Concentrations of ambient air particulates (TSP, PM$_{2.5}$ and PM$_{2.5-10}$) and ionic species at offshore areas near Taiwan Strait

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Abstract

The concentrations of total suspended particulate (TSP), fine particles PM$_{2.5}$ (with aerodynamic diameter <2.5 μm), coarse particles PM$_{2.5-10}$ (with aerodynamic diameter 2.5–10 μm,), and water-soluble inorganic ions were studied at two offshore sampling sites, Taichung Harbor (TH) and Wuci Traffic (WT), near Taiwan Strait in central Taiwan during March 2004 to January 2005. Statistical analyses were also carried out to estimate the possible sources of particulate pollution.

Experimental results showed that the average mass concentrations of TSP, PM$_{2.5}$ and PM$_{2.5-10}$ at TH and WT sampling sites were 154.54 ± 31.45 and 113.59 ± 31.94 μg m^{-3}, 54.03 ± 16.92 and 42.76 ± 12.52 μg m^{-3}, and 30.31 ± 9.79 and 24.16 ± 7.27 μg m^{-3}, respectively. The dominant inorganic ions at two sampling sites were SO$_4{}^{2-}$, NO$_3{}^-$, and NH$_4{}^+$ for TSP and PM$_{2.5}$, but that were Ca^{2+}, Cl$^-$, and Na$^+$ for PM$_{2.5-10}$. The concentrations of most particulates and inorganic ions were higher in winter at both two sampling sites, and were higher at TH than WT sampling site in each season. From statistical analysis, air-slake of crust surface, sea-salt aerosols, agriculture activities, coal combustion, and mobile vehicles were the possible emission sources of particulate pollution at TH and WT sampling sites.
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Keywords: TSP; PM$_{2.5}$; PM$_{2.5-10}$; Water-soluble; Ion

1. Introduction

The pollution of suspended particle in ambient air has become a serious problem in Taiwan recently. Air pollutants emitted from the anthropogenesis in Asia increase drastically in the past decade [1]. PM$_{2.5}$ is recognized as an important indicator for the fine particulates, which have adverse health consequences to the lower respiratory tract. These fine particles are easily retained in the alveolar walls, producing possible allergies, asthma and lung emphysema [2–4]. Although most of the PM$_{2.5}$ in the air in central Taiwan originates from fuel combustion and secondary aerosol formation, a substantial fraction is still contributed by fugitive dust from roads, construction, dry lakebeds, and disturbed grounds. In view of the fact that vehicular emissions represent a major source of fine particles in urban, chemical characterizations and sources identifications for the PM$_{2.5}$ are more useful for assessing the healthy risk and planning effective control strategies.

The coastal atmosphere adjacent to large urban and industrial centers can be strongly impacted by the emissions of air pollutants [5–10]. The airborne pollutants include the ionic species, such as sulfate, nitrate, and ammonium, etc., associated with suspended particulates from various pollution sources. High concentrations of certain ionic species in the airborne particles of coastal air could not only enhance the air-to-sea ionic deposition fluxes to coastal waters, consequently affect the coastal ecosystem [11], but could also be transported over the open ocean and affect the compositions of remote marine atmosphere. In addition, high concentrations of airborne ionic species seriously influence the air quality and human health. Fine particles produced predominantly from high-temperature sources or gas-to-particle conversion processes within the atmosphere. The major components of PM$_{2.5}$ were sulfate (SO$_4{}^{2-}$), nitrate (NO$_3{}^-$), ammonia (NH$_4{}^+$), organic carbon (OC), and elemental carbon (EC) [12,13]. Sulfate, nitrate, and ammonium are the most common components of secondary particles in the

atmosphere. These particles are usually formed from the direct emissions of sulfur dioxides (SO_2), nitrogen oxides (NO_x), and ammonia (NH_3) gases in the atmosphere. The chemical transformation and equilibrium processes for inorganic secondary aerosols have been extensively studied. The stain of building is mainly caused by the deposition of particles, particularly is the soot; while the deterioration of building is due to the corrosion, oxidation of acidic depositions, and the conversions of building materials into more water-soluble ones [14,15]. Sulfur dioxide (SO_2) and nitrogen oxides (NO and NO_2) in the atmosphere are the major contributors to the acidification.

The health-related findings of these studies were associated with either the total mass concentration of suspended particles or the mass concentration of particles with aerodynamic diameters smaller than 10 μm (PM_{10}) or smaller than 2.5–10 μm ($PM_{2.5-10}$). Considering the human health risk to airborne pollutants, the most important is the exposure to fine airborne particles of $PM_{2.5}$, sub-micrometer particles (smaller than 1 μm), and ultra-fine particles (smaller than 0.1 μm) [16]. This is why the PM_{10} and $PM_{2.5}$ measurements are included in the ambient air quality standards of United States (US-EPA, 1987 for PM_{10}; 1996 for $PM_{2.5}$).

The objectives of this study are to measure the total particulate mass and ionic (anion and cation) species in TSP, $PM_{2.5}$, and $PM_{2.5-10}$ at offshore sampling sites, Taichung Harbor (TH), Wuci Traffic (WT), near the Taiwan Strait in central Taiwan. In addition, the distributions and emission sources of different air pollution in such complex areas were also investigated.

