Source apportionment of single aerosol particles in the atmosphere of Shanghai city

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Abstract A nuclear microprobe with high spatial resolution and high analytical sensitivity was applied to analyze atmospheric aerosol at five monitoring sites in Shanghai city. Meantime, a new pattern recognition technique, which used the micro-PIXE spectrum of a single aerosol particle as its fingerprint, was developed to identify the origin of the particle. The results showed that the major contributors to the atmosphere pollution were soil dust (31.6%), building dust (30.8%), and the next were vehicle exhaust (13.7%), metallurgic industry excrements (5.6%), oil combustion (5%) and coal combustion (2.3%). Besides these, about 10% of the particles could not be identified. Based on the cluster analysis of these particles, they could be divided into eight groups. By inference, they might belong to some sub-pollution sources from soil dust, building dust and metallurgic industry excrements. Moreover, some new pollution sources from tyres and chemical plants were also revealed.

Keywords Single aerosol particle analysis, Source apportionment, Nuclear microprobe, Pattern recognition technique

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1 INTRODUCTION

Shanghai is located in the east coast of China. It covers an area of 6,341 km^2 with a population of about 13 millions. As a major economic and industrial center of China, in recent years, its rapid development has caused the urban aerosol pollution, which is from many natural and human-made sources. Therefore, much attention should be paid on the atmospheric pollution in connection with the industrial activities. One of the major goals of environmental pollution monitoring and controlling is to identify the pollution sources, to find their impact on the environment and, if necessary, to reduce it to an acceptable level[1]. There have been many reports on the source apportionment of atmospheric aerosol particles based on the bulk analysis[2]. Although the bulk analytical methods are useful for identifying sources of the aerosol particles, they have some limitations.

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Because many different particles are measured as a whole in the bulk analytical methods, ambiguities of pollution source identification occur even if a large amount of samples are measured and a time consuming statistical data handling are used[3].

However, the limitation of bulk analytical method can be avoided by the method of single aerosol particle (SAP) analysis[4]. The association of certain elements in a particle can be observed directly by the single particle measurement. Some elements tend to occur at relatively high concentration in a small particle. However, in a bulk measurement, the concentration of these elements may be at a level lower than the detection limit. If these particles are measured individually, the associated elements can be determined easily. More advantages of single particle analysis have been discussed by Orlic[5] and Grime[6]. Although the electron microprobe can measure SAP very efficiently, its relatively low analytical sensitivity restricted its application, because some important trace element features in SAP may be lost[7].

A nuclear microprobe is suitable for SAP analysis because it has reasonable spatial resolution (1μm), high analytical sensitivity, and versatile analytical techniques[8,9]. Some successful analyses of SAP by the nuclear microprobe have been reported[10~12]. However, because of the geometrical and morphological influences of a single particle, accurate quantification of the element concentration in a single particle is very difficult. Some calculation methods, which try to reduce these influences, have been discussed, but the accuracy is still not satisfied[13,14]. However, We can recognize each particle directly by its spectrum instead of its chemical composition. The PIXE spectrum pattern can be considered as the fingerprint of the particle. A method of the pattern recognition (PR) has been developed for the identification of the spectrum pattern. The strategy for the fingerprint classification and identification was used to identify each measured aerosol particle.

There were two steps for the identification of particles in the atmosphere. At first, a set of particles PM_{10} ($<10\mu$m) was collected as standard from different pollution sources, and analyzed by the nuclear microprobe. Their spectra were recorded into a database as a fingerprint library of the pollution sources. Then, other single aerosol particles, which were collected from environmental monitoring sites in Shanghai city, were analyzed by the same way and the PR program was used to compare their spectra with those in the library and to identify the origins of these particles.

2 EXPERIMENT

2.1 Sample collection and preparation

The individual aerosol particles of pollution source samples were collected from industrial trails, such as ferrous and nonferrous smelters, oil and coal combustion, building sites, leaded gasoline, unleaded gasoline, diesel fuel and soil dust et al. They contribute the majority of the aerosol particles floating in the atmosphere over Shanghai City[15]. Those of environmental samples were collected at five monitoring sites, representing the

major land use locations in Shanghai at Gong-he-xin-lu (GHXL), Ren-min-guang-chang (RMGC), Xu-jia-hui (XJH), Da-pu-qiao (DPQ), and Jian-ping-zhong-xue (JPZX) (see Fig.1). The GHXL site is close to building sites and adjacent to a road with high traffic density. The RMGC site is inner urban within a light industrial and traffic area. The XJH site is within a mixed traffic and residential area. The DPQ site is inside a highway tunnel. The JPZX site is in a middle school far away from industrial and high traffic area in suburb.

