

Title	ATMOSPHERIC PARTICLES IN HANOI-CONCENTRATIONS OF WATER-SOLUBLE INORGANIC IONS AND SOURCE REGIONS
Author(s)	Nguyen, Thi Thanh Binh; Tran, Thi Ngoc Lan; Pham, Hung Viet
Citation	Annual Report of FY 2007, The Core University Program between Japan Society for the Promotion of Science (JSPS) and Vietnamese Academy of Science and Technology (VAST). 2008, p. 40-53
Version Type	VoR
URL	<a href="https://hdl.handle.net/11094/12985">https://hdl.handle.net/11094/12985</a>
rights	
Note	

*Osaka University Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

Osaka University

# ATMOSPHERIC PARTICLES IN HANOI - CONCENTRATIONS OF WATER-SOLUBLE INORGANIC IONS AND SOURCE REGIONS

Nguyen Thi Thanh Binh<sup>1</sup>, Tran Thi Ngoc Lan<sup>1</sup>, Pham Hung Viet<sup>2</sup>

<sup>1</sup> VNU-Hochiminh, College of Natural Sciences, 227 Nguyen Van Cu, HoChiMinh

<sup>2</sup> VNU-Hanoi, Research Center for Environmental Technology and Sustainable Development, 334 Nguyen Trai, Hanoi

Corresponding author: Tran Thi Ngoc Lan

Department of Physical Chemistry, College of Natural Sciences, 227 Nguyen Van Cu, HoChiMinh, Vietnam

[ttnlan@hcmuns.edu.vn](mailto:ttnlan@hcmuns.edu.vn)

## Abstract

A study on atmospheric particles was carried out in Hanoi. TSP and concentration of water-soluble ions in TSP were low in the summer and the fall (a wet season), and high in the winter and the spring (a dry season) and varied from 51 – 655  $\mu\text{g}/\text{m}^3$  with an average concentration of 185  $\mu\text{g}/\text{m}^3$ . TSP of the dry season was more acidic than TSP of the wet season. Contribution of ions in TSP mass was 4 – 17 % for  $\text{SO}_4^{2-}$ , 1- 8% for  $\text{NO}_3^-$  and 0.2 – 6.5 % for  $\text{NH}_4^+$ . Trajectory analyses showed that the variation in concentration of atmospheric particles as well as in their chemical composition closely related with a history of incoming air parcels. Southeast region of China was the source regions of air pollutants in Hanoi in the dry season. Among them Nanning was the most influencing site. A contribution of Southeast China in particulate sulphate in Hanoi is 30%.

**Keywords:** atmospheric particles, source regions, trajectory analyses, TSP, water-soluble inorganic ions.

## 1. Introduction

Atmospheric particles consist of coarse primary particles and fine secondary particles. The most important components of secondary particles are ammonium sulphates and nitrate that are formed by atmospheric reactions between gaseous precursors like  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{NH}_3$ . Secondary particles can contain also considerable amount of chlorides originated from biomass burning. Concentration of secondary particles is related with a level of atmospheric pollution. Fine secondary particles are closely correlated with the observed adverse health effects (Thurston et al., 1994; R. Peled et al., 2005). The increasing of fine particles increased mortality and morbidity (Ozkaynak et al., 1987; L.T. Gonçalves et al., 2005). Primary particles are less harmful than secondary particles. All inorganic products of atmospheric chemistry of  $\text{SO}_2$ ,  $\text{NO}_2$  are water-soluble. Therefore water-soluble ions in particles are important indicators of pollution level; hence they are under special consideration.

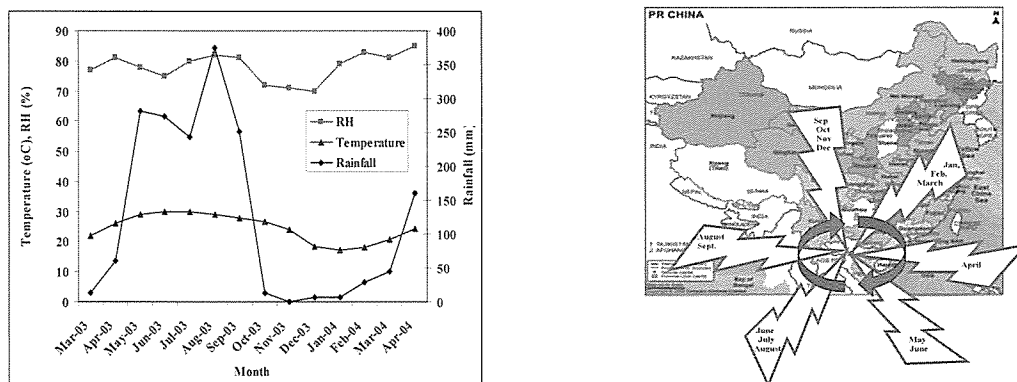
Vietnam economy grows up rapidly in the last two decades. The highest consideration is a fast development. Environmental pollution control is not adequate. Consequently air quality in the big cities like Hanoi, HoChiMinh has decreased dramatically. Particles are the most serious air pollutant nowadays in Vietnam. Hanoi is the Capital City and the second large commercial, cultural and industrial center in Vietnam with the population of 2.7 million persons, 1.7 million motorbikes and 0.12 million automobiles. The concentration of TSP in Hanoi was reported (Hien et al., 2002; Co et al. 2004). There were also some reports on concentrations of water-soluble inorganic ions in TSP (Maeda et al., 2001; Hien et al., 2002; Lan et al., 2003; and Imamura et al., 2003, 2004). However in the above listed reports the number of samples collected per year was limited; hence a statistical analysis was

unable. In this research TSP and water-soluble inorganic ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) in TSP at Hanoi were measured weekly in one-year period. Representative samples were analyzed by using XRD method in order to find possible chemical substances in which ions were bound. The ion concentrations then were examined in a relation with incoming air mass trajectories to identify source regions and to evaluate a contributions of long-range transportation in secondary particles in Hanoi.

## 2. Experimental

### 2.1. Sampling site

The sampling was conducted on the terrace of the academic building at the University of Natural Sciences in Hanoi, which was about 20 meters above the ground and 100 meters from the main street. Climatic characteristics like relative humidity, rainfall, temperature and main wind direction were obtained from the meteorological station nearby and are given in Fig. 1. Hanoi has tropical monsoon climate with four seasons: spring (January - March), summer (April – June), fall (July – September) and winter (October - December). A year was divided into a wet season (April to September) and a dry season (October to March) based on the rainfall.



**Fig. 1.** Monthly average temperature (left axis), relative humidity (left axis) and rainfall (right axis) and main wind direction in Hanoi.

