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Aerosol Wall Loss in Teflon Film Chambers Filled with Ambient Air

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Abstract

Aerosol wall loss is an important factor affecting smog chamber experiments, especially with chambers made of Teflon film. In this work, the aerosol wall loss was investigated in 2.5 and 5.8-m^3 cubic-shaped Teflon film chambers filled with ambient air. The natural change in the particle size distribution was measured using a scanning mobility particle sizer in a dark environment. The rate of aerosol wall loss was obtained from the deposition theory suggested by Crump and Seinfeld (1981). The measured rates of aerosol wall loss were in a good agreement with the theoretical and experimental values given by McMurry and Rader (1985), implying that the electrostatic effect enhances particle deposition on the chamber wall. The significance of aerosol wall loss correction was demonstrated with the photochemical reaction experiments using the ambient air.

Key words : Aerosol, Wall loss, Smog chamber, Teflon film, Ambient air

1. INTRODUCTION

Smog chambers have been used for investigating atmospheric photochemical and/or aqueous reactions. In general, the concentrations of gases and particles naturally decreased with time due to deposition on the chamber wall. In a vessel with an arbitrary shape, aerosols are transported toward the surface by convection, Brownian diffusion, gravitational sedimentation and electrostatic attraction (McMurry and Rader, 1985; Crump and Seinfeld, 1981). The wall loss of particles is an unintended and significant phenomenon in smog chamber experiments, especially using a Teflon film chamber, due to the electrostatic effect. There is static charge in a bag made of Teflon film, which enhances the wall deposition of charged particles that acquired their charge by collisions with ions existing in ambient air. Electrostatic transport has been reported to significantly affect the deposition rates of particles in the 50-1000-nm diameter range, and the wall loss rates of smaller particles are known to be dominated by Brownian diffusion (McMurry and Grosjean, 1985).

In analyses of smog chamber experiments, the wall loss of particles should be taken into account to discover a real phenomenon. Previous investigators have carried out theoretical predictions of particle deposition on the wall of a chamber or on a flat surface (Liu and Ahn, 1987; McMurry and Rader, 1985; Crump and Seinfeld, 1981). The wall loss has also been experimentally studied using monodi-

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sperse latex spheres, ambient aerosols or aerosols generated by photochemical reactions (Behnke *et al.*, 1988; McMurry and Grosjean, 1985).

In this work, the natural decay of particles was measured by using a scanning mobility particle sizer in Teflon film smog chambers filled with the ambient air. The wall loss rates, as a function of the particle size, were obtained based on the deposition theory in an arbitrary shaped vessel. The measured aerosol wall loss rates were compared with the theoretical and experimental values of McMurry and Rader (1985). The significance of aerosol wall loss correction was also demonstrated for photochemical reaction experiments using ambient air.

2. EXPERIMENTAL

An indoor smog chamber facility has been used for measuring the natural decay of ambient aerosols (Bae *et al.*, 2003). An outline of the smog chamber experiments on aerosol wall losses is summarized in Table 1. Two sizes of cubic-shaped bags, made of 2-mil (about 51 μm) thick FEP Teflon film, were used. One was small, 2.5 m^3 (1.35 × 1.35 × 1.35 m), for a single chamber experiment (Kim *et al.*, 2004), and the others were two large bags, 5.8 m^3 (1.8 × 1.8 × 1.8 m), for a twin-chamber experiment (Moon *et al.*, 2004). The surface-to-volume ratios of the small bag and two large bags were 4.4 and 3.3 m^{-1}, respectively.

Ambient air was introduced into a Teflon film bag in the morning after conditioning the bag by filling and exhausting ambient air three times. Under dark conditions the size distribution of particles within the range of 17-615 nm in a Teflon bag was measured for about four hours, using a scanning mobility particle sizer (SMPS, TSI model 3934U). For the twin-chamber experiment, the SMPS was switched to measure the particle size distributions of both chambers during the experiment.

Table 1. Outline of smog chamber experiments on aerosol wall losses.

