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Analysis of the elemental composition of fine particulate matter ($PM_{2.5}$) emitted as air pollution using triple quadrupole ICP-MS

Authors

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Keywords

Asian dust, environmental analysis, PLUS torch, $PM_{2.5}$, silicon analysis, trace elements, TQ-ICP-MS

Goal

To demonstrate the suitability of the Thermo Scientific™ iCAP™ TQ ICP-MS equipped with the PLUS torch for monitoring the elemental composition of fine particulate matter such as the $PM_{2.5}$ fraction

Introduction

Particulate matter (PM) is a significant contributor to environmental pollution globally. In particular, fine particulate matter with an aerodynamic diameter of 2.5 µm or smaller, commonly classified as $PM_{2.5}$, is of great concern on a global level. In contrast to exposure to bigger particles such as PM_{10}, which can be easily recognized and potentially avoided through protective equipment, exposure to $PM_{2.5}$ is more dangerous as the small diameter makes it effectively invisible to the human eye, and it has the potential to penetrate deep into the respiratory system when inhaled. The chemical composition of these fine particles may comprise both organic and inorganic components, and, depending on the geographical location, $PM_{2.5}$ can possibly be contaminated with toxic elements such as arsenic, cadmium, or lead. Due to its high mobility, the presence of $PM_{2.5}$ can be influenced by local environmental conditions such as location, season, weather, and other factors.

Inhalation of fine dust containing silicon particles poses serious health risks after both short- and long-term exposure; for example, the development of lung cancer.[1] In response to this particle pollution, a maximum allowable concentration of $PM_{2.5}$ of up to 12 $\mu g \cdot m^{-3}$ was set by the United States Environmental Protection Agency (EPA) in 2012,[2] and similar regulated levels have been set by the WHO and the Japanese Ministry of the Environment (Table 1).

Table 1. Maximum allowable concentration for $PM_{2.5}$

Organization	Maximum allowance (µg·m^{-3})
U.S. Environmental Protection Agency (EPA)	<12
World Health Organization (WHO)	5–10
Ministry of the Environment (MOE), Japan	<15

The composition of $PM_{2.5}$ is commonly measured using X-ray diffraction (XRD) or X-ray fluorescence (XRF), allowing direct and non-destructive analysis without prior sample preparation. However, for some lighter elements, including silicon, measuring low concentrations in the samples can be a challenge. Inductively coupled plasma mass spectrometry (ICP-MS) is the most widely employed technique for the analysis of trace elements in environmental samples, as it allows rapid multi-element analysis and enables unmatched detection limits to be achieved. Its high detection power provides a way to overcome the above stated limitations of other analytical techniques.

In this study, ambient air samples were collected using a high-volume air collector system at two different locations. The $PM_{2.5}$ fraction was collected on PTFE filters and then analyzed using a Thermo Scientific™ iCAP™ TQ ICP-MS following microwave digestion. The resulting concentrations in the measured solutions were typically below 1 µg·L^{-1}, so the high detection power of ICP-MS was needed for accurate quantitation of the elemental composition.

Experimental

Experimental optimization of instrument parameters

An iCAP TQ ICP-MS was used for all measurements. The instrument used in this study was equipped with the hydrofluoric acid resistant sample introduction kit (i.e., PFA cyclonic spray chamber, PFA nebulizer, sapphire injector, platinum interface cone) and a PLUS torch[3]. The PLUS torch, together with superior interference removal based on the use of triple quadrupole technology, enabled the detection of silicon at concentration levels well below the regulatory requirement. To remove all potentially occurring interferences, the ICP-MS was operated in He KED,[4] TQ-H_2 and TQ-O_2 modes. Table 2 gives an overview of the full configuration of the system.