### 2.2. Sampling procedure

Particles were collected on silica filters with a size of 18cm x 22cm by using a high-volume sampler (Kimoto, Japan). The sampling was carried out for 24 hours based on weekly frequency at a flow rate of 850 L/min. The filters were preheated in an electric furnace at 850°C for 4h before sampling and equilibrated in desiccators for 24 hours before weighing. All filters were kept in clean plastic bags that were sealed in aluminum envelopes before and after the samplings, and during the transportation. Collected samples were stored in a refrigerator at 5°C until chemical analysis. Total 48 samples were collected in the period from 17<sup>th</sup> March 2003 to 5<sup>th</sup> April 2004.

### 2.3. Chemical analyses

1/32 of each filter was used for analyses. The filters were cut into pieces and extracted ultrasonically for 20 minutes by 20mL of pure water in clean plastic vials. A pH meter B-212 (Horiba) and a conductivity meter B-173 (Horiba) were used to determine pH and conductivity of the extracts. The pH and conductivity meters were calibrated before measurements. The extracts were analyzed by using ion chromatography system Dionex DX 500 IC equipped with an auto-suppressed conductivity detector. A

Dionex CS12A (2\*250mm) was used with 25mM H<sub>2</sub>SO<sub>4</sub> eluent at a flow rate of 0.25mL/min and injection volume of 50μL for determination of cations. The detection limits were 0.02, 2, 0.2, 0.3 and 0.5 ppb for Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, respectively. A Dionex AS12A (4\*250mm) column with Na<sub>2</sub>CO<sub>3</sub> 2.7 mM, NaHCO<sub>3</sub> 0.3 mM eluent at a flow rate of 1.5mL/min and injection volume of 25μL was used for anion detection. The detection limits were 3, 6, 10, 30 and 9 ppb for Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>, respectively. Concentrations of TSP, as well as water-soluble ions in particles were estimated. The obtained results were analyzed based on daily as well as monthly-average concentrations. Na<sup>+</sup> ion was selected as an indicator for sea-salt aerosols. Correlations between ions were estimated. Three representative samples collected in rainy season, winter and spring were analyzed by XRD method to identify chemical formulas of sulphates and nitrate.

#### 2.4. Source region identification

Air mass back trajectories for the sampling days were computed using Transport and Dispersion Model “Hybrid Single-Particle Lagrangian Integrated Trajectory version 4” (HYSPLIT 4) developed by the US National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (<http://www.arl.noaa.gov/ready/hysplit4.html>). The important factors in trajectory analyses are 1) pollution level in region that trajectory passed through, 2) heights of air parcels over polluted regions, 3) advection velocity of the trajectories and 4) rainfall during the trajectory. The trajectories were computed for each quarter of day from the beginning of sampling day using three starting heights (20 m, 50 m, and 100 m above the ground level). Each set of trajectories then was analyzed to determine source regions and their contribution in particle pollution in Hanoi.

### 3. Result and discussion

#### 3.1. Mass concentration of TSP

Daily and monthly-average TSP concentrations are given in Fig. 2. The daily TSP concentration varied strongly, especially in the dry season, from 51 – 655 μg/m<sup>3</sup> with an annual average concentration of 185 μg/m<sup>3</sup>. It changed by factor of 5 even in one week. Commonly TSP reduced along with the wet season, increased along with the dry season. It was low in the period from May to September and March, and high in the period from October to February and April. Thus air quality in Hanoi in winter and spring is in critical conditions. Among 48 collected samples 18 samples showed TSP concentration higher than the Vietnamese standard for 24-hour TSP concentration which is 200 μg/m<sup>3</sup>. These 18 samples were collected in the period from September to April.

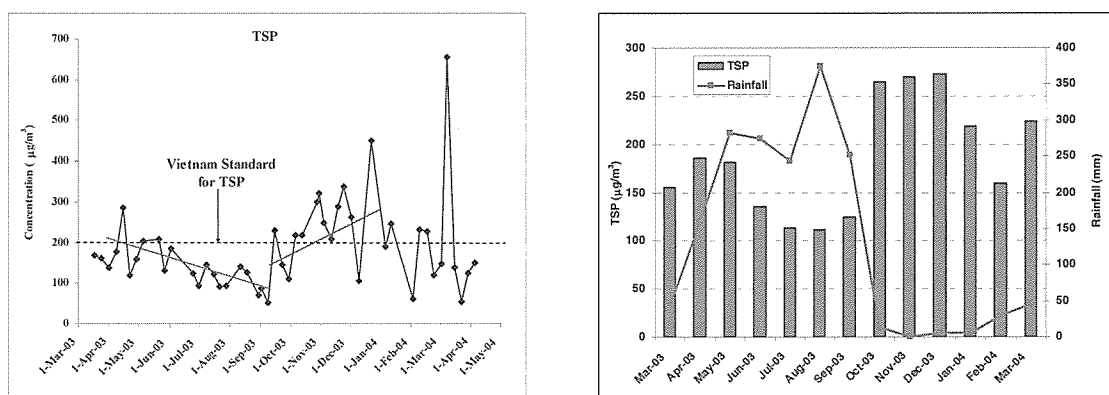


Fig. 2. TSP concentration: a) daily (left) and b) monthly average (right).

### 3.2. Acidity and ion balance of the extracts

Fig. 3 shows pH of the extracts of particles. About 40% of the extracts had pH higher than 7 and about 30% of the extracts had pH lower than 6. Most of the particles collected in the period from September to April were acidic, while those in the period from May to August were neutral and basic. Fig. 4 gives an ion balance, where the concentrations of ions are expressed in  $\text{neq/m}^3$ . The dash line in Fig. 4 represents balance between anions and cations. The dash line represents balance between anions and cations. The regression equation showed that obtained data is adequate.

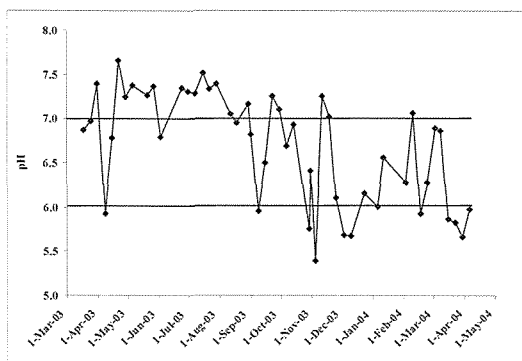


Fig. 3. pH of aqua-extracts of particles

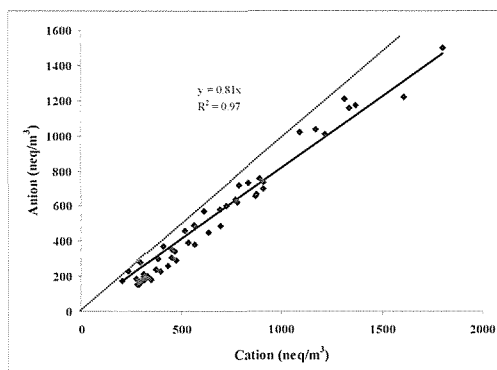


Fig. 4. Ion balance

### 3.3. Concentration of water-soluble ions

Fig. 5 shows the total concentration of common inorganic water-soluble ions and their weight percentage in TSP. The total concentration of ions varied from  $13 \mu\text{g/m}^3$  to  $113 \mu\text{g/m}^3$  correspondently to the weight percentage in TSP from 10% up to 38%. The total concentration of ions as well as their weight percentage in TSP followed the same trend as TSP, i.e. they were much higher in the dry season than in the wet season. This implies that the contribution of secondary particles in atmospheric particles of the dry season was much higher than those of the rainy season.