Experiment	Single chamber	Twin chamber	
Chamber	Left	Left	Right
Bag size (m^3)	2.5	5.8	5.8
Date	August 21, 2002	July 31, 2003	July 31, 2003
Weather	Cloudy and foggy	Clear	Clear
Run time	10:06-13:44 (218 min)	11:35-15:26 (231 min)	11:41-15:42 (231 min)
Temperature (°C)/RH (%)	NM[1]/NM	24/75	24/79
Sample number (valid/total)	106/111	105/105	24/24
Initial NO/NO_2 (ppb)	16/18	0.3/49	0.3/49
Initial O_3 (ppb)	1	59	56
Initial N_p[2] (particles/cm^3)	8,085	9,723	9,486
Initial M_p[2] (μg/m^3)	18.3	22.6	24.6
Initial mean diameter (nm)	156	145	152

[1] Not measured, [2] Particles in the range of 20-300 nm.

3. RESULTS AND DISCUSSION

3.1 Aerosol wall loss

The typical change in the particle size distribution with time is shown in Figure 1 for the left chamber in the twin-chamber experiment. Here, the elapsed time starts just after the complete filling of ambient air into the 5.8-m^3 Teflon bags. The shape of the particle size distribution remained nearly unchanged; however, a natural decay in the particle number concentration was observed over the whole particle size range, which was due to the wall loss. A similar change in the particle size distribution in a 2.5-m^3 Teflon bag filled with ambient air was shown in our previous paper (Bae *et al.*, 2003).

Crump and Seinfeld (1981) described the wall deposition rate of particles in a vessel of arbitrary shape, as shown by Equation (1). This theory accounted for aerosol transport by convection, Brownian diffusion and gravitational sedimentation.

$$\frac{\partial N(D_p, t)}{\partial t} = -\beta(D_p) N(D_p, t) \quad (1)$$

where $N(D_p, t)$ is the number concentration of aerosols with diameter D_p at time t, and fractional loss rate, $\beta(D_p)$ is the wall deposition or wall loss rate. McMurry and Rader (1985) extended this

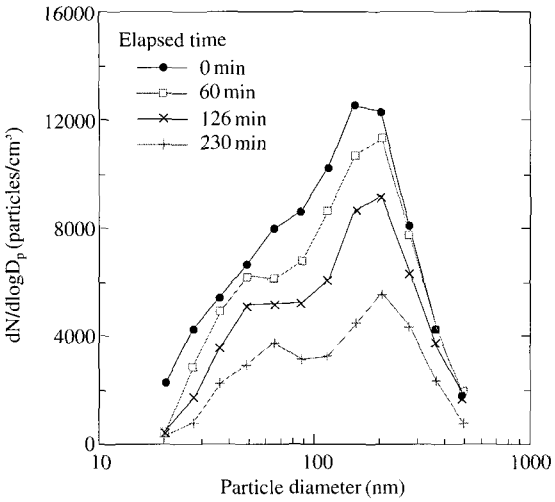

Fig. 1. Change in the particle size distribution due to the wall loss in a 5.8-m^3 Teflon film bag filled with ambient air.

theory to include electrostatic deposition caused in Teflon bags.

The SMPS provides size distribution data with 64-channel size resolution per decade. The raw size distribution data can be transformed to data sets of 4-, 8- and 16-channel size resolutions. For a 2.5-m^3 Teflon film bag, the natural decays in the number concentration for particles ranging 18-31, 57-98 and 20-300 nm in diameter are shown in Figure 2, together with normalized regression curves. The regression equation in the form of an exponential function for each particle size range was automatically derived using the Excel program. Comparing the regression equation for the above particle ranges with Equation (1), the wall loss rates were 1.6×10^{-4}, 6.5×10^{-5} and 8.4×10^{-5} sec^{-1}, respectively. The wall loss rate might be underestimated around initial state, as shown in Figure 2. The wall loss rate depends on the particle size, as shown in Equation (1). If the wall loss rate obtained with the size range 20-300 nm is applied to the chamber experimental data, the corrected values might be underestimated for particles in the size range 18-31 nm and overestimated for particles in the size range 57-98 nm in diameter.

