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Key Points:

- Some models fail to acknowledge actual particle deposition data
- Reasons for differences between observations and predictions remain obscure
- Modern instrumentation allows the matter to be addressed experimentally

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Dry deposition of particles to canopies—A look back and the road forward

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Abstract The so-called accumulation-size range of airborne particles is the center of a continuing disagreement about the formulation of dry deposition. Some contemporary meteorological and air quality models use theoretical developments based on early wind tunnel and other controlled experiments, while other models consider the bulk properties of the underlying surface and the ability of atmospheric turbulence to deliver particles to it. This dichotomy arose when the first micrometeorological measurements of particle deposition velocities became available, yielding numbers exceeding the highest expectations of the then-current models based on assumptions about inertial impaction and interception. The model predictions had previously been shown to be in accord with theoretical treatments of filtration. A common reaction was to distrust the field experimental results, but the experimental findings were supported by subsequent studies. The difference between model predictions and field measurements appears greatest for densely vegetated canopies. Ongoing research is investigating factors that could give rise to the discrepancy, e.g., turbulence intermittency, leaf orientation, leaf morphology, leaf flutter, electrical charges, and a number of phoretic effects. In the meantime, many investigators are faced with a decision as to whether to make use of parameterized field results or theoretical descriptions of behaviors that are not yet well examined. Here the history of the ongoing disagreement is reviewed, and some possible resolutions are presented.

1. Introduction

The contemporary suite of air quality models contains a wide variety of expressions describing the processes causing dry deposition of particles. This variability is a good illustration of the complexities involved in extrapolating understanding of individual contributing processes from laboratory situations to the real vegetated world and in assembling knowledge of these individual processes into a working description of whole-canopy behavior. Although the scientific investigation of atmospheric particle dry deposition stretches back more than 50 years, it is apparent that substantial uncertainties remain in our basic understanding [e.g., *Sportisse*, 2007].

Dry deposition is the net flux of airborne gases and particles to exposed surfaces associated with the turbulent transport of trace gases and small particles and the gravitational settling of larger particles. There are at least three major areas of modeling currently involved: (a) estimating the air quality consequences of emissions of chemicals from various sources for regulatory or predictive purposes (e.g., CAMx [see *Emery et al.*, 2012]), (b) interpreting routinely collected air quality data to yield site-specific estimates of dry deposition of ecologically important chemicals (as in CASTNet [*Clarke et al.*, 1997]), and (c) refining basic understanding of the roles of the processes involved [e.g., *Katul et al.*, 2010]. The existence of uncertainties in dry deposition formulation is reflected in many different particle dry deposition results that regional-scale air quality models produce [see *Rao et al.*, 2011].

Pryor et al. [2008] and *Petroff et al.* [2008] have summarized key aspects of the particle dry deposition phenomenon, focusing on recent experimental results and developments in the understanding of relevant processes. It is not the present purpose to repeat the summations of these reviews, or to endorse or to criticize any particular models or model constructs, but rather to give an outline of how early disparities between theoretical developments and field measurements are slowly being resolved and to suggest paths by which the remaining divergences might be reconciled, with an emphasis on the need to address issues of biological variability [see *Wesely and Hicks*, 2000].

Figure 1 presents CAMx results demonstrating that dry deposition is a critical component of the overall atmospheric aerosol budget, a matter that has been well addressed elsewhere [e.g., *Fowler et al.*, 2009].