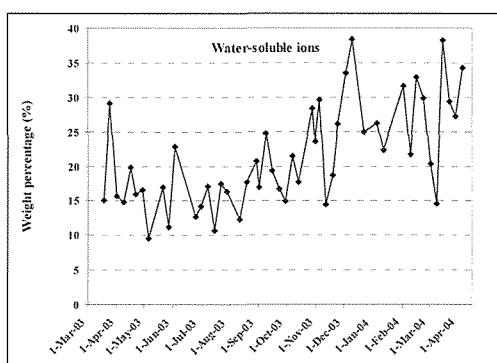
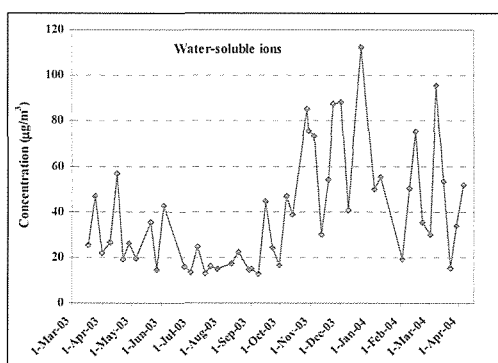


Fig. 5. Total concentration of inorganic water-soluble ions and their weight percentage in TSP

To see better a seasonal variation in water-soluble composition of particles, a daily concentration of each ion is given in Fig.6.  $\text{SO}_4^{2-}$  was the most abundant ion followed by  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ .  $\text{SO}_4^{2-}$  ion was  $5\text{--}46 \mu\text{g/m}^3$  and contributed 4 – 12 % TSP mass in the wet season, 5 – 17 % in the dry season.  $\text{Ca}^{2+}$  was the second abundant ion with the concentration of  $1\text{--}17 \mu\text{g/m}^3$  and contributed 2.3 – 5.3 %

TSP mass.  $\text{Ca}^{2+}$  has crustal origination. In average  $\text{Ca}^{2+}$  in the wet season was much lower than in the dry season. In addition a daily variation in  $\text{Ca}^{2+}$  concentration in the dry season was larger than in the wet season too. However its percentage in TSP mass varied in the range 2.5 – 5% fluctuated around 4% not depending on season.  $\text{Mg}^{2+}$  has crustal origination like  $\text{Ca}^{2+}$ . It was about 0.1 – 0.3% TSP mass only. Since  $\text{Mg}^{2+}$  was minor among other ions in TSP, therefore it was left out of consideration.

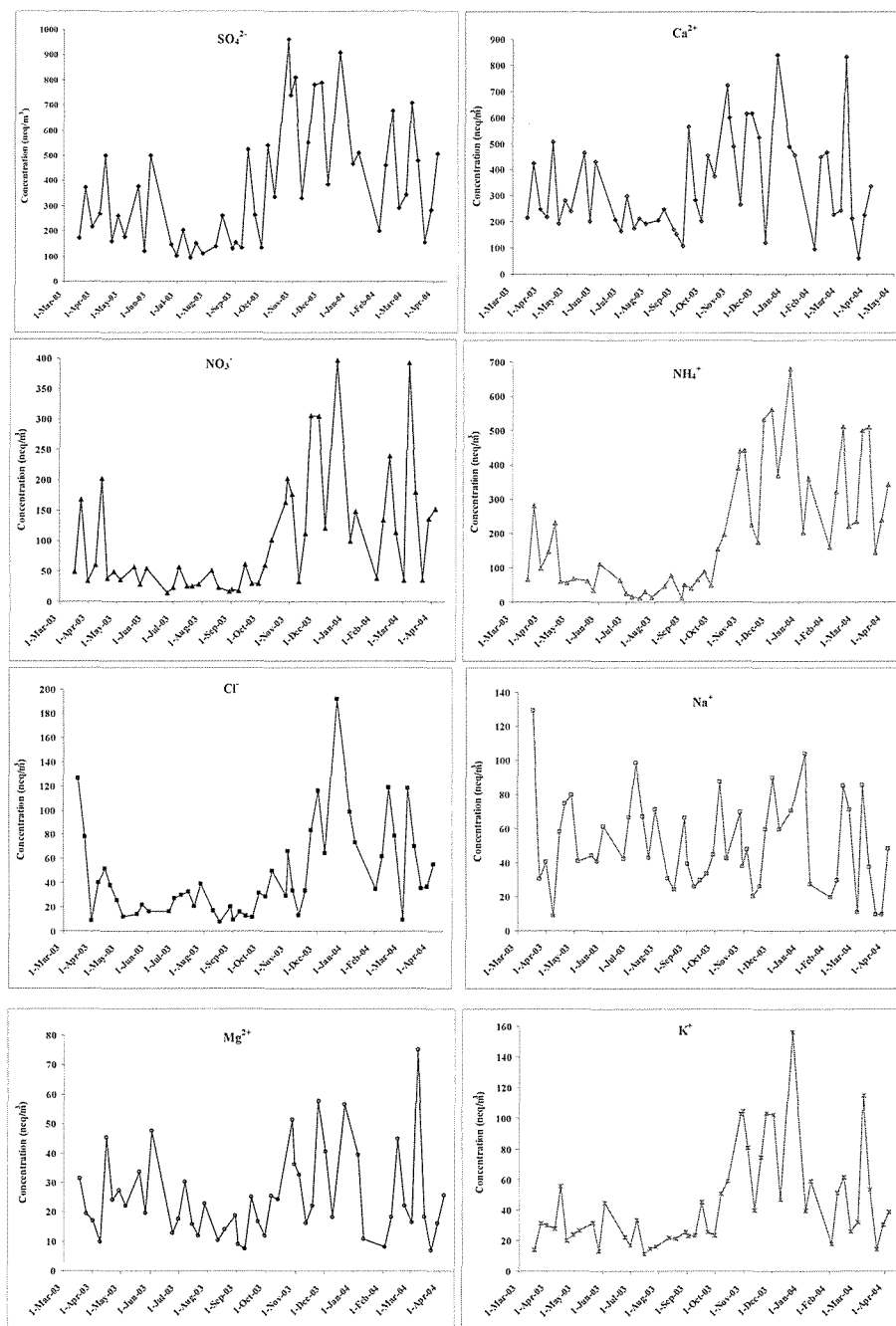
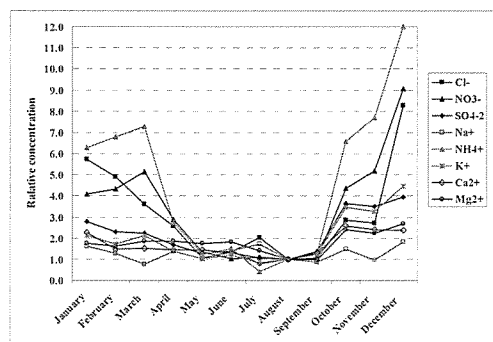


Fig. 6. Daily concentrations of inorganic water-soluble ions.

