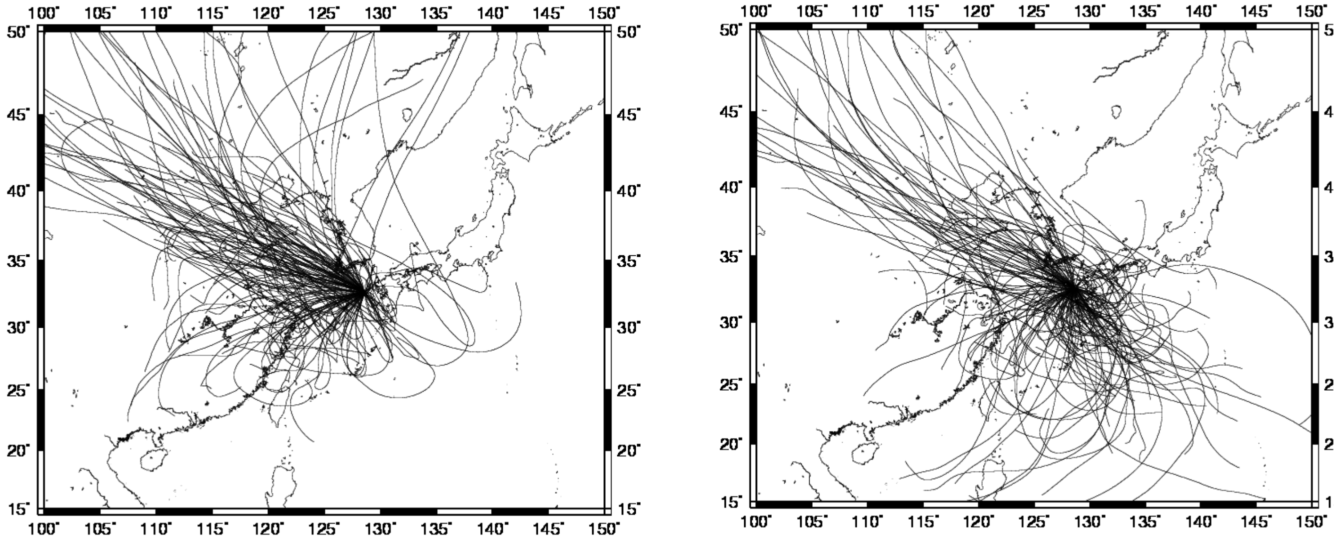


winter autumn



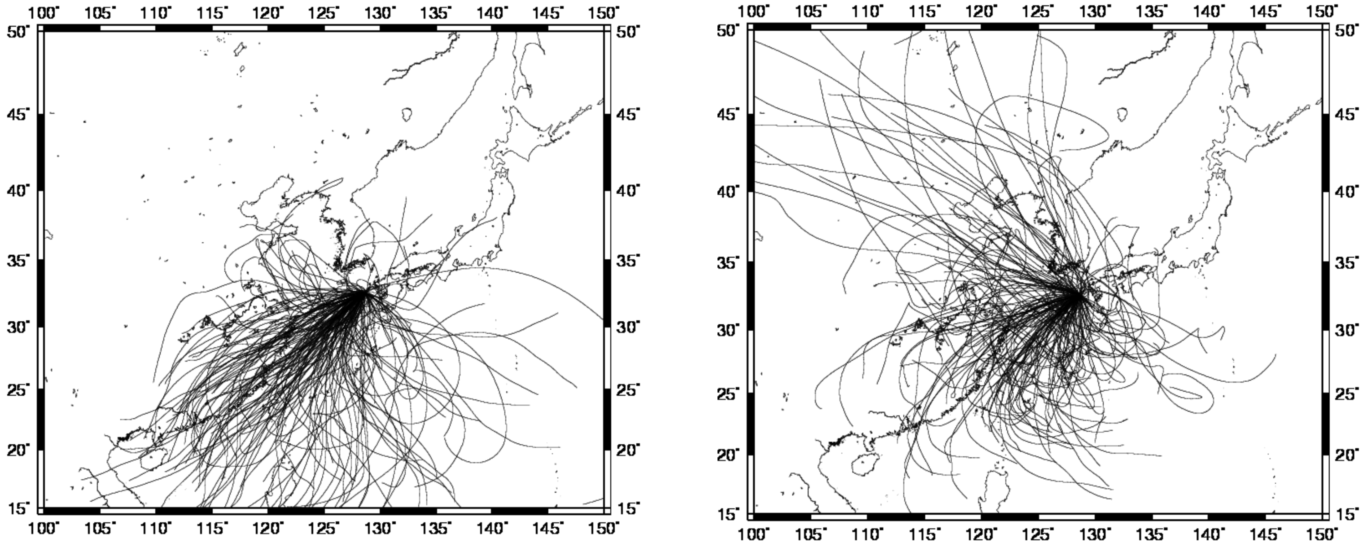
summer spring

Fig. 9a Back-trajectories in seasons at Echizen. Each trajectory started at 0300 UTC for daily precipitation events and persisted for 72 hours.



winter

autumn



summer

spring

Fig. 9b Back-trajectories in seasons at Goto. Each trajectory started at 0300 UTC for daily precipitation events and persisted for 72 hours.

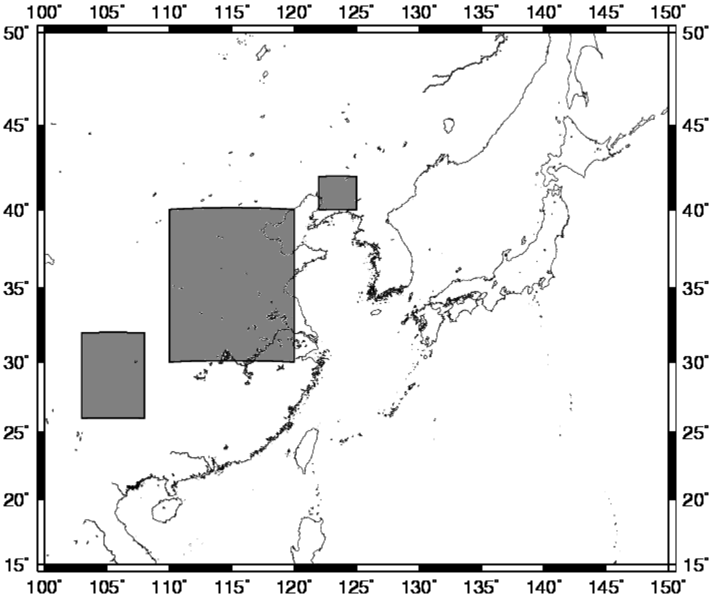


Fig. 10 High SO_2 concentration areas in Asia estimated by Lin et al. (2008a).