2. Experimental

2.1. Sampling sites and meteorological conditions

Two sampling sites were selected to characterize the ionic species concentrations in central Taiwan. Atmospheric particulates were collected by PS-1 and Universal samplers at Taichung Harbor and Wuchi Traffic 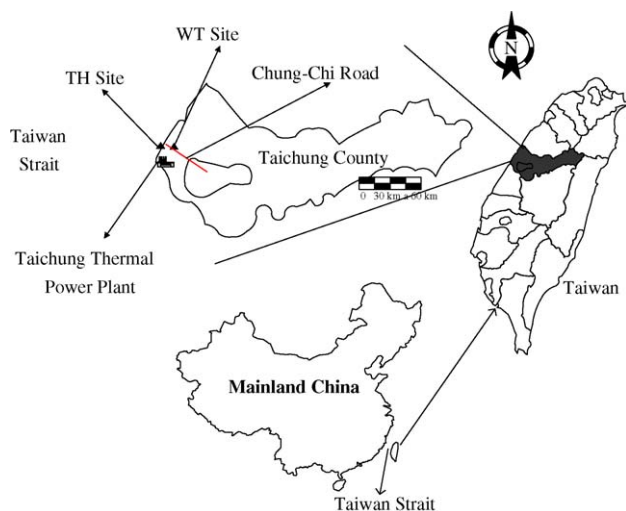sites simultaneously (Fig. 1). Twenty-four hours sequential samplings for PAHs in ambient air were performed between February 2004 and January 2005. Wind speed and direction, barometric pressure and relative humidity (RH) were recorded using a Weather Monitor II (#7440).

Taichung Harbor is located in the western side of central Taiwan. It occupies about 1540 ha, which include 390 ha water and 1150 ha land. Taichung Harbor is an artificial harbor and has up to 83 ports. The sampling site for this study was located at the chemical port area, which is about 400 m on the east side of Taiwan Strait. The sampling height of this sampling site was about 10 m. It was also the highest building in this region. In addition, Taichung Thermal Power Plant (TTPP) occupies a site of 281 ha located along the coast about 15 km south of the sampling site. It is a coal-combustion TPP supplying about 4400 MW electricity to central Taiwan. It is located southeast (about 15 km) of TH and southwest (about 12 km) of WT sampling sites.

Table 1 showed the meteorological information at TH and WT sites during the sampling period in this study. The average temperature, relative humidity, wind speed and atmospheric pressure were $24.60 \pm 5.14\,°C$, $73 \pm 4\%$, $7.15 \pm 2.58\,m\,s^{-1}$ and $1010.38 \pm 4.85\,hPa$, respectively. The seasonal prevailing wind directions of spring, summer, autumn, and winter were NE, SWW, NE, and NNW.

2.2. PS-1 sampler

The PS-1 sampler (GPS1 PUF sampler, General Metal Work) consists of nine basic assemblies: dual chamber, sampling module, flow vent, electromagnetic gauge, voltage, elapsed time indicator, pump, 7-day skip timer, exhaust hose and aluminum shelter. The PS-1 sampler is a complete air sampling system designed to simultaneously collect suspended airborne particles at flow rates up to $280\,L\,min^{-1}$ and the flow rate was controlled at $200\,L\,min^{-1}$ in this study. The quartz filters (10.2 cm in diameter) were used to catch the suspended particles in the study, and were first conditioned for 24 h in an electronic desiccator at humidity $50 \pm 5\%$ and temperature $25 \pm 5\,°C$ prior to weighting both before and after exposure. Filters were placed in a sealed CD box during transport and storage. An analytical balance (AND GR-202) with a reading precision of 0.01 mg was used to measure the ambient air particulate mass.

2.3. Universal sampler

The Model 310 Universal Air Sampler[TM] (UAS[TM]) is a general-purpose air sampler for TM atmospheric aerosol sampling and for mass concentration, and organic or inorganic analysis. The sampler has a design inlet sampling flow rate of $300\,L\,min^{-1}$. The sampler is provided with an omni-directional inlet, a PM10 virtual impactor classifier, a fine particle filter and a PUF sampler. This allows operation as a high volume dichotomous sampler for size fractionation of airborne particles in the 0–2.5 and 2.5–10 μm aerodynamic size range. Air is sampled at $300\,L\,min^{-1}$ (10.6 acfm) from the ambient atmosphere through an omni-directional, cylindrical inlet. Particles greater

Fig. 1. Locations of offshore sampling sites, Taichung Harbor (TH) and Wuci Traffic (WT), near Taiwan Strait in central Taiwan.

Table 1
Mass concentrations of particulates ($\mu g \, m^{-3}$) and meteorological conditions at TH and WT sampling sites during March 2004 to January 2005