For a 2.5-m^3 Teflon film bag, the wall loss rates as a function of particle size for three different size-channel resolutions are shown in Figure 3. The dependency of the size-channel resolution seems to be insignificant. In obtaining a regression curve, the coefficient of determination, R^2, increases with decreasing size-channel resolution. The range of R^2 for 4-channel resolution is 0.61-0.87, which is higher than the 0.50-0.80 for 8-channel resolution or the 0.37-0.68 for 16-channel resolution. This tendency was also found in 5.8-m^3 bag experiments. Therefore, the wall loss rate derived from 4-channel resolution data should be highly recommended.

Twin smog chamber experiments were conducted to find the effect of specific parameters, such as light intensity, initial aerosol concentration and toluene concentration, etc (Moon *et al.*, 2004). In our study, the twin chambers generally consisted of a left chamber filled with uncontrolled ambient air and a right chamber filled with controlled ambient air. However, uncontrolled ambient air was introduced into both chambers for natural decay experiments. The wall loss rates of the two large bags derived from 4-channel resolution data are shown in Figure 4 and listed in Table 2. In determining the wall loss rates for large chambers, the values of R^2 range from 0.93 to 0.99. The wall loss rates for the small bag seemed to be slightly higher than those for the large bags due to the differences in the surface-to-volume ratios.

Wall loss rates have been reported to vary with time as the charge distribution is time-dependent due to collisions with ions existing in ambient air (McMurry and Rader, 1985). Wall loss rates will theoretically decrease with time because charged particles are more rapidly deposited than neutral particles, and ion concentrations that cause charging of particles decrease with time (McMurry and Rader, 1985). The time-averaged wall loss rates of particles ranging from 20 nm to 300 nm for both small and large bags are shown in Figure 5. Over time intervals of about 1-2 hours the wall loss rates for a small bag decrease as time elapses, whereas, for large bags they slightly increase.