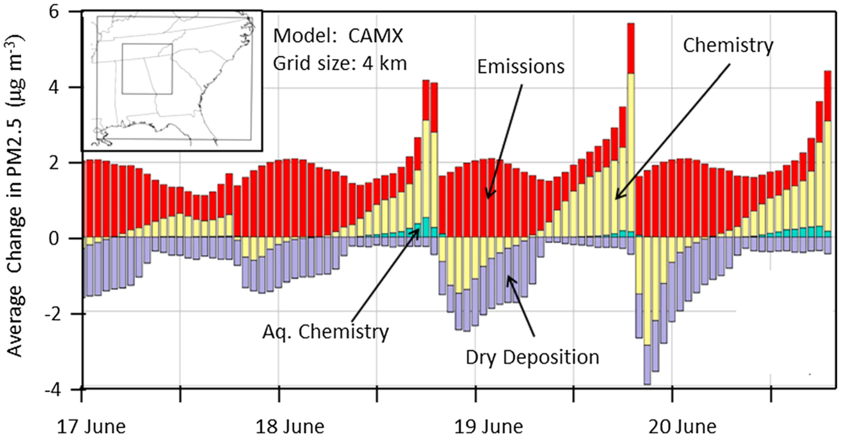

Figure 1. Comparison of the nontransport processes that affect $PM_{2.5}$ concentration in the lowest 100 m of the atmosphere as estimated from a regional-scale air quality model simulation for June 2013. The area over which the results (averages) apply is about 500 km × 500 km, as indicated by the inner square of the CAMx domain illustration inset. The time scale markings indicate noon (EST). The dry deposition estimates result from an assumption about the deposition velocity that is a focus of the current presentation. The time period selected for this illustration was free of rainfall.

In particular, it comprises a significant fraction of total chemical deposition to aquatic and terrestrial ecosystems, of major contemporary relevance in the context of "critical loads" (e.g., *Pardo* [2010]: "... one can generate a value for any site regardless of whether any data exist for that site"). It should be noted that the version of CAMx used here makes use of the deposition/particle size formulation developed by *Zhang et al*. [2001].

The schematic simplification of Figure 2 presents a familiar way of differentiating atmospheric particles by diameter. Ultrafine particles ($< \sim 0.2\ \mu m$) are primarily affected by turbulence and coarse particles ($>2\ \mu m$) primarily by gravity. The intermediate size range (0.2–2 μm), known as the "accumulation mode," is affected by both gravity and turbulence. The term accumulation mode refers to the dominant process of their generation—from interactions among the ultrafine particles that are themselves the consequence of chemical reactions and gas-to-particle conversion occurring in the air. The mechanisms that determine the rate of dry deposition of particles are well known for both coarse particles whose deposition is dominated by gravitational settling and for ultrafine particles that deposit via turbulent exchange and Brownian diffusion. It is the accumulation mode size range that will be the primary focus of the discussion to follow.

Different research communities have different ideas of what constitutes dry deposition. Among materials deterioration experts and chemical engineers, the important factor is the rate of accumulation on the surfaces of buildings, statues, pipes, etc. These surfaces may be in any conceivable configuration; they are rarely horizontal or uniform. The important considerations relate to the characteristics of the air to which a receptor surface is exposed, the concentration of the depositing material in this air, and a number of surface factors—e.g., the texture and composition of the surface under consideration, its size and shape, its temperature and electrical charge, and its angle to the flow in which it is exposed. Radioactivity presents an additional factor sometimes of importance.

Consider a metal plate or some other receptor exposed to an air stream containing a concentration (χ) of particles. All other factors being equal, the rate of deposition (the flux, f_χ) is assumed to be proportional to χ. Standard practice has then evolved to account for this first-order association by considering the ratio of the flux to the concentration, so defining a deposition velocity, $v_d = f_\chi/\chi$. Having accounted for the association of fluxes and concentrations, it then remains to explore the dependence of f_χ on the remaining set of influential properties. It is this intent that underpinned most of the laboratory studies which initiated related research, with the particle size being the focus. Studies of this kind have also given clear evidence of the complexities introduced when the receptor surfaces are foliage. For example, *Beckett et al*. [2000] report wind tunnel studies that show a clear distinction between the particle capture efficiencies of coniferous (*Pinus nigra*, in their study) and a variety of deciduous foliage.

