Research Report

Time and Space Variations of Main Species Concentration of Fine Particulate in the Kanto Region

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関東地域における微小粒子中主要成分の時空間変動

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Abstract

The main component concentrations of fine particulate were measured at 17 sites by 24-hr sampling for two weeks by JCAP (Japan Clean Air Program) in the winter of 1999. The following results were obtained by multivariate data analysis using the data sets.

(1) The ratio of fine particulate to SPM was about 2/3 and a large difference between the observation points was not observed although some low values were indicated in the clean region.

(2) The fluctuation factor and Max/Min of Cl^- concentration for space variation were the highest and those of SO_4^{2-} were the lowest among the six components.

(3) The deviations of space variation for Cele (elemental carbon) and NO_3^- concentrations were larger than for SO_4^{2-} concentrations. The peak concentration of Cele and NO_3^- for a site sometimes appeared at different dates. The fluctuation factor of space variation for the SO_4^{2-} concentrations was smaller than that of time variation. SO_4^{2-} concentration is thought to change similarly in a wide mesoscale area.

(4) Three factors were extracted by factor analysis of all data. Factor 1 is representative of the ammonium salt that is the main component of the secondary formatted inorganic particulate. Factor 2 is representative of the combustion source including vehicle exhaust and the secondary formatted organic particulate. Factor 3 is representative of sea salt and fine soil particulate.

Keywords: Fine particulate, Field investigation, Daily variation, Factor analysis, Elemental carbon, Nitrate, Sulfate, Kanto, JCAP

要　旨

JCAP (Japan Clean Air Program) は1999年冬季に微小粒子中の主要成分濃度を関東地域の17地点において，1日毎に2週間測定した。このデータセットを用いて多変量解析を行い，次のことを明らかにした。

(1) 微小粒子のSPMに対する質量濃度比は約2/3であり，清浄地域はわずかに小さい値を示したものの，都市域と大差はなかった。

(2) 測定期間中の各成分の平均値を地点別に求めると，地点間の振動係数と最大値／最小値は6主要成分中Cl^-が最も大きく，SO_4^{2-}は最も小さい値を示した。

(3) Cele (元素状炭素)とNO_3^-の日平均濃度の空間変動はSO_4^{2-}のそれよりも大きかった。同じ測定局でもCeleとNO_3^-の極大値は日付の異なる場合があった。SO_4^{2-}の空間変動は明らかに時間変動よりも小さく，メソスケール内でかなり同じ濃度レベルで変化すると予測される。

(4) 全測定データを用いた因子分析により，3因子を抽出した。第1因子は無機イオンの二次生成を，第2因子は自動車排気粒子を含む燃焼系発生源と有機二次粒子を，第3因子は海塩粒子と土壌粒子の微小粒径区分をそれぞれ代表することがわかった。

キーワード　微小粒子，フィールド観測，日変動，因子分析，元素状炭素，ナイトレート，サルフェート，関東地域，JCAP

1. Introduction

Health effects of exposure to ambient fine particulate matter have mainly been investigated in epidemiological studies in the United States.[1-3] After the United States enacts the air quality standards of PM2.5 (particles with aerodynamic diameter d_p < 2.5 μm) in 1997, the concern for PM2.5 has risen in Japan. The Japanese Ministry of the Environment started monitoring PM2.5 mass concentration[4] in 1998.

Recently the characterization of chemical species and annual mean concentrations in PM2.5 has been reported. Wei et al.[5] investigated eight sites in four Chinese cities by random 24-hr sampling on 40-70 days. He et al.[6] researched two sites in Beijing by weekly sampling. Kavouras et al.[7] investigated five sites in Chile by 24-hr sampling every four days. In the Kanto region, eight prefectures and three cities have investigated cooperatively 18 sites by 96-hr sampling[8] twice a year. However, field studies that measure the main components of fine particulate simultaneously at several sites by 24-hr sampling for at least one week are seldom conducted.

The air modeling research group of JCAP (Japan Clean Air Program) has conducted air quality studies on the Kanto region in the summer and winter of 1999 and in the summer of 2000. In winter 1999 campaign[9], the main component concentrations of fine and coarse particulate were measured at 17 sites by 24-hr sampling for two weeks. The purpose of this study is to analyze the behavior of the main composition of fine particulate. This paper reports time and space variations of main compositions including a multivariate data analysis using the JCAP data sets.