Sample date	Sample no.	TH[a]			WT[b]			T^c (°C)	RH[d] (%)	WS[e] (m s^{-1})	PWD[f]	P^g (hpa)
		TSP	PM$_{2.5}$	PM$_{2.5-10}$	TSP	PM$_{2.5}$	PM$_{2.5-10}$					
3, 4 March	1	184.78	84.59	40.75	166.70	62.61	31.95	19.6	75	10.8	NNE	1021.7
16, 17 March	2	210.94	97.48	45.87	171.63	66.48	37.46	18.4	71	11.3	NE	1018.6
18, 19 March	3	152.25	92.81	41.65	135.59	63.21	30.49	19.0	70	12.2	NNE	1017.5
24, 25 March	4	198.21	74.29	31.85	152.31	55.31	29.42	18.5	72	12.7	NE	1012.6
8, 9 April	5	209.59	65.87	33.59	168.23	65.26	38.20	20.6	74	10.2	NW	1007.5
11, 12 April	6	157.59	77.29	39.36	129.42	79.85	41.43	22.4	76	8.6	NNW	1010.2
20, 21 April	7	146.56	75.51	51.82	101.12	62.29	37.73	21.9	74	7.4	NW	1011.6
7, 8 May	8	164.59	67.32	40.85	100.25	58.81	33.26	23.5	77	8.2	NNW	1005.8
12, 13 May	9	155.56	69.78	39.59	97.28	45.10	24.92	24.1	74	5.1	N	1001.9
24, 25 May	10	161.75	77.26	31.85	104.85	40.27	23.42	25.6	76	7.3	N	1010.5
9, 10 June	11	112.87	50.48	27.89	82.55	47.48	29.13	27.8	69	7.5	NNE	1012.2
17, 18 June	12	148.21	61.35	26.18	97.16	50.42	28.19	27.5	70	6.2	NNE	1011.8
21, 22 June	13	169.56	63.62	37.26	74.38	42.85	28.16	27.1	71	4.3	NE	1008.4
8, 9 July	14	92.45	45.44	13.54	71.72	51.05	27.90	29.3	78	3.6	NNE	999.5
13, 14 July	15	105.78	30.45	11.45	75.86	45.13	24.10	29.7	76	4.9	NE	1003.7
28, 29 July	16	107.30	45.26	25.43	65.82	30.85	14.32	30.1	75	4.5	NE	1013.2
6, 7 August	17	100.67	43.85	10.76	72.93	36.25	17.58	30.8	79	5.1	SW	1011.4
9, 10 August	18	89.86	32.14	9.36	76.85	38.41	20.08	29.5	80	6.2	SWW	1012.8
18, 19 August	19	102.45	30.25	17.19	65.20	35.22	21.64	29.8	78	5.7	SW	1012.5
23, 24 August	20	112.31	35.85	14.87	89.57	46.25	22.18	28.6	79	4.8	SWW	1010.7
3, 4 September	21	142.85	36.89	22.78	78.16	31.42	16.5	27.1	72	5.1	SWW	1007.1
17, 18 September	22	126.31	33.65	17.97	81.26	27.65	11.97	27.8	75	7.6	SW	1003.6
17, 18 September	23	163.86	38.75	16.58	79.24	25.42	12.58	26.7	72	6.9	SW	1008.4
4, 5 October	24	151.25	31.92	16.3	85.11	28.57	15.8	26.4	75	7.1	NNE	1010.5
18, 19 October	25	147.84	38.59	22.66	93.45	29.4	12.61	22.8	70	6.7	NNE	1011
23, 24 October	26	175.42	42.73	18.94	125.92	38.45	20.1	24.2	70	5.3	N	1011.6
25, 26 October	27	155.71	34.45	23.89	103.64	31.14	13.74	23.3	73	8.3	N	1009.8
3, 4 November	28	163.37	48.24	21.3	115.58	37.94	17.51	21.8	67	5.3	ENE	1014.3
5, 6 November	29	187.73	34.36	21.76	121.42	36.68	19.27	22.7	70	6.2	NE	1011.2
8, 9 November	30	140.76	46.3	25	166.70	41.49	27.85	21.4	69	6.4	NE	1010
6, 7 December	31	179.32	58.23	37.4	171.63	57.14	23.17	18.6	74	5.3	N	1013.5
8, 9 December	32	181.23	64.57	37.83	135.59	75.86	24.63	19.2	78	6.2	NE	1015.2
14, 15 December	33	152.65	67.85	36.19	142.75	68.7	23.7	18.3	76	4.3	NNE	1018.5
21, 22 December	34	164.87	59.12	34.75	152.33	63.26	34.42	19.4	81	5.7	N	1014.2
23, 24 December	35	195.71	76.36	29.63	137.74	75.1	30.67	19.7	79	6.2	NNW	1015.6
28, 29 December	36	172.54	71.32	37.15	147.85	68.53	36.87	13.4	77	7.5	NNE	1014.8
30, 31 December	37	169.92	68.73	35.56	161.92	65.19	28.32	12.1	75	9.4	NE	1015.4
1, 2 January	38	164.23	72.26	41.41	177.74	61.25	33.28	9.6	68	8.1	N	1022.6
4, 5 January	39	172.67	68.61	38.5	147.85	75.47	39.64	16.5	76	6.2	NNW	1016.8
6, 7 January	40	189.94	77.18	35.75	161.92	68.52	37.13	17.8	78	8.4	NNW	1015.2
Average		154.54	54.03	30.31	113.39	42.76	24.16	24.60	73	7.15	–	1010.38
S.D.		31.45	16.92	9.79	31.94	12.52	7.27	5.14	4	2.58	–	4.85

[a] Taichung Harbor sampling site.
[b] Wuci Traffic sampling site.
[c] Temperature.
[d] Relative humidity.
[e] Wind speed.
[f] Prevalent wind direction.
[g] Atmospheric pressure.

than 10 μm aerodynamic equivalent diameter are removed from the sampled air stream by the PM$_{10}$ classifier and discarded. Particle less than 10 μm flow to the PM$_{2.5}$ classifier located downstream. Particles in the 2.5–10 μm range are collected on a 62 mm × 165 mm filter and those smaller than 2.5 μm are collected on a 200 mm × 250 mm final filter. The filtered air stream is then directed through the PUF sampler to collect the volatile organic compounds in the filtered air stream.

