

# Where Do Particulate Toxins Reside? An Improved Paradigm for the Structure and Dynamics of the Urban Mid-Atlantic Aerosol

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Discussions of excess mortality and morbidity from exposure to urban aerosol particles typically invoke the now 20-year-old trimodal aerosol paradigm proposed by Whitby to explain the structure and behavior of ambient aerosol volume and its major constituent, sulfate. However, this paradigm largely ignores the primary high-temperature combustion (HTC) components of the urban aerosol, which contribute minor amounts of the aerosol mass, but carry the bulk of the particulate toxins and numbers of aerosol particles. Studies encompassing the analyses of >100 size distributions of important intrinsic tracers of primary particles from HTC sources collected over the past decade in various environments show that urban aerosol contains a complex mixture of physically-discrete fresh and aged, primary particle populations from a variety of sources. Furthermore, whereas the behavior of fine-particulate aerosol mass and sulfate was described in terms of coagulation and accumulation aerosol scavenging of new secondary sulfate nuclei, studies reviewed herein suggest that the behavior of primary aerosol is mediated more by hygroscopic growth and cloud processing, accompanied by oxidation of SO<sub>2</sub> on wet particles and droplets. We conclude that the distribution of airborne particulate toxins and their atmospheric behavior is far more complex than commonly conceptualized on the basis of the classical trimodal model, and we develop an extended paradigm in which the focus is on the primary accumulation aerosol.

## Introduction

Numerous epidemiological studies suggest that serious health effects including mucosal injury, respiratory distress, and early death are associated with exposure to respirable aerosol particles present in urban areas, especially those <2.5 μm in diameter (1–7). In urban areas of the northeastern United States, where the composition of fine aerosol mass is typically dominated by secondary sulfate formed from the oxidation of SO<sub>2</sub> (which is emitted almost entirely from coal and oil power plants; 8), the size distribution and behavior of both mass and sulfate are well described by the trimodal paradigm

developed in the 1970s by Whitby (9). However, a great deal of evidence suggests that ambient urban aerosol is comprised of a complex mixture of physically discrete fresh and aged, primary aerosol particle populations from a variety of individual high-temperature combustion sources (HTCS) (10–12) upon which the secondary aerosol mass resides. Masked by the overwhelming presence of the secondary aerosol, these primary aerosol populations are not readily detected in aerosol mass or sulfate size distributions and were virtually excluded from the Whitby paradigm. The primary components are important as they are frequently enriched in toxic substances (e.g., Cd, Pb, As, and Hg; 13) which differ for different sources, have long atmospheric residence times, and are efficiently deposited in the human respiratory tract. Furthermore, HTCSs emit an enormous number of particles, a metric that is potentially important in driving pathophysiological responses (14).

Neither the precise mechanism nor the specific pollutants associated with particulate toxicity have been identified. However, a growing body of evidence suggests that metallic components of primary aerosol particles are important. For example, Carter et al. (15) have shown that exposure of human airway epithelial cells to residual oil fly ash (ROFA) particles enhances the production of inflammatory mediators such as cytokines. This response is also elicited by V, an important constituent of ROFA particles, but not Fe or Ni, indicating that the response is metal specific. Furthermore, animal studies by Costa and Dreher (16) indicate that the dose of soluble metals, not particle mass, relates most closely with associated cardiopulmonary effects in both healthy and compromised hosts. These observations are especially important in view of the fact that the masses of various inorganic constituents, including first-series transition metals (many of which are capable of producing reactive oxygen species), heavy metals, and toxic metalloids, are predominately associated with primary aerosol emissions from high-temperature combustion sources (HTCS), such as coal- and oil-fired power plants (CFPP and OFPP), municipal and medical incinerators, diesel-powered vehicles, and residential furnaces. It is clear, therefore, that toxic effects might be associated with discrete aerosol populations from individual sources or generic source types. Despite this possibility, discussions of the health effects of urban aerosols almost always invoke the now 20-year-old trimodal aerosol paradigm, i.e., a paradigm that is largely inappropriate for describing primary aerosol structure and behavior and one that does not encompass important new information on its nature and behavior.

Several years ago, Hasan and Dzubay (17) identified ambient accumulation aerosol from motor vehicles burning leaded fuel. More recently, Dodd et al. (10) showed that important information on the structure and dynamics of primary particulate emissions from generic sources could be inferred from the size distributions of intrinsic tracer species derived from ultratrace analysis of highly resolved submicrometer aerosol fractions. Later, Divita (12, 18, 19) developed size distributions for >20 elements (including V, As, Se, Sb, Zn, and S, i.e., elements strongly associated with oil combustion, coal combustion, municipal incineration, and intraregionally transported secondary aerosol) in >50 samples collected in nonindustrial and industrial urban environments in and around Washington, DC, and Philadelphia, PA. Herein, we review the pertinent findings of these and other studies and use the information to develop the extended paradigm shown in Figure 1. The intent is to extend the Whitby paradigm to encompass primary accumulation

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instead, nuclei particles are scavenged by *preexisting* accumulation aerosol of *unspecified origin*, a process that Whitby argued governed the growth of the accumulation aerosol mode. But despite this supposition, Whitby suggested that only about 5% of the total aerosol volume formed is accounted for by new particle formation (9). More recent measurements show that mixing ratios of sulfuric acid, i.e., formed from homogeneous processes, are negligible (i.e., on the order of ppt) as compared with other processes that contribute to the mass loading (23). Clearly, homogeneous nucleation cannot be the source of sulfate in the accumulation region.

### Other Atmospheric Aerosol Growth Processes

In Whitby's paradigm, accumulation aerosol growth is considered to occur mainly by condensation of sulfate photochemical oxidation products. He made little mention of the effects of hygroscopic growth, heterogeneous  $\text{SO}_2$  conversion on existing aerosol particles, and cloud processing in his description of ambient aerosol dynamics.

About 70% of urban submicrometer particle mass is composed of hygroscopic compounds, largely ammonium sulfates, that deliquesce (becoming liquid droplets) at relative humidities (RH) between 40 and 80% (24). Below the deliquescence point, these particles may exist as crystalline solids, for which particle size is unaffected by changes in RH. Above the deliquescence point particles grow when exposed to higher RH (hygroscopic growth) and shrink when ambient RH declines. In studies by McMurry and Stolzenburg (25), ambient Los Angeles aerosol particles grew by up to 50% when the RH was increased from 50 to 90%. Above 90% RH, droplet growth continues until droplets with significant liquid water content and settling velocities are produced, as occurs in fog and clouds. Hygroscopic growth is reversible provided that nonvolatile mass is not added during this process.