2. Method

2. 1 Sampling sites

Coarse particulate (PM7-2.1: particle with aerodynamic diameter d_p, 2.1 μm < d_p < 7 μm) and fine particulate (PM2.1: particle with aerodynamic diameter d_p, d_p < 2.1 μm) were simultaneously collected at 17 points in winter 1999 (see **Fig. 1**). In Fig. 1, sites 11 and 12 are the rooftop of a skyscraper, namely the Ikebukuro Sunshine 60 Building (226 m above ground level), and the Omiya Sonic City Building (137 m above ground level). The name of site, height above sea level, height above ground level, mean concentration ratio of NO_2 to NO, mean concentration of NO_X in December, and the population density of the administrative division are shown in **Table 1**. A ground observation point at the Ikebukuro site was set up in a schoolyard near the Sunshine 60 Building (SS60). The Jyomine and Akagi sites are both in clean rural regions. The Jyomine site is on the top of mountain Jyomine (1,037 m above sea level) that is located 67 km northwest of central Tokyo. The Akagi site (470 m above sea level) is on the south slope of mountain Akagi, which is located 20 km north of the Jyomine site. The Ichinomiya site is in a rural area near the Pacific Ocean. Kudan, Ikebukuro, Urawa, Omiya and Yokosuka are located in the industrial region and business district of Tokyo and Yokohama. Koga (population 60,000), Fukaya (population 100,000) and Hiratsuka (population 250,000) are located in urban areas of mid-sized cities. Toke and Hachioji are semi urbanized residential areas. Umihotaru is located on an artificial island in Tokyo bay and near an expressway.

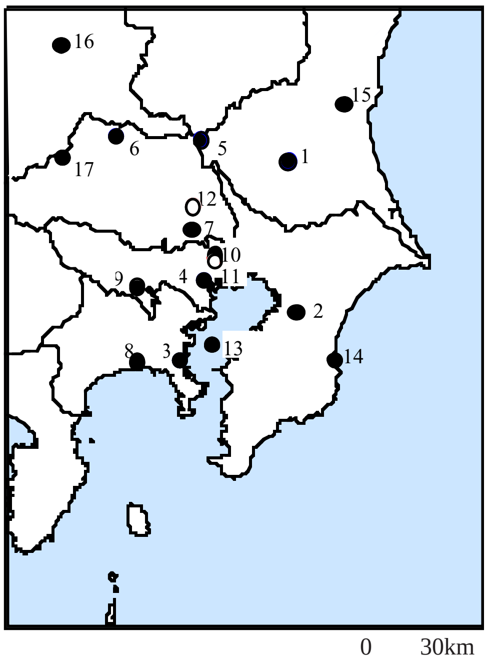


Fig. 1 The fine and coarse particulate sampling points in the Kanto region in 1999 winter. ● ; Site on ground or of height less than 35m above ground level, ○ ; Site of height more than 35m above ground level.

2. 2 Sampling and chemical analysis

Fine and coarse particulate was collected using an Andersen three-stage low-volume air sampler (Tokyo Dylec, AN200). The collected particulate matter was divided into three fractions, $PM_{2.1}$, $PM_{7\text{-}2.1}$ and $PM_{7<}$ (particles of aerodynamic diameter d_p , 7 μm < d_p). The sampler was equipped with quartz fiber filters (Gelman Science, PALLFLEX 2500QAT-UP, ϕ80 mm) that were baked at 650°C in air for three hours. Twenty-four-hour samplings of 17 sites was started at 10 o'clock AM on Monday Nov. 29 and ended on Monday Dec. 13 in 1999. The flow rate was 28.3 L /min.

The all filters used to collect $PM_{7\text{-}2.1}$ and $PM_{2.1}$ were maintained at 50% RH and 25°C for 24 hr or more and were weighted before and after sampling. After measuring PM mass, the filter was treated as shown in **Fig. 2**. Two portions were used for the carbon analysis, and one portion was used for the inorganic ion analysis. As shown in Fig. 2, one portion measured Ct (total carbon), and other portion was measured Corg (organic carbon) using the CHN meter (Yanagimoto, MT-5). Cele (elemental carbon) is calculated by the difference between Ct and Corg Standard deviation of Ct on twenty blank filters was about 1 μg.