2.4. Chemical analysis

After sampling, all filters were put into 200 mL bottles and immersed in distilled-deionized water. The bottles were sent to ultrasonic process for about 120 min and then diluted to 30 mL with distilled-deionized water. Ion Chromatography (DIONEX-100) was used to analyze the water-soluble ions (Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Ca^{2+}, and Mg^{2+}) in the samples.

2.5. Quality control

2.5.1. Blank test

Background contamination was routinely monitored by using operational blanks (unexposed filters), which were processed simultaneously with field samples. The results of the blank test in this study were 0.20, 0.30, 0.20, 0.17, 0.15, 0.30 and 0.40 μg for Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+} and Ca^{2+}, respectively. The background contamination is insignificant and can be ignored.

2.5.2. Detection limit

The detection limit was used to determine the lowest concentration level that can be detected to be statistically different from a blank. The detection limits of ions were 0.010, 0.010, 0.010, 0.015, 0.021, 0.023 and 0.024 mg L^{-1} for Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+} and Ca^{2+}, respectively. The method detection limit (MDL) was determined from $3 \times S$, where S is the standard deviation (S) estimated from repeating the concentration slightly higher than the lowest concentration of standard line for 12 times.

3. Results and discussion

3.1. Concentrations of ambient air particulate

The average mass concentrations of TSP at TH and WT sampling sites were 154.54 ± 31.45 and 113.59 ± 31.94 μg m^{-3}, both of them were within the regulation limits (150–230 μg m^{-3}) of the World Health Organization (WHO). On the whole, the particulate mass concentrations at TH site were higher than that at WT site. Many sea droplets and salts were considered to be blown toward the Taichung Harbor. The average concentrations of PM$_{2.5}$ at TH and WT were 54.03 ± 16.92 and 42.76 ± 12.52 μg m^{-3}, and the average PM$_{2.5–10}$ concentrations at TH and WT were 30.31 ± 9.79 and 24.16 ± 7.27 μg m^{-3}, respectively. Fine particles (PM$_{2.5}$) were found to dominate the total suspended particles at offshore sampling sites (TH and WT) near the Taiwan Strait in central Taiwan. On the other hand, the TSP concentration measured in winter was 70% higher than that in the summer, because many agricultural activities (burning rice straw) were carried out in winter. Many farmers burned rice straw to fertilize the land for the coming year. Therefore, episode days were almost all observed in winter in central Taiwan [17].

3.2. Concentrations of water-soluble ions in TSP

The seasonal variation of water-soluble ionic components is shown in Fig. 2. A clear seasonal pattern for the concentrations of all water-soluble inorganic ions in TSP at both TH and WT sampling sites during March 2004 to January 2005 was observed. The concentrations of NH_4^+, NO_3^- and SO_4^{2-} were higher in winter and lower in summer at both two sites. The concentrations of NH_4^+, NO_3^- and SO_4^{2-} obtained at TH sampling site were higher than that at WT sampling site in each season. Statistical analysis of the average TSP concentration in each season for NH_4^+, NO_3^- and SO_4^{2-} at TH and WT sampling sites yielded a

T statistic of 11.27, 2.87, and 5.86, respectively, which is greater than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were not equal. A similar seasonal variation of NO_3^- was also observed in Qingdao (China), which was attributed to gas-to-particle conversion depending on the ambient temperature [18]. Because SO_4^{2-} is associated with the ambient gaseous SO_2, the higher levels of SO_4^{2-} in winter are much related to the increase of coal consumption (Taichung Thermal Power Plant) at this season. The mass ratio of $[NO_3^-]/[SO_4^{2-}]$ has been used as an indicator of the relative importance of stationary versus mobile sources of sulfur and nitrogen in the atmosphere [19,20]. Gasoline and diesel fuel contain 0.12 and 0.2% sulfur, the estimated ratios of SO_x to NO_x in the emission of gasoline and diesel fuel burning were 1:13 and 1:8, respectively [21]. Another study has also indicated that the sulfur content in coal was 1% and the estimated ratio of NO_x to SO_x is 1:2 from coal burning [20]. The ratios of $[NO_3^-]/[SO_4^{2-}]$ obtained in this study were 0.4 in winter, that was higher than that 0.28 in summer. The maximum ratio of $[NO_3^-]/[SO_4^{2-}]$ was occurred in December. This result was attributed to the ammonium nitrate volatilizing at higher air temperature in summer and the ratio was decreased. A similar phenomenon has also been reported by other studies [18]. In addition, the lower levels of NH_4^+ in summer might be closely associated with the higher pH values of TSP [22].

The seasonal concentrations of Ca^{2+} and Mg^{2+} did not show similar variations as those of NH_4^+, NO_3^- and SO_4^{2-}, indicating that they were from different sources. The T statistic of average TSP for Mg^{2+} and Ca^{2+} at two sampling sites were 1.18 and 0.03, respectively, which are lower than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were equal. Since Ca^{2+} and Mg^{2+} are typical crustal elements, the air-slake of earth's surface, which is mainly dependent on air temperature and rainfall should be the major contributor of TSP (The weather is hot and rainy in Taichung City during June–September.). This result was consistent with the previous study, which addressed the concentrations of Ca^{2+} and Mg^{2+} with the air-slake of the earth's surface were higher in summer and autumn than that in winter and spring [22].