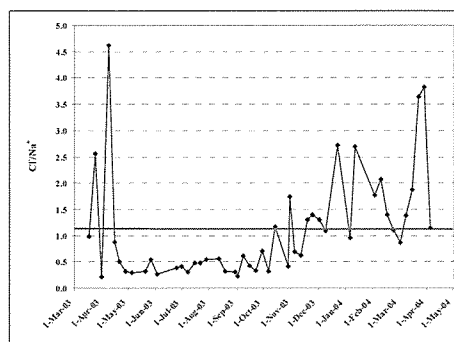
$\text{NO}_3^-$  was  $1\text{--}25 \mu\text{g}/\text{m}^3$  and contributed 1 - 8% TSP mass. For  $\text{NH}_4^+$  these parameters were  $0.2\text{--}13 \mu\text{g}/\text{m}^3$  and 0.2 – 6.5 %, respectively. In addition  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were high in the dry season but very low in the wet season. It was not surprising. Ammonium is the most important basic atmospheric component that neutralizes acidic species in the atmosphere like  $\text{SO}_2$ ,  $\text{HNO}_3$ , and  $\text{HCl}$ ... All ammonium salts are known very soluble, hence they deposit along with rains. The above suggestion is proved by the results obtained in study on rain in Vietnam (Lan, 2004). Lan found that sulphate and ammonium are predominating ions in rainwater.

Each of  $\text{Na}^+$ ,  $\text{Cl}^-$  ions was less than 2.5% of TSP mass.  $\text{Na}^+$  is considered to originate mainly from sea-salt aerosols that have the same composition as sea water. Therefore  $\text{Na}^+$  was chosen as the indicator of a contribution of sea-salt aerosols in atmospheric particles. Since in sea-water  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{K}^+$  contribute very small percentage in comparison with  $\text{Na}^+$  ions, but in atmospheric particles they were higher than  $\text{Na}^+$  ions; consequently they have anthropological originations.  $\text{Cl}^-$  and  $\text{K}^+$  originate from sea-salt aerosols as well as from biomass burning. In sea-water the equivalent ratio  $\text{Cl}^-/\text{Na}^+$  is 1.1. Sea-salts aerosols in the atmosphere can react with acidic species like  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  to form volatile  $\text{HCl}$ ; consequently  $\text{Cl}^-$  is lost into gas phase. Fig. 7 gives an equivalent ratio  $\text{Cl}^-/\text{Na}^+$  in the particles. The ratio  $\text{Cl}^-/\text{Na}^+$  lower than 1.1 observed in the wet season implied that reaction between sea-salt aerosols and gaseous substances in the air occurred intensively. The ratio  $\text{Cl}^-/\text{Na}^+$  much higher than 1.1 in the dry season points out that in the dry season a big part of  $\text{Cl}^-$  originated from biomass burning. The mass content of  $\text{K}^+$  ions in particle was around 0.6% in the wet season and 0.8 – 1.8% in the dry season. As  $\text{Cl}^-$  ions, besides sea-salt origination  $\text{K}^+$  ions in the dry season have addition biomass burning sources.

The concentrations of ions as well as of TSP were the lowest in the August. Therefore August was chosen for evaluating average monthly relative concentrations of ions. The monthly relative concentrations were evaluated as ratios between monthly average concentrations of the other months and those in the August. These relative concentrations are given in Fig. 8. Among ions  $\text{Na}^+$  concentration in TSP was the most stable. Ions with anthropological origination and biomass burning ( $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{K}^+$ ) showed stronger seasonal dependence than the ions with natural originations ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ ). However like TSP all ions presented big daily variation in their concentration, especially in the dry season when there was no rain and a washing effect of rain was excluded. Since human activity in the city could not vary so much from week to week the above observed suggests that besides common local sources there might be additional unexpected sources of air pollution in Hanoi.



**Fig. 7.** Average monthly relative concentrations of ions in comparison of those in the August.



**Fig. 8.** Equivalent ratio  $\text{Cl}^-/\text{Na}^+$  ions. The line represents the  $\text{Cl}^-/\text{Na}^+$  ratio in sea-salt aerosols.

### ***3.4 Source region identification and background level of particulate sulphate in Hanoi***

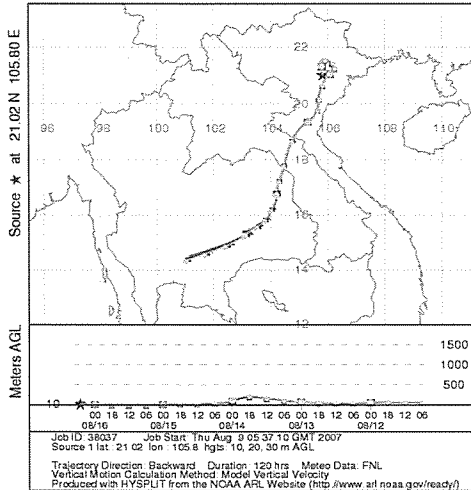
Long-range transportation of pollutants by air mass is known as important source of particles. Coarse particles settle fast. They can not transport far in the air. Secondary particles are small hence their exhibit long life in the air, travel a long distance from their sources before sinking by a wet or dry deposition. Sulphate ammonium contributes a big part of secondary particles. For this reason in this study sulphate was chosen for evaluating a contribution of trans-boundary sources. Fig. 9 shows four representative directions of 5-day backward trajectories of incoming air parcels a) southwest, b) southeast, c) north-northeast, and d) east-northeast.

In the period from April to the middle of September the trajectories of air parcels coming to Hanoi went from middle part of Vietnam, Laos, Cambodia and Thailand (Fig.9 a, b) in accordance with wind direction given in Fig. 1. The above mentioned regions have no industry and are clean areas. Therefore air pollutants originated from local source only. Also, there were a lot of rains this period. Rains washed off air pollutants. Hence concentrations of TSP as well as particulate sulphate and nitrate were very low as showed in the previous sections.