One portion of the filter was soaked in 10 mL of ion exchanged water and soluble inorganic salt was extracted by a supersonic wave washing machine for 15 minutes. The extract was filtered with a 0.45 μm PTFE filter (GL Sciences, 13AI) and analyzed by ion chromatography (DIONEX, IC20) to detect the amounts of seven inorganic ionic species (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+ and Mg^{2+}) according to the

Table1 Atmospheric feature of the sampling points.

NO.	name of site	abbreviation	ASL$ (m)	AGL# (m)	NO_2 / NOx * (%)	NOx * (ppb)	population density (n/km^2)	urban or rural
1	Tsukuba	Tsu	27	1	43[c]	56[c]	552 ('99)	semi urban
2	Toke	Tok	90	5	62[a]	73[a]	3,238 ('99)	semi urban
3	Yokosuka	Yok	5	1	47[c]	71[c]	4,260 ('02)	urban
4	Kudan	Kud	35	31	47[c]	95[c]	3,097 ('00)	urban
5	Koga	Kog	19	1	36[b]	71[b]	2,830 ('99)	urban
6	Fukaya	Fuk	37	1	52[b]	47[b]	1,504 ('01)	urban
7	Urawa	Ura	8	21	41[c]	89[c]	6,915 ('01)	urban
8	Hiratsuka	Hir	9	10	42[c]	97[c]	3,757 ('00)	urban
9	Hachioji	Hac	124	20	61[c]	32[c]	2,727 ('99)	semi urban
10	Ikebukuro	Ike	30	1	48[a]	93[a]	17,978 ('99)	urban
11	SS60 R	SS6	30	226	41[a]	80[a]	17,978 ('99)	urban
12	Omiya R	OmR	13	137	43[c]	91[c]	5,130 ('01)	urban
13	Umihotaru	Umi	2	1	38[a]	51[a]	-	in the bay
14	Ichinomiya	Ich	6	3	70[b]	22[b]	527 ('02)	rural
15	Ibaraki	Iba	26	2	38[b]	52[b]	293 ('02)	semi urban
16	Akagi	Aka	470	2	90[a]	13[a]	173 ('02)	rural
17	Jyomine	Jyo	1,027	1	100[a]	7[a]	93 ('00)	rural

$; ASL = above sea level #; AGL = above ground level *; Monthly mean value in Dec. 1999 or during this campain
a; Original measurment data of the JCAP campain
b; Data of the public monitoring station where we used particulate matter sampling
c; Data of the nearby public monitoring station

analysis condition of **Table 2**.

3. Results

3. 1 PM concentrations

In the two-week sampling period, PM mass concentrations were periodically decreased at four times, Nov. 29, Dec. 3, Dec. 7 and Dec. 12, when the distributions of atmospheric pressure were of the typical "west-high and east-low pattern" and during a strong northwest wind. After the typical pressure contribution was reduced and the migratory anticyclone had covered the Honshu Island for few days, PM mass concentration increased greatly.

Mean mass concentrations of $PM_{2.1}$ and PM_7 for each sampling site are compared in **Fig. 3**.

There is not a large difference in mean PM_7 concentrations between the metropolitan urban sites like Kudan or Ikebukuro and the urban sites in mid-sized cities like Koga and Fukaya. The mean PM_7 concentration of Hiratsuka was the highest for the measurement period at 75 $\mu g/m^3$. The mean PM_7 concentration of Jyomine, a clean area in the Kanto region, was 40% of the mean value of Hiratsuka and was higher than author's forecast.

SPM that is defined to be particulate matter with a diameter of 10 μm or less in the 100% cut-off diameter is different from PM_{10} defined to be particulate matter with a diameter of 10 μm or less in the 50% cut-off diameter. If PM_7 is assumed to be an almost equal to SPM, it is possible to consider that sum of mass concentration of coarse particulate ($PM_{7-2.1}$) and fine particulate ($PM_{2.1}$) is the SPM mass concentration. The ratio of the fine particulate to SPM was about 2/3 and was not largely different from the observation points, although that of Jyomine became slightly lower.