The concentrations of Cl^- and Na^+ obtained at TH were higher than that at WT sampling site in each season. The T statistic of average TSP for Cl^- and Na^+ at two sampling sites were 8.59 and 2.98, respectively, which are greater than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were not equal. This result indicated that sea-salt aerosols were also contributors of TSP at offshore sampling sites (TH and WT) near the Taiwan Strait of central Taiwan.

3.3. Concentrations of water-soluble ions in PM$_{2.5}$

Fig. 3 showed the seasonal variation of water-soluble ions in PM$_{2.5}$. The results also showed the major soluble inorganic species were NH_4^+, NO_3^- and SO_4^{2-}, and their concentrations at both TH and WT sampling sites were higher in winter and lower in summer. The concentrations of NH_4^+, NO_3^- and SO_4^{2-} obtained at TH were higher than that at WT sampling site in each season. Statistical analysis of average PM$_{2.5}$ concentration in each season for NH_4^+, NO_3^- and SO_4^{2-} at TH and
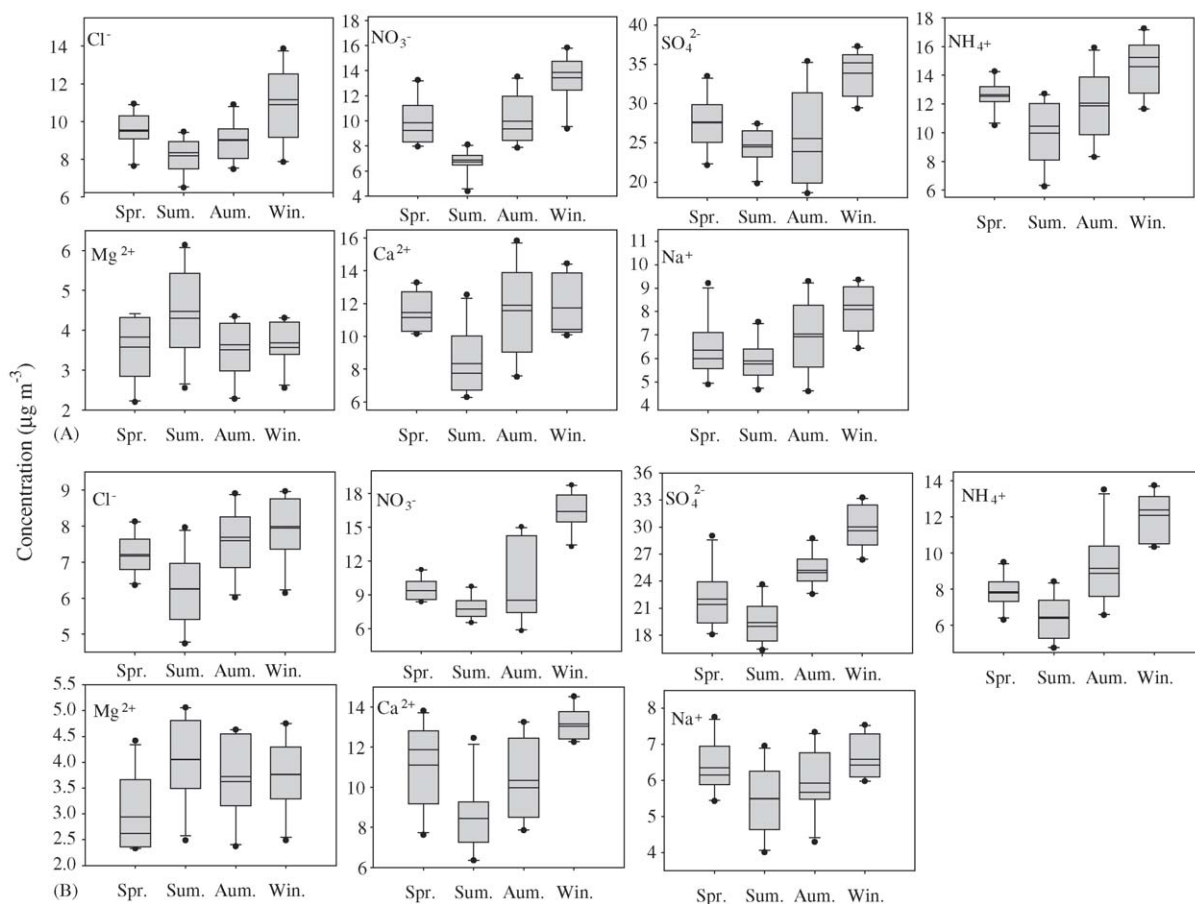
Fig. 2. Seasonal concentrations of water-soluble ions in TSP at: (A) TH; and (B) WT sampling sites during March 2004 to January 2005. The boundary of the box indicates the 25th and 75th percentile. The thin and thick lines within the box mark the median and the mean, respectively. Whiskers above and below the box indicate the 90th and 10th percentiles.

