Annual Variations of the Elemental Concentrations of PM₁₀ in Ambient Air of Nagoya City as Determined by ICP-AES and ICP-MS

Eiji FUJIMORI,[†] Tatsuya KOBAYASHI, Masanori AOKI, Masahiro SAKAGUCHI, Tsuyoshi SAITO, Taku FUKAI, and Hiroki HARAGUCHI

*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa, Nagoya 464-8603, Japan*

PM₁₀ samples were collected at an urban site of Nagoya City during September, 2003, to August, 2004, and annual variations of the concentrations of the elements in PM₁₀ samples were examined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). The annual concentration variations of *ca.* 30 elements in ambient air were in the range from sub-ng m⁻³ to several µg m⁻³. From an evaluation by the enrichment factors of the elements, elements such as Al, Ca, Fe, Mg, Ti, Mn, Ba, Sr, Ce, La, Nd, Co, Cs, and Pr, in PM₁₀ samples were found to have originated mostly from natural sources, while the elements such as S, Zn, Pb, Cu, Ni, Sb, Sn, Cd, Bi, W, Tl, and In originated from anthropogenic emission sources. Furthermore, in seasonal variations of the elemental concentrations of PM₁₀ samples in ambient air, the elements originated mostly from natural sources provided significantly high concentrations in spring during the “Kosa” period (the dust season from March to May). On the other hand, the elements mainly from anthropogenic emission sources provided relatively higher concentrations in autumn and winter, which may be explained by the fact that the urban atmospheric structure is stabilized by the temperature-inversion layer formed over the city in those seasons. In addition, all of the elements provided significantly low concentrations in the summer, due to the dilution effect of the oceanic winds as well as due to the convection of air mass up to the high levels.

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Introduction

The anthropogenic emission of diverse elements into the atmosphere has become one of the most serious problems in modern society. This problem occurs mostly in urban areas because various stationary and mobile emission sources, such as industrial activities, energy production, building and road construction, urban waste treatment, and vehicle exhausts, release large amounts of diverse elements into the atmosphere, in addition to natural emission sources such as soils, crustal minerals, volcanic dust and gases, sea spray, and biogenic particles. It is well known that atmospheric particulate matter (APM) often causes serious infection on human health due to toxic and hazardous elements. APM also plays an important role as transport carriers of various elements in the atmosphere. Therefore, it is urgently required to elucidate the emission sources of various elements in APM as well as the kinetic behaviors of APM in the atmosphere in order to protect our health and environment. Thus, chemical characterizations of APM have been performed by many workers.¹⁻⁷

In previous work,⁸ we carried out multielement determinations

of the elements in PM₁₀ (APM smaller than 10 µm in size) samples at the urban area of Nagoya City, Japan, where PM₁₀ samples were collected during one month (8 September – 9 October, 2003) on the campus of Nagoya University. It was found from analytical results that lithophile and siderophile elements, originated from natural sources, were distributed more than 50% in the coarse-particle fraction (> 2.1 µm) of PM₁₀, while chalcophile elements were more than 50% in the fine-particle fraction (< 2.1 µm) of PM₁₀, originated from anthropogenic emission sources.

In the present work, the annual variations of the elemental concentrations of PM₁₀ samples in ambient air of Nagoya City was further examined, where PM₁₀ samples were collected at the same sampling site almost every day throughout the year from September, 2003, to August, 2004. Major-to-ultratrace elements in PM₁₀ samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) after sample decomposition by microwave-assisted acid digestion. Then, the characteristic behaviors of PM₁₀ in ambient air of Nagoya City were examined throughout the year on a multielement basis, while taking into consideration the meteorological conditions, such as the formation of a temperature-inversion layer and wind directions.

[†] To whom correspondence should be addressed.

E-mail: EIJI_FUJIMORI@env.go.jp

E. F. present address: National Environmental Research and Training Institute, 3-3 Namiki, Tokorozawa, Saitama 359-0042, Japan.

