ELSEVIER

The Science of the Total Environment 153 (1994) 267–273

the Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Man

Short communication

The indoor/outdoor relationship of acid aerosols in Taipei

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Received 29 September 1993; accepted 12 October 1993

Abstract

In order to estimate personal exposure to acid aerosols indirectly, we designed this study to characterize the relationship between indoor and outdoor acid aerosol concentrations in Taipei. The acid aerosols were collected using a Harvard-EPA annular denuder and analyzed by ion chromatography. Samples were collected on 4 sampling days at two sampling sites in May, 1992, and on 39 sampling days at four sampling sites from January to April, 1993. At each sampling site, both indoor and outdoor samples were collected concurrently. On each sampling day, we collected two 12-h samples in the summer and one 24-h sample in the winter. We found that acid aerosols in Taipei are rich in SO_2, NH_3, ammonium nitrate and sulfate. We also found that indoor/outdoor ratios were > 1 for HNO_2, NH_3, NO_3^-, NH_4^+ and H^+, but < 1 for SO_2, SO_4^{2-} and HNO_3. The outdoor SO_4^{2-} levels were correlated with outdoor SO_2 levels, while the indoor SO_4^{2-} levels were correlated with indoor NH_4^+ levels. The indoor SO_4^{2-} may originate from outdoor SO_2 emissions and then penetrate indoors in the form of $(NH_4)_2SO_4$ or $(NH_4)HSO_4$ in Taipei. We conclude that mobile sources can be one important source of acid aerosols in Taipei. The concentrations of acid aerosols, indoors and outdoors, are possibly controlled by factors such as hot and humid weather and crowded living space in Taipei.

Keywords: Acid aerosols; Indoor/outdoor ratio; Denuders; Ion chromatography; Taipei

1. Introduction

Many epidemiological and clinical studies have indicated that exposure to acid aerosols, i.e. SO_4^{2-}, NO_3^-, NO_2^-, SO_2 and NO_2, may cause respiratory health effects [1–4]. In order to accurately quantify personal exposure and identify the sources of acid aerosols, some studies were designed to investigate the relationship between indoor and outdoor measurements of acid aerosols [5,6]. The prevalence of asthma in children aged from 7 to 15 years has increased 4.75 times for males and 3.78 times for females between 1974 and 1986 in Taipei, Taiwan [7]. The deterioration of air quality has been considered as an important contributing factor to such a rising trend in asthmatics in the Taipei metropolitan areas. According to

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SSDI 0048-9697(94)4083-L

the ambient air monitoring data of the Taiwan Environmental Protection Agency (EPA), PM_{10}, NO_2 and SO_2 have been the three most important pollutants in urban areas for years. In 1991, the annual average concentrations of PM_{10}, SO_2 and NO_2 were ~ 77–119 $\mu g\ m^{-3}$, 21–27 ppb and 22–37 ppb in Taipei, respectively [8]. In addition to these primary air pollutants, we think that various secondary air pollutants, such as acid aerosols, can be formed in the climate of Taiwan, which is usually warm, humid and with much sunshine. This study is, therefore, designed to construct a database of acid aerosols in ambient air in Taipei, and to compare the relationship between indoor and outdoor acid aerosol levels in non-asthmatic and asthmatic homes. These measurements will serve as a database of exposure in a large follow-up study on investigating the causal relationship between asthma and acid aerosols in Taiwan.

