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Empirical Models to Predict Parsimoniously the Mass and Number Concentrations of Ultrafine Particulate in Ambient Atmosphere

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Abstract The main objective of this study was to develop parsimonious empirical models for predicting the mass and number concentrations of ultrafine particulate (UFP, aerodynamic diameter < 0.1 or 0.18 μm) in the atmospheric environment. We found strong correlations existed between the mass/number concentration of UFP and the mass concentration of $PM_{2.5}$ (aerodynamic diameter < 2.5 μm) by fitting the experimental data. Therefore, we were easily able to obtain UFP mass and number concentrations by using the presented empirical models. The empirical equations should be used with care since limitations existed.

Keywords Ultrafine particulate (UFP) · $PM_{2.5}$ · Mass and number concentrations

There have been many cohort studies documenting adverse health outcomes related to particulate air pollution with total suspended particulate of aerodynamic diameter (d_a) < 100 μm, PM_{10} (d_a < 10 μm), $PM_{2.5}$ (d_a < 2.5 μm), and ultrafine particulate (UFP, d_a < 0.1 or 0.18 μm) (Samet et al. 2000; Ibald-Mulli et al. 2002). Evidence from epidemiological studies indicates that ambient particulate, especially UFP, is significantly correlated with adverse health effects, including lung inflammation, chronic bronchitis, airway obstruction, heart attacks, stroke, heart rhythm disturbances, and sudden death (Nel 2005). In order to evaluate the effects on human health of UFP (or nanoparticulate, NP) in ambient and occupational environments, a new discipline of nanotoxicology has been formulated (Oberdörster et al. 2005; Nel et al. 2006). The related issues of how UFP/NP acts within and impacts upon the environment have been discussed intensively in recent years (Maynard and Kuempel 2005). Many studies have indicated that the number concentration and surface area of UFP are more significant than its mass concentration (Oberdörster et al. 2005; Nel et al. 2006).

In the past decade, PM_{10} and $PM_{2.5}$ mass concentrations have been frequently and widely measured in Taiwan. But only few studies (Hung and Wang 2001; Lin et al. 2005; Fang et al. 2006, Chio et al. 2007) have focused on UFP/NP and its impact on environment and health. The major reason for this is that UFP/NP measurement needs precise sizing technologies and financial funding. Hence, the purpose of this study was to develop and present a useful empirical equation that enables the prediction of mass and number concentrations at the ultrafine- or nano-size particulate levels from existing $PM_{2.5}$ mass concentrations in the atmospheric environment.

Materials and Methods

Two datasets were utilized to assess the mass and number concentrations of UFP. Chio (2005) conducted an experiment to measure the mass concentrations of $PM_{2.5}$, PM_1 (d_a < 1 μm), and $PM_{0.18}$ (d_a < 0.18 μm or 180 nm) from

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Table 1 Original data of last six stages from MOUDI sampler

d_a^a (μm)	Sample number (mass unit as μg m^{-3})										Mean[b]	SD[b]
	1	2	3	4	5	6	7	8	9	10		
Non-episodic days ($N = 10$)												
3.2	1.78	3.80	5.40	15.69	6.11	2.84	3.75	3.55	3.94	4.37	5.12	3.90
1.8	1.33	4.74	9.62	11.11	4.83	5.44	4.25	7.81	6.48	5.09	6.07	2.82
1.0	2.00	5.93	11.73	20.26	5.60	7.33	4.50	8.75	10.88	6.07	8.31	5.11
0.56	0.67	3.56	7.74	14.38	7.12	4.73	5.01	5.20	6.71	5.34	6.05	3.54
0.32	1.56	4.51	7.98	13.07	3.56	4.73	2.75	3.55	4.40	2.67	4.88	3.35
0.18	3.11	4.74	7.27	10.46	6.11	5.44	3.00	3.08	8.33	3.64	5.52	2.54
Biomass burning episodic days ($N = 4$)												
3.2	11.67	17.64	12.53	14.06							13.97	2.64
1.8	34.76	42.44	35.37	26.42							34.75	6.55
1.0	38.57	43.16	33.41	20.61							33.94	9.74
0.56	25.71	28.14	19.90	13.33							21.77	6.60
0.32	16.19	9.30	6.39	7.03							9.73	4.49
0.18	2.86	4.77	2.46	0.97							2.76	1.56