WT sampling sites yielded a T statistic of 8.43, 10.7, and 8.48, respectively, which is greater than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were not equal. Sulfate accounted for 47.51–51.58% (on average) of the total mass of inorganic ions, and nitrate accounted for 12.33–18.77%. The annual average concentrations of NO_3^- at TH and WT sites were 6.16 and 8.47 $\mu g\,m^{-3}$, and that of ammonium were 9.06 and 6.63 $\mu g\,m^{-3}$, respectively. The annual average ratio of $[NO_3^-]/[SO_4^{2-}]$ at TH and WT sites were 0.24 and 0.4, respectively. The measured ratios were similar with previous studies which ratios were 0.53–0.95 in Taichung city (about 60 km from TH and WT) [23] and 0.79–0.86 in Kaohsiung city (about 200 km from TH and WT) [24]. The low mass ratios of $[NO_3^-]/[SO_4^{2-}]$ suggested that stationary emissions were the important sources of $PM_{2.5}$ than vehicle emissions.

The annual average concentrations of Mg^{2+} and Ca^{2+} in $PM_{2.5}$ were 0.40 and 1.72 $\mu g\,m^{-3}$ at TH site and were 0.54 and 1.28 $\mu g\,m^{-3}$ at WT site. Mg^{2+} and Ca^{2+} accounted for 0.8–3.45% of the total mass of inorganic ions, respectively. The T statistic of average $PM_{2.5}$ for Mg^{2+} and Ca^{2+} at two sampling sites were 2.93 and 4.96, respectively, which are greater than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were not equal. Ca^{2+} and Mg^{2+} did not show the same seasonal

variations as those of NH_4^+, NO_3^- and SO_4^{2-}, indicating that they were from different sources.

The annual average concentrations of Cl^- and Na^+ in $PM_{2.5}$ were 2.73 and 4.12 $\mu g\,m^{-3}$ at TH site and were 2.33 and 4.44 $\mu g\,m^{-3}$ at WT site. Cl^- and Na^+ accounted for 5.16–9.83% of the total mass of the inorganic ions. Statistical analysis of average $PM_{2.5}$ concentration in each season for Cl^- at two sampling sites yielded a T statistic of 4.04, which is greater than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were not equal. However, the T statistic of average $PM_{2.5}$ for Na^+ at two sampling sites was -1.98 which is greater than $-t_{\alpha/2,39} = -2.021$, suggesting that the sample population means were equal. This implied that the major source of $PM_{2.5}$ was sea-salt. The concentrations of Cl^- and Na^+ at TH and WT sampling sites were both higher in winter and lower in summer. The concentrations of Cl^- and Na^+ obtained at TH were higher than that at WT sampling site in each season.

3.4. Concentrations of water-soluble ions in $PM_{2.5–10}$

The seasonal variation for water-soluble ions in $PM_{2.5–10}$ was shown in Fig. 4. The concentrations of NH_4^+, NO_3^- and SO_4^{2-} at TH and WT sampling sites were also higher in winter and
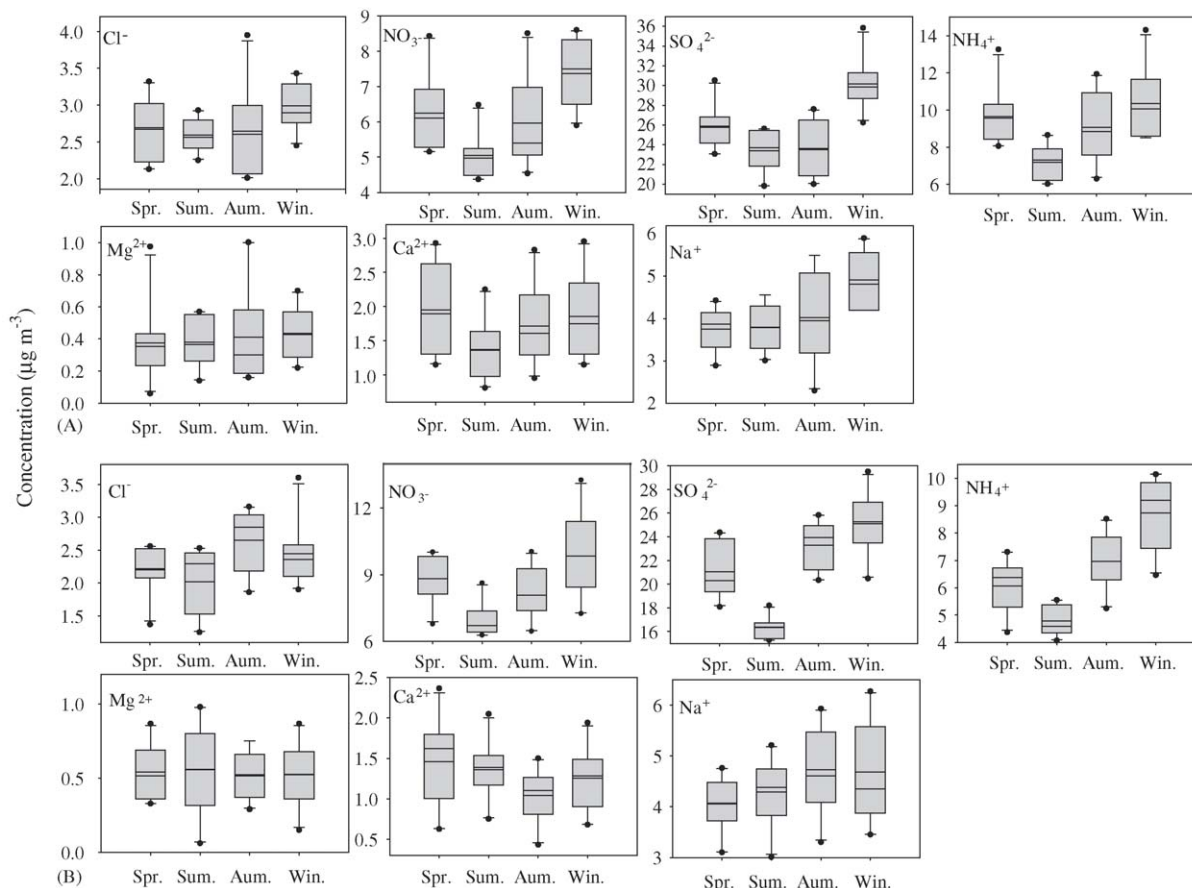
Fig. 3. Seasonal concentrations of water-soluble ions in PM$_{2.5}$ at: (A) TH; and (B) WT sampling sites during March 2004 to January 2005. The boundary of the box indicates the 25th and 75th percentile. The thin and thick lines within the box mark the median and the mean, respectively. Whiskers above and below the box indicate the 90th and 10th percentiles.