In the period from middle of September to March wind changed direction and air masses came from land of China (Fig.9 c, d), where there a lot of seriously polluted sites. Thus period from middle of September to March is dangerous period from view point of pollution. This is approved by the observed level of TSP and particulate sulphate given in Figs. 2-7. Among 22 trajectory set related to the 22 samples of this period only one set began in the East and passed over the East sea to Hanoi. The trajectories in other 21 sets began in the North or Northeast, and traveled over one or some polluted sites in Southeast area of China like Nanning, Guilin, Changsha, Wuhan, Hefei, Shanghai, Haikou, Beihai, Quinzhou, Guangzhou, Hongkong, Zhenghoau, Fuzhou, Xiamen, Guiyang, and Chongqing (Fig. 10) before coming to Hanoi. The above mentioned sites are the big industrial centers in China. Chongqing, Guiyang, Guangzhou, and Shanghai are in the list of 11 most polluted sites in the world. The others sites are the big emission sources of SO<sub>2</sub> in China also, especially Nanning, Wuhan, Changsha, Hongkong, Guilin and Haikou. In this period 14 samples (64%) showed TSP concentration higher Vietnamese standard and 18 samples (82%) showed the sulphate concentration higher 20 µg/m<sup>3</sup>, 11 samples (50%) showed the sulphate concentration higher 25 µg/m<sup>3</sup> (American standard for particulate sulphate). It was observed that highly polluted days in Hanoi corresponded to the trajectories that passed highly polluted sites in China. The more polluted sites a trajectory passed the higher concentration of TSP and particulate sulphate in TSP at Hanoi was. Low height of air parcels and low advection velocity over polluted area corresponded to high pollution level in Hanoi also. Rain improved air quality. An example is March 22<sup>nd</sup> 2004. The backward trajectories of this day passed through Nanning city, but there were rains along with the trajectories, hence the concentrations of TSP and particulate sulphate were low.

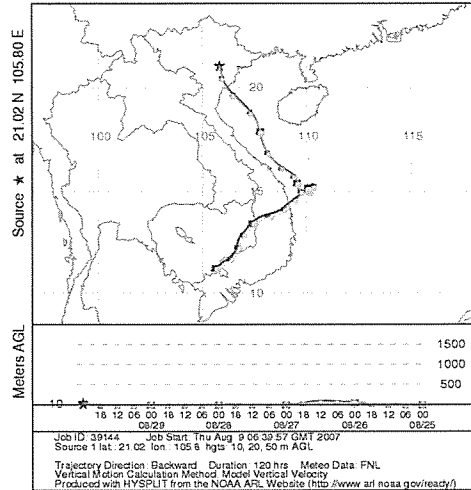


NOAA HYSPLIT MODEL  
Backward trajectories ending at 05 UTC 16 Aug 03  
FNL Meteorological Data



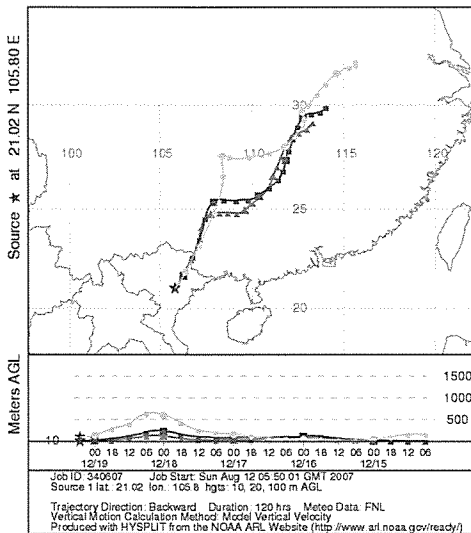
(a)

NOAA HYSPLIT MODEL  
Backward trajectories ending at 00 UTC 30 Aug 03  
FNL Meteorological Data



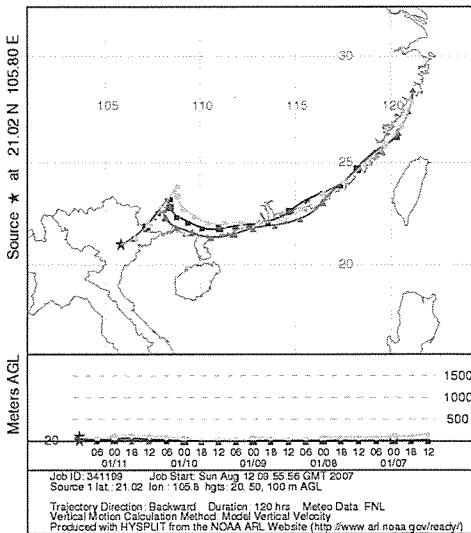
(b)

NOAA HYSPLIT MODEL  
Backward trajectories ending at 05 UTC 19 Dec 03  
FNL Meteorological Data



(c)

NOAA HYSPLIT MODEL  
Backward trajectories ending at 12 UTC 11 Jan 04  
FNL Meteorological Data



(d)

**Fig. 9.** Representative directions of 5-day backward trajectories of incoming air parcels

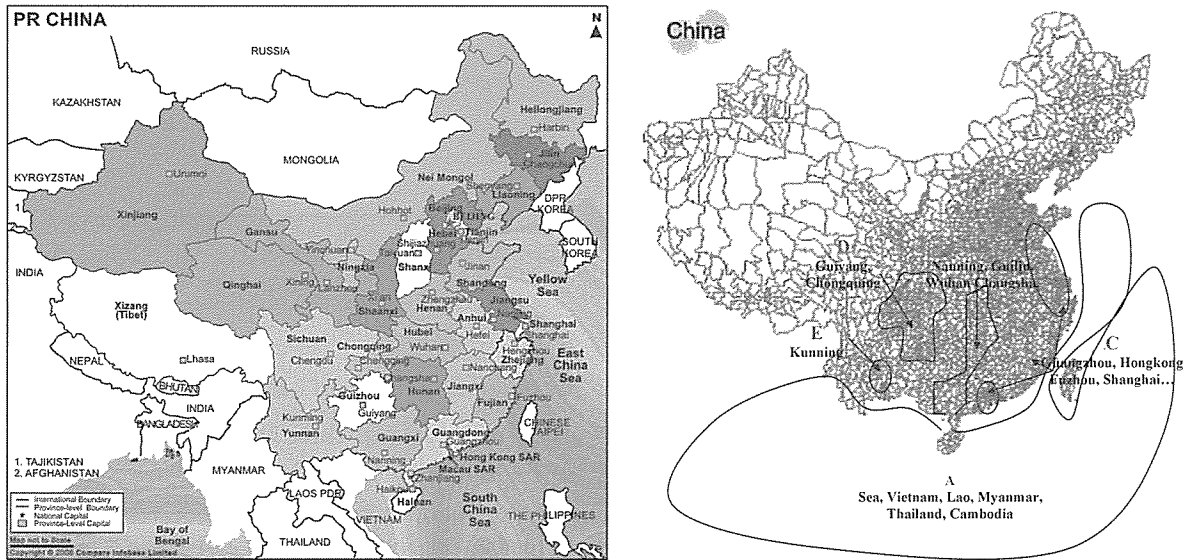
a) southwest, b) southeast, c) north northeast, and east northeast (d). Three heights (10m, 25 m and 50 m) were used as starting heights.