[a] d_a denotes the cut aerodynamic diameter of each stage in MOUDI sampler

[b] Mean and SD denote the mean value and standard deviation of samples, respectively

late summer to early winter in 1998 using a Micro-Orifice Uniform Deposition Impactor (MOUDI, MSP model 100) in Taichung, Taiwan. The details of sampling, weighing and elemental analyses are described in the previous work (Chio et al. 2004). The number of samples used in the Taichung urban area was 14 (Table 1). Ten were taken on non-episodic days and four during biomass burning episodic days. In the present study, $PM_{2.5}$ mass concentrations were derived from the total masses under 1.8 μm of cut diameter (the second to sixth row in Table 1) plus half of the mass in the range 1.8–3.2 μm of cut diameter (the first row in Table 1). Mass concentrations of PM_1 (the third to sixth row) and $PM_{0.18}$ (the last row) can be obtained from Table 1.

Number concentration was modeled from the AirCARE1 program conducted in SW Detroit (Keeler et al. 2005). AirCARE1 was designed and constructed collaboratively by Michigan State University and the University of Michigan to study the effects of air pollution on human health. Extensive measurements of ambient PM were performed in SW Detroit in a custom-designed mobile air research laboratory during the five summer periods from 2000 to 2004 (Morishita et al. 2004; Keeler et al. 2005). $PM_{2.5}$ samples were collected using an annular denuder filter pack system to gather the acidic gaseous species and inorganic fine particulate ions. A scanning mobility particle sizer (SMPS, TSI model 3936) system measured 5-min average concentrations of sub-micrometer aerosols in the range 20–800 nm in diameter. In the present study, we focused on the $PM_{2.5}$ mass concentrations and the number concentrations of UFP via an analysis of forty-eight of the samples.

We reanalyzed two datasets mentioned above. The mass concentration data collected using a MOUDI was quantified and classified as general and episodic events for $PM_{2.5}$, PM_1 and $PM_{0.18}$ (refer to UFP). The original AirCARE1 data was divided into several groups of specified ranges of the independent variable (mass concentration of $PM_{2.5}$), and the dependent variable (number concentration of UFP) was grouped simultaneously. Subsequently, a regression analysis can be carried out based on the grouping data.

Results and Discussion

The reanalyzed series mass concentrations of $PM_{2.5}$, PM_1 and $PM_{0.18}$ measured by using a MOUDI, empirical equations were developed to allow the estimation of $PM_{0.18}$ mass concentration when both $PM_{2.5}$ and PM_1 are known. The equations obtained allow the estimation of $PM_{0.18}$ mass concentration during non-episodic and biomass burning episodic days (Table 2),

$$PM_{0.18} = 0.223PM_1 \text{ or } 0.165PM_{2.5} \quad \text{(for Non-episodic days)}, \tag{1}$$

$$PM_{0.18} = 0.041PM_1 \text{ or } 0.025PM_{2.5} \quad \text{(for Biomass burning episodic days)}. \tag{2}$$

Regressions were performed on the non-episodic and episodic PM_1 and $PM_{2.5}$ data to estimate the mass concentration of $PM_{0.18}$ and these estimations were compared with the original datasets. The coefficients

Table 2 Measured and estimated concentrations of $PM_{0.18}$ and their regression parameters