Table 2. Instrument configuration and operating parameters

Parameter	Value		
Nebulizer	ESI™ PFA ST nebulizer, 100 µL·min^{-1}, pumped at 40 rpm		
Pump tubing	Orange–green, 0.38 mm i.d.		
Spray chamber	PFA cyclonic, cooled at 2.7 °C		
Torch	PLUS torch		
Injector	2.0 mm i.d., sapphire		
Interface	Platinum sampler and platinum skimmer cone with high sensitivity skimmer cone insert		
Plasma power	1,550 W		
Nebulizer gas	0.98 L·min^{-1}		
QCell setting	**TQ-O_2**	**TQ-H_2**	**He KED**
Gas flow	100% O_2, 0.36 mL·min^{-1}	100% H_2, 9.7 mL·min^{-1}	100% He, 4.8 mL·min^{-1}
CR bias	-6.3 V	-6.3 V	-21 V
Q3 bias	-12 V	-12 V	-18 V
Scan settings	0.1 s dwell time, 10 sweeps, 3 main runs		

Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to create LabBooks for sample analysis, data acquisition, processing, and reporting. The Reaction Finder Method Development Assistant was used to set up the method, with settings for specific analytes (i.e., using H_2) being manually modified.

Sample collection and preparation

Each air sample was collected from two different locations in Kanagawa prefecture in Japan over 24 hours onto a 47 mm diameter PFTE filter (PALL Corporation) with 2 µm pore size, using a Thermo Scientific™ Partisol™ sequential ambient particulate sampler (Figure 1) at 16.7 L·min^{-1} (or 1 m^3·hr^{-1}). One sampling location was within a municipal area, whereas the second location chosen was close to a motorway.

Figure 1. Sample collection at Kanagawa prefecture (location 1) using the Partisol 2025i system

To monitor and potentially quantify changes over time in the elemental composition of $PM_{2.5}$, air samples were collected over a period of 14 days at one of the sampling sites. In a second study, the influence from climate effects, such as the wind conditions, were evaluated at the second sampling location. For example, Asian dust is a seasonal metrological phenomenon, where large amounts of yellow sand are transported from the deserts of Western Asia (Kazakhstan, Mongolia, and northern China) eastward towards China, the Korean Peninsula, and Japan. Due to industrial pollution in the dust, this phenomenon has become an increasing concern. A summary of the sampling details is shown in Table 3.

Table 3. Details on the sampling locations and conditions, including sampling duration

Location	Season	Weather conditions	Remark	# of testing days
1	Winter	N/A	Municipal area (near to an airport)	14
2	Winter	Normal weather conditions	Sampling location was close to a motorway	1
	Winter	Strong wind from northwest	Sampling occurred during a day with a strong wind from northwest of Japan	1

The filters with collected air were digested using a mixture of 5 mL HNO_3 (68% Optima™ grade, Fisher Chemical), 2 mL HF (48% Optima™ grade, Fisher Chemical) and 1 mL H_2O_2 (31% Optima™ grade, Fisher Chemical) in a microwave digestion system (Milestone ETHOS™ 1). After digestion, the samples were made up to a volume of 50 mL using ultrapure water. In all digestions, an unused filter was digested using the same procedure as a control to assess potential contamination in the process of sample preparation. All blanks and calibration standards were prepared from 2% (v/v) HNO_3 with multi-element standards (XSTC-1667 and XSTC-1668, SPEX™ CertiPrep™, Metuchen, NJ, USA). An internal standard solution containing 5 $\mu g \cdot L^{-1}$ lithium, yttrium, indium, and thallium was added to all samples. Table 4 shows the details of the final calibration standard concentration ranges for each element.

Table 4. Concentrations of calibration solutions

Element	Calibration standard concentration range ($\mu g \cdot L^{-1}$)
Na, Al, K, Ca	1, 5, 10, 25, 50, and 100
Si	5,10, 25, 50, and 100
Sc, Cr, Mn, Co, Ni, Sb, Cs, Ba, La, Ce, Sm, Hf, Ta, W, Pb, Th	0.01, 0.05, 0.1, 0.25, 0.5, 1, 5, and 10
Fe	0.5, 1, 5, 10, 25, and 50
Ti, Cu	0.1, 0.25, 0.5, 1, 5, 10, and 25
Zn	0.25, 0.5, 1, 5, 10, 25, 50, and 100
V, As, Se, Rb, Mo, Cd	0.05, 0.1, 0.25, 0.5, 1, 5, and 10

Results and discussion

Improved detection of silicon

Silicon is an analyte of special importance for the evaluation of the elemental composition of fine dust due to its potential to cause severe respiratory diseases (such as silicosis) when able to penetrate deeply into the human body. Silicon is often one of the main components of $PM_{2.5}$ and current legislation set by the Ministry of the Environment in Japan sets a minimum required detection limit (MRDL) of 10 $ng \cdot m^{-3}$ for this element. It is therefore necessary to detect this element with high sensitivity and low background. The regulatory limit corresponds to a final concentration of less than 5 $\mu g \cdot L^{-1}$ in a sample collected over 24 hours and following the above stated sample preparation. Often, the filter sample may be split in half to allow additional measurements to be performed, further reducing the concentration in the analyzed solution for this critical contaminant.