In the atmosphere, water vapor concentrations are large; hence, the time scale for achieving hygroscopic equilibrium is short. As a result, water can be assumed to be in equilibrium between the vapor and condensed phases under nearly all conditions (22). Atmospheric growth equations developed for the other processes, i.e., condensation, coagulation, and aqueous-phase reactions, have been examined by Kerminen and Wexler (26). For conditions prevalent in urban areas, neither Brownian, turbulent, nor kinematic coagulation appreciably alter the mass vs size distribution of urban aerosol particle modes except in extreme cases, e.g., in the near plume region of a combustion source (22). Essentially, self-coagulation of accumulation aerosol particles is slow and rapidly quenched by concomitant decline in number concentration as coagulation proceeds and, more importantly, with rapid dilution in dispersing plumes. The time scale for dilution and coagulation are compared in Kerminen and Wexler (27). Under conditions prevalent in the South Coast Air Basin of Los Angeles, growth of particles from 0.1 to 0.4  $\mu\text{m}$  occurs by aqueous-phase  $\text{SO}_2$  oxidation on a time scale of from 30 s to 3 h. The corresponding time scales for condensational and coagulation growth are on the order of days or longer (26).

Growth law and field data analyses lead McMurry and Wilson (28) to conclude that liquid-phase heterogeneous sulfur conversion dominated the formation of new aerosol particle volume in the urban plume of Columbus, OH, when RH exceeded 75%. Conversion was said to have occurred in "liquid aerosol droplets". In the South Coast Air Basin of Los Angeles, conditions are such that Kerminen and Wexler (26) estimate that accumulation mode particles cannot easily grow by heterogeneous  $\text{SO}_2$  oxidation, except in clouds, because the water content of wet particles is otherwise too small and high particle acidity inhibits oxidation by some

processes. In clouds, the rate of  $\text{SO}_2$  oxidation by heterogeneous processes can be 10–100-fold greater than homogeneous rates. In clouds and fog, supersaturated conditions causes aerosol particles to grow above a critical diameter and, ultimately, to diameters of 5–10  $\mu\text{m}$  in fog and 10–20  $\mu\text{m}$  in clouds. These act as discrete atmospheric processing cells wherein oxidants and  $\text{SO}_2$  partition into the droplets according to their Henry's law constants. The  $\text{SO}_2$  is oxidized by hydrogen peroxide, ozone, and metal-catalyzed reactions with dissolved oxygen, adding to aerosol mass during the lifetime of the cloud (29, 30). Note that the time scale for cycling urban air through clouds, i.e., hours, is relatively short and cloud height is generally lower at higher surface-level RH. Therefore, we suspect that the  $\text{SO}_2$  conversion in the Columbus urban plume might have occurred in quite large "liquid aerosol droplets" that exist in clouds and not in wet aerosol particles below the cloud level.

Most clouds are nonprecipitating, so that residue particles are formed after the cloudwater evaporates. The resulting residue particle diameter depends on the amount of sulfate deposited and the ambient RH. Model calculations (31) suggest that at 80% RH the resultant particles will be 0.6 and 0.8  $\mu\text{m}$  after 1 h of processing in fog with a droplet diameter of 5  $\mu\text{m}$  for  $\text{SO}_2$  concentrations of 1 and 10 ppb, respectively. For clouds with 10- $\mu\text{m}$  droplets, 0.9 and 1.5  $\mu\text{m}$  residue particles can be formed at these  $\text{SO}_2$  levels. Growth law analyses suggest that droplet-phase sulfate production in nonprecipitating clouds and fog is the only mechanism that can account for 0.7- $\mu\text{m}$  "droplet modes" observed by John et al. (32) in urban southern California aerosol (26). We note also that major fractions of the new aerosol mass detected in the Columbus urban plume were observed in 0.7- $\mu\text{m}$  particles, which supports our contention that cloud processing and not below-cloud liquid-phase conversion was responsible for aerosol particle growth at high RH.

In power plant plumes,  $\text{SO}_2$  concentrations are far greater than those of the surrounding air, and homogeneous conversion competes favorably with heterogeneous conversion. The overall conversion rate in plumes is therefore largely governed by the ambient RH and the volume fraction of the plume that interacts with clouds. On a typical midwestern summer day, about two-thirds of the  $\text{SO}_2$  conversion in the Cumberland Power Plant plume was accounted for by heterogeneous liquid-phase mechanisms, two-thirds of which occurred in 1 or 2 h in the morning, when the rising mixing height carried scattered clouds across the elevated plume (33).

According to Friedlander (34), the  $\sigma_g$  of an aging (initially broad) polydisperse aerosol should approach 1.5 as a result of preferential coagulation between the smaller and larger particles of the distribution. This process likely controls the width of fresh accumulation aerosol particles in smoke stacks. Condensational growth can lead to even more narrow distributions because small particles tend to grow faster than larger particles during this process. Such is the case for water vapor, which often precipitates on combustion aerosol particles in the near plume (as evidenced by white plumes) but quickly evaporates as the plume mixes with the drier air around it. However, as discussed below, hygroscopic growth accompanied by aqueous-phase reactions forming one or more nonvolatile components or condensation of some other nonvolatile component, e.g., organic compounds, should lead to a narrowing of the distribution. The underlying principle is described by Kerminen and Wexler (26). Essentially when the droplet size becomes large enough, the rate of mass influx to the droplet becomes small relative to the droplet volume and the time scale for growth becomes disproportionately large. At this point, smaller particles continue to grow to the limiting size.