2. Materials and methods

2.1. Sampling and analysis

We used Harvard-EPA annular denuder systems to collect acid aerosols outdoors in two seasons and indoors in the summer only [9,10]. Briefly, the air enters the system at a flow rate of 10 l min^{-1} through a glass inlet-impactor which removes coarse particles (d_a < 2.5 μm). The air then passes through a sodium chloride coated denuder which collects the acidic gas HNO_3, two sodium carbonate coated denuders which collect the acidic gases SO_2 and HNO_2, and a citric acid coated denuder which traps NH_3. Downstream of the denuders a Teflon filter is mounted to collect fine particles and a nylon filter to trap volatilized vapors from the previous filter. In the winter, samples inside the homes of asthmatic children were collected with a personal annular denuder system, which is a miniaturization of the previous one and operates at a flow rate of 2 l min^{-1}. The personal annular denuder system consists of two short denuders. The first one is coated with sodium carbonate to collect gaseous HNO_2, HNO_3 and SO_2, and the second one is coated with citric acid to collect NH_3. The particulate nitrate, sulfate and ammonium are collected on the filters downstream. In analysis, all denuders and filters are first extracted with either deionized water or extraction solution and then analyzed by ion chromatography (Dionex 4500i). Anions, such as, Cl^-, NO_2^-, NO_3^- and SO_4^{2-}, were analyzed using a Dionex AS4A column (eluent, 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$; regenerent, 0.025 N H_2SO_4). Cations, such as, NH_4^+, Na^+ and K^+, are analyzed using a Dionex CS10 column (eluent, 20 mM HCl and 2 mM DL-2,3-diaminopropionic acid monohydrochloride; regenerent, 100 mM tetrabutyl ammonium hydroxide). An aliquot of the Teflon filter extract was analyzed for aerosol acidity (H^+) by a pH method which considered the influence of the extraction solution and the existence of the filter [11]. Among the analyzed anions and cations, only five species, HNO_2, HNO_3, SO_2, NO_3^- and SO_4^{2-}, were measured both in summer and winter. The data on Cl^-, Na^+ and K^+ will not be discussed in this paper.

2.2. Sampling site and period

We conducted our field sampling in two seasons. The summer season was in May, 1992, while the winter season was from January to April, 1993. In the summer, we monitored indoor and outdoor acid aerosols in two homes of non-asthmatics for 4 days. In each sampling day, two 12-h samples were taken to compare the difference between the day time and the night time. In the winter, the sampling scale was expanded. We monitored 2 days a week in four outdoor sites near the residence of 18 asthmatic children recruited from the pediatric clinic of the National Taiwan University Hospital. In each sampling day, one 24-h sample was taken. The outdoor samplers were placed ~ 3 m above the ground, while the indoor samplers were ~ 1.5 m above the ground and ~ 1 m away from the walls.

3. Results and discussion

The results of the summer and winter sampling are summarized in Table 1. Among the gaseous components, the outdoor acid aerosols in Taipei are rich in SO_2, while poor in HNO_3. In the summer, the average outdoor concentrations of gaseous HNO_2, HNO_3 and SO_2 were 1.65, 0.52

Table 1

Summary statistics for indoor and outdoor concentrations of particulate (nmol m^{-3}) and gas (ppb) compounds measured during the summer and winter sampling seasons

Compound	Season	Location	N	Mean	S.D.
HNO_2	Summer	Indoor	16	6.6	3.7
		Outdoor	15	1.7	0.9
	Winter	Indoor	96	8.0	4.8
		Outdoor	36	2.7	1.5
HNO_3	Summer	Indoor	16	0.7	1.2
		Outdoor	15	0.5	0.5
	Winter	Indoor	90	0.3	0.2
		Outdoor	38	0.5	0.6
SO_2	Summer	Indoor	16	2.5	1.9
		Outdoor	15	7.6	4.6
	Winter	Indoor	100	2.4	2.9
		Outdoor	37	8.2	4.6
NH_3	Summer	Indoor	NA	NA	NA
		Outdoor	NA	NA	NA
	Winter	Indoor	98	43.7	18.5
		Outdoor	38	8.0	5.5
NO_3^-	Summer	Indoor	15	7.8	8.1
		Outdoor	15	17.5	12.0
	Winter	Indoor	98	76.3	62.8
		Outdoor	38	52.3	43.3
SO_4^{2-}	Summer	Indoor	15	58.8	38.8
		Outdoor	15	68.7	40.8
	Winter	Indoor	94	98.3	67.0
		Outdoor	38	113.5	193.7
NH_4^+	Summer	Indoor	NA	NA	NA
		Outdoor	NA	NA	NA
	Winter	Indoor	90	250.4	187.9
		Outdoor	37	176.7	116.3
H^+	Summer	Indoor	NA	NA	NA
		Outdoor	NA	NA	NA
	Winter	Indoor	101	6.0	13.1
		Outdoor	39	4.6	11.6

N, number of observations; NA, samples not analyzed. Samples in which the filter extract was clearly alkaline were excluded for H^+.