Experimental

Samples

The metropolitan area of Nagoya City is one of the most urbanized and industrialized areas in Japan, as shown in Fig. 1. Nagoya City is located at the southern edge of the Nobi plain in the central part of Japan and in front of the Pacific Ocean in the south. In the present work, PM₁₀ samples were collected on the rooftop of a building on the campus of Nagoya University (20 m above ground level), which was located near a residential area of Nagoya City. Meteorological data of temperature, relative humidity, wind velocity, and wind direction observed at the Nagoya Local Meteorological Observatory located about 2 km north from the campus of Nagoya University, were also used for analysis in the present work.

The sampling of PM₁₀ samples was carried out almost every day during the sampling period from 1 September, 2003, to 31 August, 2004. PM₁₀ samples were collected on quartz fiber filters (QR-100, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) by using a high-volume air sampler installed with a 10- μ m cut-off filter (HV-500F-10, Shibata Scientific Technology, Tokyo, Japan) at a flow rate of 800 l min⁻¹ for 10 h (14:00 – 24:00). The weights of the PM₁₀ samples were measured with an electric balance after the PM₁₀ samples were dried to constant weights in a desiccator for 24 h.

Meteorological conditions

The amounts and compositions of PM₁₀ are significantly affected by the meteorological conditions. Thus, the seasonal meteorological data during September, 2003, to August, 2004,

Fig. 1 Location of the sampling site for PM₁₀ samples and observatory of the meteorological data in Nagoya City. PM₁₀ samples were collected on the campus of Nagoya University (●), and meteorological data observed at the Nagoya Local Meteorological Observatory (×) were used for analysis.

are summarized in Table 1, where the data for autumn, winter, spring, and summer were calculated as the averaged values during September – November, 2003, December, 2003 – February, 2004, March – May, 2004, and June – August 2004, respectively. It is noted here that the seasonally-averaged temperatures varied over a wide range, *i.e.*, the averaged temperature in the summer was more than 20°C higher than that in the winter. Other meteorological data of relative humidity and wind velocity were almost at the same levels through the year.

Chemicals

Nitric and hydrochloric acids of electronics industry grade and perchloric acid of analytical grade, and hydrofluoric acid for semiconductor industry used for sample pretreatment were purchased from Kanto Chemicals (Tokyo, Japan), and Stella Chemifa (Osaka, Japan), respectively. Multielement standard solutions for making the working calibration curves were prepared by mixing single-element stock solutions for atomic absorption spectrometry (1000 μ g ml⁻¹), which were purchased from Wako Pure Chemicals (Osaka, Japan). Deionized water prepared by a Milli-Q Plus water purification system (Nihon Millipore Kogyo, Tokyo, Japan) was used throughout the present experiment.

Digestion procedure of PM₁₀ sample

The sample decomposition procedure was almost similar to that described in previous paper.⁸ The quartz fiber filter used for collecting the PM₁₀ sample was dissected into two halves, and only the half part of it was used for sample decomposition. The PM₁₀ sample on the quartz fiber filter was put in a PFA decomposition vessel (Model P-70, San-ai Science, Nagoya, Japan) and the sample was digested with 10 ml of an acid mixture (HNO₃:HClO₄:HF = 5:3:2) by heating in a kitchen-type microwave oven (500 W). After cooling, the decomposed sample solution was heated almost to dryness to remove excess HF, and the residue was dissolved with 100 ml of 1 M HNO₃, which contained the internal standard elements (Rh and Re; 5 ng ml⁻¹ each) for correcting any matrix effects in ICP-MS measurements.