lower in summer. The concentration of NO$_3^-$ obtained at TH was higher than that at WT sampling site for each season. Statistical analysis of average PM$_{2.5-10}$ concentration in each season for NO$_3^-$ at two sampling sites yielded a T statistic of -8.98, which is lower than $-t_{\alpha/2,39} = -2.021$, suggesting that the sample population means were not equal. However, the T statistic of average PM$_{2.5-10}$ for NH$_4^+$ and SO$_4^{2-}$ at two sampling sites were 1.94 and 1.67, which is lower than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were equal. This implied that the possible sources of PM$_{2.5-10}$ were agriculture activities and coal combustion. In addition, sulfate accounted for 6.77–8.25% (on average) of the total mass of inorganic ions, and nitrate accounted for 18.13–27.34%. The annual average concentrations of NO$_3^-$ at the two sampling sites were 6.04 and 8.47 µg m^{-3}, and that of ammonium were 2.81 and 2.59 µg m^{-3}, respectively. The annual average ratio of [NO$_3^-$]/[SO$_4^{2-}$] at TH and WT sites were 2.20 and 4.04, respectively. The measured ratios were also similar with previous studies which ratios were 1.3–4.2 in Taichung city (about 60 km from TH and WT) [23] and 0.76–0.99 in Kaohsiung city (about 180 km from TH and WT) [24].

The annual average concentration of Mg^{2+} and Ca^{2+} in PM$_{2.5-10}$ were 3.48 and 9.46 µg m^{-3} at TH site and were 3.39 and 8.51 µg m^{-3} at WT site. Mg^{2+} and Ca^{2+} accounted for

10.44–28.39% of the total mass of inorganic ions. The T statistic of average PM$_{2.5-10}$ for Mg^{2+} and Ca^{2+} at two sampling sites were 0.52 and 1.79, respectively, which are lower than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were equal. This implied that the possible sources of PM$_{2.5-10}$ were air-slake of crust surface. Ca^{2+} and Mg^{2+} did not show the same seasonal variations as those of NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$, indicating that they were from different sources.