For evaluating influence of long-range transboundary pollution surrounding Hanoi regions were divided into groups based on directions of incoming air parcels as given in Fig. 10 and Table 1. Table 1 also gives number trajectory sets that passed each group and contribution of each group in air pollution in Hanoi. In the 2<sup>nd</sup> group backward trajectories passed Nanning region, went to the northeast direction and might pass other sites in the group. Backward trajectories of the 3<sup>rd</sup> group went to east (to the sea) and then to north east direction, swept coastal area of China, passed one or some of the sites in the

group. Those of the 4<sup>th</sup> group had north direction, passed Guiyang and might pass Chongqing region. Trajectories of the 6<sup>th</sup> group went to northeast direction passed one or some of the sites in the group, but did not pass Nanning region. In the 7<sup>th</sup> group backward trajectories passed in the east-northeast direction on land, passed Nanning, and Guangzhou or Hongkong. In the 8<sup>th</sup> groups backward trajectories passed clean China land.

**Table 1** Main direction of incoming air parcels to Hanoi and number of trajectories in each group

		Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
Sites that air parcels pass		Sea	Nanning*	Haikou	Guiyang*	Kunning	Changsha	Nanning (surub) <sup>#</sup>	Unpolluted regions in China
		Middle Vietnam	Guilin	Guangzhou	Chongqing		Wuhan	Guangzhou	
		Laos	Wuhan	Hongkong				Hongkong	
		Thailand	Hefei	Quinzhou					
		Myanmar		Zhenghoau					
	Cambodia			Xiamen					
				Fuzhou					
				Shanghai					
48 coll samples		17	17	10	0	0	1	3	0
Whole year	day	171	93	30	13	2	19	5	33
	%	47	25	8	4	0.5	5	1,5	9
Contribution			19	6	3	0.4	2	1	



**Fig. 10.** Important economical centers and discharge of SO<sub>2</sub> in China.

Among 48 collected samples 31 samples associated with the trajectories that traveled over polluted regions in China, the 17 other samples associated with the trajectories that traveled over clean regions or the sea. Samples associated with groups 2 and 7 in no-rain time corresponded to highest pollution level. This fact is reasonable since Nanning is located close to Vietnam - China border line, about 300 km in the northeast of Hanoi hence air pollutants in Nanning strongly affect air quality in Hanoi. Groups 3 and 6 are in the second order. Most of samples associated with these groups corresponded to high pollution level, but some of them corresponded to middle pollution level. Samples associated with group 8 corresponded to middle pollution level. Samples associated with group 1 corresponded to low pollution level. Although none of collected samples associated with groups 4 and 5, it was expected that pollution level would be high due to high pollution level at sources.

Based on the results observed for the collected samples the following idea was proposed to estimate contribution of regional sources to air pollution in Hanoi. Approximately the groups 2, 3, 4, 5, 7 are considered to result on the highest pollution level of sulphate P1. The groups 6 correspond to pollution level of sulphate P2. The group 8 corresponds to pollution level of sulphate P3 and the group 1 corresponds to pollution level of sulphate P4. P1, P2, P3 and P4 were estimated as average concentrations of sulphate measured for collected samples of corresponding groups. The obtained values are 26, 21, 14 and 8  $\mu\text{g}/\text{m}^3$ . P1 and P4 are pollution level in the rainy and dry season respectively, when local source is the only source of air pollution. Thus approximately an annual average real concentration of particulate sulphate R can be estimated as follows

$$R = (25\% + 8\% + 4\% + 0.5\% + 1.5\%) \cdot 26 \mu\text{g}/\text{m}^3 + 5\% \cdot 21 \mu\text{g}/\text{m}^3 + 9\% \cdot 14 \mu\text{g}/\text{m}^3 + 47\% \cdot 8 \mu\text{g}/\text{m}^3 = 16.2 \mu\text{g}/\text{m}^3$$

If the days correspond to groups 2-8 have no rain than an annual average concentration of particulate sulphate R from local source would be

$$53\% \cdot 14 \mu\text{g}/\text{m}^3 + 47\% \cdot 8 \mu\text{g}/\text{m}^3 = 11.2 \mu\text{g}/\text{m}^3$$

Thus a contribution of air pollutants coming from China to Hanoi for the whole year is

$$(16.2 \mu\text{g}/\text{m}^3 - 11.2 \mu\text{g}/\text{m}^3) : 16.2 \mu\text{g}/\text{m}^3 \cdot 100 \% = 31 \%$$

The contribution of group 1 is the highest due to the low distance from Nanning to Hanoi as well as high frequency of air parcels passing sites in this group.

For the period from October to March a contribution of air pollutants coming from China to Hanoi about 40% and an average concentration of particle sulphate is about 22  $\mu\text{g}/\text{m}^3$ . This level is really high and harmful to human being.

### 3.5. Chemical composition of sulphate and nitrate

Table 2 shows chemical composition of sulphate and nitrate in particles obtained by XRD analyses. Sulphate in particles is in the form of neutral and acidic ammonium salts, and neutral iron and calcium salts. As known from literature ammonium salts are in fine particles, while iron and calcium salts are in coarse particles. Sulphates and nitrates in super fine particles are formed by atmospheric reactions between  $\text{SO}_2$ ,  $\text{NH}_3$  and oxidizing agent in the air or by gaseous  $\text{H}_2\text{SO}_4$  condensation. In larger fine particles sulphates and nitrate are formed by coagulation or hygroscopic growth of smaller particles, or evaporation of sulphate-containing cloud water (Whitby, 1978; Hering and Friedlander, 1982; John et al., 1990; Ondov and Wexler, 1998; Meng and Seinfeld, 1994). The formation of calcium or iron sulphates in coarse particles is due to the reaction between solid crustal components, absorbed moisture and  $\text{SO}_2$  (Lun, 2003; Ikuko, 2003; and LAN, 2004).