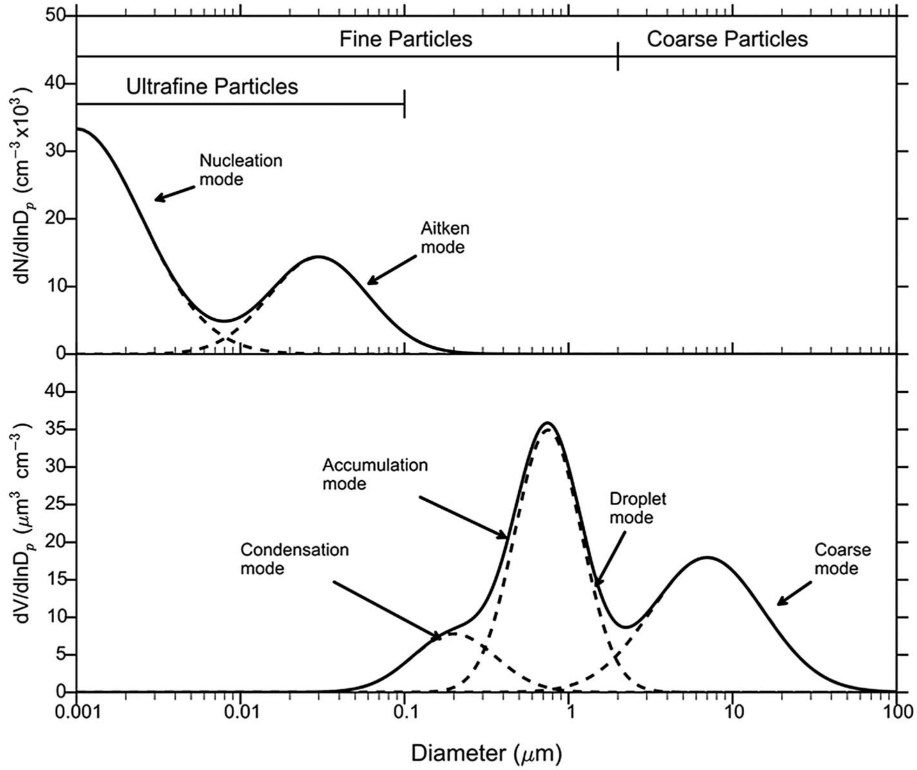

Figure 2. A schematic depiction of the size modes of atmospheric aerosol particles.

In other contexts, dry deposition is viewed as a removal mechanism for trace materials (gases as well as particles) carried by the wind. Above the level of immediate influence of surface obstacles and vegetation, the spatially averaged removal rate of atmospheric contaminants is represented by a vertical flux (F_χ), partially associated with turbulent exchange, as in the case of the usual micrometeorological quantities (heat, moisture, and momentum), but for particles also influenced by particle properties and by gravity. By extension of the surface-specific work of early studies, the concept of a deposition velocity is also widely used in this context [see *Gregory*, 1945; *Chamberlain*, 1953]: as the ratio of the vertical flux F_χ through a horizontal plane in the air to the concentration in the air at that level, χ_z (for height z). If there are no sources or sinks of particles between the level of interest and the surface itself, then F_χ is constant with height below z. The deposition velocity of relevance here is then $V_d = F_\chi/\chi_z$.

Note that herein there is a deliberate differentiation of nomenclature, with lower case symbols referring to deposition to some selected surface of an exposed object, while upper cases are used to describe the deposition from the air aloft to the complex array of surfaces that constitutes the deposition sink as seen by the atmosphere. The challenge dominating much of the literature over the last many decades has centered on the way in which knowledge of v_d can be used to estimate the canopy-average and landscape-relevant quantity V_d. The matter is complicated by the simple fact that V_d is aligned with the vertical (or alternatively oriented normal to the plane of atmospheric streamlines), but v_d is not. In early work, *Monteith* (1963) bypassed this complexity by conceptually replacing a canopy with a single surface that had the process characteristics of a single leaf—the so-called big leaf model. An alternative approach has been to assemble all of the receptor-specific values of v_d in layers within a vegetated canopy and then to compute the effective value of V_d on the basis of these layer-by-layer computations. *Meyers et al*. [1998] present such a multilayer model which has received practical application in the Clear Air Status and Trends Network (CASTNet) program of the U.S. Environmental Protection Agency [*Clarke et al*., 1997]; however, some of the original problems remain unanswered. The difficulties appear to be most apparent for the case of depositing particles in the accumulation mode.

In the following, there will be frequent reference to the diameter of the particle(s). In some instances, this refers to the aerodynamic diameter—the diameter of a sphere with unit density that has the same aerodynamic characteristics as the particle in question. However, the distinctions and usages are vague, since clearly the shape and composition of particles are key considerations that cannot be easily combined into a single convenient descriptor.