TABLE 1. Accumulation Aerosol Distribution Parameters for Several High-Temperature Combustion Sources

	analysis <sup>a</sup>	mmad <sup>b</sup> (μm)	σ <sub>g</sub> <sup>b</sup>	mass fraction accounted for %
Alexandria Municipal Incinerator				
270 ton/day unit w/spray-baffle scrubber (36, 37)	Zn, Cl	0.24, 0.33, 0.39, 0.50, 0.63	nd <sup>c</sup>	87, 87, 90, 84, 95
	Pb, Cl	0.30, 0.34	nd	92, 93
oil-fired boiler, Vienna, VA (Unit 7, 35)	V, Cl	0.22, 0.25, 0.19, 0.21, 0.19	nd	80, 76, 74, 76, 80
coal-fired boilers				
430 MW(e), ESP-equipped CFPP (39)	SEM	0.14	1.37	
750 MW(e), ESP-equipped CFPP (39)	SEM	0.13	1.42	
hot-side ESP-equipped CFPP (38)	EAA/OPA	0.13	1.57	36
520 MW(e) ESP-equipped CFPP (41)	EAA	0.14–0.168	1.18–1.48	20
180 MW(e) Venturi scrubber-equipped (42)	SEM	0.33 and 0.8	1.57 and 1.20	20 and 80
430 MW(e) ESP- & FGD-equipped (40)	HPDCI	0.11	nd	~2
motor vehicles				
Baltimore Harbor Tunnel (45)	Pb, Cl	0.33–0.41	nd	90–95
Sepulveda Traffic Tunnel (43)	EC, LPI	0.13	1.28	98
individual sanitation trucks (44)	mass, MOI	0.12 and 0.43	1.43 and 1.49	51 and 28

<sup>a</sup> Cl, in-stack cascade impactor; SEM, scanning electron microscopy; EAA, electric aerosol analyzer; OPA, optical particle size analyzer; HPDCI, high-pressure drop in-stack cascade impactor; MOI, microorifice impactor; LPI, low-pressure impactor; EC, elemental carbon. Concentrations of Zn and Pb in Alexandria incinerator aerosol averaged 12 and 9.7%, respectively. V is a minor components of emitted particles. <sup>b</sup> mmads were estimated by the authors for the Alexandria incinerator, Vienna boiler, hot-side ESP- and FGD-equipped power plants, Baltimore and Sepulveda tunnel studies, and the sanitation truck study. Where indicated, accurate geometric standard deviations could not be determined because of poor resolution achieved by the cascade impactors used in these studies. <sup>c</sup> nd, not determined.

## Sources and Atmospheric Behavior of Primary Aerosol

**Characteristics of Primary Aerosol Emissions.** An important source of fresh accumulation aerosol, and one not discussed by Whitby, is high-temperature combustion. Natural and anthropogenic high-temperature combustion sources (HTCSs), e.g., biomass burning, coal- and oil-fired power plants (CFPPs and OFPPs), incinerators, cement kilns, smelters, residential oil furnaces, fire places, and motor vehicles, i.e., virtually all of the major sources of anthropogenic particulate pollutants, emit copious quantities of atmospheric fine particles (10). Most HTCSs are controlled, and therefore nuclei particle emission is suppressed by accumulation mode scavenging and efficient removal by control devices prior to atmospheric discharge. These accumulation aerosols are initially formed by condensation and grow by coagulation and condensation within the source and to some extent, immediately after release, before dilution quenches the process. As shown in Table 1, primary particles are typically emitted in accumulation aerosols with modal diameters between 0.05 and 0.35 μm. For example, in size distributions developed for two OFPPs (35) and a municipal incinerator (36, 37), >80% of the particulate mass emissions are emitted in accumulation aerosol peaks. Reanalysis of these data suggest mean diameters of 0.19 and 0.29 μm for the OFPPs and typically from 0.24 to 0.33 μm for the incinerator (see Table 1 for details). Pulverized coal-fired utility boilers are a special case in that the mass distributions of emitted aerosol contain both an accumulation mode derived ultimately from nuclei condensation and a substantial larger particle mode reflecting unburned mineral matter (fly ash). From 10–90% of the aerosol mass is emitted from coal-fired plants in the accumulation aerosol peak depending largely on the type of particulate control device (38). Mean diameters for accumulation aerosol particles emitted from four coal-utility boilers equipped with cold- or hot-side electrostatic precipitators (ESP) or a cold-side ESP with flue-gas desulfurization (FGD) ranged from 0.11 to 0.168 μm (39–41). It is noteworthy that the mean diameter for the fine-particle component emitted from a coal-fired utility unit equipped with a venturi wet scrubber was somewhat larger, i.e., 0.33 μm, and that the distribution also contained a droplet/residual fly ash mode at 0.7 μm (42). Relative to unscrubbed units, the larger size from scrubbed units is

attributed to accumulation of the scrubbing agent (aqueous CaCO<sub>3</sub>) and heterogeneous conversion of SO<sub>2</sub> in droplets and wet fly ash particles. Furthermore, the scrubbed aerosol contained new particles generated by flash evaporation of droplets.

Mass emissions from uncontrolled diesel and gasoline engines also peak in the accumulation region (43, 44). For example, mean sizes for (background corrected) aerosol particles from motor vehicles burning leaded fuel sampled in the Baltimore Harbor Tunnel ranged from 0.33 to 0.41 μm, and these particles contained >90% of the aerosol mass (45, 46). Likewise, 98% of the elemental carbon (EC) in particles emitted from unleaded fueled vehicles in the Sepulveda Tunnel were contained in a narrow accumulation peak with a mean diameter of 0.13 μm (43). Mass-size distributions of soot aerosol emitted from individual diesel sanitation trucks in normal operation contained peaks at 0.12 and 0.43 μm (44). The larger accumulation mode was attributed to particles released during acceleration and changes in engine load.

**Ambient Air Observations.** Accumulation aerosol populations from these sources are preserved after discharge into ambient air and have been observed in size distributions of sulfate in ground-level plumes of CFPPs (47, 48). After emission, atmospheric aging processes, e.g., cloud processing, hygroscopic growth, and growth by heterogeneous conversion of SO<sub>2</sub> in wet particles tend to increase particle size, add secondary aerosol mass, and modify particle chemistry (especially aerosol acidity). In HTCSs, particle composition as well as size is controlled by fuel composition, time-temperature history, and the type and efficiency of emission control devices (38). The unique compositions of particles from various sources provide the basis for receptor modeling wherein individual elements or groups of elements serve as intrinsic tracers (49). Some tracers appropriate to the discussion below are as follows: Pb, for leaded motor vehicle aerosol; Zn and Cd, municipal incineration; Se, local CFPPs; V, OFPPs; Ti, paint manufacturing/spraying; elemental C, diesel soot; and S, secondary sulfate. However, Pb has been largely eliminated from U.S. motor vehicle fuel.