**Table 2.** Composition of particles identified by XRD method.

<i>Sampling day</i>	<i>CaSO<sub>4</sub>·2H<sub>2</sub>O</i>	<i>KCl</i>	<i>Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></i>	<i>K<sub>3</sub>Fe(SO<sub>4</sub>)<sub>3</sub></i>	<i>NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub></i>
11/08/ 03	*		*		?
4/11/03			*	*	
8/03/ 04	*	*	*	*	*
<i>Sampling day</i>	<i>NH<sub>4</sub>HSO<sub>4</sub></i>	<i>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub></i>	<i>(NH<sub>4</sub>)<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub></i>	<i>(NH<sub>4</sub>)<sub>4</sub>(NO<sub>3</sub>)SO<sub>4</sub></i>	<i>NH<sub>4</sub>Cl</i>
11/08/ 03	?	?	?		
4/11/03	*			*	
8/03/ 04	*	*	*	*	*

### 3.6. Implementation to particle pollution in Hanoi

Exposure to strongly acidic sulfate particles was found to cause an alteration in lung function and particle clearance rates (Amdur et al., 1978; Koenig et al., 1983; Bauer et al., 1988; Leikauf et al., 1984; Schlesinger et al., 1983; Lippmann et al., 1982, 1989). However, these effects were not observed following exposure to the weakly acidic ammonium sulfate particles (Schlesinger, 1989; Utell et al., 1982). Some studies have demonstrated a stronger association between  $\text{SO}_4^{2-}$  and mortality and morbidity than with any of the other measures of PM, such as total suspended particulate TSP,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  (Ozkaynak and Thurston, 1987; Thurston et al., 1994). 30 % of air particles in Hanoi come from China. The situation is serious since trans-boundary particles come to Hanoi mainly in winter time, when above 40% of secondary particles come from China. As a result concentration of particles, especially secondary particles in winter should be very high. Secondary particles contain a lot of acidic sulphate. Thus particles in winter are more harmful than particles of the wet season especially in a cold weather. Perhaps this is a reason of increased number of people suffered respiratory diseases in Hanoi in winter (Co et al., 2004). Implemented measures to reduce particles in Hanoi can decrease only particles from local source. This means that is difficult to reduce significantly air particles in Hanoi in winter time. However, Hanoi EPA should implement urgent issues to prevent health effect of air particles. At least it can inform people about incoming situation of air pollutant so each person could have own measure to save himself.

## 4. Conclusion

The mass concentrations of particles as well as the concentrations of common soluble inorganic ions in particles were measured in Hanoi from March 2003 to April 2004. In summer and fall TSP was lower than the standard, but in winter and spring more than 60% of sampling days showed concentrations higher than the standard. Particles in winter and spring contained more secondary particles than the particles of summer and fall. Particles in the winter and the spring were more acidic hence more harmful than particles of the summer and the fall. Annually 30% of secondary particles come from China, but mainly in winter and spring. Nanning, Changsha, Fuzhou, Guilin, Guangzhou, Xiamen, Haikou, Wuhan, Suzhou, Shanghai, Beihai, Hefei, Hongkong, Quinzhou, Zhengzhou in the Southeast region of China are the source regions of air pollutants in Hanoi. Among them Nanning is the most influencing site.

## References

1. Amdur, M.O., Dubriel, M., Creasia, D., 1978. Respiratory response of guinea pigs to low levels of sulfuric acid. *Environmental Research* 15, 418–423.
2. Anh, M.T., Triet, L.M., Sauvain, J.-J., Tarradellas, J., 1999. PAH Contamination Levels in Air Particles and Sediments of Ho Chi Minh City, Vietnam. *Bull. Environ. Contam. Toxicol.* 63, 728 – 735.
3. Bauer, M.A., Utell, M.J., Speers, D.M., Gibb, F.R., Morrow, P.E., 1988. Effects of near ambient levels of sulfuric acid aerosol on lung function in exercising subjects with asthma and COPD. *American Review of Respiratory Disease* 137, A167.
4. Cabada J. C., Rees S., Takahama S., Khlystov A., Pandis S. N., Davidson C. I. and Robinson A. L., 2004. Mass size distributions and size resolved chemical composition of fine particulate matter at the Pittsburgh supersite. *Atmospheric Environment* 38, 3127-3141.
5. Co, H. X., Dung, N. T., 2004. Improving air quality in Vietnam. Regional Research Programme on Environmental Technology (ARRPET). Phase I Final Report.
6. Funasaka, K., Sakai M., Shinya M., Miyazaki T., Kamiura T., Kaneco S., Ohta K. and Fujita, T., 2003. Size distributions and characteristics of atmospheric inorganic particles by regional comparative study in Urban Osaka, Japan. *Atmospheric Environment* 37, 4597-4605.
7. Gonçalves, L.T., Carvalho, L.M.V., Conde, F.C., Latorre, M.R.D.O., Saldiva, P.H.N. and Braga, A.L.F., 2005. The effects of air pollution and meteorological parameters on respiratory morbidity during the summer in Sao Paulo City. *Environment International* 31, 343-349.
8. Gottlieb, J., Mamane, Y., 1989. Heterogeneous reactions of minerals with sulfur and nitrogen oxides. *Journal of Aerosol Science* 20, 303–311.
9. Hazi Y., Heikkinen M. S. A. and Cohen B. S., 2003. Size distribution of acidic sulfate ions in fine ambient particulate matter and assessment of source region effect. *Atmospheric Environment* 37, 5403-5413.
10. Hering, S., Eldering, A., Seinfeld, J.H., 1997. Bimodal character of accumulation mode aerosol mass distributions in Southern California. *Atmospheric Environment* 31, 1–11.
11. Hien, P. D., Bac, V. T., Tham, H. C., Nhan, D. D., and Vinh, L. D., 2002. Influence of meteorological conditions on PM<sub>2.5</sub> and PM<sub>2.5-10</sub> concentrations during the monsoon season in Hanoi, Vietnam. *Atmospheric Environment* 36, 3473-3484.
12. Hien, P. D., Binh, N. T., Ngo, N. T., Ha, V. T., Truong, Y., and An N. H., 1997. Monitoring lead in suspended air particulate matter in Ho Chi Minh City. *Atmospheric Environment* 31, 1073-1076.
13. Imamura, K., Maeda, Y., Lan, T.T.N., Thao, N.T.P., Viet, P.H., 2003. Investigation on Air Pollutants in Vietnam - Components of Water- soluble ions in airborne particulate matter. 12<sup>th</sup> Symposium on Environmental Chemistry, Japan, June 2003, 546-547.
14. Imamura, K., Maeda, Y., Lan, T.T.N., Thao, N.T.P., Viet, P.H., 2003. Investigation on Air Pollutants in Vietnam – Metal compounds in airborne particulate matter. 12<sup>th</sup> Symposium on Environmental Chemistry, Japan, June 2003, 158-159.
15. Imamura, K., Maeda, Y., Lan, T.T.N., Thao, N.T.P., Viet, P.H., 2003. Investigation on Air Pollution in Vietnam - Concentration of water- soluble ions in suspended particulate matters. The 4<sup>th</sup> General Seminar of The Core University Program. Environmental Science and Technology for Sustainable Development. Osaka, Japan July 2003, p. 105-109.
16. John, W., Wall, S.M., Ondo, J.L., Winklmayr, W., 1990. Modes in the size distributions of atmospheric inorganic aerosol. *Atmospheric Environment* 24A, 2349–2359.