2. Historical Origins

Because of the need to assess the risk to people and the environment from the radioactive products produced in nuclear weapons tests, deposit gauges of varying configurations became favored measurement devices during the era of atmospheric nuclear testing starting in the late 1940s. A major risk of local exposure was then due to "hot" radioactive particles, usually associated with fragments of the weapon casing and its supporting structures, and the suspension of irradiated soil in the vicinity of the explosion. These large (and exceedingly hazardous) particles fell over an area of rather limited extent downwind of the explosion —hence, radioactive "fallout." These particles fell from the air quickly, leaving behind an atmospheric inventory of much smaller particles, dominated by fission products. In the lack of something better, the same collection vessels that worked well for close-in fallout studies were then employed far beyond the region of large-particle dominance, despite recognition of the fact that such methods failed to reproduce the microscale roughness features of natural surfaces. In nature, and depending on the vegetative species, leaf characteristics such as their size and the presence of protuberances such as leaf hairs can influence the generation and continuity of laminar boundary layers adjacent to the surface itself. The collection efficiency of small particles can be substantially affected. In an early recognition of the central role of biological factors in the deposition process, efforts were made to "calibrate" collection vessels in terms of fluxes to specific types of vegetation, soils, etc. [*Hardy and Harley*, 1958].

Figure 3 illustrates one of the dry- and wet-bucket devices of the 1960s and later. Two collection buckets were used. A protective cover moved from one bucket to the other whenever precipitation was detected, so that separate measurements were made of deposition associated with the precipitation process and deposition occurring at all other times. In practice, the "dry bucket" collected particles large enough to be falling according to gravity but sampled finer particles imperfectly. Nevertheless, data obtained using collection vessels are, at times, interpreted as if they accurately sample the deposition of particles in the accumulation-size range and smaller, to a natural landscape in which the sampler is situated. To those who so interpret, a simple question has produced some new understanding (and considerable discussion) in the past—"Should the deposition to the inside of the measurement vessel be measured, or that to the outside, and why?" The use of collection surfaces, dishes, and buckets continues to this day, often in the context of substances of some special interest [e.g., *Holsen et al*., 1991; *Lyman et al*., 2009].

The step from a dominant interest in coarse particle deposition (e.g., for soil particles, dust, and near-field radioactive fallout) to that of smaller particles generated considerable theoretical and laboratory research. In early modeling work, *Friedlander and Johnstone* [1957] assumed that particles are carried with atmospheric turbulence until they are within one stopping distance (as determined by inertia and the turbulent velocity) of the surface. *Sehmel* [1970] assumed an effective sink at one particle radius from the surface—thus, assuming that particles contacting the surface will be captured by it. It was studies such as these that predicted very low deposition velocities to smooth surfaces, particularly for particles in the accumulation-size range. Wind tunnel studies [*Sehmel*, 1970, 1979] largely confirmed this expectation. *Sehmel et al*. [1973] and *Chamberlain* [1986] summarize much of the early work related to surface capture of particles.

3. Deposition Processes

Attention was initially concentrated on the processes of impaction and interception, the main mechanisms by which filters remove particles from airstreams [see *Davies*, 1967; *Friedlander*, 1977]. Interception occurs when a particle following velocity streamlines comes within one particle radius from the surface that is causing streamline bending. Impaction occurs when the mass/inertia of a particle is sufficient to prohibit it from following a bending streamline, so that it is impacted on the surface of the obstruction. Studies of fibrous filters showed that there was a minimum in the efficiency of scavenging, which is also a feature of particle retention in human lungs [*Lee and Liu*, 1980]. Figure 4a illustrates the efficiency associated with filtration by a fibrous membrane (with arbitrary units). In practice, the details of the efficiency curve depend on many factors, such as the characteristics of both the filter and the particles, and the speed of air flow. Not

Figure 3. A wet/dry sampler (initially the “HASL collector,” after the US Atomic Energy Commission Health and Safety Lab., New York) as used in studies of acid rain, when the emphasis was on the deposition of anions and cations [see *Bogen et al.*, 1980].

surprisingly, extension of the interception and impaction filtration model to the case of deposition of airborne particles yields a similar picture, as illustrated in Figure 4b. The model predictions illustrated in Figure 4b were largely supported by wind tunnel investigations, starting with studies of flat test surfaces and ending up with tests involving swaths of vegetation.