Instrumentation

The major and minor elements in PM₁₀ samples were determined by an ICP-AES instrument equipped with a polychromator (Model Plasma AtomComp Mk II; Jarrell Ash, Franklin, MA, USA). An ICP-MS instrument equipped with a quadrupole mass spectrometer (Model HP 4500, Agilent Technologies, Tokyo, Japan) was used for the determination of trace and ultratrace elements in PM₁₀ samples. Matrix effects and spectral interferences due to major elements in the ICP-MS measurement were corrected by the internal standard method⁹ and the interference correction coefficient method,¹⁰ respectively. The operating conditions of the ICP-AES and ICP-MS instruments were as usual, as reported in previous work.¹¹

Table 1 Meteorological data during sampling duration

Season	Time period	Averaged value		
		Temperature/°C	Relative humidity, %	Wind velocity/m s ⁻¹
Autumn	Sep., 2003 – Nov., 2003	19.0	71	2.70
Winter	Dec., 2003 – Feb., 2004	5.9	65	3.21
Spring	Mar., 2004 – May, 2004	14.9	63	3.23
Summer	Jun., 2004 – Aug., 2004	26.7	69	3.07

Fig. 2 Annual variations of the particulate and elemental concentration of PM_{10} samples.

Results and Discussion

Annual variations of elemental concentrations of PM_{10} samples

In the present work, PM_{10} samples were collected almost every day during the period from 1 September, 2003, to 31 August, 2004. As a result, 334 samples (days) were obtained during the above sampling period. The analytical results for PM_{10} samples are shown as the annual variations of the particulate and elemental concentrations in Fig. 2. In the figure, the elements are arranged in the order of their averaged concentrations, which are given in Table 2 (discussed later).

Concentrations of the elements in PM_{10} samples

The concentrations of 26 elements in PM_{10} samples could be obtained in the range from sub- $ng\ m^{-3}$ to several $\mu g\ m^{-3}$, and the results for their annually-averaged concentrations are summarized in Table 2. The feasibilities of the present analytical method were discussed in detail in a previous paper.⁸ The filter blank values were estimated by analyzing only a collection filter in the same manner as the PM_{10} sample. The filter blank values and the analytical detection limits were expressed as the concentrations in the ambient air, considering the total volume of the air sample. As described in previous work,⁸ the analytical data could be regarded as “available”, when the analytical values were larger than the halves of the filter blank values. Therefore, the analytical data obtained in the present work were also treated in the same manner. The numbers of available data for analyte elements are given in the second column of Table 2. It can be seen in Table 2 that the numbers of available data for Al, Ba, Ce, La, Nd, and Pr were relatively small, because their analytical values close to the filter blank values were discarded. In Table 2, the maximum and minimum values are also listed to indicate the elemental

concentration ranges of the PM_{10} samples. It can be seen from the results in Table 2 that a concentration variation for diverse elements occurred within 1 – 2 orders of magnitude.

In Table 2, the enrichment factors (EFs) of the elements,^{8,12,13} which indicate the degree of enrichment of analyte elements in PM_{10} samples, as compared to the continental crust, are also shown in parentheses. As described in a previous paper, elements with EF values larger than 5 are widely used as composite materials in industrial production, while elements with EF values smaller than 5 are mostly derived from soils and crustal minerals. Thus, elements with EF values larger than 5 were referred to as “anthropogenic-source elements”, and those with smaller than 5 as “natural-source elements”.⁸ It can be seen in Table 2 that the EF values for S, Zn, Pb, Cu, Ni, Sb, Sn, Cd, Bi, W, Tl, and In were larger than 5 in PM_{10} samples. Therefore, these elements are also hereafter referred to as anthropogenic-source elements. On the other hand, Al, Ca, Fe, Mg, Ti, Mn, Ba, Sr, Ce, La, Nd, Co, Cs, and Pr with EF values smaller than 5 are referred to as natural-source elements.