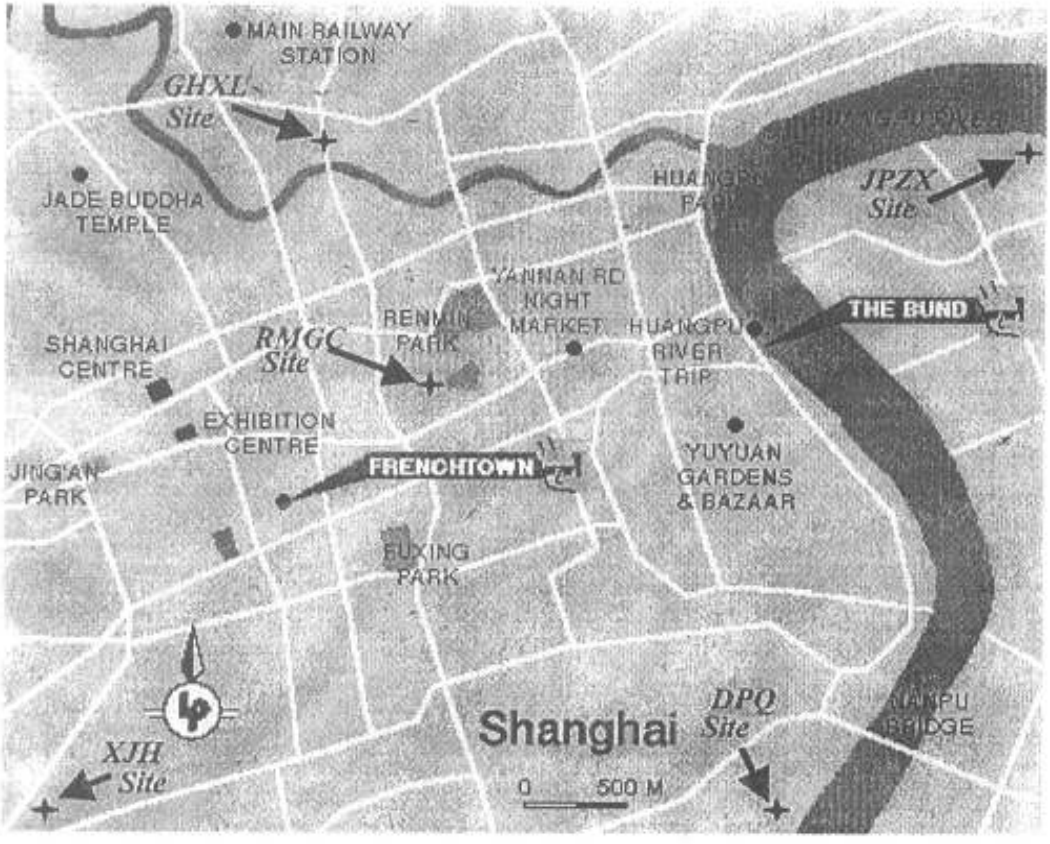

Fig.1 Map of Shanghai city, showing the five enviornmental monitoring sites

A cascade impact sampler (model HY-1) was used and the aerosol particles were collected on polystyrene fiber filters. 97% of the collected particles are smaller than 10μm and 70% of them are smaller than 3 μm. Several methods for individual aerosol particle preparation have been reported in our earlier work[16]. However, none of them could separate small particles (<3 μm) clearly and only groups of the individual aerosol particles had been measured[17]. In order to measure the single particles one by one, it is essentially important to isolate the particles from each other on a thin foil. The isolated particles should be close enough to be found easily during a beam scanning. Keeping these requirements in mind, a new method for individual aerosol particle preparation was developed.