The annual average concentrations of Cl$^-$ and Na$^+$ in PM$_{2.5-10}$ were 5.59 and 3.20 µg m^{-3} at TH site and were 3.80 and 3.08 µg m^{-3} at WT site. Cl$^-$ and Na$^+$ accounted for 9.50–16.70% of the total mass of the inorganic ions. Statistical analysis of average PM$_{2.5}$ concentration in each season for Cl$^-$ at the two sampling sites yielded a T statistic of 14.65, which is greater than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were not equal. However, the T statistic of average PM$_{2.5-10}$ for Na$^+$ at two sampling sites was 0.56, which is lower than $t_{\alpha/2,39} = 2.021$, suggesting that the sample population means were equal. This implied that the possible sources of PM$_{2.5-10}$ were sea-salt aerosols. The concentrations of Cl$^-$ and Na$^+$ at TH and WT sampling sites were both higher in the winter and lower in summer. The concentrations of Cl$^-$ and Na$^+$ obtained at TH sampling site was higher than that at WT sampling site in each season.
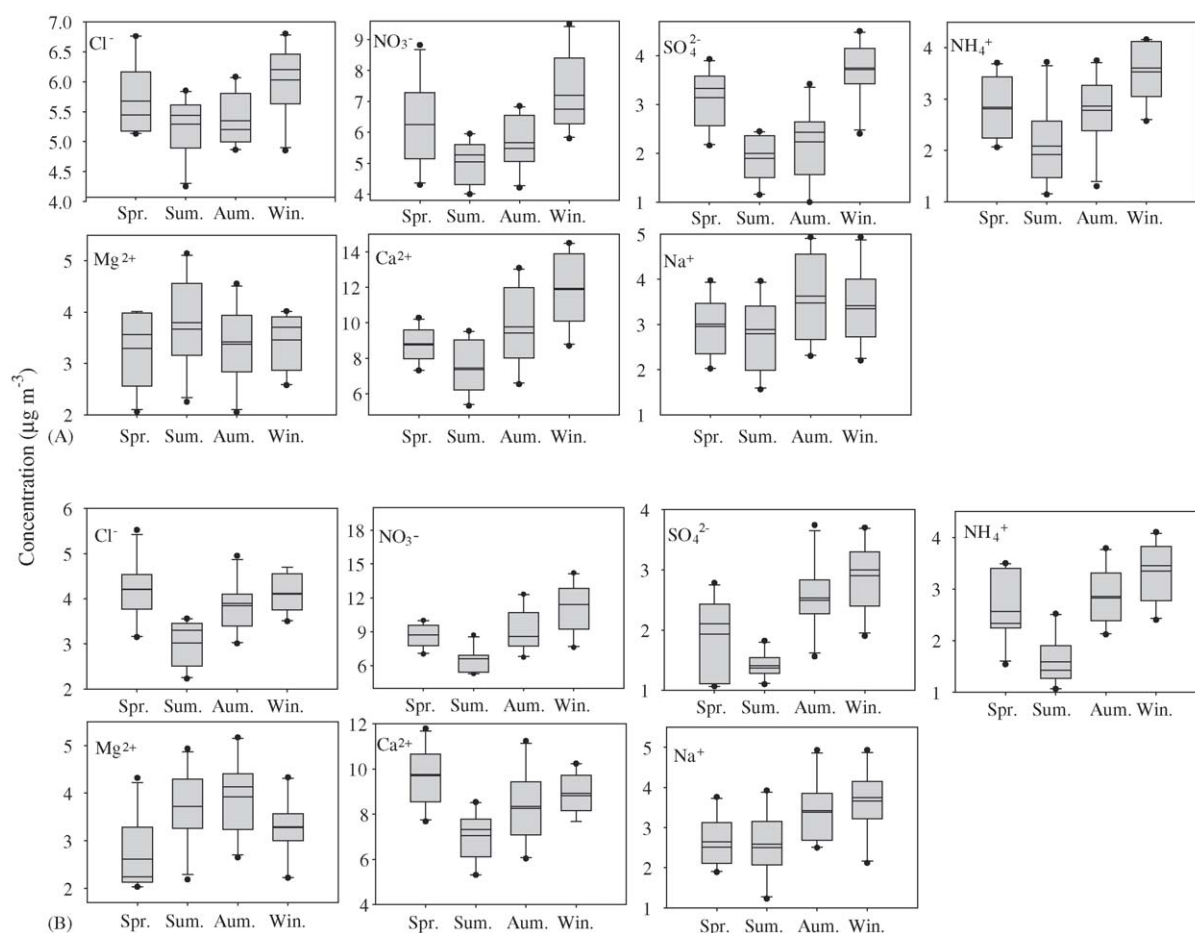
Fig. 4. Seasonal concentrations of water-soluble ions in PM$_{2.5-10}$ at: (A) TH; and (B) WT sampling sites during March 2004 to January 2005. The boundary of the box indicates the 25th and 75th percentile. The thin and thick lines within the box mark the median and the mean, respectively. Whiskers above and below the box indicate the 90th and 10th percentiles.

4. Conclusion

The average mass concentrations of TSP, PM$_{2.5}$ and PM$_{2.5-10}$ at TH and WT sampling sites were 154.54 ± 31.45 and $113.59 \pm 31.94\,\mu g\,m^{-3}$, 54.03 ± 16.92 and $42.76 \pm 12.52\,\mu g\,m^{-3}$, and 30.31 ± 9.79 and $24.16 \pm 7.27\,\mu g\,m^{-3}$, respectively. Fine particles (PM$_{2.5}$) dominated the TSP at offshore sampling sites near the Taiwan Strait in central Taiwan. The concentrations of TSP, PM$_{2.5}$ and PM$_{2.5-10}$ at TH site were all higher than that at WT site. The concentrations of TSP measured in winter were 70% higher than that in summer due to the agricultural activities (burning rice straw) in winter.

The dominant inorganic ions at two sampling sites were SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ for TSP and PM$_{2.5}$, but that were Ca^{2+}, Cl$^-$, and Na$^+$ for PM$_{2.5-10}$. The concentrations of most inorganic ions were higher in winter at both two sampling sites, and were higher at TH than WT sampling site in each season. From statistical analysis, the population of TSP was equal to Ca^{2+} and Mg^{2+}. The air-slake of crust surface and sea-salt aerosols were considered to be the major contributors of TSP at offshore sampling sites (TH and WT) near the Taiwan Strait of central Taiwan. Statistical analyses also indicated that the population of PM$_{2.5}$ was equal to Na$^+$, the major source of PM$_{2.5}$ was sea-salt

aerosols; and that of PM$_{2.5-10}$ was equal to NH^{4+}, SO$_4^{2-}$, Ca^{2+}, Mg^{2+} and Na$^+$, the major sources of PM$_{2.5-10}$ were agriculture activities, coal combustion, and sea-salt aerosols.

From estimating the ratios of [NO$_3^-$]/[SO$_4^{2-}$], the particulates were emitted mainly by stationary sources in winter and by mobile sources in summer at WT sampling site; however, the particulates were emitted mainly by stationary sources for each season at TH sampling site.

Acknowledgements

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