3. 2 Mean compositions

The two-week averaged concentrations of mass and six main components (Cele, Corg, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) of fine particulate are shown in **Table 3** for each of the 17

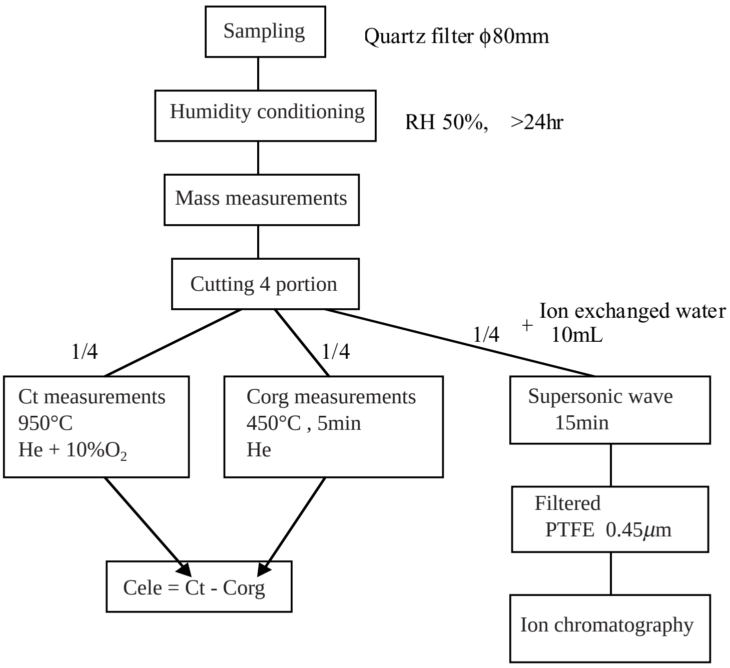


Fig. 2 Outline chart of carbon analysis.

Table 2 Analytical conditions of ion chromatograph.

	anion	cation
Pretreatment column	AG12A (DIONEX)	CG12A (DIONEX)
Separation column	AS12A (DIONEX)	CS12A (DIONEX)
Temperature	35°C	35°C
Detector	conductivity	conductivity
Mobile phase	2.7mM Na_2CO_3 + 0.3mM $NaHCO_3$	20mM methanesulfonic acid
Flow rate	1.3 mL/min	1.0 mL/min
Injection volume	25μ L	25μ L

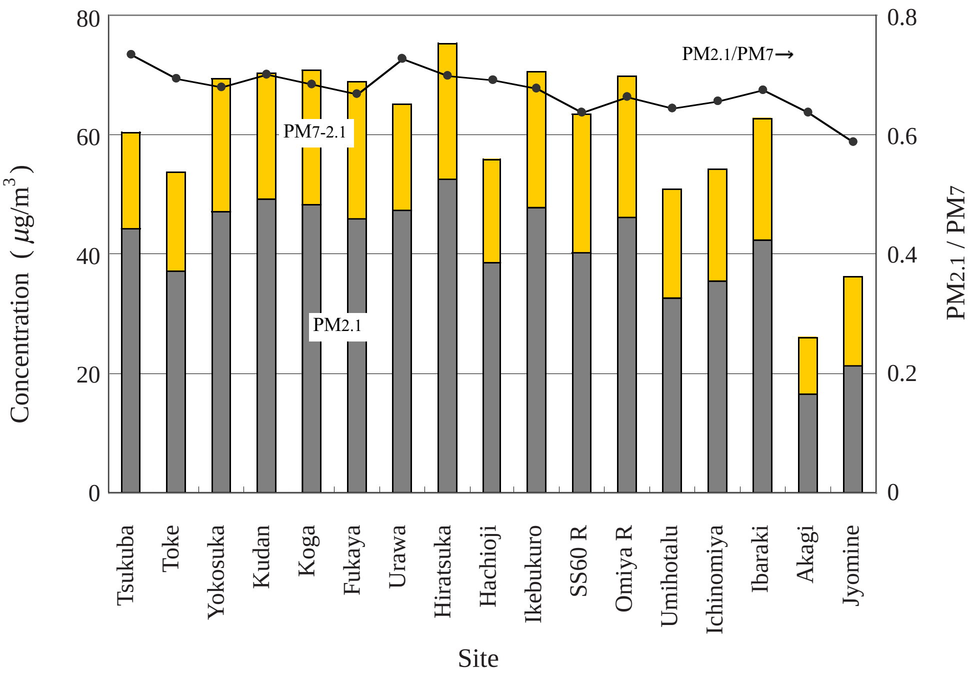


Fig. 3 Contributions of $PM_{2.1}$ and PM_7 mass concentrations (From Nov. 29 to Dec. 13 in 1999).