and 7.6 ppb, respectively. In the winter, the average outdoor concentrations of gaseous HNO_2, HNO_3 and SO_2 were 2.7, 0.5 and 8.2 ppb, respectively. The average concentrations of NH_3 outdoors was ~ 8.0 ppb in the winter. Among the particulate matter, although SO_4^{2-} is the dominant component outdoors, the concentrations of NO_3^- are also relatively high. In the summer, the average outdoor concentrations of particulate NO_3^- and SO_4^{2-} were 17.5 and 68.7 nmol m^{-3}, respectively. In the winter, the averaging outdoor concentrations of particulate NO_3^- and SO_4^{2-} were 52.3 and 113.5 nmol m^{-3}, respectively. The average concentrations of NH_4^+ outdoors was ~ 176.7 nmol m^{-3} in the winter. The nitrogen-related sources seemed to play a relatively important role in the formation of acid aerosols in Taipei. One major local source of nitrogen oxides is the tail-pipe exhausts of ~ 10 million vehicles and motorcycles in Taipei metropolitan areas. The NH_3 is possibly emitted from sources such as densely populated residential areas in Taipei and landfills and rice fields in the suburban areas. The relatively low aerosol acidity in Taipei, consequently, is a result of the neutralization effects by these ammonia-related sources. The indoor acid aerosols are rich in HNO_2, NH_3, SO_4^{2-} and NH_4^+. In the summer, the average indoor concentrations of HNO_2 and SO_4^{2-} were 6.60 ppb and 58.8 nmol m^{-3}, respectively. In the winter, the average indoor concentrations of HONO, NH_3, SO_4^{2-} and NH_4^+ were 8.0 ppb, 43.7 ppb, 98.3 nmol m^{-3} and 250.4 nmol m^{-3}, respectively. In addition to the outdoor sources discussed above, indoor HNO_2 can also be partially produced by some indoor sources, such as gas stoves in kitchens. We found no significant difference between the acid aerosol concentrations during day and night in the summer sampling. However, a seasonal difference was significant for some species. The outdoor concentrations of SO_2 and HNO_3 in the summer were significantly higher than those in the winter, while SO_4^{2-} and NO_3^- were significantly higher in the winter ($P < 0.05$). The indoor concentrations of SO_4^{2-} and NO_3^- in the winter were significantly higher than those in the summer ($P < 0.05$) (Table 2).

In order to investigate the relationship between indoor and outdoor acid aerosols, we first divided indoor measurements by matched outdoor measurements and then calculated geometric means and standard deviations of the ratios (Table 3). We found that indoor/outdoor ratios were > 1 for HNO_2, NH_4^+, H^+ and NH_3, but < 1 for SO_2 and HNO_3. For SO_4^{2-}, the indoor/outdoor ratios were ~ 1. The higher NH_3 concentrations indoors are probably due to greater emissions from humans during their indoor activities. The contribution of indoor sources and the lower decay rate of HNO_2 indoors are two possible reasons for the higher indoor HNO_2 concentrations. The commonly used gas stoves in kitchens and living rooms are believed to be the main indoor sources of HNO_2 emissions in Taipei. Additionally, the rate of HNO_2 photolysis indoors is much slower than outdoors due to the availability of sunlight. In contrast, NO_2 and SO_2 are mainly from outdoor sources, such as gasoline-powered motorcycles and cars, and diesel-powered trucks and buses in Taipei. This may explain the phenomenon of higher NO_2 and SO_2 concentrations outdoors. In the urban atmosphere, HNO_3 is mainly formed through the photochemical reactions of NO_2, O_3 and volatile organic compounds. Therefore the rate of HNO_3 formation is higher in outdoor environments [12]. Another possibility is that the deposition velocity of HNO_3 is greater in indoor environments where more surfaces are available for the adsorption of HNO_3 [13].

We also found a significant seasonal change of indoor/outdoor ratios for HNO_2 which decreased from 4.29 to 2.59 from summer to winter. This indicated that the source strength for generating HNO_2 was greater in the summer in these participant's houses. Moreover, the poor regression slopes between indoor and outdoor measurements for acid aerosols (Table 4) indicated that the concentrations of indoor acid aerosols were influenced by some mechanisms in forming and removing acid aerosols indoors. In contrast, the indoor/outdoor ratios for NO_3^- increased from 0.44 to 1.32 from summer to winter. The increase of indoor/outdoor ratios for NO_3^- is possibly due

Table 2
The P-value of the t-test for the comparison of particulate and gas concentrations in summer and winter