Effects of meteorological conditions on the particulate concentrations of PM_{10}

It is generally known that the particulate concentrations of PM_{10} in ambient air are affected by various meteorological conditions, such as temperature, wind velocity, wind direction, rainfall and relative humidity.¹⁴ Therefore, the correlation between the particulate concentrations of PM_{10} and those meteorological conditions are shown in Fig. 3. In general, a negative correlation between the particulate concentrations of PM_{10} and the meteorological conditions is found, as can be seen in Fig. 3. These results coincide with observations in the literature.^{14,15} Because the height of the mixing layer of ambient air increases with increasing temperature,¹⁶ the particulate concentrations of PM_{10} had a negative correlation with

Table 2 Annually-averaged concentrations of the elements in PM₁₀ samples during September, 2003, to August, 2004

Element ^a	Number ^b	Analytical value/ng m ⁻³				Filter blank value ^d /ng m ⁻³	Analytical detection limit/ng m ⁻³
		Averaged value ^c		Range			
				Max	Min		
S	334	1540	(230)	5630	100	—	80
Al [†]	252	564	(0.75)	3590	181	362	3
Ca [†]	302	525	(1.4)	2980	109	212	3
Fe [†]	334	460	(1.1)	2360	57	63	2
Mg [†]	317	145	(0.69)	970	27	53	3
Zn [†]	334	90.1	(150)	456	9.1	—	0.7
Ti [†]	334	38.1	(1.0)	386	3.6	4.0	0.3
Pb	334	19.3	(140)	103	0.604	0.333	0.006
Mn [†]	334	19.1	(2.8)	101	1.7	0.9	0.2
Ba [†]	292	17	(3.1)	145	8	6	2
Cu [†]	334	12.2	(51)	47.4	2.1	—	0.4
Sr	327	4.5	(1.4)	23.9	0.9	1.8	0.1
Ni	312	3.36	(6.3)	19.9	0.73	1.45	0.04
Sb	334	3.26	(1100)	16.2	0.389	—	0.003
Sn	333	3.2	(150)	19.9	0.5	—	0.1
Ce	276	1.06	(1.9)	7.96	0.333	0.667	0.002
Cd	326	0.526	(550)	3.08	0.045	—	0.008
La	271	0.441	(1.5)	2.13	0.159	0.317	0.001
Bi	334	0.418	(520)	4.36	0.0202	—	0.0009
Nd	186	0.366	(1.4)	1.91	0.173	0.347	0.005
W	334	0.277	(29)	1.73	0.015	0.023	0.001
Co	331	0.240	(1.1)	1.28	0.020	0.037	0.002
Cs	332	0.134	(4.2)	0.809	0.0137	—	0.0005
Pr	249	0.0951	(1.5)	0.504	0.0392	0.0783	0.0005
Tl	331	0.073	(15)	0.457	0.005	—	0.001
In	304	0.021	(44)	0.124	0.004	—	0.001

a. Elements with [†] were determined by ICP-AES and the others by ICP-MS. b. The numbers of available data during the sampling period. c. Values in parentheses are the enrichment factors of the elements. d. Blank values attributed to the impurities of the collection filter.

Fig. 3 Correlation between the meteorological conditions and the particulate concentrations of PM₁₀ samples. (a) Temperature, (b) relative humidity, (c) wind velocity.

temperature (Fig. 3(a)). The negative correlation between the relative humidity and the particulate concentration of PM₁₀ (Fig. 3(b)) was attributed to an increase of the wet deposition of PM₁₀ under high relative humidity. It is clearly seen in Fig. 3(c) that the particulate concentrations of PM₁₀ were lower under a stronger wind, while they were higher under a weaker wind, because the dispersion of particulate matter in ambient air was occurred more under stronger winds.

Seasonal variation of the elemental concentrations of PM₁₀ samples

In order to discuss the seasonal variations of the concentrations of the elements in PM₁₀ samples, the seasonally averaged concentrations of the elements were estimated from the data shown in Fig. 2. The seasonally-averaged concentrations for autumn were compared with those for other seasons, and the significance of the variations was evaluated by the two-tailed *t*-test. In Fig. 4, the elements with significant variations (*p* < 0.01) are marked with double asterisks (**) on the bar graph. The results for natural- and anthropogenic-source elements are shown in Figs. 4(a) and 4(b), respectively.