Table 3 Mean components of fine particulate for each site.

(μg/m³)

	$PM_{2.1}$	Cele	Corg	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+
Tsukuba	44.3	9.5	8.3	2.27	3.39	2.41	3.16
Toke	37.2	7.8	7.7	1.89	2.96	2.59	2.49
Yokosuka	47.0	8.9	7.7	2.41	4.26	3.06	2.93
Kudan	49.3	10.8	8.9	3.28	5.16	2.64	3.61
Koga	48.3	8.9	10.0	3.31	3.80	2.82	3.31
Fukaya	45.9	6.3	7.7	2.57	3.62	2.50	3.17
Urawa	47.3	10.3	11.8	2.73	4.05	2.46	3.36
Hiratsuka	52.6	11.2	10.3	3.16	4.53	2.77	3.72
Hachioji	38.7	7.7	9.5	1.62	4.00	2.09	2.68
Ikebukuro	47.8	10.8	9.3	2.55	4.26	2.21	3.59
SS60 R	40.3	7.1	6.6	1.99	4.21	2.43	2.84
Omiya R	46.2	5.9	8.8	1.99	3.93	2.26	3.17
Umihotaru	32.8	6.7	6.3	2.07	3.71	2.71	3.02
Ichinomiya	35.4	7.0	7.1	1.57	2.67	2.55	2.26
Ibaraki	42.4	9.6	10.0	1.29	2.08	1.24	2.31
Akagi	16.6	2.6	5.1	0.41	1.58	1.47	1.56
Jyomine	21.2	2.3	4.6	0.29	1.36	1.52	1.29
Mean	40.8	7.9	8.2	2.08	3.50	2.34	2.85
SD	9.8	2.6	1.9	0.88	1.05	0.51	0.69
FF	24.1	33.3	23.2	42.0	30.0	21.6	24.2
Max/Min	3.2	4.8	2.6	11.3	3.8	2.5	2.9

SD ; Standard Deviation
FF ; Fluctuation Factor (%)