For flat test surfaces (and for a water surface) the well in the deposition velocity curve was found to have a minimum value approximating 0.001 cm s^{-1} for particles in the 0.4 to 0.5 μm size range, depending on the circumstance. As particle sizes increased, the deposition velocities trended toward the predictions of the Stokes-Cunningham relationship. These experiments provided a foundation for extending understanding to the case of particle deposition to vegetation [*Chamberlain*, 1967, 1975; *Wedding et al.*, 1977; *Beckett et al.*, 2000]. As wind tunnel studies progressed, support for the general feature of minimum deposition velocity corresponding to a particle diameter of about 0.5 μm was repeatedly confirmed although with some disagreement regarding its depth. Subsequently, *Sehmel* [1980] updated his wind tunnel work to provide estimates of deposition velocities to canopies of a range of geometries in different meteorological conditions. As is shown in Figure 4b, increasing surface roughness enhanced deposition [see *Sehmel and Hodgson*, 1978]. However, in the case of a natural vegetated surface, the appropriate velocity field is hard to specify and is certainly a function of the mix of plant species involved. In any case there are several other mechanisms at

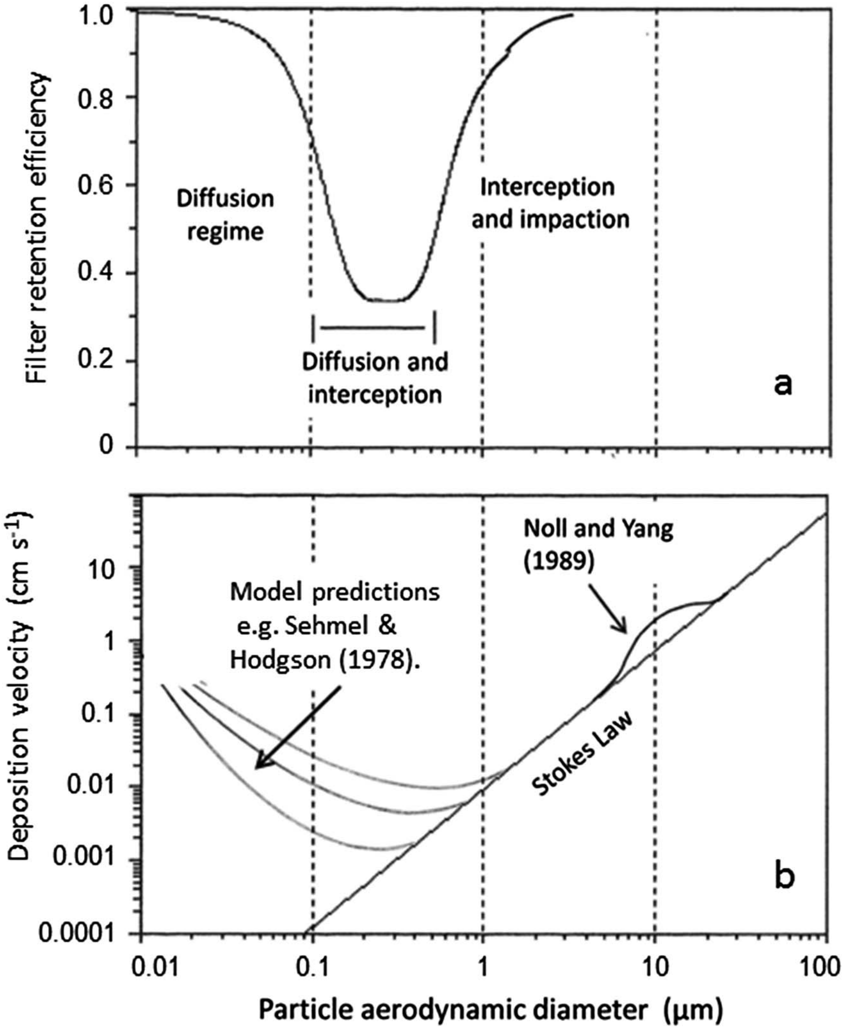

Figure 4. Schematic representations of (a) the efficiency of a fibrous filter for removing particles from an airstream, following *Davies* [1967] and *Friedlander* [1977], and (b) examples of particle deposition velocity models based on wind tunnel studies by *Sehmel and Hodgson* [1978] and on collection by a water surface outdoors [*Noll and Fang*, 1989]. The Sehmel and Hodgson results indicate shallower "wells" as the surface roughness length increases. Many such depictions exist, all supported by experimental data obtained in laboratory situations.

play. It is the goal of much contemporary research to explore and describe these additional mechanisms, so as to construct a model more representative of a natural landscape.