In addition, silicon is known as a challenging analyte in ICP-MS, mostly due to polyatomic interferences arising from nitrogen in the ambient atmosphere (creating ${}^{14}N_2^+$ on the most abundant isotope ${}^{28}Si$), but also contamination from the ubiquitous presence of the element in the laboratory and the glassware used in the ICP-MS source. The excellent calibration curve achieved for silicon (Figure 2) in this work was obtained using a mass shift reaction with oxygen (Figure 3) to eliminate the polyatomic interferences using TQ-O_2 mode. Thanks to the PLUS torch, minimization of the Si background from the ICP-MS sample introduction parts was achieved, resulting in an instrumental detection limit (IDL) of 0.081 µg·L^{-1}, blank equivalent concentration (BEC) of 1.9 µg·L^{-1}, and coefficient of determination (R^2) of 0.9991. The IDL was calculated using three times the standard deviation of ten replicate measurements of the calibration blank.

Sensitivity and linearity

Table 5 summarizes the obtained analytical figures of merit (IDL, BEC, and R^2) for all 31 elements analyzed in this study. The typically achieved instrumental detection limits were well below 0.1 µg·L^{-1}, even for often challenging analytes such as arsenic, selenium, and cadmium.

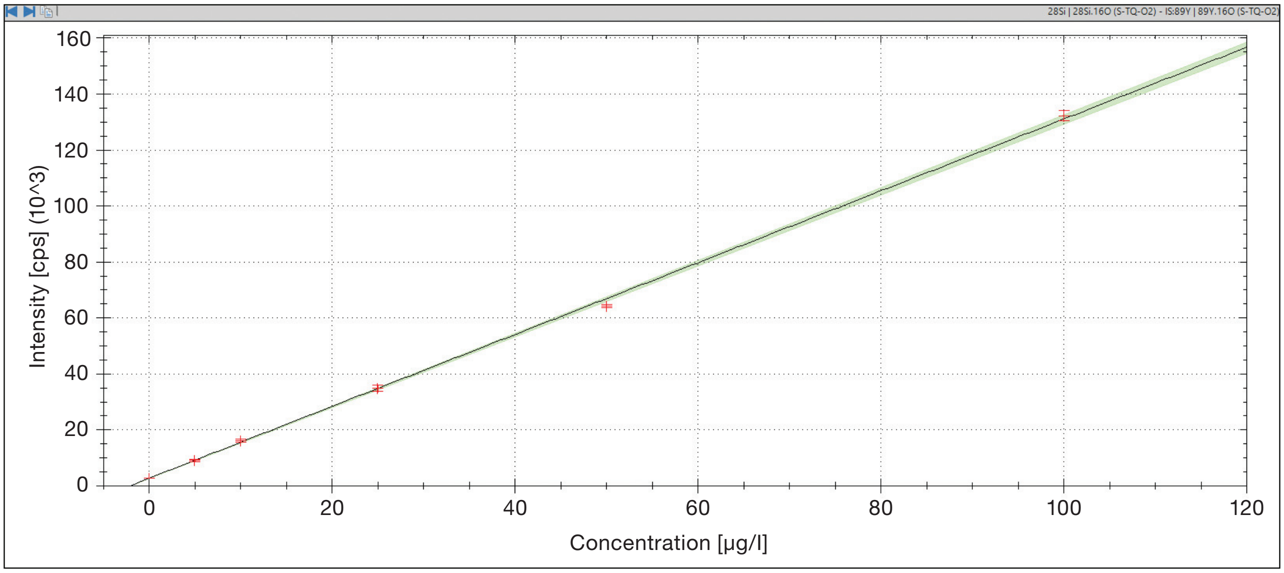

Figure 2. Calibration curve for silicon from 5 to 100 µg·L^{-1}

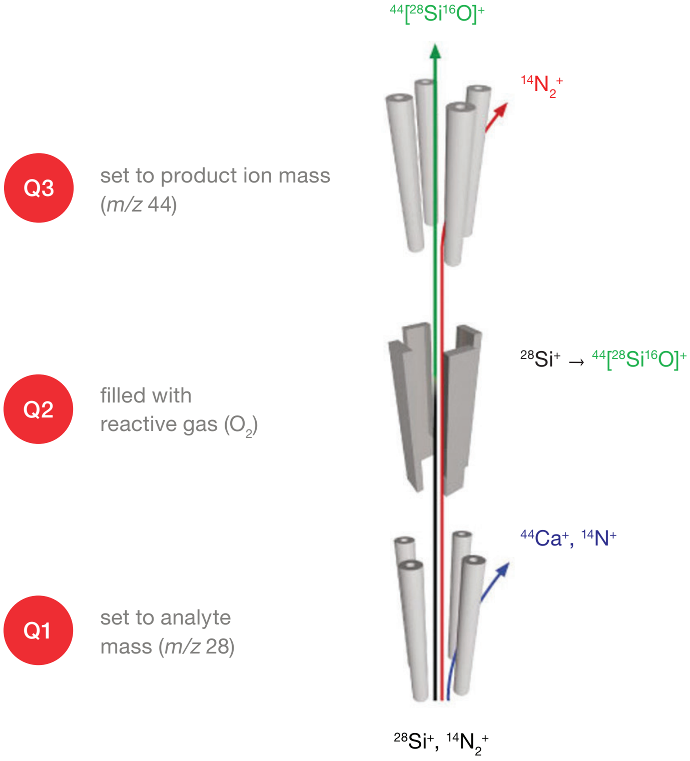

Figure 3. Schematic diagram showing the use of TQ-O_2 mode to selectively analyze silicon as ${}^{28}Si^{16}O$

Table 5. Summary of analysis modes, internal standards, and calibration results (LODs, BECs) for all target analytes