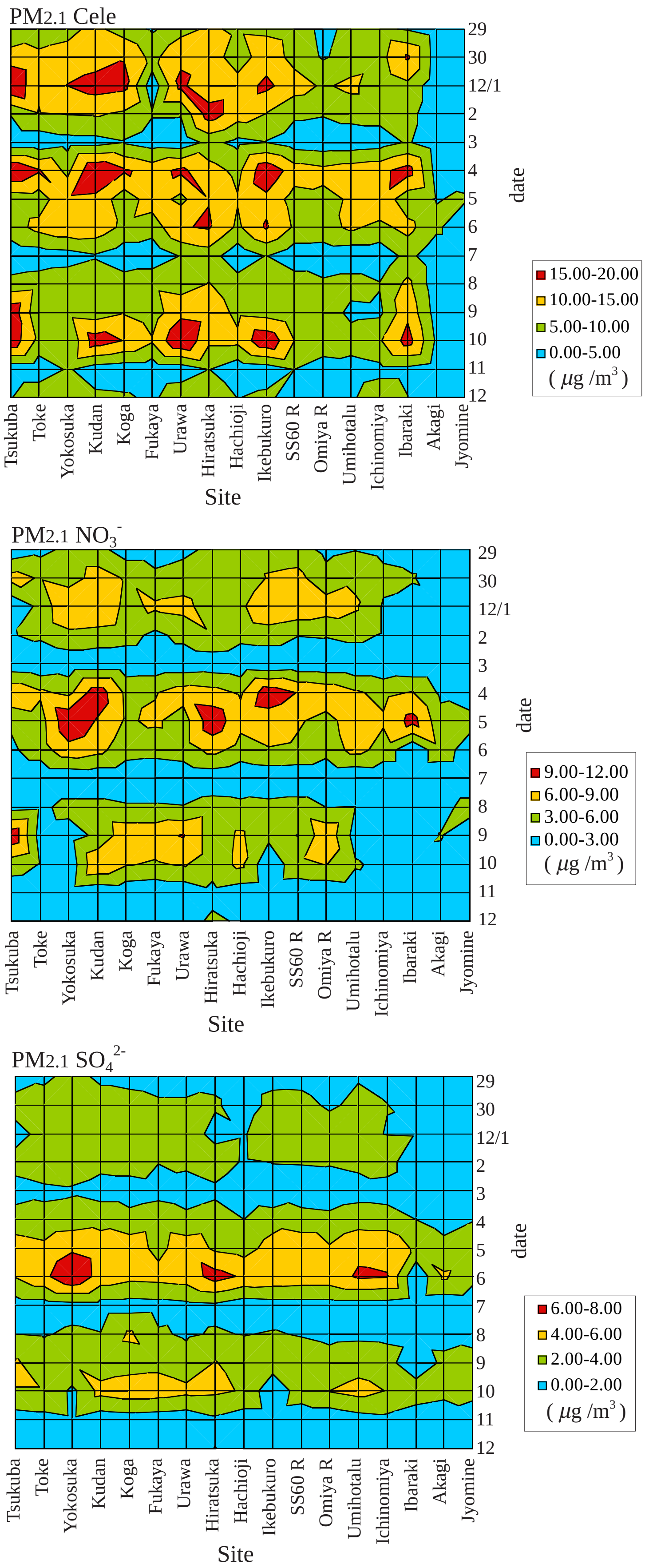


Fig. 4 Time and space variations of Cele, NO_3^- and SO_4^{2-} concentrations from Nov. 29 to Dec. 12 in 1999.

sampling points. The mean weight of the six main components occupied 56-77% of fine particulate. It is expected that the remainder of PM2.1, particulate other than the six main species, is made up of water and other elements, such as O, N, H, alkali and metal elements.

Cele concentration was considerably high at Hiratsuka, Kudan, Ikebukuro and Urawa, and the ratio of Cele concentration at urban sites to those at clean area sites was the second highest in the six components. Corg mean concentrations at Urawa, Hiratsuka, Koga and Ibaraki were higher than those at Kudan and Ikebukuro. It is expected that Corg at suburban sites, such as Koga and Ibaraki, are influenced considerably by the secondary organic aerosol, thus increasing the concentration. Corg/Cele was the highest at clean region such as Akagi and Jyomine.

The fluctuation factor and Max/Min (see Table 3) of Cl^- were the highest, and those of SO_4^{2-} were the lowest of the six components. The main source of Cl^- in fine particulate is not sea salt, but rather public incinerators. The deposition rate coefficient of HCl gas is larger than those of NO or SO_2, so the difference in Cl^- concentrations in rural and urban areas was larger than those of other main components. SO_4^{2-} concentration was highest at Yokosuka site in the industrial area, and differences in SO_4^{2-} concentrations between rural and urban areas was smallest among the main components.

NO_3^- concentration was considerably high at Kudan and Ikebukuro, sites in the center of Tokyo. The fluctuation factor of mean NH_4^+ was almost the same value as fluctuation factor of mass concentration.

3. 3 Time and space variations

Figure 4 shows the variation of daily mean concentrations of Cele, NO_3^- and SO_4^{2-} in PM2.1 for each site. Concentrations of three components were clearly decreased on Dec. 3, Dec. 7 and Dec. 11 as well as PM2.1 mass concentration. The deviations of space variation for Cele and NO_3^- concentrations seem to have been larger than for SO_4^{2-} concentrations. The peak concentrations of Cele and NO_3^- for a site appeared sometimes at different dates. For instance, Cele concentrations at Ikebukuro and Ibaraki on Dec. 10 were extremely high, but NO_3^- concentrations on the same day at the same site were low. The difference is thought to have been caused by the time delay of photooxidation of NO_X to HNO_3. The arithmetical mean of the fluctuation factor of space variation for SO_4^{2-} concentrations was 33%, and that of the fluctuation factor of time variation was 63%. The arithmetical mean of fluctuation factor of space variation for the NO_3^- concentrations was 49%, and that for Cele was 47%. It is expected that SO_4^{2-} concentration changes similarly in a wide mesoscale area of about 200 km × 200 km.

As shown in Fig. 4, one day was required for Cele to increase from local minimum concentration to local maximum concentration, and three days were required for this to occur for SO_4^{2-}.