As can be seen in Fig. 4(a), natural-source elements, such as Al, Fe, Mg, Ti, Ce, La, Nd, and Pr, provided significantly high concentrations in the spring. This result may be attributed to yellow sand (so-called “Kosa” in Japanese) transported from China to Japan with the westerly wind in the spring. On the other hand, anthropogenic-source elements, such as Zn, Cu, Sb, Sn, and Bi, provided relatively high concentrations in the autumn and winter, as can be seen in Fig. 4(b). In autumn and winter in the Nagoya City area, it is known that the temperature-inversion layer is formed over the city, so that the urban and suburban areas are covered with a stabilized atmospheric layer.¹⁷ Such a formation of the temperature-inversion layer in the Nagoya City area has been elucidated from monitoring the concentrations of CO₂ and CH₄ in the atmosphere.¹⁷ Therefore, anthropogenic particulate matter may be accumulated at low altitude of a stabilized urban atmosphere. As a result, the concentrations of anthropogenic-source elements become apparently high in the autumn and winter.

It is noted here that all of the elements, except for S, provided

Fig. 4 Seasonal comparison of the concentrations of the elements in PM_{10} samples. The error bar on the bar graph indicates the standard deviation. The double asterisks (**) on the bar graph indicate that the seasonally-averaged concentrations of the elements for winter, spring, and summer were different from those for autumn with significant level of 0.01 ($p < 0.01$). (a) Natural-source elements, (b) anthropogenic-source elements. ▨, Autumn; □, winter; ▤, spring; ■, summer.

Fig. 5 Distribution of the wind direction around Nagoya University, represented as 16 compass expressions, where the radial axis shows the frequency (%) during September, 2003, to August, 2004. (a) Autumn, (b) winter, (c) spring, (d) summer.

significantly low concentrations in the summer. In the summer, the westerly winds were replaced by oceanic winds that contained less particulate matter.¹⁸ Therefore, the statistical data for the wind direction frequencies on the 16 compass expression in Nagoya City during September, 2003, to August, 2004, were obtained from the Nagoya Local Meteorological Observatory;

the results are shown in Fig. 5. As can be seen in Fig. 5, the dominant wind directions in Nagoya City in autumn, winter, and spring were WNW, NW, and NNW due to the westerly winds. On the other hand, the dominant wind directions in the summer were S, SSE, and SE from the ocean side. Thus, in order to examine the dependence of the particulate concentrations of

Table 3 Particulate concentrations of PM₁₀ samples obtained under different wind directions during summer, autumn, and winter

Season	Wind direction	Particulate concentration/ $\mu\text{g m}^{-3}$	Temperature/ $^{\circ}\text{C}$	Relative humidity, %	Wind velocity/ m s^{-1}
Summer	Southern	18.0 ± 8.3	26.7 ± 2.3	72 ± 10	3.1 ± 1.2
Summer	Northern	20.2 ± 10.0	26.7 ± 3.0	66 ± 11	3.1 ± 0.9
Autumn	Northern	21.8 ± 14.2	17.5 ± 4.6	70 ± 13	3.1 ± 1.2
Winter	Northern	24.7 ± 14.1	5.6 ± 2.4	65 ± 11	3.5 ± 1.2

The values in the table are expressed as mean $\pm$ standard deviation.

Fig. 6 Dendrograms of a hierarchical cluster analysis of the particulate and elemental concentrations of PM₁₀ samples during September, 2003, to August, 2004 (cluster method, Ward's method). Anthropogenic- and natural-source elements are shown by normal and italic fonts, respectively. (a) Autumn, (b) winter, (c) spring, (d) summer.