A solution of nylon powder in Iso-Butyl alcohol was prepared at temperature of

80°C. A droplet of the solution was dropped onto a rotary beaker of deionized water at room temperature. The droplet stretched and a very thin (0.2 μm) nylon foil was formed on the water surface. Just after the formation of the foil (in a few seconds), the collected single particles were dropped dispersedly from the sampling filter onto the sticky foil by a small shaker. After five minutes solidification, the foil attached on a stainless steel frame was taken out of the water. The single particles were separately embedded in the thin, taut and flat nylon foil. After 24 hours baking at temperature of 60°C, the individual aerosol particle was ready for single particle analysis by the nuclear microprobe.

2.2 SAP measurement by the nuclear microprobe

A reliable and efficient experiment for single aerosol particle analysis demanded good performances of the nuclear microprobe. Because most of the particles were smaller than 3 μm, both high spatial resolution and beam current were needed. The Leipzig nuclear microprobe, LIPSION, satisfied the experimental requirements. A detailed description of LIPSION can be found elsewhere[18]. A 100 μm object diaphragm and a 100 μm aperture diaphragm were used to produce a focused beam spot with 1 μm size and 80 pA beam current for most single particle measurements. The particles were so small that it could be considered as thin target measurements. The 2.5 MeV protons could penetrate most of the particles. The beam charge was collected by a downstream Faraday cup. There was no conductive coating on the sample surface and no data correction for the effects of the particle matrix and shapes. A 20 nC integrated beam charge was required for each particle measurement. Much experimental time was spent on searching for isolated small particles. A proper searching procedure was important for high efficiency of this work. At first, a big scan area in size of 70 μm was needed to survey the sample in order to find areas where the isolated small particles were cultivated with high distribution density. The coordinates of each small particle in the big scanning area were digitized and recorded for further small scans. And then, set up the small scan area in size of 6~10 μm and moved one or more isolated small particles into the viewing area. The three dimensional movement of the sample stage was precisely digit controlled. The accuracy of the sample displacement was better than 1 μm. One or more isolated small particles were covered by the beam within the scanning areas. Each single particle measurement took about 15 minutes. The characteristic spectrum of single particle was extracted from raw data according to the particle shape in the small scanning area.

2.3 Pattern recognition

Based on the artificial neural network (ANN) technique, a pattern recognition procedure was developed for the identification of single aerosol particles. The ANN technique attempts to simulate the function of human brains for qualitative assessment in many fields. It has been used for the interpretation of various spectra in the fields of infrared[19], ultraviolet[20], gamma-ray[21], and X-ray spectroscopy[22,23]. An extensive description of ANN by McClelland and Rumelhart[24] is available. An artificial neuron receives signals

from external sources or from other neurons and produces one output value that can be used as an input to other neurons or an output result of the network. The topology of an ANN depends on the complexity of application. The algorithm used in this study was standard back-propagation (BP)[24]. The algorithm employs processing neurons connected by links; there is a coefficient (the "weight") associated with each link. The neurons receive inputs from the external world or from other neurons, and sum the signals feeding to them and output this sum to each driven connection scaled by a "squashing" function with a sigmoid shape, typically the function $f = 1/(1 + e^{-x})$, where $x = \sum$inputs. Then the signal was passed to the other neurons or to external world. The ANNs constitute a means of pattern classification in which an input pattern (i.e., a normalized PIXE spectrum) is transformed into an output pattern (i.e., a vector whose values represent the desired classification of the PIXE spectrum). Herein the input and output patterns are called training pattern. An ANN is always trained over a number of training pairs; this group is collectively called the training set. The difference between the actual and desired output, taken over the entire training session, feeds back through the network in the reverse direction to signal flow (hence back-propagation) modifying the weights as they go. Repeat this process until a suitable level of error is achieved.

The ANNs architectures implemented in this work consisted of three layers (input, hidden, and output layer). The input layer contains 1024 channels of a spectrum. The output layer contains N neurons corresponding to the number of reference patterns (pollution sources). Each of the neurons in the output layer produces an output value 1 or 0 (i.e., >0.7 or <0.3).

Like a real brain, an ANN has to take a training course before doing any identification jobs. The purpose of the network training is to find the right combination of all parameters in a network, which can produce a desired output code for every reference pattern. While the network reads a reference pattern, the modification of the parameters take place in the backward direction, which is from the output layer to the input layer. After several periods of modification and regressions, the final total error for all of the input patterns reaches a low criterion. The training course is then finished and all the "knowledge" learned in the course is stored in a matrix. The neural network is now able to perform a reliable identification job for any unknown input pattern. Only when an unknown spectrum fits one of the reference patterns well enough, does its corresponding neuron give out a value of 1. All others give an output of zero.