d_a (μm)[a]	Sample number (mass unit as μg m^{-3})										Mean[c]	SD[c]
	1	2	3	4	5	6	7	8	9	10		
Non-episodic days ($N = 10$)												
$PM_{2.5}$	9.56	25.39	47.03	77.12	30.28	29.08	21.40	30.16	38.77	24.99	33.38	18.30
PM_1	7.34	18.74	34.72	58.17	22.39	22.22	15.27	20.58	30.32	17.71	24.75	13.97
$PM_{0.18}$	3.11	4.74	7.27	10.46	6.11	5.44	3.00	3.08	8.33	3.64	5.52	2.54
UFP_{m1}[a]	1.58	4.19	7.76	12.73	5.00	4.80	3.53	4.98	6.40	4.12	5.51	3.02
(%)	32.6	18.7	15.5	13.6	20.2	18.7	14.0	10.2	21.5	14.6	16.5	
UFP_{m2}[a]	1.64	4.18	7.74	12.97	4.99	4.96	3.53	4.59	6.76	3.95	5.52	3.11
(%)	42.4	25.3	20.9	18.0	27.3	24.5	19.7	14.9	27.5	20.5	22.3	
Regression parameters: $UFP_{m1} = 0.165 \times PM_{2.5}$; $UFP_{m1} = 1.06 \times PM_{0.18} - 0.32$, $R^2 = 0.79$												
$UFP_{m2} = 0.223 \times PM_1$; $UFP_{m2} = 1.12 \times PM_{0.18} - 0.66$, $R^2 = 0.83$												
Biomass burning episodic days ($N = 4$)												
$PM_{2.5}$	123.9	136.6	103.8	75.4							109.9	26.70
PM_1	83.33	85.36	62.15	41.94							68.19	20.41
$PM_{0.18}$	2.86	4.77	2.46	0.97							2.76	1.56
UFP^{b}_{m3}	3.10	3.42	2.59	1.88							2.75	0.67
(%)	2.3	3.5	2.4	1.3							2.5	
UFP^{b}_{m4}	3.42	3.50	2.59	1.88							2.80	0.76
(%)	3.4	5.6	4.0	2.3							4.1	
Regression parameters: $UFP_{m3} = 0.025 \times PM_{2.5}$; $UFP_{m3} = 0.40 \times PM_{0.18} + 1.63$, $R^2 = 0.90$												
$UFP_{m4} = 0.041 \times PM_1$; $UFP_{m4} = 0.47 \times PM_{0.18} + 1.45$, $R^2 = 0.78$												

[a] UFP_{m1} and UFP_{m2} denote the modeled (1 and 2) UFP ($PM_{0.18}$) mass concentrations using $PM_{2.5}$ and PM_1 measured during non-episodic days, respectively

[b] UFP_{m3} and UFP_{m4} denote the modeled (3 and 4) UFP ($PM_{0.18}$) mass concentrations using $PM_{2.5}$ and PM_1 measured during biomass burning episodic days, respectively

[c] Mean and SD denote the mean value and standard deviation of samples, respectively

applied in Eq. (1), 0.165 for $PM_{2.5}$ and 0.223 for PM_1 (models 1 and 2), were calculated statistically. Results show that these coefficients produced adequate estimated data ($R^2 = 0.79$–0.83, $N = 10$) for non-episodic days. The slope in the regression equation and the interception were closed to 1 and 0, respectively. For biomass burning episodic days, the estimated $PM_{0.18}$ data resulting from the coefficients applied (0.025 for $PM_{2.5}$ and 0.041 for PM_1, models 3 and 4), also fitted well ($R^2 = 0.78$–0.90) with the measured values (Eq. (2)). However, because they were obtained using only four samples and the regression parameters (slope and interception) were not good, these results were deemed inadmissible. Limitations of the regression equations include the necessity for at least one of the mass concentrations of $PM_{2.5}$ and PM_1 to be known. Also, the ratios of $PM_{0.18}$ to $PM_{2.5}$ and PM_1, respectively, would be varied and also be depended on nearby emission sources. In previous study (Ntziachristos et al. 2007) similar to the present one, the ratios of $PM_{0.18}$ to $PM_{2.5}$ were about 22.7–23.9% on sampling sites near a freeway, whereas Lin et al. (2005) reported that the ratio of $PM_{0.18}$ to $PM_{2.5}$ sampled near a heavily trafficked road was 48.8%. Additionally, Hung and Wang (2001) demonstrated that the ratio of $PM_{0.18}$ to PM_1 sampled from a sidewalk and underpass in Taipei ranged from 37.7 to 54.3%.

When we attempted to fit the relationship between UFP number concentration and $PM_{2.5}$ mass concentration, a scatter plot indicating a poor relationship ($N = 48$, $R^2 = 0.2274$) was obtained (Fig. 1a). We subsequently divided the $PM_{2.5}$ mass data into 4 groups (<20, 20–25, 25–30, and >30 μg m^{-3}) (Table 3) with sample sizes of 7, 17, 20 and 4, respectively. The mean values in the higher and lower $PM_{2.5}$ intervals were 16.80 ± 2.15 (mean ± SD) and 31.53 ± 1.15 μg m^{-3}. The UFP number concentrations were therefore also divided into four groups corresponding to $PM_{2.5}$ mass concentrations, and their mean values were 1.58 ± 0.47, 1.98 ± 0.55, 2.27 ± 0.64 and 2.30 ± 1.00 (10^4 cm^{-3}), respectively. The elevations of SD in group concentrations were associated with the elevations of corresponding mean values, and this can be easily observed. Through the data transformation, we were able to obtain an equation of good fit ($N = 4$, $R^2 = 0.9149$) to describe the relationship between $PM_{2.5}$ mass and UFP number concentrations (C_{UFP}) (Fig. 1b),