PM₁₀ samples on the wind direction in the summer, the averaged particulate concentrations of PM₁₀ were estimated from data obtained in the cases of the northern winds (WNW, NW, and NNW) and the southern winds (S, SSE, and SE). These results are given in Table 3. It can be seen from Table 3 that the particulate concentrations of PM₁₀ in the summer provided lower concentrations in the southern winds than in the northern winds, although the meteorological conditions were almost the same. These results indicate that the elements in ambient air were diluted by the ocean winds, which contained less particulate matter. In Table 3, the particulate concentrations in the northern winds in autumn and winter are also listed so as to examine the seasonal variations. The results for spring were not used here because the particulate concentrations of PM₁₀ were strongly affected by Kosa in then. As can be clearly seen in Table 3, the particulate concentration of PM₁₀ in the northern winds provided a lower concentration in the summer than in autumn and winter, which showed an inverse correlation with the temperature. Therefore, the significant decrease in the particulate concentrations of PM₁₀ during the summer was attributed to the convection of air mass up to a high level due to the higher temperature as well as a dilution effect of the oceanic winds. Consequently, the concentrations of both anthropogenic- and natural-source elements in PM₁₀ samples were significantly

low in the summer.

Statistical evaluation of the particulate and elemental concentration variations of PM₁₀ samples

In order to examine the variation behaviors of PM₁₀ in ambient air, the concentration variations of the elements in PM₁₀ samples of each season were statistically analyzed by cluster analysis. Since reliable analytical data for Al, Ba, Ce, La, Nd, Pr, and In were less than 85% in the summer because of their low concentrations, the concentration variations for these elements were not used here. In the present work, thus, the concentration variations of other 19 elements were used for the cluster analysis. The results are summarized in Fig. 6, as the dendrograms for (a) autumn, (b) winter, (c) spring, and (d) summer.

As is seen in Fig. 6(a), the particulate and elemental concentrations of PM₁₀ samples consisted of two major clusters in autumn. The first major cluster was formed by anthropogenic-source elements, such as Cu, Zn, Sb, Cd, Pb, Ni, Bi, Sn, S, and Ti. As described in a previous paper,⁸ these anthropogenic-source elements in ambient air were mostly distributed in the fine-particle fraction of PM₁₀. On the other hand, the second major cluster consisted of natural-source elements, such as Fe, Mn, Sr, Ca, Mg, Ti, and Co, which were

Fig. 7 Variations of the enrichment factors of anthropogenic-source elements (Pb, Bi, Tl, Zn, Cu, and Sb) during 1 – 31 July, 2004. ●, Northern winds; ○, southern winds.

Fig. 8 Backward trajectories of the air parcels that arrived at Nagoya University on 1, 13, 17, and 21 July, 2004 at every 1 h from 14:00 to 24:00. Lat, 35.15N; Log, 136.97E.

contained more in the coarse-particle fraction of PM_{10} . The result for winter (Fig. 6(b)) was similar to that of autumn, although some elements were involved in different major clusters. In addition, it should be noted here that the particulate concentration variations of PM_{10} in the autumn and winter were involved in major clusters consisting of anthropogenic-source elements. These results indicate that anthropogenic-source fine particles played important roles in the behaviors of PM_{10} in the autumn and winter.

In spring (Fig. 6(c)), the variation behaviors of PM_{10} in the Nagoya City area were clearly influenced by natural-source particles, including Kosa, because the particulate concentration of PM_{10} formed the first major cluster with natural-source elements.

In the case of summer (Fig. 6(d)), anthropogenic-source elements were involved in two different major clusters. Anthropogenic-source elements, such as S, Pb, Cd, Tl, and Bi,

Table 4 Comparison of the elemental concentrations of PM_{10} samples in the ambient air of Nagoya City between 1974 to 1996 and September, 2003, to August, 2004

	Average concentration from 1974 to 1996 ^a [A]/ng m ⁻³	Present work (Sep., 2003 – Aug., 2004) [B]/ng m ⁻³	Concentration ratio [B]/[A]
<i>Al</i>	440	564	1.28
<i>Ca</i>	328.5	525	1.59
<i>Fe</i>	418	460	1.10
<i>Zn</i>	196.3	90.1	0.45
<i>Ti</i>	34.2	38.1	1.11
<i>Pb</i>	71.5	19.3	0.27
<i>Mn</i>	26.4	19.1	0.72
<i>Cu</i>	15.5	12.2	0.79
<i>Ni</i>	5.28	3.26	0.60