3 RESULTS AND DISCUSSION

3.1 Characterization of pollution sources

The discrimination of different pollution sources was enhanced by investigating single aerosol particles. 356 SAPs from pollution sources were measured with the same facilities. These micro-PIXE spectra were classified into six categories according to the corresponding sources. They were building dust (mainly cement dust), metallurgic indus-

try excrements, automobile exhaust including excrements from leaded gasoline, unleaded gasoline and diesel fuel, soil dust, oil combustion, and coal combustion.

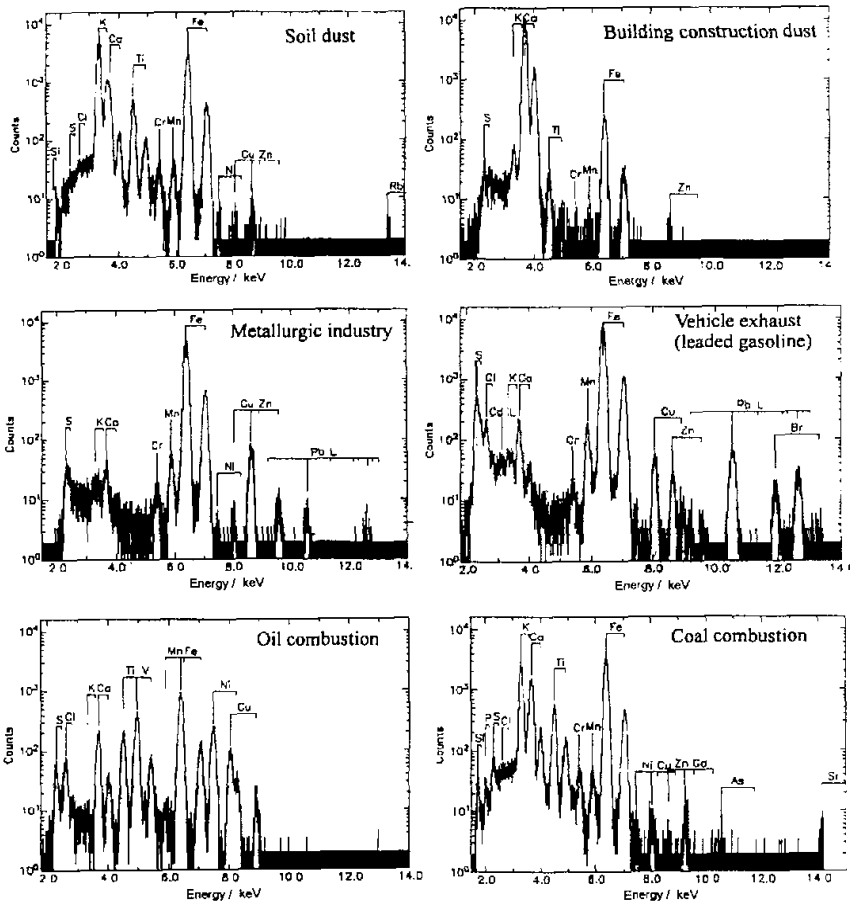

Fig.2 Six typical micro-PIXE spectra from pollution sources

Fig.2 shows six typical micro-PIXE spectra from pollution sources. The spectral patterns can be considered as the fingerprints of the single aerosol particles. Each source has its typical fingerprint with its characteristic elements. The main feature of aerosol particles from building dust had high loading for Ca and Fe, followed by a lower loading for elements such as K, Zn. High iron concentration could be found in the particles from the metallurgic industry. Other trace elements, such as Cr, Mn, Pb, were also found in these industrial pollution sources. They might come from raw materials used or catalysts added. The single particles from different automobile exhaust were measured. Because the organic tetra-alkyl-lead ($Pb(C_2H_4)_5$) as an anti-knock-agent and the ethylene dihalide

($C_2H_4Cl_2$ and $C_2H_4Br_2$) as scavengers were added to the leaded petrol, high loading for Pb and Br was found in the particles from leaded petrol. However, in this experiment, low lead concentration was also detected in the particles from unleaded gasoline. Probably, the lead in the unleaded gasoline was derived from the crude oil. Meanwhile, Br and Cl were also found in the particles from unleaded gasoline, which could be a feature used to distinguish them from other pollution sources. The particles from diesel fuel were characterized by S, Ti and Cu, Zn in low concentration.