At Deep Creek Lake, highly resolved aerosol particulate size fractions were collected in a shallow (~200 m) trough between the Negro and Meadow mountain chains, which

TABLE 2. Accumulation Aerosol Distribution Parameters for Intrinsic Tracers of HTCS

location and tracer species <sup>a</sup>	av RH range (%)	mmad ( $\mu\text{m}$ )	$\sigma_g$
incinerator plume, Camden, NJ (18, 19) (roof-top level, 5 km downwind)			
Zn, Cd, Cr; MOI (bgnd corrected)	60, 45–85	0.23	1.21
Zn, Cd, Cr; MOI	79, 62–99	0.51	3.16
Deep Creek Lake (10) (rural mountainous region of western, MD, 150 km downwind of the industrial Ohio Valley)			
MOI sample, winds not recorded			
Se, As, Sb Fe <sup>b</sup>	not recorded	0.22, 0.21, 0.16, 0.41	1.45, 1.32, 1.45, 1.40
MOI samples, northeasterly winds			
As; Pb, La; Ti (Ce)	48–74	0.11	<1.8 (1.36)
day/night & two 23-h MOI samples, northeasterly winds			
As	47–72	0.44, 0.33, 0.32, 0.30	1.93, 1.85, 1.81, 1.96
day and night MOI samples, westerly winds			
As, Sb, S, V, run 13, day <sup>b</sup>	48	0.41, 0.42, 0.41, 0.42	1.36, 1.53, 1.4, 1.45
As, Sb, run 14 night	50–70	0.41, 0.50	1.76, 1.82
S, V, run 29 day	57	0.51, 0.54	1.60, 1.60
S, V, run 30 day	59–74	0.52, 0.54	1.70, 1.66
College Park, MD, fresh/aged (11, 12, 18)			
fresh aerosol			
As, Se, Sb, Zn	61, 54–72	0.30 $\pm$ 0.03, 0.33 $\pm$ 0.06, 0.39 $\pm$ 0.03, 0.39 $\pm$ 0.06	1.79, 1.82, 2.35, 2.29
aged aerosol			
As, Se, Sb, Zn	61, 51–82	0.46 $\pm$ 0.04, 0.54 $\pm$ 0.04, 0.53 $\pm$ 0.04, 0.53 $\pm$ 0.08	1.79, 1.59, nd, <sup>c</sup> nd
V	61, 51–82	0.31	1.5
Andrews Air Force Base (12, 18)			
V in oil-fired boiler plume, 100 m downwind	65, 50–92	0.23	1.48
	76, 55–93	0.27	1.53
	97, 93–100	0.3	1.31
motor vehicles			
ambient air, Dever, CO; Pb/MOI (17)		0.15	2.44
ambient air, Upland, CA; EC/LPI (43)		0.14	1.42
sanitation truck fleet, Baltimore, MD; Ir/MOI (44)		0.05, 0.12, 0.4, 2.4	nd

<sup>a</sup> CI, in-stack cascade impactor; SEM, scanning electron microscopy; EAA, electric aerosol analyzer; OPA, optical particle size analyzer; HPDCI, high-pressure drop in-stack cascade impactor; MOI, microorifice impactor; LPI, low-pressure impactor. <sup>b</sup> Parameters determined from fitting log-normal distribution functions to the histogram data, see ref 11. <sup>c</sup> nd, not determined.

run northeast–southwest for more than 60 km from the site. A cluster of four CFPPs lie from 32 to 100 km westward along prevailing wind trajectories, and the heavily industrial Ohio River Valley lies about 200 km to the west. At this site, size distributions developed for As, Pb, and Ti often contained narrow accumulation aerosol peaks at  $\sim 0.11 \mu\text{m}$ . In addition, Ce and La peaks in this range correlated well with Pb size distributions and were thought to be coemitted with Pb as a result of dispersal from zeolite automotive catalyst or, perhaps, motor oil combustion. These tenth-micrometer peaks were interpreted to be the signatures of “fresh” accumulation aerosol from nearby HTCSs. They often appeared to be surprisingly narrow, more so than commonly observed for sulfur and other elemental markers associated with particles between 0.4 and  $1 \mu\text{m}$ . For example, standard deviations ( $\sigma_g$ ) as small as 1.2 for Sb and Se were observed (50). (Note that Sb is typically a good marker of incinerator aerosol whereas Se is mostly associated with primary coal-combustion aerosol, mainly from utility power plants.) Furthermore, most unimodal distributions had standard deviations  $< 1.5$  (50). As shown in Table 1, standard deviations for accumulation aerosol determined from utility coal-fired power plants equipped with cold-side electrostatic precipitators are typically  $\geq 1.4$ . However, for a plant equipped with a flue gas scrubber, a value of 1.2 was reported (see Table 1). Similar values of the standard deviation, i.e., 1.23–1.31, are reported (50) for Sb, Zn, Mn, and Na in accumulation aerosol sampled via aircraft from the Pleasants (coal-fired) Power Plant plume, approximately 200 km west of Deep Creek Lake. The Pleasants Plant is equipped with a wet-lime scrubber system. In contrast, standard deviations in accumulation aerosol likewise sampled from the cold-side ESP-equipped Harrison coal-fired Power Plant (about 60 km from Deep Creek Lake) were typically 1.4, in agreement with in-

stack measurements for this type of plant. Clearly, the narrowness and mean diameter of aerosol particle distributions observed in stacks are preserved after release into the ambient air. It is noteworthy that many of these distributions are far more narrow than those observed by Whitby for the total accumulation aerosol.

Despite the presence of narrow accumulation aerosol peaks for some elements in size distributions for Deep Creek Lake and elsewhere, most of the mass for most of the elements in 12- and 24-h samples was typically contained in broad peaks ( $\sigma_g$  1.8–2.0) with modal diameters of 0.4–0.56  $\mu\text{m}$  (where indicated, mean diameters listed for As in Table 2 were derived from reanalysis of the original Deep Creek Lake data). In addition, great similarity was observed in the structure of peaks for Sb, Se, and S and to a lesser extent As and V.