Analyte	Internal standard	Mode	LOD ($\mu g \cdot L^{-1}$)	BEC ($\mu g \cdot L^{-1}$)	R^2
^{23}Na	^{7}Li	TQ-H_2	0.091	0.900	>0.9999
^{27}Al	^{7}Li	TQ-H_2	0.009	0.079	>0.9999
^{28}Si as ^{28}Si.^{16}O *m/z* 44	^{89}Y	TQ-O_2	0.081	1.969	0.9991
^{39}K	^{7}Li	TQ-H_2	0.030	0.714	>0.9999
^{40}Ca	^{7}Li	TQ-H_2	0.012	0.12	>0.9999
^{45}Sc as ^{45}Sc.^{16}O at *m/z* 61	^{89}Y	TQ-O_2	0.001	0.001	>0.9999
^{48}Ti as ^{48}Ti.^{16}O at *m/z* 64	^{89}Y	TQ-O_2	0.0004	0.004	>0.9999
^{51}V as ^{51}V.^{16}O at *m/z* 66	^{89}Y	TQ-O_2	0.003	0.003	>0.9999
^{52}Cr	^{89}Y	SQ-KED	0.009	0.060	>0.9999
^{55}Mn	^{89}Y	SQ-KED	0.006	0.012	>0.9999
^{56}Fe	^{89}Y	SQ-KED	0.006	0.195	0.9999
^{59}Co	^{89}Y	SQ-KED	0.002	0.010	>0.9999
^{60}Ni	^{89}Y	SQ-KED	0.0002	0.014	>0.9999
^{63}Cu	^{89}Y	SQ-KED	0.004	0.020	0.9999
^{66}Zn	^{89}Y	SQ-KED	0.023	0.030	>0.9999
^{75}As as ^{75}As.^{16}O at *m/z* 91	^{89}Y	TQ-O_2	0.002	0.010	0.9999
^{78}Se as ^{78}Se.^{16}O at *m/z* 94	^{89}Y	TQ-O_2	0.008	0.025	>0.9999
^{85}Rb	^{89}Y	SQ-KED	0.006	0.060	>0.9999
^{95}Mo	^{89}Y	SQ-KED	0.011	0.014	>0.9999
^{111}Cd	^{89}Y	SQ-KED	0.007	0.007	>0.9999
^{121}Sb	^{115}In	SQ-KED	0.0003	0.001	>0.9999
^{133}Cs	^{115}In	SQ-KED	0.007	0.016	>0.9999
^{137}Ba	^{115}In	SQ-KED	0.006	0.007	>0.9999
^{139}La	^{115}In	SQ-KED	0.006	0.006	>0.9999
^{140}Ce	^{205}Tl	SQ-KED	0.006	0.006	>0.9999
^{149}Sm	^{205}Tl	SQ-KED	0.006	0.006	>0.9999
^{178}Hf	^{205}Tl	SQ-KED	<0.0001	<0.0001	>0.9999
^{181}Ta	^{205}Tl	SQ-KED	0.0001	0.0002	>0.9999
^{182}W	^{205}Tl	SQ-KED	0.0002	0.0003	>0.9999
^{208}Pb	^{205}Tl	SQ-KED	0.006	0.009	>0.9999
^{232}Th	^{205}Tl	SQ-KED	0.005	0.006	>0.9999