The characteristic elements of single aerosol particles from oil combustion were V, Ni, Cu. Those from soil dust and coal combustion were Rb and Sr. But particles from coal combustion contained As and Ga which were not found in the soil dust. The correlation coefficient between them was less than 0.8. Other sub-fingerprints were included in some pollution sources, such as metallurgic industry excrements, depending on the chemical composition of raw material used and the type of the combustion process.

3.2 Source apportionment of single aerosol particles

About seven hundred single aerosol particles of environmental samples were collected at the five monitoring sites. The environmental samples were measured with the same facilities as described above . Then, by PR program, the pollution sources of these particles were identified. Table 1 shows the results of the source apportionment at the different monitoring sites. On average, the major components in the PM_{10} samples were soil dust (31.6%) and building dust (30.8%). It is true that the municipal construction has been the largest business in the city recently. But automobile exhaust was also an important pollution source which should not be ignored. Its contribution to the atmosphere pollution was 13.7%. However, the largest contributor in the automobile exhaust was leaded gasoline (8.4%). During the last five years, annually consumed gasoline in Shanghai has surpassed one milliontons[25]. Enormous lead was emitted to the atmosphere, which would affect human health and ecological environment. Fortunately, Shanghai municipal government has paid much more attention on it and phased out of the leaded gasoline.

Due to close to building work area, the contribution of the particles from building dust was higher at the GHXL site (46.3%). The samples from sites within industrial or high traffic density area, such as GHXL, DPQ and XJH, had higher aerosol contributions from vehicle exhaust and metallurgic industry excrements. However, it is also clear that the air quality was better at the JPZX site, which is buffered from the road traffic and distant from the industrial sources. The aerosol particles in the atmosphere of JPZX mainly came from soil dust (53.7%). But minor particles from vehicle exhaust and metallurgic industry were also found there, which indicates that industrial and road traffic emissions could be widely distributed in the atmosphere.

Table 1 Source apportionment at the five sample sites

Sample site	Number of samples	Building dust /%	Soil dust /%	Vehicle exhaust (leaded gasoline)/%	Industry combustion /%	Coal combustion /%	Oil component /%	Unidentified
GHXL	120	46.3	2.3	16.8(9.5)	12.3	2.3	6.4	13.6
RMGC	231	26.5	36.7	9.2(6.1)	2.0	4.1	8.2	13.3
XJH	116	32.1	29.1	17.6(8.9)	1.7	2.0	3.2	14.3
DPQ	108	22.6	36.2	18.4(12.3)	5.7	3.0	7.3	6.8
JPZX	117	26.7	53.7	6.5(5.1)	6.5	0.0	0.0	6.6
Average	138	30.8	31.6	13.7(8.4)	5.6	2.3	5.0	10.9

3.3 Hierarchical cluster analysis of unidentified particles

About 10% of the aerosol particles were not able to not be identified by PR program. It was suggested that they might come from other pollution sources, which had not yet been included in our investigation list. It gave hints for discovering new pollution sources. A hierarchical clustering technique was used to group these unidentified particles. The results from the cluster analysis are shown in Table 2. The unidentified particles were clustered into eight groups. According to the characterization of their elemental spectra and our experiences, the origins of these particles could be deduced. The first group and second group had high loading for K or Ca and low loading of Fe. They were probably derived from the sub-pollution sources from soil dust or building dust.

Table 2 Characterization of element spectrum

Group (Number of particles)	Characterization of element spectrum	
	Major elements	Minor elements
No.1(34)	K	Fe
No.2(54)	Ca	Fe
No.3(11)	Ti,Fe	S
No.4(5)	S, Ca, Fe	Ti, Zn, Pb
No.5(4)	Cl, Ca, Cr, Fe, Zn	S, Ti
No.6(7)	S, Cl, Ca, Ti, Fe, Zn	Cr, Mn, Cu
No.7 (1)	K, Ba	Fe, Cu
No.8 (1)	Fe, La, Ce	Cu, Zn

There was a common characteristics of Fe-rich in the third, fourth, fifth and sixth group. Besides, other metallic elements such as Ti, Cr, Mn, Zn at high concentration were found in these groups. This kind of particles may be related to the industrial activities. However, in this study, two peculiar particles were found. The particle in the seventh group was mainly composed of K and Ba. Ba may come from the wear and tear of tyres on the road, as it is used in the manufacturing of rubber[26]. In the atmosphere, the concentration of La and Ce is very low, but the particle in the eighth group was enriched in these rare-earth elements, its origin is difficult to trace back but that may be related to the chemical plant producing catalytic promoters. It is obvious that single aerosol particle analysis has the ability to detect the particles with peculiar elements, which is important to apportion atmospheric pollution sources.