In a later study (18, 19), size-segregated aerosol was simultaneously collected for 11 h in Camden, NJ, 5 km downwind of a municipal incinerator and at a background site in a suburb of Philadelphia, 12 km to the northwest (see Figure 2). Two sets of samples were collected when the Camden site was downwind of the incinerator. One set was collected at average and maximum RH of 60 and 85%, respectively, whereas the other set was collected at an average RH of 79% but with a maximum RH near 100%, i.e., conditions more conducive to hygroscopic growth. Chemical mass balance calculations on the full (month-long) data set suggested that about 85% of the Zn and  $> 60\%$  of the Cd in Camden aerosol were typically associated with a municipal incinerator source. In the high RH sample, Zn and Cd were observed in a broad ( $\sigma_g$  3.16) peak at 0.51  $\mu\text{m}$ . Whereas, in the low RH sample, Zn, Cd, Cr, and Cl all occurred in a single, narrow accumulation aerosol peak with a median diameter of 0.23  $\mu\text{m}$ , a size consistent with in-stack aerosol measure-

## Camden, NJ

## Deep Creek Lake

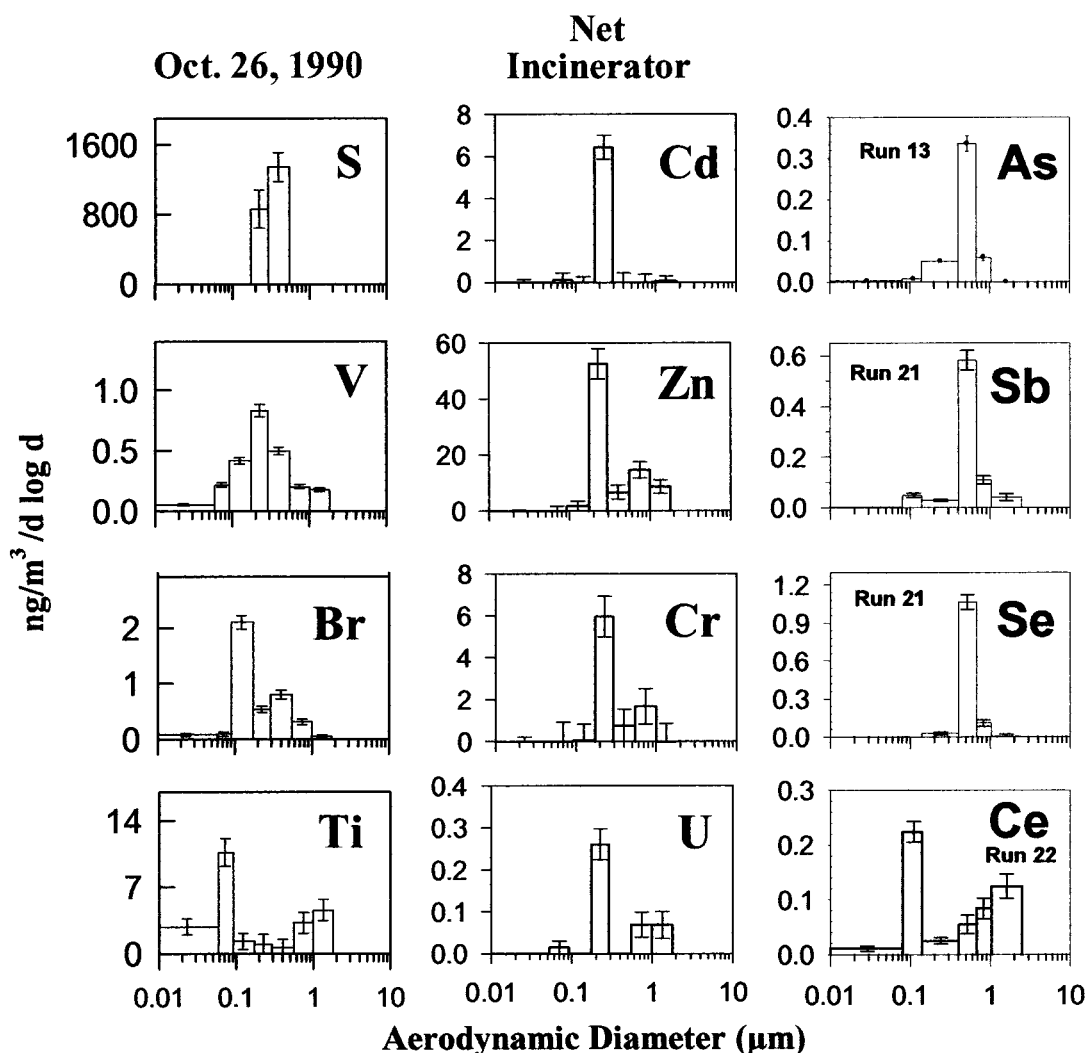


FIGURE 2. Size distributions reported by Divita (12) for aerosols in the heavily industrial Camden, NJ, area are shown in the first two columns. Size distributions shown in the second column represent fresh accumulation aerosol collected at a ground-based sampling site, 5 km down wind from an incinerator, when the ambient relative humidity averaged 60%. The series developed for the October 26th clearly show the presence of four distinctly different aerosol populations, as revealed by the different modal diameters for S-, V-, Br-, and Ti-containing particles. Exceedingly narrow distributions are evident in the ambient size distributions of elemental markers of particles produced by condensational growth in incinerators (Cd and Zn, second column) and, possibly, Ti pigment manufacture. Narrow distributions were also observed for As, Sb, Se, and Ce in aerosol collected at Deep Creek Lake (data of Dodd et al., 1991, column 3). Selenium and, to a lesser extent, As are associated with particulate emissions from coal-fired boilers. Such narrow distributions have been observed in plants with wet scrubbers and are substantially more narrow than the more abundant nonscrubber-equipped plants. Another possible explanation is that narrowing results from liquid-phase conversion of SO<sub>2</sub> during atmospheric transport, quite possibly, in nonprecipitating clouds.

ments. In the latter sample, mass concentrations of these elements in the 0.23-μm particles exceeded those in the corresponding upwind sample by 8-fold. This information, taken together with wind direction and composition data, is nearly definitive evidence of the influence of "fresh" accumulation aerosol in the incinerator plume.

Perhaps the most striking feature of many of these data is the observation of such narrow accumulation modes. In Camden, accumulation peaks attributed to the incinerator and observed at low RH were only 1.2, i.e., substantially smaller than typically observed for ESP-equipped CFPPs (see Table 1) but similar to those observed for scrubbed-power plant accumulation aerosol. In incinerators, kinetic modeling suggests that metal-containing particles are formed primarily by condensation of volatile chlorides (51). As discussed above, in condensational growth, small particles grow quickly

whereas large particles grow slowly, so that the  $\sigma_g$  of a polydisperse aerosol growing by vapor condensation will approach 1. Biswas et al. (52) predicted a standard deviation of 1.34 for Pb aerosol made in a rotary-kiln incinerator. The major constituents of aerosol particles emitted from the Philadelphia incinerator were determined via stack sampling and are as follows: chlorine, 29%; Zn, 10%; K, 7.6%; sulfate, 6.8%; Na, 6.6%; and Pb, 5.8% (53). Zinc and lead chlorides are especially volatile (boiling points are 732 and 950 °C, respectively). These are totally vaporized at combustion temperatures but are fully condensed on particles at ambient atmospheric temperatures; hence, condensation occurring during aerosol formation in the plant likely explains the narrow standard deviations. Apparently, this feature is preserved during atmospheric transport, at least over a distance of 5 km.