Extrapolation from laboratory understanding to open-air vegetated surfaces necessarily involves the development of models that assemble the overall consequences of the many contributing processes in a realistic manner. Most considerations of the physics of particle deposition to vegetation (or other complex surfaces) start with the filtration basics—interception and impaction and add other contributing processes to the overall system. *Hicks* [1984] presented a schematic diagram (like Figure 5) identifying the many processes relevant in the present context. As originally presented, the listing of processes omitted turbophoresis.

Thermophoresis drives particles away from hot surfaces, because of the higher energy of gas molecules impacting the side of a particle facing the surface [see *Davies*, 1967]. Thermophoresis depends on the local temperature gradient in the air, on the physical and thermal properties of the particle, and on the nature of the interaction between the particle and air molecules [see *Derjaguin et al.*, 1972]. The thermophoretic velocity of very small particles ($<0.03\ \mu$m diameter, and at times of peak temperature of the surface(s)) is likely to be less than $0.03\ \mathrm{cm\ s^{-1}}$ (estimated from values quoted by *Davies* [1967]). It is not clear how larger particles may be influenced, but radiometric forces can also become important [*Cadle*, 1966].

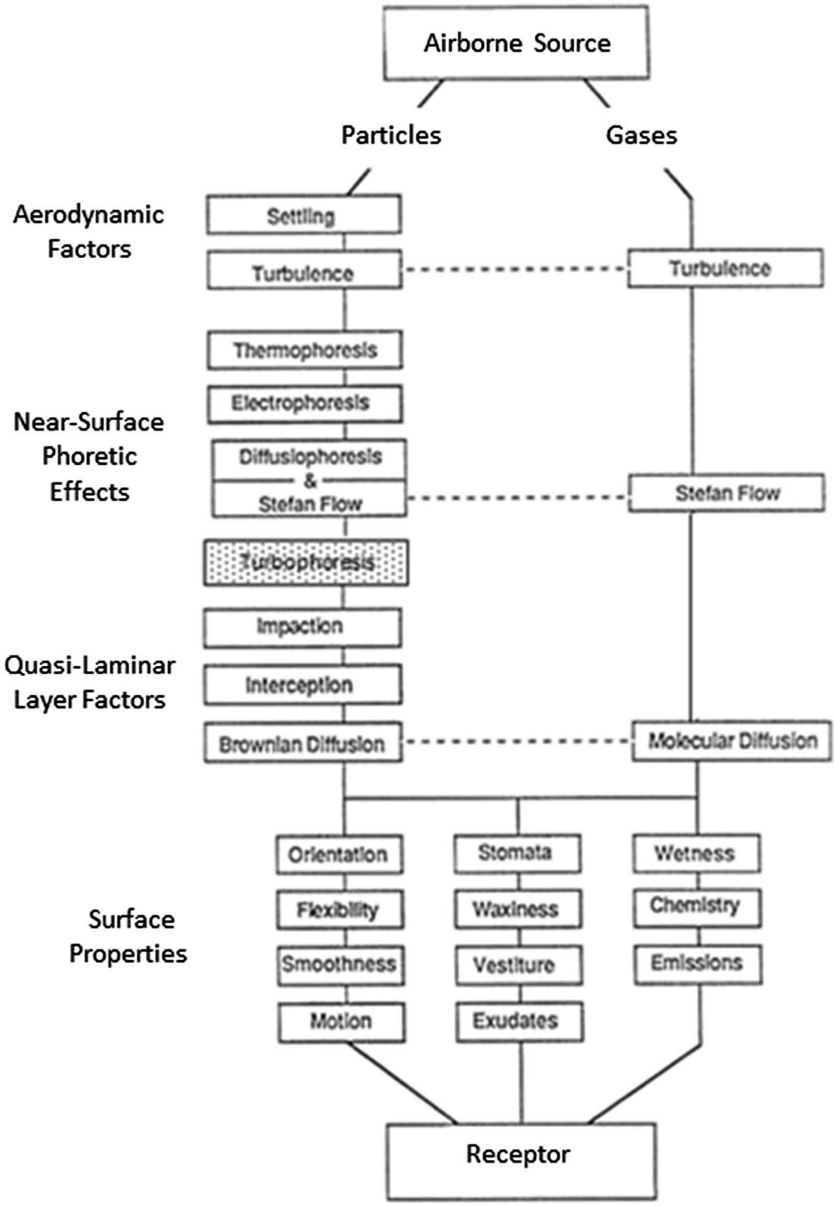

Figure 5. A depiction of the processes contributing to the deposition of airborne particles and trace gases. Turbophoresis is a recent addition to the suite of mechanisms.

Diffusiophoresis results when particles reside in a mixture of several gases, with a concentration gradient of one of them. In most natural circumstances, the principle concern is the water vapor concentration. Close to an evaporating surface, a particle will be impacted by more water molecules on the nearer side. Because these water molecules are lighter than air molecules, there will be a net "diffusiophoresis" toward the evaporating surface.

Diffusiophoresis and thermophoresis both depend on the interaction between atmospheric molecules and the particle. The size and shape of the particle are likely to be critical considerations, although neither can be predicted with precision. Moreover, these subjects are sufficiently complicated that generalizations cannot be easily made; they constitute specialties in their own right. The phoretic effects are generally small, and their influence on dry deposition in field situations can often be disregarded. However, it is relevant to note that these effects are independent of the orientation of the surface to which deposition occurs. In the case of a deep and complex canopy (e.g., a forest), ignoring them might be unwise.