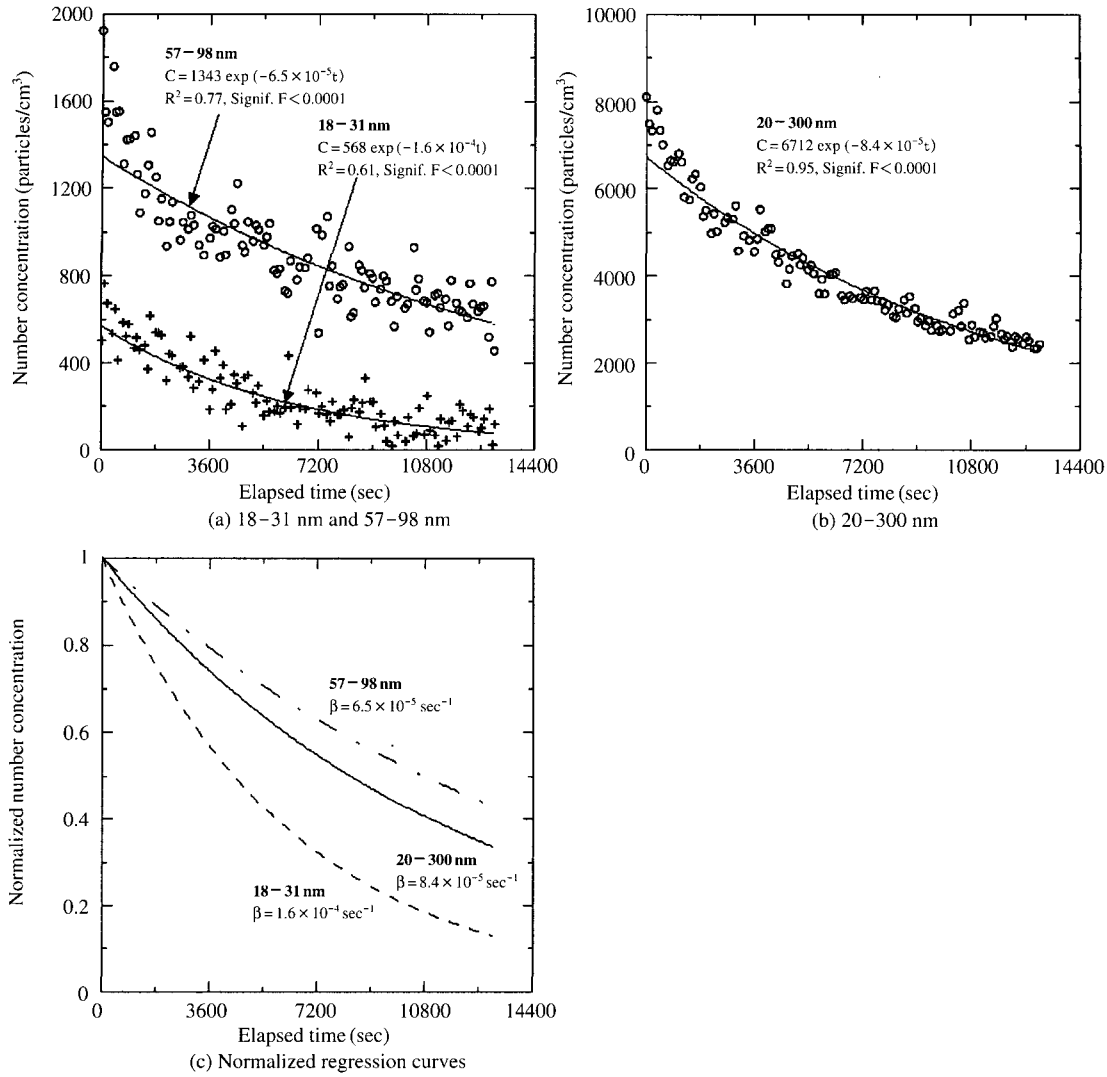

Fig. 2. Natural decay of specific size-ranged particles in a 2.5-m^3 Teflon film bag filled with ambient air.

The measured wall loss rates for large bags are illustrated in Figure 6, together with the results from previous studies. The measured wall loss rates showed big difference compared with the theoretical values suggested by Crump and Seinfeld (1981) for particles larger than 100 nm. However, they were in good agreement with the theoretical and experimental values obtained by McMurry and Rader (1985) for a 60-m^3 pillow-shaped bag with a surface-to-volume ratio of 2.1 m^{-1}. Theoretical values were calculated assuming the ion concentration to be 20 ions/cm^3. McMurry and Rader (1985) pointed out that electrostatic forces affected the overall deposition rates for particles in the diameter range 50 to 1,000 nm.

In conclusion, the theoretical wall loss rates suggested by McMurry and Rader (1985) can be used to correct the measured data from smog chamber experiments using 5.8-m^3 Teflon film bags filled with the ambient air. For particles in the diameter

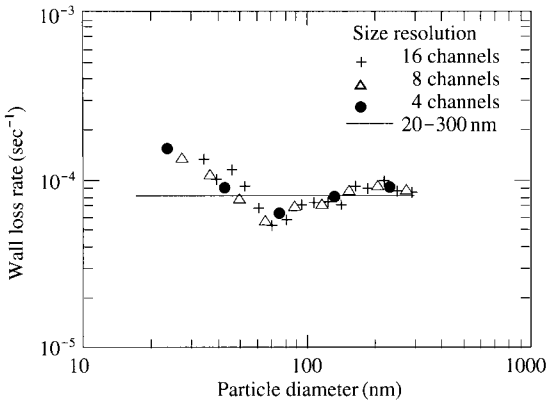

Fig. 3. Wall loss rate as a function of particle size in a 2.5-m^3 Teflon film bag filled with ambient air.

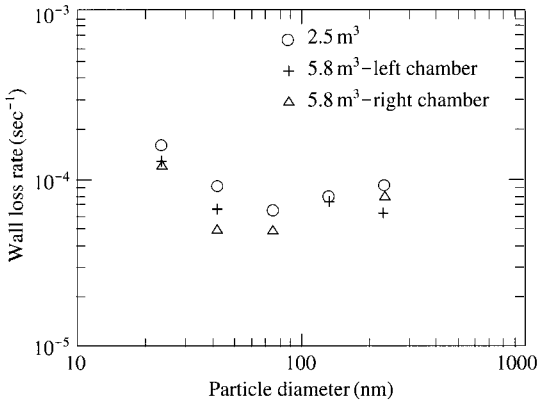

Fig. 4. Comparison of wall loss rates between small and large bags.