Why then do size distribution measurements often show a broad accumulation mode? The reason is that both fresh and aged primary particles typically contain sulfates, secondary polar organic compounds, and other deliquescent materials. Their size is, therefore, variable during sampling as it is modulated by hygroscopic growth in concert with temporal changes in RH, which, in the middle Atlantic region, often varies between 100% in the early morning to a low of 40 or 50% in the warmer midafternoon. In the case of the incinerator, particulate emissions typically contain from 20 to 50% deliquescent zinc chloride by mass (36, 37, 53). Thus, the broad peaks observed in size distributions of the high RH incinerator sample result from the integration of a single narrow peak whose size is modulated by hygroscopic growth in concert with temporal changes in RH during the sampling period. Conversely, an instantaneous "snapshot" of the aerosol spectrum would contain a narrow accumulation aerosol peak at a mean diameter consistent with the RH of its environment as would a spectrum obtained at constant RH.

The principle source of Ti in submicrometer particles is probably aerosol emitted from Ti pigment manufacture or, perhaps, spray painting. Titanium dioxide pigment particles are formed by evaporation as volatile  $\text{TiCl}_4$  and condensation after gas-phase oxidation. Thus, if Ti pigment manufacturing is the source, Ti aerosol is likely to be emitted in narrow condensation peaks. Evidence for this was observed in Camden (11, 18) and Deep Creek Lake (10).

Interestingly, the modal diameters of peaks for S, Sb, Se, and V in Deep Creek Lake aerosol were nearly always about  $0.4\ \mu\text{m}$ . The differences between the size distributions for these elements appear to result from the influence of aerosol of different age or source(s). Evidence for this is found in S:Se ratios for the various size particles. Gaseous Se emissions from CFPPs rapidly become associated with primary particles a short distance from the stack due to cooling and concomitant condensation (49). As the plume ages, the S:Se ratio for plume particles increases as sulfate is accumulated from  $\text{SO}_2$  conversion. The  $\text{SO}_2$  conversion rate in plumes is typically between 0.4 and 10%/h; hence, the S:Se ratio increases slowly with aerosol age. However, air arriving at Deep Creek Lake from the west is subject to enhanced  $\text{SO}_2$  conversion by orographic projection into clouds. Here, S:Se ratios for 1.8- and  $0.8\text{-}\mu\text{m}$  particles were typically double those for  $0.5\text{-}\mu\text{m}$  particles, indicating greater aerosol age or a greater degree of cloud processing. Thus, it is possible that sulfur-containing aerosol observed in the  $0.8\text{--}1.8\ \mu\text{m}$  size range represented either cloud-processed material of the same origin or older aerosol of a different origin (i.e., sources located further away). Furthermore, on the basis of observed elemental concentrations and Gaussian plume dispersion estimates for stationary sources lying upwind, Dodd et al. argued that the peaks at  $0.4\ \mu\text{m}$  diameters must have contained contributions from multiple sources (10). Taken together and in view of the narrow peaks observed for "fresh" accumulation aerosol, these observations are consistent with the interpretation that broad peaks observed at Deep Creek Lake represent the influence of multiple, narrowly distributed particle populations from individual sources, some or, perhaps, many of which may have been aggregated into new larger particles inside clouds. The good correlation in the structure of peaks for marker elements of decidedly different sources, e.g., V versus Se versus Sb is consistent with the homogenization expected by nucleation/coalescence in turbulent clouds. If so, then we could infer from the Deep Creek Lake size distributions that the  $\sigma_g$  for cloud-processed primary accumulation aerosol is probably  $<1.8$ . However, the overlap of many peaks whose mean size and width are limited by aqueous droplet growth dynamics is also consistent with this observation.

In College Park, MD, a suburb of Washington, DC, major sources of As, Sb, Se, and Zn lay within 50 km (11, 18). These include CFPPs located to the southwest and northwest; two large municipal incinerators, a blast furnace, and two CFPPs to the northeast and two incinerators to the southwest. In contrast, the closest major source lying to the west of College Park is the CFPP at Mount Storm 180 km away. Furthermore, emissions from CFPPs in the Ohio River Valley  $>300\ \text{km}$  to the west account for major fractions of the sulfate aerosol and associated elemental components observed at College Park. At College Park, mean diameters for aerosol particles containing As, Se, Sb, and Zn increased continuously with increasing RH but along different curves for samples influenced by local and distant sources (11). The mean diameters derived from samples influenced by winds from the direction of local sources were uniformly smaller than those influenced by westerly winds bearing aerosol from distant sources to the west. For example, at 60% RH, gmmads were As  $0.30 \pm 0.03$  and  $0.46 \pm 0.04$ ; Se  $0.33 \pm 0.06$  and  $0.54 \pm 0.04$ ; Sb  $0.39 \pm 0.03$  and  $0.53 \pm 0.04$ ; and Zn  $0.39 \pm 0.06$  and  $0.53 \pm 0.08$ , respectively, for curves influenced by local and distant sources. The near perfect collinearity of the curves for Sb and Zn supports the observation that both elements are mainly derived from the same source in this area, i.e., municipal incineration. The differences in RH response curves and size distributions for As, Se, and Sb/Zn indicate that these elements reside, entirely or partly, on physically separate particle populations. In westerly samples, sulfur concentrations were 4-fold greater than those for the other directions and increased more or less monotonically with increasing size and RH. This trend was also evident in samples affected more by local sources, but only at average RH  $>70\%$ . This is consistent with the hypothesis that once particles become wet, hygroscopic growth of both fresh and aged primary aerosol is accompanied by heterogeneous sulfur oxidation, although as described above, a portion of the growth may actually occur in nonprecipitating clouds.