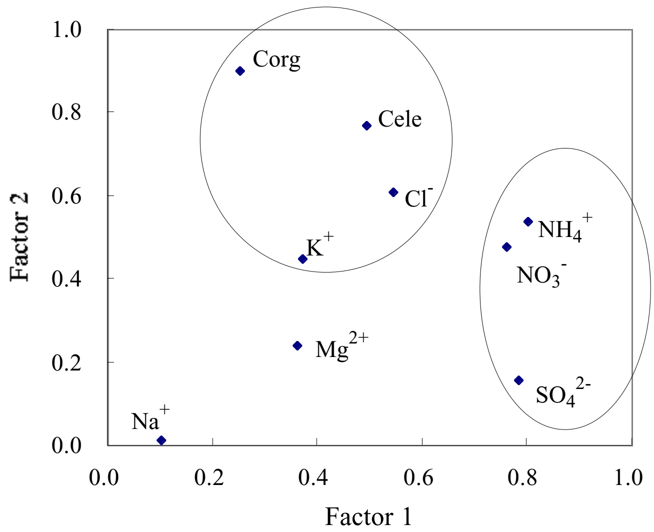
4. Discussion

4. 1 Factor analysis

Some latent factors that represent source type were extracted from 238 data sets of composition concentrations (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Cele and Corg) of fine particulate by a factor analysis. The multivariate data analysis software, S-PLUS[10] (Ver 4.5, Mathematical system) was used for the factor analysis.

It was assumed that the number of latent factors was three, and the factor loading for each factor was calculated after the varimax rotation. The scatter charts of the factor loading are shown between factor 1 to factor 2 and factor 2 to factor 3 in **Fig. 5**. The contribution rate of factor 1, factor 2 and factor 3 became, respectively, 30.2, 28.7, and 19.4%. Factor 1 has an especially high amount of factor loading for NH_4^+, SO_4^{2-} and NO_3^- (Fig. 5) and is representative of the ammonium salt that is the main component of the secondary formatted inorganic particulate. Factor 2 has a high amount of factor loading for Corg, Cele and Cl^-, and seems representative of combustion sources, including vehicle exhaust and the secondary formatted organic particulate. Factor 3 has a high amount of factor loading for Na^+ and K^+, and is representative of sea salt and fine soil particulate.

Because quantitative analysis of trace metallic elements was not performed, three factors were not able to be divided in further detail. In particular, it is



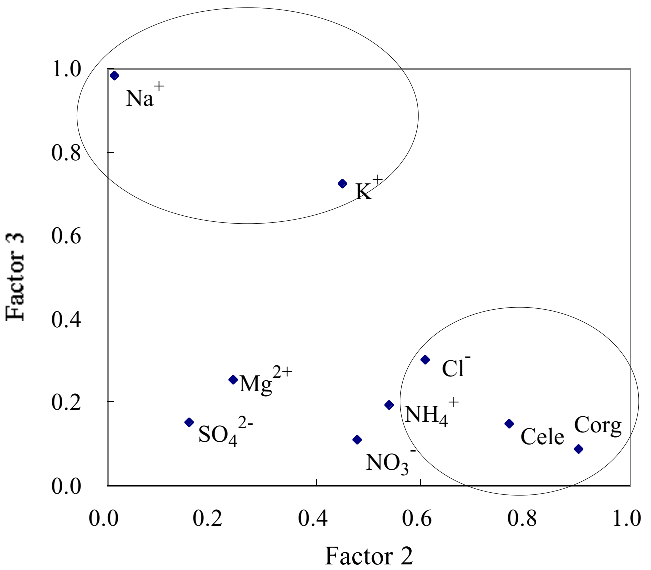


Fig. 5 Scatter chart of the factor loading.

considered that factor 2 concerns several types of diesel exhaust particulate (DEP), various types of incinerators, boilers and secondary organic particulate, and it is thought that more detailed chemical analysis is necessary in order to reveal the source apportionment.

4. 2 Cluster analysis

A hierarchical clustering technique was used to group 17 sampling sites for each of three main and specific components, Cele, NO_3^- and SO_4^{2-} in PM2.1. The cluster analysis and dendrogram charts were obtained by statistics analysis software[11] that Hayakari developed to be convenient for atmospheric researchers. A complete linkage dendrogram for 17 sites is shown in **Fig. 6**. The degree of non-similarity was expressed as 1 - | correlation coefficient |, and the crowd mean method[10] was used to combine clusters.

The distance of each site in the dendrogram of SO_4^{2-} is smaller than in the dendrogram of Cele and NO_3^- (Fig. 6). The Akagi and Tsukuba cluster or the Hachioji and Urawa cluster showed a high degree of similarity for the three components. It becomes clear that Cele concentration variations at SS60 R and Ibaraki and SO_4^{2-} concentration variations at Fukaya displayed unique behavior.