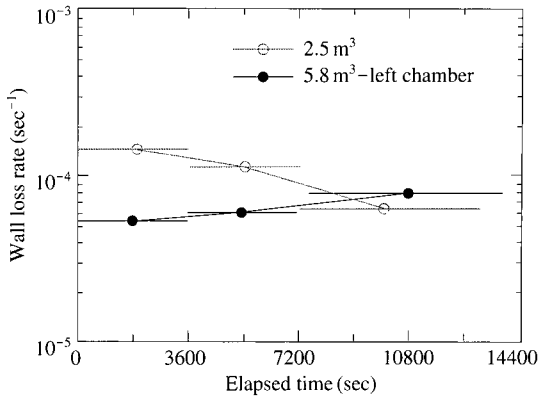

Fig. 5. Time dependency with wall loss rates. The horizontal line represents the time interval.

Table 2. Summary of wall loss rates for three bags filled with ambient air.

	Wall loss rate, β ($\times 10^{-5}$ sec^{-1})					
	Particle size range (midpoint diameter) (nm)					Wide range (nm)
Teflon bag	18-31 (23.7)	32-55 (42)	57-98 (75)	102-175 (133)	181-311 (237)	20-300
2.5 m^3	16	9.2	6.5	8.0	9.1	8.4
5.8 m^3-left chamber	13	6.6	6.4	7.5	6.3	6.9
5.8 m^3-right chamber	13	5.1	5.0	7.7	8.0	6.9

range 20-300 nm, the theoretical wall loss rate suggested by McMurry and Rader (1985) ranged from 5.8×10^{-5} to 1.4×10^{-4} sec^{-1}, which was slightly higher than the 2.5×10^{-5} to 5×10^{-5} sec^{-1} for a cubic-shaped 28-m^3 Teflon chamber, but was similar to the range 3.0×10^{-5} to 6.5×10^{-4} sec^{-1} for a 2-m^3 Teflon chamber (Cocker III *et al.*, 2001; Hurley *et al.*, 2001).

The overall wall loss rate for particles in the range of 20-300 nm well indicates the size-dependent wall loss rate for particles larger than 30 nm. Considering the uncertainty in the measured values, the overall wall loss rate can also be used in the correction of chamber data as this makes the data process simple and easy.

3.2 Correction of aerosol wall loss

In smog chamber experiments, time-series size distribution data can be obtained during the course of the experiment. For a specific particle size bin, the corrected particle number concentration, N_c, at a given time is the measured value N_m at a given time plus the sum of the decrement of the particle concentration due to wall losses from time = 0 up to the given time, as shown in Equation (2).

$$N_c(D_p, t_i) = N_m(D_p, t_i) + \sum_{j=0}^{j=i-1} N_m(D_p, t_j)\,[1-\exp\{-\beta(D_p)(t_{j+1}-t_j)\}] \quad (2)$$

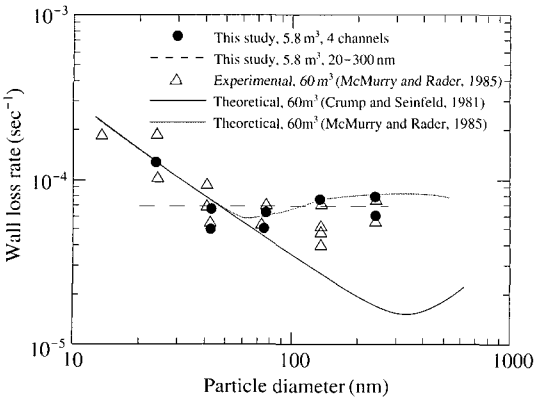

Fig. 6. Comparison of wall loss rates with previous works.

As an example, the changes in the particle number and mass concentrations with irradiation time during the photochemical reactions in a 5.8-m^3 Teflon bag filled with ambient air are shown in Figure 7 (Moon *et al.*, 2004). The size-dependent theoretical wall loss rates for 20 ions/cm^3 given by McMurry and Rader (1985), and the overall wall loss rate derived in this study were applied to correct the measured data. The aerosol wall loss correction started when the blacklights were turned on. In Figure 7(a), the measured number concentration of particles in the range of 20-300 nm increased about 1 hour after turning the blacklights on due to the formation of secondary organic aerosols, and then decreased slowly after two hours due to the condensational growth and/or wall loss of particles. However, the corrected number concentration increased continuously during the irradiation, although it increased relatively slowly after two hours.