Divita et al. also investigated the atmospheric behavior of V (12). Vanadium is highly enriched relative to many other metals in fuel oil due to the presence of V porphyrins and is extensively used as a tracer of emissions from fuel oil combustion. In OFPPs, which are the major source of atmospheric V aerosol in the summer, stack gases contain up to 50 ppm  $\text{SO}_3$  and 14% water vapor, which at temperatures  $<350\ ^\circ\text{C}$  readily condense on the primary particles to form highly concentrated droplets of sulfuric acid. After atmospheric discharge, these highly hygroscopic particles grow in the near plume by condensation of additional sulfuric acid and water vapor, sometimes resulting in fallout of highly acidic droplets. Oil-fired boilers represent a potentially important source of acid aerosol, a respiratory irritant of national concern. At College Park, mmads for V aerosol ranged from  $0.3$  to  $0.42\ \mu\text{m}$  at RH ranging from 60 to 79% but modal diameters for V aerosol were typically less than those of tracers of other stationary sources. At a site located on a roof 100 m downwind of a small oil-fired boiler, the mmad for V-containing aerosol was only  $0.23\ \mu\text{m}$  at 65% RH and  $\sigma_g$  was 1.48. A similar  $\sigma_g$  (1.53) was observed when the average RH was 76% and the mean diameter was  $0.27\ \mu\text{m}$ , but very small  $\sigma_g$  values (1.31 and 1.35) were observed for RH  $>82\%$  at this site. Thus, "fresh" and "aged" aerosol from OFPPs also appear to exhibit important differences in particle size. Moreover, it appears that processes accompanying hygroscopic growth can narrow the size distribution even in plumes.

In summary, observations taken from several hundred ambient size distributions of intrinsic tracers of generic high-temperature combustion sources reveal the following information appropriate for the U.S. mid-Atlantic region.



(1) "Fresh" accumulation aerosols from HTCSs are preserved after atmospheric discharge and probably account for the unspecified, preexisting accumulation aerosol described in Whitby's trimodal paradigm. Their size distributions and atmospheric behavior can be observed by studying size distributions of intrinsic elemental tracers.

(2) Furthermore, their size distribution parameters appear to be preserved during transport on the urban scale. Mean diameters of fresh primary accumulation aerosol particles are typically between 0.1 and 0.3  $\mu\text{m}$ , and standard deviations are typically 1.2–1.45 for many combustion sources.

(3) Accumulation aerosol emitted from incinerators and power plants equipped with scrubbers, i.e., sources wherein condensational growth is important, have exceedingly narrow size distributions ( $\sigma_g$  1.2–1.3).

(4) The data strongly suggest that fresh accumulation aerosol size distributions are rapidly modified by vapor deposition in concert with temporal changes in ambient RH, i.e., by hygroscopic growth.

(5) Growth after particle deliquescence is probably accompanied by heterogeneous conversion of  $\text{SO}_2$  in both wet particles and in clouds and is therefore largely irreversible on the time scale of hours. The concurrent accumulation of nonvolatile materials during atmospheric transport may further narrow ambient accumulation aerosol particle distributions ( $\sigma_g \sim 1.2$ ). These, however, appear broad in time-integrated samples due to hygroscopic modulation by the strong diurnal RH cycle typical of the mid-Atlantic region of the United States.

(6) In urban areas, size distributions typically differ for tracer elements of different generic sources. Fresh and aged accumulation aerosols follow different growth curves.

(7) Cloud processing of air advected over the Appalachians appears to "prematurely" age aerosol from sources to the west and produces aerosol with modal diameter in the 0.8–1.8  $\mu\text{m}$  range. During violent storms, coalescence of droplets probably combines particles from different sources, which would tend to homogenize aerosol composition; however, these particles will be removed in rain. Most clouds are nonprecipitating, and in these, turbulence may be too low to facilitate appreciable coalescence. Thus, the capacity of clouds to bring together particles from different sources may be small, and their net effect may be to narrow the distributions of primary particle populations. However, the coexistence of processed and unprocessed aerosol likely broadens the apparent distribution observed in time-integrated samples.

(8) Cloud processing may account for much of the aerosol particle growth attributed to liquid-phase heterogeneous conversion of  $\text{SO}_2$ .

Taken together, these observations strongly suggest that many toxic substances in urban mid-Atlantic aerosols are contained in a multiplicity of separate fresh primary aerosol populations from a multiplicity of individual sources as well as one or more aged primary aerosol populations. Ultimately, if pathophysiological links are to be made between health effects and aerosol particles, then it may be necessary to describe toxic doses in terms of exposures to the multiplicity of chemically distinct fresh and aged primary particle populations and not in terms of a single internally homogeneous secondary aerosol population as is connoted by the Whitby paradigm.