17. Kleeman M. J., Scauer J. J. and Cass G. R., 2000. Size and composition distribution of fine particulate matter emitted from motor vehicle. *Environmental Science & Technology* 34, 1132-1142.
18. Lan, T.T.N., Maeda, Y., Nishimura, R., Imamura, K., Viet, P. H., and Thao, N. T. P., 2003. Dry deposition monitoring in Vietnam and removal of air pollutants by using biodiesel fuel. The 4<sup>th</sup> General Seminar of The Core University Program. *Environmental Science and Technology for Sustainable Development*, Osaka, 2003, 7-12.
19. Lan, T.T.N., Nishimura, R., Tsujino, Y., Imamura, K., Maeda, Y., Hoang, N.T., 2004. Atmospheric Concentrations of Sulfur Dioxide, Nitrogen Oxides, Ammonia, Hydrogen Chloride, Nitric Acid, Formic and Acetic Acids in the South of Vietnam Measured by the Passive Sampling Method. *Analytical Sciences* 20, 213-217.
20. Lan, T.T.N., Thoa, N. T. P., Nishimura, R., Tsujino, Satoh, Y., Yokoi, M., Maeda, Y., 2005. New model for the sulphation of marble by dry deposition. Sheltered marble – the indicator of the air pollution by sulphur dioxide. *Atmospheric Environment* 39, 913–920.
21. Leikauf, G.D., Spector, D.M., Albert, R.E., Lippmann, M., 1984. Dose-dependent effects of submicrometer sulfuric acid aerosol on particle clearance from ciliated human lung airways. *American Industrial Hygiene Association Journal* 45, 285–292.
22. Lestari P., Oskouie A. K. and Noll K. E., 2003. Size distribution and dry deposition of particulate mass, sulfate and nitrate in an urban area. *Atmospheric Environment* 37, 2507-2516.
23. Lestari, P., 1996. Atmospheric sulfate and nitrate: distribution, formation and deposition. Ph.D. Thesis. Illinois Institute of Technology, Chicago, IL.
24. Lippmann, M., 1989. Background on health effects of acid aerosols. *Environmental Health Perspectives* 79, 3–6.
25. Lippmann, M., Schlesinger, R.B., Leikauf, G., Spector, D., Albert, R.E., 1982. Effects of sulfuric acid aerosols on the respiratory tract airways. *Annals of Occupational Hygiene* 26, 677–690.
26. Lun, X, Zhang, X, Mu, Y, Nang, A. and Jiang, G, 2003. Size fractionated speciation of sulfate and nitrate in airborne particulates in Beijing, China. *Atmospheric Environment* 37, 2581-2588.
27. Maeda, Y., Imamura, K., Lan, T. T. N., Thoa, N. T. P., Nam, V. D., and Viet, P. H., 2001. Air pollution caused by exhaust gas from 2-cycle engine in Vietnam. *Joint Research on Environmental Science and Technology for the Earth. Annual Report of FY 2001*, Osaka, 75-80.
28. Meng, Z., Seinfeld, J.H., 1994. On the source of the submicrometer droplet mode of urban and regional aerosols. *Aerosol Science and Technology* 20, 253–265.
29. Mori, I., Nishikawa, M, Tanimura, T, and Quan, H, 2003. Change in size distribution and chemical composition of kosa (Asian dust) aerosol during long-range transport, *Atmospheric Environment* 37, 4253-4263.
30. Ondov, J.M., Wexler, A.S., 1998. Where do particulate toxins reside? An improved paradigm for the structure and dynamics of the urban mid-Atlantic aerosol. *Environmental Science and Technology* 32, 2547–2555.
31. Ozkaynak, H., Thurston, G.D., 1987. Associations between 1980 US. mortality rates and alternative measures of airborne particle concentration. *Risk Analysis* 7, 449–461.
32. Pakkanen, T.A., Kerminen, V.M., Hillamo, R.E., Makinen, M., Makela, T., Virkkula, A., 1996. Distribution of nitrate over sea-salt and soil derived particles—implications from a field study. *Journal of Atmospheric Chemistry* 24, 189–205.
33. Peled, R., Friger, M., Bolotin, A., Bibi, H., Epstein, Pilpel, L., D. and Scharf, S., 2005. Fine particles and meteorological conditions are associated with lung function in children with asthma living near two power plants. *Public Health*, 418-425.
34. Rocha, G. O., Allen, A. G., Cardoso A. A., 2005. Influence of Agricultural Biomass Burning on Aerosol Size Distribution and Dry Deposition in Southeastern Brazil. *Environment Science & Technology* 39, 5293-5301.
35. Rodhe, H., Grandell, J., 1981. Estimates of characteristic times for precipitation scavenging. *Atmospheric Science Journal* 38, 370–386.

36. Rosenbohm E., Vogt R., Scheer V., Nielsen O.J., Dreiseidler A., Baumbach G., Imhof D., Baltensperger U., Fuchs J. and Jaeschke W., 2005. Particulate size distributions and mass measured at a motorway during the BAB II campaign. *Atmospheric Environment* 39, 5696-5709.
37. Schlesinger, R.B., Naumann, B.D., Chen, L.C., 1983. Physiological and histological alterations in the bronchial mucociliary clearance systems of rabbits following intermittent oral or nasal inhalation of sulfuric acid mist. *Journal of Toxicology and Environmental Health* 12, 441-465.
38. Sillanpää M., Saarikoski S., Hillamo R., Pennanen A., Makkonen U., Spolnik Z., Grieken R., Koskentalo T. and Salonen R. O., 2005. Chemical composition, mass size distribution and source analysis of long-range transported wildfire smokes in Helsinki. *Science of The Total Environment* 350, 119-135
39. Thurston, G.D., Ito, K., Hayes, C.G., Bates, D.V., Lippmann, M., 1994. Respiratory hospital admissions and summertime haze air pollution in Toronto, Ont.: consideration of the role of acid aerosols. *Environmental Research* 65, 271-290.
40. Utell, M.J., Morrow, P.E., Hyde, R.W., 1982. Comparison of normaland asthmatic subjects' response to sulfate pollutant aerosols. *Annals of Occupational Hygiene* 26, 691-697.
41. Whitby, K.T., 1978. The physical characteristics of sulfur aerosols. *Atmospheric Environment* 12, 135-159.
42. Xiaohong Yao, Arthur P. S. Lau, Ming Fang, Chak K. Chan and Min Hu," Size distributions and formation of ionic species in atmospheric particulate pollutants in Beijing, China: 1—inorganic ions". *Atmospheric Environment*. (2003) 37, Pages 2991-3000.
43. Xiu G., Zhang D., Chen J., Huang X., Chen Z., Guo H. and Pan J., 2004. Characterization of major water-soluble inorganic ions in size-fractionated particulate matters in Shanghai campus ambient air. *Atmospheric Environment* 38, 227-236.
44. Yu J. Z., Yang H., Zhang H. and Lau A. K. H., 2004. Size distributions of water-soluble organic carbon in ambient aerosols and its size-resolved thermal characteristics, *Atmospheric Environment* 38, 1061-1071.