$PM_{2.5}$ analysis results

To comply with applicable legislation, all analysis results (obtained as µg·L^{-1}) were converted into mass per volume in the $PM_{2.5}$ fraction (in ng·m^{-3}) using the following equation:

$$C = \frac{(M_s - M_b) \cdot E \cdot S}{s \cdot V}$$

Where:

C Mass of analyte in fine particulate matter $PM_{2.5}$ in 1 m^3 of sampled air (ng·m^{-3})

M_s Result of the analysis of the sample (ng·mL^{-1})

M_b Result of the analysis of the preparation blank (ng·mL^{-1})

E volume of test solution (mL)

S $PM_{2.5}$ filter area where the sample was collected (cm^2)

s Filter area used for analysis (¼ of S, (cm^2))

V Collected volume of ambient air (m^3)

Table 6 shows the results for all elements under study across both sampling locations. The results obtained for the analysis of the elemental composition of the $PM_{2.5}$ fraction clearly provide meaningful data to evaluate the pollution level due to the ability of ICP-MS to measure a wide range of elements in a single analysis.

Table 6. Summary of ambient air analysis results, maximum allowable concentration in Japan, and method detection limits (MDLs). All results are in ng·m^3. The high RSDs observed for the measurements over 14 days can be explained by the significant influence of weather conditions (such as rain) on the formation and transportation of $PM_{2.5}$.

	MDL	Required MDL*	Maximum allowable concentration	Location 1	Location 2	
				Average concentration of 14 days in winter	Normal weather conditions	With strong wind
Na	0.76	10	–	66.1 ± 39.5	<MDL	<MDL
Al	0.08	6	–	29.8 ± 19.9	<MDL	42.38
Si	1.4	10	–	45.1 ± 40.4	<MDL	125.48
K	0.25	10	–	65.6 ± 45.6	62.72	197.74
Ca	0.1	10	–	23.7 ± 15.9	24.69	99.65
Sc	0.01	0.04	–	0.005 ± 0.004	<MDL	0.01
Ti	0.004	0.7	–	3.44 ± 1.99	2.34	7.59
V	0.02	0.2	–	0.61 ± 0.85	0.24	0.64
Cr	0.07	0.4	–	0.88 ± 0.70	1.8	<MDL
Mn	0.05	0.5	140	5.55 ± 3.20	15.99	27.36
Fe	0.05	10	–	92.8 ± 55.0	188.24	368.87
Co	0.02	0.04	–	0.04 ± 0.02	0.03	0.07
Ni	0.002	0.2	25	0.46 ± 0.53	1.18	1.4
Cu	0.03	0.4	–	2.50 ± 1.38	9.01	14.65
Zn	0.19	3	–	16.6 ± 12.4	60.41	84.45
As	0.02	0.09	6	0.41 ± 0.24	<MDL	<MDL
Se	0.06	0.2	–	1.56 ± 2.93	0.85	0.94
Rb	0.005	0.03	–	0.18 ± 0.11	0.1	0.41
Mo	0.009	0.07	–	0.84 ± 1.07	1.23	1.54
Cd	0.006	0.02	–	0.09 ± 0.06	0.16	0.29
Sb	0.001	0.09	–	0.72 ± 0.45	1.81	2.97
Cs	0.006	0.02	–	0.02 ± 0.01	<MDL	0.02
Ba	0.005	0.3	–	2.07 ± 1.20	5.44	11.4
La	0.005	0.02	–	0.04 ± 0.03	0.09	0.17
Ce	0.005	0.02	–	0.08 ± 0.05	0.22	0.32
Sm	0.005	0.03	–	0.001 ± 0.001	<MDL	<MDL
Hf	0.0002	0.03	–	0.02 ± 0.03	0.02	0.03
Ta	0.0005	0.02	–	0.001 ± 0.001	<MDL	0.01
W	0.002	0.05	–	0.14 ± 0.13	0.29	0.28
Pb	0.005	0.6	–	3.43 ± 1.67	6.1	11.76
Th	0.004	0.02	–	0.004 ± 0.003	<MDL	<MDL