Anthropogenic-source elements (Zn, Pb, Cu, and Ni) and natural-source elements (Al, Ca, Fe, Ti, and Mn) are shown by normal and italic fonts, respectively.

a. Cited from Ref. 18.

formed a sub-cluster with the particulate concentration of PM_{10} , and this sub-cluster formed the first major cluster with sub-cluster of natural-source elements. On the other hand, anthropogenic-source elements, such as Zn, Cu, Sb, and Sn, formed the second major cluster. These results indicate that the behaviors of anthropogenic-source elements, such as Zn, Cu, Sb, and Sn, were different from those of other anthropogenic-source elements, such as S, Pb, Cd, Tl, and Bi.

As mentioned earlier, the dominant wind directions in the summer were S, SSE, and SE, while those of other seasons were WNW, NW, and NNW. Thus, in order to examine the dependence of the relative concentrations of anthropogenic-source elements in PM_{10} samples on the wind direction in the summer, the daily variations of the EF values of Pb, Bi, Tl, Zn, Cu, and Sb for July, 2004, are given in Fig. 7, where the results in the northern and southern winds are plotted by black and white circles, respectively. As can be seen in Fig. 7, the EF values for Pb, Bi, and Tl varied regardless of the wind directions. Therefore, it is considered that these elements were emitted from anthropogenic emission sources around the industrial area of Nagoya City. On the other hand, the EF values of Zn, Cu, and Sb provided larger EF values in the northern winds. These results indicate that anthropogenic-source elements, such as Zn, Cu, and Sb, were transported into the urban area of Nagoya City from the northern area.

Atmospheric trajectory models are commonly applied for identifying the source of atmospheric particulate matter.¹⁹ In this work, to estimate the source region of anthropogenic-source elements such as Zn, Cu, and Sb, a trajectory model of the National Oceanic Atmospheric Administration (NOAA) HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLOT)²⁰ was employed. The backward trajectories for air parcels that arrived at the sampling site of PM_{10} (Nagoya University) every 1 h during the sampling period (14:00 – 24:00), which were calculated from HYSPLIT, are shown in Fig. 8. The backward trajectories indicate the routes of the air parcels during 24 h before arriving at the sampling site. In the cases of the northern winds with the large EF values of Zn, Cu, and Sb (13 and 17 July, 2004), air parcels came from northwestern directions after traveling above the industrial areas located in the western areas of Japan (Figs. 8(b) and (c)). On the other hand, in the cases of the northern winds with small EF values of Zn, Cu, and Sb

(1 and 17 July, 2004), air parcels came from northeastern directions (Figs. 8(a) and (d)). These results suggest that the source region of anthropogenic-source elements, such as Zn, Cu, and Sb, may be the industrial area in the western part of Japan, although further investigations to identify their emission sources should be carried out in the future.

Evaluation of the present status of the atmospheric environment in Nagoya City

Finally, in order to evaluate the present status of the atmospheric environment in Nagoya City, the analytical results for the elemental concentrations of PM₁₀ samples obtained here were compared with literature values, which were the average values in ambient air of Nagoya City from 1974 to 1996, investigated by the National Air Surveillance Network (NASN).¹⁸ The results are summarized in Table 4. As can be seen from Table 4, the concentrations of anthropogenic-source elements, such as Zn, Pb, Cu, and Ni, were significantly lower than the literature values. These results indicate that anthropogenic particulate matter in ambient air has been reduced in recent years by the atmospheric pollution control. In particular, a significant decrease in Pb can certainly be attributed to the use of unleaded gasoline in recent years. On the other hand, the concentrations of natural-source elements, such as Al, Fe, and Ti, were almost at the same levels during the last *ca.* 30 years. The significant decrease in Mn may suggest that Mn had been emitted from anthropogenic emission sources in the past years, although Mn was regarded as being a natural-source element in the present work.

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