4 CONCLUSION

It was better to do the aerosol source apportionment by using the nuclear microprobe analysis coupled with pattern recognition than by the traditional bulk analysis. SAP analysis was able to discriminate different particle types and to clarify atmospheric processes in a unique way. The analytical results showed that the soil dust and building dust contributed most of the atmospheric pollution in the Shanghai city. However, automobile exhaust, especially leaded gasoline, should not be ignored. More attention must be paid on it. Besides, about 10% aerosol particles could not be identified. By means of cluster analysis, the unidentified particles could be clustered into eight species, which was useful for seeking new pollution sources. Henceforth, our next work should continue to ascertain the origins of the unidentified particles.

References

1 Watson J G, Chow J C. Aerosol measurement: principles, techniques and applications. New York: Van Nostrand Reinhold, 1993: 1~20
2 Chow J C, Watson J G, Lowenthal D H et al. Atmos Environ, 1992, **26a**:3335~3354
3 Wei F, Teng E, Wu G *et al.* Environ Sci Tech, 1999, **33**:4188~4193
4 Maenhaut W, Salomonbic R, Ptasinski J *et al.* Nucl Instr Meth, 1997, **B130**:576~581
5 Orlic I, Osipowicz T, Watt F *et al.* Nucl Instr Meth, 1995, **B104**:630~637
6 Grim G W. X-ray spectrosc, 1998, **27**:221~231
7 Jambers W, Grieken R V. Trends Anal Chem, 1996, **15**:114~122
8 Hickmott D D, Herrin J M, Abell R *et al.* Nucl Instr Meth, 1997, **B130**:564~570
9 Orlic I. Nucl Instr Meth, 1995, **B104**:602~611
10 Artaxo P, Rabello M L C, Watt F *et al.* Nucl Instr Meth, 1993, **B75**:521~525
11 Orlic I, Watt F, Loh K K *et al.* Nucl Instr Meth, 1994, **B85**:840~844
12 Cohen D D, Garton D, Stelcer E. Nucl Instr Meth, 2000, **B161/163**:775~779
13 Jaksic M, Bogdanovic I, Gereda E **et al.** Nucl Instr Meth, 1993, **B77**:505~508
14 Orlic I, Zhou S, Watt F. Nucl Instr Meth, 1999, **B158**:505~510
15 Chen M, Chen J, Li D. Shanghai Environ Sci (in Chinese), 1997, **16**(10):15~17
16 Sha Y, Gu Y, Liu G *et al.* Nucl Instr Meth, 1996, **B109/110**:79~84
17 Sha Y, Shi J, Gu Y *et al.* Nucl Sci Tech (China), 1996, **7**:61~64
18 Butz T, Flagmeyer R -H, Heitmann J etal. Nucl Instr Meth, 2000, **B161/163**:323~327
19 Tanabe K, Tamura T, Uesaka H. Appl Spectrosc, 1992, **46**(5):807~810
20 Mitternayr C R, Drouen A C J H, Otto M. Anal Chim Acta, 1994, **294**(2):227~242
21 Cheng Z, Li M, Xu S. Nucl Tech (in Chinese), 1996, **19**(8):449~452
22 Bos M, Weber H T. Anal Chim Acta, 1991, **247**(1):97~105
23 Allanic A L, Jezequel J Y, Andre J C. Anal Chem, 1992, **64**(21):2618~2622
24 McClelland J L, Rumelhart D E. Parallel distributed processing. Cambridge: MIT Bradfort Press, 1986
25 Fan X, Zhang W, Han S. Environ Sci (in Chinese), 1999, **20**(5):102~108
26 Weingartner E, Kelles C, Stahel W A *et al.* Atmos Environ, 1997, **31**:451~462