In Figure 7(b), the measured mass concentration decreased very slowly. Here, the aerosols were assumed as 1-g/cm^3 spheres. However, the corrected mass concentration increased continuously during the irradiation. Therefore, the correction of aerosol wall loss is more significant in the analysis of mass concentration or aerosol yield. From Figures 7(a) and 7(b), the final corrected concentrations of number and mass were found to be about twice those of the measured values. Namely, after 4 hours of irradiation the number and mass of particles lost

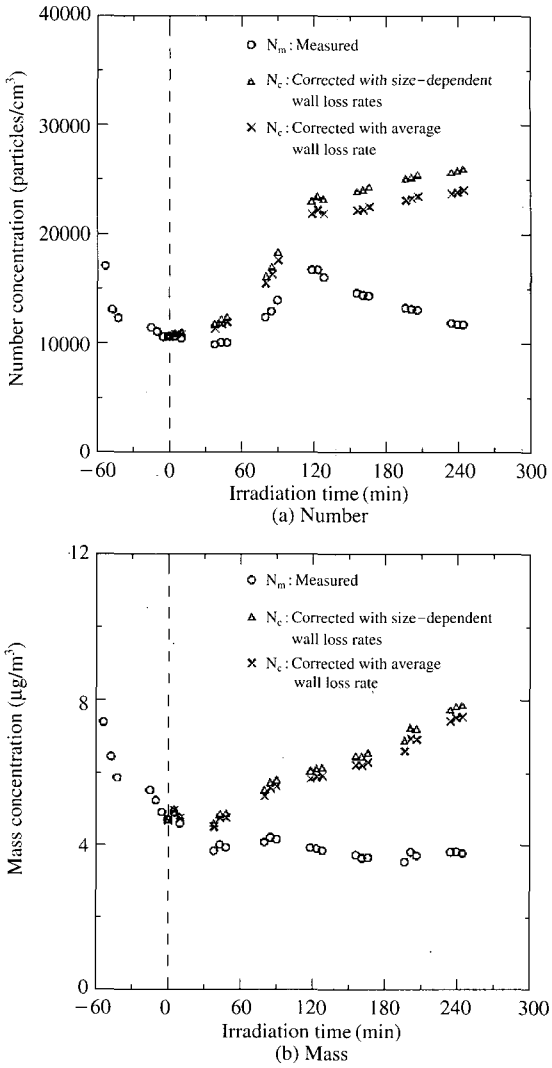

Fig. 7. Wall loss correction for particles of 20-300 nm in photochemical reactions of ambient air in a 5.8-m^3 Teflon bag on April 16, 2004.

to the wall were about 16,000 particles/cm^3 and 3 μg/m^3, respectively.

Although the corrected concentrations with an overall wall loss rate were slightly lower than those with size-dependent theoretical wall loss rates, the difference between the two correction methods was insignificant. Therefore, the use of average wall loss rates could be considered to save effort for simple corrections of wall losses.

4. SUMMARY

In this work, the natural change in the particle size distribution was investigated in 2.5-m^3 and 5.8-m^3 cubic-shaped Teflon film chambers filled with ambient air under dark conditions. The measured aerosol wall loss rate was obtained based on the deposition theory suggested by Crump and Seinfeld (1981). The measured wall loss rates showed big differences with the theoretical values suggested by Crump and Seinfeld (1981) for particles larger than 100 nm. However, they were in good agreement with the theoretical and experimental values obtained by McMurry and Rader (1985) for a 60-m^3 pillow-shaped bag. Therefore, the theoretical wall loss rates that account for the electrostatic effects suggested by McMurry and Rader (1985) can be used to correct the measured data from smog chamber experiments using ambient air.

For photochemical reaction data obtained from smog chamber experiments, the trends of the particle number and mass concentrations are seriously altered as time elapses when considering the aerosol wall loss. After 4 hours of irradiation, the corrected particle number and mass concentrations become about twice those of the measured values. Therefore, the correction of aerosol wall losses should be considered in the analysis of smog chamber experimental data.

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