Many workers include Stefan flow in general discussions of diffusiophoresis, but because of the conceptual difference between the mechanisms involved it is of current relevance to consider it separately. Stefan flow results from the injection into the gaseous medium of new gas molecules at an evaporating or subliming surface. Every gram-mole of substrate material that becomes a gas displaces 22.41 L of air, at standard temperature and pressure. Thus, at STP a Stefan flow velocity of 22.41 mm s^{-1} will result when 18 g of water evaporates from a 1 m^2 area every second. Daytime evaporation rates from natural vegetation often exceed 0.2 g m^{-2} s^{-1} for considerable times during the midday period, resulting in Stefan flow of more than 0.2 mm s^{-1} away from the surface. For the present, it is sufficient to note that Stefan flow is capable of modifying surface deposition rates by an amount that is larger than the predicted deposition velocity appropriate for many small particles to aerodynamically smooth surfaces exposed in wind tunnels.

Turbophoresis results from the inability of particles being transported in a three-dimensional field of turbulence to respond quickly to velocity fluctuations in the immediate vicinity of a receptor surface (*Caporaloni et al.*, 1975; *Reeks*, 1983; *Guha*, 1997; *Katul and Poggi*, 2010). The net consequence is that particles are moved by turbulence toward regions of lower turbulent kinetic energy and hence toward any surface exposed in a field of turbulence largely regardless of the orientation of the surface. Since the time of first presentation of the conceptual flow diagram illustrated in Figure 5, turbophoresis has arisen as a major factor for situations in which turbulent kinetic energy is high—over rough surfaces or in strong winds, or both.

Electrostatic attraction has often been proposed as a mechanism for promoting deposition of small particles. *Chamberlain* [1960] reported that electrostatic attraction can modify the deposition velocities of small particles to vegetation, when electrical fields are sufficiently high, of the order of 1000 V/cm. However, in fair-weather conditions, field strengths are typically less than 10 V/cm, so the net effect on particle transfer is likely to be small. Biological research [e.g., *Leach*, 1987; *Fromm and Fei*, 1998] has led to an understanding of the role of electrical signals in plant physiology, and it is now clear that surface electrical charge could play a part in the overall deposition process, at least for some plant species and in some situations. "Leaves exhibited a diurnal rhythm of potentials, with highest voltages after midday (+120 V max. recorded) and minimum potentials, near zero, at night" [*Leach* 1987]. There have been other investigations of electrostatic attraction as a deposition process [e.g., *Langer*, 1965; *Rosinski and Nagamoto*, 1965; *Hidy*, 1973], but at the time of this writing (2016) the issue is still obscure. It should be noted, however, that (a) the electrical mobility of a particle is a strong negative function of particle size, so that electrostatically enhanced deposition should be most important for very small particles, and (b) the net consequences must be expected to vary with the circumstances in ways that are presently obscure. Electrostatic effects have also been proposed as a mechanism for submicrometer particle generation over forested areas [*Fish*, 1972]. Thus, the consequences of electrical charges on foliage could range from promoting particle generation to accelerating particle deposition.