5. Conclusions

The main component concentrations of fine particulate were measured at 17 sites by 24-hr sampling for two weeks by JCAP in the winter of 1999. The following results were obtained by multivariate data analysis using the data sets.

(1) The ratio of fine particulate to SPM was about 2/3 and a large difference between the observation points was not observed although some low values were indicated in the clean region.

(2) The fluctuation factor and Max/Min of Cl^- concentration for space variation were the highest and those of SO_4^{2-} were the lowest among the six components.

(3) The deviations of space variation for Cele and NO_3^- concentrations were larger than for SO_4^{2-} concentrations. The peak concentration of

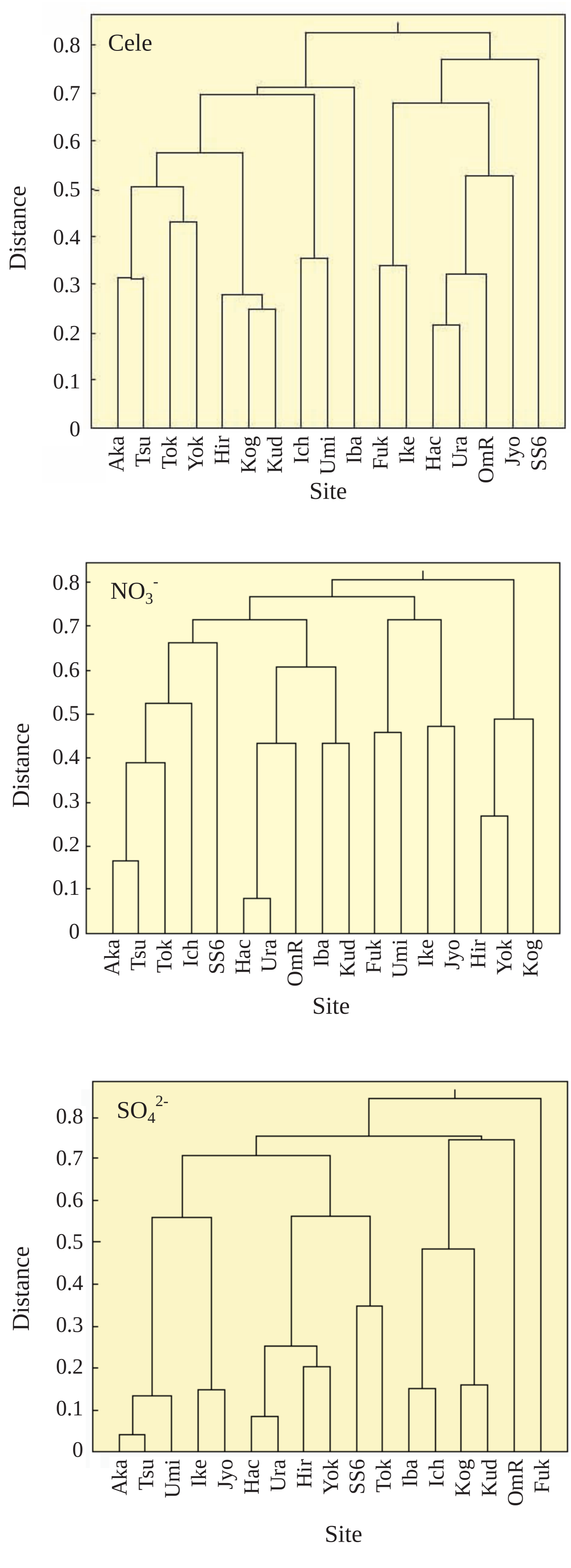


Fig. 6 Complete linkage dendrogram for 17 places in Cele, NO_3^- and SO_4^{2-} of fine particulate.

Cele and NO_3^- for a site sometimes appeared at different dates. The fluctuation factor of space variation for the SO_4^{2-} concentrations was smaller than that of time variation. SO_4^{2-} concentration is thought to change similarly in a wide mesoscale area

(4) Three factors were extracted by factor analysis of all data. Factor 1 is representative of the ammonium salt that is the main component of the secondary formatted inorganic particulate. Factor 2 is representative of the combustion source including vehicle exhaust and the secondary formatted organic particulate. Factor 3 is representative of sea salt and fine soil particulate.

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