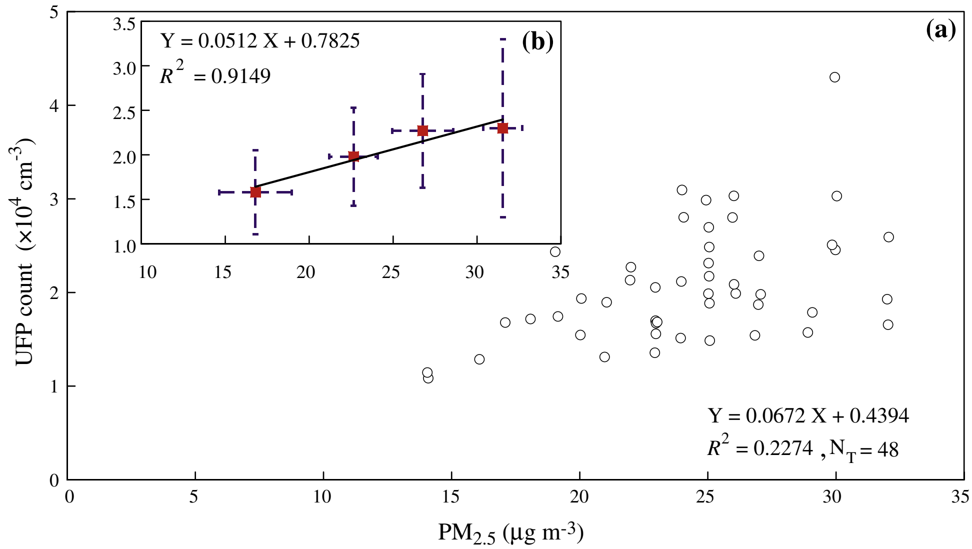

Fig. 1 The original (a) and treated (b) relationships between C_{UFP} and $PM_{2.5}$ mass concentration measured on 08/16/04 in SW Detroit. The $PM_{2.5}$ mass concentration and C_{UFP} were performed in X- and Y-axis, respectively

Table 3 Mean values and their standard deviations of $PM_{2.5}$ mass and UFP number concentrations in different $PM_{2.5}$ ranges

$PM_{2.5}$ range (μg m^{-3})	Samples	$PM_{2.5}$ mass concentration (X-axis, μg m^{-3})	UFP number concentration[a] (Y-axis, 10^4 # cm^{-3})
<20	7	16.80 (2.15, 12.8%)[b]	1.58 (0.47, 29.7%)
20–25	17	22.64 (1.43, 6.3%)	1.98 (0.55, 27.8%)
25–30	20	26.76 (1.82, 6.8%)	2.27 (0.64, 28.2%)
>30	4	31.53 (1.15, 3.6%)	2.30 (1.00, 43.5%)

[a] UFP number concentration (C_{UFP}) was counted for particle size less than 100 nm

[b] Mean (SD, RSD(%))

$$C_{UFP} = 0.051 PM_{2.5} + 0.783 (10^4 \text{ cm}^{-3}). \qquad (3)$$

The regression equation for UFP number concentration is applicable only when the $PM_{2.5}$ level is less than 35 μg m^{-3}. On the other hand, this estimation method for UFP number concentration is only suitable for use in clear air quality conditions. In comparison to the recent study in Los Angeles (Fruin et al. 2008), our predictions of UFP number concentrations, using Eq. (3), were about 8.5–40.6% lower than the measured data. Lack of precision was a problem when the $PM_{2.5}$ was outside the suitable range. In the future, we need more data to verify the usability of the regression equation.

By fitting the experimental data, we found that there was a strong correlation between the mass concentration of UFP and the mass concentration of $PM_{2.5}$. However, the regression equations should be used with care since limitations existed. On the other hand, we also predicted the number concentration of UFP estimated from the mass concentration of $PM_{2.5}$ in the atmospheric environment. These characteristics (mass and number concentrations) and even surface area could be used to assess UFP-induced health risk in the near future.

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