*** Required MDLs are from the guidelines of the Ministry of Environment (MOE) in Japan.**

The composition of $PM_{2.5}$ at sample location 2 (under normal weather conditions) shows a higher presence of typical wear metals such as iron, nickel, copper, or zinc compared to location 1. Other metals, such as molybdenum, antimony, and lead were also significantly increased in samples from this location. This is very likely related to the higher urbanization and the specific sampling location near a motorway.

The composition of the $PM_{2.5}$ fraction obtained under the influence of the strong wind clearly differs from the composition under normal weather conditions. Considering the climate (wind direction) information and the $PM_{2.5}$ simulation results in Japan on the same day as the measurements, a possible impact of Asian dust on the results can be assumed.

The iCAP-TQ ICP-MS analysis results also show that typical soil components, such as Si, Al, Ti, and Fe, which are thought to be derived from Asian dust, are clearly found in higher concentrations under the likely influence of Asian dust (in location 2) as compared to normal weather conditions. This technique can be used to improve the accuracy of analysis of potential sources of anthropogenic pollution, transported by meteorological phenomena such as Asian dust.

However, whether this is due to transportation from other locations or contamination within the area around the sampling location could not be confirmed without additional research data, which were not in the scope of this work.

Also, to presume Asian dust effects, it is important to obtain data from multiple sampling locations and include data for other species, for example the water soluble ionic components (e.g., NH_4^+, Cl^-, NO_3^-, SO_4^{2-}) and the weather conditions.

Conclusion

A highly sensitive method for the analysis of the elemental composition of $PM_{2.5}$ was developed and applied to the analysis of samples collected from two sampling locations in Japan using the iCAP TQ ICP-MS equipped with the PLUS torch:

- Using a combination of TQ-O_2, TQ-H_2, and He KED mode, common interferences on important contaminants were eliminated and excellent signal-to-noise (S/N) ratios were obtained for all the elements studied, with detection capability well below global $PM_{2.5}$ analysis requirements.
- As an analyte of concern, silicon could be detected at levels well below the minimum required detection limit, because of the superior interference removal obtained with the iCAP TQ ICP-MS and the reduced backgrounds achieved using the PLUS torch.
- The method allowed the simultaneous assessment of 31 elements in one analysis, helping to get a better understanding of the natural and anthropogenic processing contributing to the composition of $PM_{2.5}$.
- In summary, the combination of sample collection using the Partisol 2025i and analysis with the iCAP TQ ICP-MS has been successfully demonstrated for the characterization of the inorganic components in the composition of $PM_{2.5}$.

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References

1. Sato, T.; Shimosato, T. Silicosis and lung cancer: current perspectives, *Lung Cancer: Targets and Therapy* **2018**, 9, 91–101.
2. National Ambient Air Quality Standards for Particulate Matter, Final Rule, United States Environmental Protection Agency, 2013.
3. Thermo Scientific Product Spotlight 44485: Thermo Scientific iCAP Qnova Series ICP-MS PLUS Torch for improved ICP-MS analysis of challenging samples.
4. Thermo Scientific Smart Note 44415: iCAP RQ ICP-MS. **https://assets.thermofisher.com/TFS-Assets/CMD/brochures/sn-44415-icp-ms-single-quadrupole-sn44415-en.pdf**
5. Ministry of the Environment Air Pollutant Wide Area Monitoring System, Japan Homepage: **https://soramame.env.go.jp/**

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