Compound	Indoor P-value	Outdoor P-value
HNO_2	0.504	0.124
HNO_3	0.220	0.023
SO_2	0.016	0.000
NO_3^-	0.000	0.000
SO_4^{2-}	0.000	0.002

Table 3
Geometric mean (and geometric S.D.) of indoor/outdoor concentration ratios for particulate and gaseous compounds of acid aerosols

Compound	Summer I/O ratio (geomeric mean, (G.S.D.))	Winter I/O ratio (geometric mean, (G.S.D.))
HNO_2	4.29 (2.85)	2.59 (1.89)
HNO_3	0.98 (1.65)	0.69 (2.44)
SO_2	0.24 (2.46)	0.23 (2.30)
NO_2	NA	0.91 (1.11)
NH_3	NA	5.65 (1.90)
NO_3^-	0.44 (1.73)	1.32 (1.51)
SO_4^{2-}	0.74 (2.11)	0.96 (1.87)
NH_4^+	NA	1.28 (1.70)
H^+	NA	1.24 (4.17)

Table 4
Regression of indoor concentrations on the outdoor concentrations

Gas, aerosol	N	Slope (SE)	Intercept (SE)	R2
[w]HNO_2	78	0.56 (0.10)	1.37 (0.12)	0.28
[w]HNO_3	76	0.35 (0.06)	−1.99 (0.09)	0.28
[w]SO_2	82	0.77 (0.13)	−1.02 (0.28)	0.30
[w]NH_3	81	0.26 (0.06)	3.20 (0.13)	0.19
[w]NO_2	66	0.72 (0.15)	NS	0.25
[w]NO_3^-	82	0.83 (0.05)	0.93 (0.19)	0.79
[w]SO_4^{2-}	79	0.61 (0.08)	1.71 (0.34)	0.46
[w]NH_4^+	73	0.81 (0.07)	1.20 (0.36)	0.65
[s]HNO_2	7	0.72 (0.15)	NS	0.59

NS, not significant at $P < 0.05$; N, number of observations.

[s]Summer samples.

[w]Winter samples.

Relationships not included in the table had non-significant slopes ($P < 0.05$).

Table 5
Correlation coefficients for particulate and gaseous compounds

HNO_2	HNO_3	SO_2	NH_3	NO_3^-	SO_4^{2-}	NH_4^+	H^+
HNO_2	[a]—	—	NA	—	—	NA	NA
	[b]—	—	NA	—	0.72	NA	NA
	[c]—	—	—	—	—	—	—
	[d]—	0.83	0.73	0.84	—	0.74	—
HNO_3		—	—	—	—	—	NA
		—	—	—	—	—	NA
			—	—	—	—	—
			—	0.73	—	—	—
SO_2			—	—	—	NA	NA
			—	—	0.73	NA	NA
			—	—	—	—	—
			0.70	—	—	—	—
NH_3				NA	NA	NA	NA
				NA	NA	NA	NA
				—	—	—	—
				0.72	—	0.74	—
NO_3^-					—	NA	NA
					—	NA	NA
					—	0.77	—
					0.72	0.75	—
SO_4^{2-}						NA	NA
						NA	NA
						—	—
						0.79	—
NH_4^+							NA
							NA
							—
							—
H^+							

[a]Indoors during summer sampling period.

[b]Outdoors during summer sampling period.

[c]Indoors during winter sampling period.

[d]Outdoors during winter sampling period.

Values listed were significantly correlated at $P < 0.01$. NA, samples not analyzed.

Table 6

Summary statistics for indoor and outdoor concentrations of aerosol (nmol m^{-3}) and gas (ppb) species measured in Taipei, Boston and Chicago