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## Literature Cited

- (1) Schwartz, J.; Dockery, D. W. *Am. Rev. Respir. Dis.* **1992**, *145*, 600–604.
- (2) Thurston, G. D.; Ito, K.; Hayes, C. G.; Bates, D. V.; Lippmann, M. *Environ. Res.* **1994**, *65*, 271–290.
- (3) Schwartz, J. *Am. J. Epidemiol.* **1994**, *139*, 589–598.
- (4) Dockery, D. W.; Pope, C. A., III. *Annu. Rev. Public Health* **1994**, *15*, 107–132.
- (5) Health Effects Institute. *Particulate Air Pollution and Daily Mortality: Replication and Validation of Selected Studies*; Health Effects Institute: Cambridge, MA, 1995.
- (6) National Center for Environmental Assessment. *Air Quality Criteria for Particulate Matter*, Vol. I; U.S. Environmental Protection Agency: Research Triangle Park, April 1996; EPA/600/P-95/001aF.
- (7) Office of Air Quality Planning and Standards. *Review of the National Ambient Air Quality Standards for Particulate Matter: Policy Assessment of Scientific and Technical Information*; Staff Paper PB97-115406; EPA-452/R-96-013; U.S. EPA: Washington, DC, 1996.
- (8) Warneck, P. *Chemistry of the Natural Atmosphere*; Academic Press: New York, 1988; p 506.
- (9) Whitby, K. T. *Atmos. Environ.* **1978**, *12*, 135–159.
- (10) Dodd, J. A.; Ondov, J. M.; Tuncel, G. *Environ. Sci. Technol.* **1991**, *25*, 890–903.
- (11) Ondov, J. M.; Divita, F., Jr.; Suarez, A. J. *Radioanal. Nucl. Chem.* **1995**, *192*, 215–228.
- (12) Divita, F., Jr.; Ondov, J. M.; Suarez, A. E. *Aerosol Sci. Technol.* **1996**, *25*, 256–273.
- (13) Niragu, J. O.; Davidson, C. I., Eds. *Toxic Metals in the Atmosphere*; Advances in Environmental Science and Technology, Vol. 17; John Wiley & Sons: New York, 1986.
- (14) McClellan, R., Miller. *CIIT Act.* **1997**, *17*, 1–22.
- (15) Carter, J. D.; Ghio, A. J.; Samet, J. M.; Devlin, R. B. *Toxicol. Appl. Pharmacol.* **1997**, *146*, 180–188.
- (16) Costa, D. L.; Dreher, K. L. *Environ. Health. Perspect.* In press.
- (17) Hasan, H.; Dzubay, T. G. *Aerosol Sci. Technol.* **1987**, *6*, 29–39.
- (18) Divita, F., Jr. Characterization and Sources of Atmospheric Submicrometer Particles in Washington, D.C. and Philadelphia, PA. Ph.D. Thesis, University of Maryland, College Park, 1993.
- (19) Kidwell, C.; Divita, F., Jr.; Ondov, J. M. *J. Aerosol Sci.* **1996**, *27*, S29–S30.
- (20) Davies, C. N. *J. Aerosol Sci.* **1974**, *5*, 293–300.
- (21) Sverdrup, G. M. Parametric Measurement of Submicron Atmospheric Aerosol Size Distributions. Ph.D. Thesis, University of Minnesota, Minneapolis, MN, 1977.
- (22) Wexler, A. S.; Lurmann, F. W.; Seinfeld, J. H. *Atmos. Environ.* **1994**, *28*, 531–546.
- (23) Hegg, D. A.; Hobbs, P. V.; Lyons, J. H. *Atmos. Environ.* **1985**, *19*, 1147–1167.
- (24) Warneck, P. *Chemistry of the Natural Atmosphere*; Academic Press: New York, 1988; p 301.
- (25) McMurry, P. H.; Stolzenburg, M. R. *Atmos. Environ.* **1989**, *23*, 497–507.
- (26) Kerminen, V.-M.; Wexler, A. S. *Atmos. Environ.* **1995**, *29*, 3263–3275.
- (27) Kerminen, V.-M.; Wexler, A. S. *Atmos. Environ.* **1995**, *29*, 361–375.
- (28) McMurry, P. H.; Wilson, J. C. *J. Geophys. Res.* **1983**, *99*, 5101–5108.
- (29) Gillani, N. V.; Colby, J. A.; Wilson, W. E. *Atmos. Environ.* **1983**, *17*, 1753–1763.
- (30) Pandis, S. N.; Seinfeld, J. H. *Atmospheric Chemistry and Physics*; John Wiley & Sons: New York, 1998; p 23.
- (31) Meng, Z.; Seinfeld, J. H. *Aerosol Sci. Technol.* **1994**, *20*, 253–265.
- (32) John; et al. *Atmos. Environ.* **1990**, *24A*, 2349–2359.
- (33) Gillani, N. V.; Colby, J. A.; Wilson, W. E. *Atmos. Environ.* **1983**, *17*, 1752–1763.
- (34) Friedlander, S. K. *Smoke, Dust, Haze*; John Wiley & Sons: New York, 1977; p 223.
- (35) Mroz, E. J. The Study of the Elemental Composition of Particulate Emissions from an Oil-Fired Power Plant. Ph.D. Thesis, University of Maryland, College Park, 1976.
- (36) Greenberg, R. R. A Study of Trace Elements Emitted on Particles from Municipal Incinerators. Ph.D. Thesis, University of Maryland, College Park, 1976.
- (37) Greenberg, R. R.; Zoller, W. H.; Gordon, G. E. *Environ. Sci. Technol.* **1978**, *12*, 566–573.
- (38) Ondov, J. M.; Biermann, A. H. Physical and Chemical Characterization of Aerosol Emissions from Coal-Fired Power Plants. In *Environmental and Climatic Impact of Coal Utilization*; Singh, J. J., Deepak, A., Eds.; Academic Press: New York, 1979.
- (39) Ondov, J. M.; Ragaini, R. C.; Biermann, A. H. *Environ. Sci. Technol.* **1979**, *13*, 946–953.



- (40) Ondov, J. M.; Biermann, A. H.; Heft, R. E.; Koszykowski, R. F. Elemental Composition of Atmospheric Fine Particles Emitted from Coal Burned in a Modern Electric Power Plant Equipped with a Flue-Gas Desulfurization System. In *Atmospheric Aerosol: Source/Air Quality Relationships*; ACS Symposium Series 167; Macias, E. S., Hopke, P. K., Eds.; American Chemical Society: Washing, DC, 1981; pp 173–186.
- (41) Markowski, G. R.; Ensor, D. S.; Hooper, R. G.; Carr, R. C. *Environ. Sci. Technol.* **1980**, *14*, 1400–1402.
- (42) Ondov, J. M.; Ragaini, R. C.; Biermann, A. H. *Environ. Sci. Technol.* **1979**, *13*, 598–567.
- (43) Venkataraman, C.; Lyons, J. M.; Friedlander, S. K. *Environ. Sci. Technol.* **1994**, *28*, 555–562.
- (44) Suarez, A. E.; Caffrey, P. F.; Ondov, J. M.; Thaung, K. C. *J. Aerosol Sci.* **1996**, *27*, S697–S698.
- (45) Ondov, J. M. A Study of Trace Elements on Particles from Motor Vehicles. Ph.D. Thesis, University of Maryland, College Park, 1974.
- (46) Ondov, J. M.; Zoller, W. H.; Gordon, G. E. *Environ. Sci. Technol.* **1982**, *16*, 318–328.
- (47) McMurry, P. H.; Rader, D. J.; Stith, J. L. *Atmos. Environ.* **1981**, *15*, 2315–2327.
- (48) Annegarn, H. J.; Leslie, A. C. D.; Winchester, J. W.; Sellschop, J. P. F. *Aerosol Sci. Technol.* **1983**, *2*, 489–498.
- (49) Gordon, G. E. *Environ. Sci. Technol.* **1988**, *22*, 1132–1142.
- (50) Dodd, J. A. The Elucidation of Submicrometer Aerosol Structure and Properties in Source and Ambient Samples at Deep Creek Lake Maryland. M.S. Thesis, University of Maryland, College Park, 1989.
- (51) Wu, C. Y.; Biswas, P. *Combust. Flame* **1993**, *93*, 31–40.
- (52) Biswas, P.; Lin, W. Y.; Wu, C. Y. Formation and Emission of Metallic Aerosols from Incinerators. Presented at the 1992 European Aerosol Conference, Oxford.
- (53) Olmez, I.; Sheffield, A. E.; Gordon, G. E.; Houck, J. E.; Pritchett, L. C.; Cooper, J. A.; Dzubay, T. G.; Bennett, R. L. *JAPCA* **1988**, *38*, 1392–1402.

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