Compound	Location	Mean Concentrations					
		Taipei	*N*	Boston	*N*	Chicago	*N*
HNO_2	Indoor	8.0 (4.8)	96	5.4 (3.4)	29		
	Outdoor	2.7 (1.5)	36	0.7 (0.6)	24	0.5 (0.3)	81
HNO_3	Indoor	0.3 (0.2)	90	0.03 (0.06)	29		
	Outdoor	0.5 (0.6)	38	0.6 (0.5)	24	0.3 (0.4)	81
SO_2	Indoor	2.4 (2.9)	100	0.4 (0.4)	23		
	Outdoor	8.2 (4.6)	37	4.7 (2.5)	24	8.1 (7.4)	81
NO_2	Indoor	45.2 (1.6)	100				
	Outdoor	67.4 (1.4)	37				
NH_3	Indoor	43.7 (18.5)	98	19.3 (6.4)	18		
	Outdoor	8.0 (5.5)	38	1.1 (0.9)	18	2.3 (2.4)	81
NO_3^-	Indoor	76.3 (62.8)	98	5.5 (5.6)	30		
	Outdoor	52.3 (43.3)	38	11.8 (11.3)	24	67.9 (61.3)	81
SO_4^{2-}	Indoor	98.3 (67.0)	94	31.5 (17.0)	24		
	Outdoor	113.5 (193.7)	38	42.6 (15.3)	24	57.8 (60.5)	81
NH_4^+	Indoor	250.4 (187.9)	90	66.4 (34.6)	18		
	Outdoor	176.7 (116.3)	37	66.8 (32.2)	18	152.2 (127.2)	78
H^+	Indoor	6.0 (13.1)	101	2.4 (1.8)	11		
	Outdoor	4.6 (11.6)	39	11.1 (8.6)	18	7.7 (11.6)	81

N, number of observations.

to the different formation rates of NH_4NO_3 indoors during the two seasons. The correlation coefficients for different species of acid aerosols can be used to investigate the mechanisms of aerosol formation (Table 5). The outdoor SO_4^{2-} levels were correlated with outdoor SO_2 levels in the summer (r = 0.73). The indoor SO_4^{2-} measurements, however, were correlated with indoor NH_4^+ measurements in the winter (r = 0.79). The molar concentration ratios between H^+ and SO_4^{2-} averaged at 0.2 indoors and 0.1 outdoors. It has been reported that the dominant species of acid aerosols collected on the filters are mainly $(NH_4)_2SO_4$, $(NH_4)HSO_4$ and $(NH_4)_3H(SO_4)_2$ when the ratio was < 1 [14]. Therefore, indoor SO_4^{2-} in Taipei is believed to originate from outdoor SO_2 emissions, and then penetrate indoors in the form of $(NH_4)_2SO_4$, $(NH_4)HSO_4$ or $(NH_4)_3H(SO_4)_2$. Apparently, the acidity of both indoor and outdoor aerosols has been largely neutralized by ammonium in Taipei.

In comparison with the components of acid aerosols in Boston and Chicago (Table 6), the acid aerosols in Taipei are similar to those in Chicago [15]. Both sulfate and nitrate are the main sources of acidity in the aerosols in Taipei and Chicago. In contrast, the main cause of acidity in the aerosols in Boston is sulfate. The aerosols in Taipei and Chicago also contained more ammonium. The ammonium concentrations in Taipei and Chicago are approximately twice as high as the concentrations in Boston. Accordingly, the aerosols in these two cities show less acidity. The relatively high HNO_2 concentrations in the aerosols in Taipei is a significant feature compared with the other two cities. The emissions from a large number of cars and motorcycles without catalysts in the congested traffic provide stocks of NO_x in the atmosphere in Taipei. The NO_x is then quickly transformed into HNO_2 through photochemical reactions in the hot (25–30°C) and humid (80–90% RH) weather in Taipei. Indoors, the HNO_2 can also be emitted directly from gas stoves, which are commonly used for cooking and making tea in Taiwanese homes.

4. Conclusion

We have identified that ammonium, nitrate and sulfate are important components of acid aerosols in Taipei. The main sources of acid aerosols are vehicles outdoors and gas stoves indoors. In most cases, the outdoor sources play a more important role in forming the acidity in aerosols. The formation, removal and penetration of acid aerosols indoors and outdoors are strongly influenced by climatic conditions and house settings. The year-round high temperature and high humidity are favorable meteorological conditions in forming acid aerosols, such as HNO_2. The crowded living spaces provide a strong source of NH_3 emissions as well as a large surface for the deposition of acid aerosols [16]. However, more studies are needed to understand the kinetics and mechanisms in controlling the apportionment of various species in acid aerosols in Taipei.

Acknowledgements

We would like to thank the support of the Taiwan Environmental Protection Agency (contract No. EPA-82-E3F1-09-01) in funding this study. We would especially like to thank all the participants who allowed us to measure acid aerosols in their homes.

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