Condensation of water reduces the effectiveness of electrostatic adhesion forces, because leakage paths are then set up and charge differentials are diminished. However, the presence of liquid films at the interfaces between particles and surfaces causes a capillary adhesive force that compensates for the loss of electrostatic attraction. These "liquid-bridge" forces are most effective in high humidities, and for coarse particles $> 20\ \mu\text{m}$, according to *Corn* [1961].

Even in the earliest studies, the fine-scale complexity of vegetated surfaces was acknowledged as a contributing factor. For example, *Chamberlain* [1967] tested the roles of leaf stickiness and hairiness in his wind tunnel tests. He concluded that "with the large particles (32 and 19 μm) the velocity of deposition to the sticky artificial grass was greater than to the real grass, but with those of size 1 μm and less, it was the other way, thus confirming....... that hairiness is more important than stickiness for the capture of the smaller particles." The importance of leaf hairs was verified by studies of the uptake of Pb and ^{210}Po particles by tobacco leaves [*Martell*, 1974; *Fleischer and Parungo*, 1974]. *Wedding et al.* [1975] reported increases by a factor of 10 in deposition rates for particles to pubescent leaves compared to smooth, waxy leaves. This was confirmed by further wind tunnel studies reported by *Wedding et al.* [1977] and in recent work by *Huang et al.* [2015].

All of these surface-specific "phoretic" mechanisms apply to the individual surface components. While their magnitudes discussed above are small, there must be consideration of canopy density before any of them might be dismissed. None of these mechanisms depends on the orientation of the particular surface element under consideration; however, the orientation of leaves remains an intriguing factor. In daytime, with strong solar radiation, the orientation of leaves is likely to influence their temperature. For those particles that are slightly affected by gravity, combining the orientation-specific gravitational considerations with the effects of the various phoretic mechanisms and the velocity-dependent interception and impaction processes presents an intriguing intellectual challenge. However, it is clear that whatever the way in which these many deposition mechanisms contribute to the overall deposition phenomenon, their consequence in the real world will be influenced by the leaf area index (or its equivalent)—the amount of exposed surface area per unit horizontal area—and the velocity/turbulence field.

4. Introducing Micrometeorology

For many decades, descriptions of such near-surface processes have been assembled in models constructed on the basis of accepted micrometeorology. The assumption of perfect capture once a particle comes in contact with a surface is a common feature. Several authors have approached the problem as one of filtration theory, as illustrated in Figure 4 above, in which aerosols are scavenged as air permeates through a collecting medium [e.g., *Slinn*, 1977; *Davidson and Friedlander*, 1978; *Hidy and Heisler*, 1978]. All of these early models built upon the wind tunnel work of *Chamberlain* [1974], *Wedding et al*. [1977], and others. These early workers recognized the importance of considering such matters as the density of the canopy and its biological characteristics, but the modeling capabilities then available limited the extent to which such processes could be simulated in deposition and air quality models.

Chamberlain [1967] extended the familiar micrometeorological concepts of roughness length and zero-plane displacement to the case of particle fluxes. Such treatments were considered to be extensions of simulations developed for the case of gaseous deposition to vegetation, which in turn were based on an extensive background of agricultural and forest meteorology, especially concerning evapotranspiration [*Monteith*, 1965] and introducing the now-familiar multiple-resistance model. In much later work, *Venkatram and Pleim* [1999] and *Seinfeld and Pandis* [2012] have drawn attention to the inadequacies of the multiple-resistance framework in the case of particle fluxes; however, the errors involved might often be small. *Lewellen and Sheng* [1980] used formulations describing subcanopy turbulence to reproduce the main features of subcanopy flow and combined these with particle deposition formulations like those resulting from the laboratory and wind tunnel work as described above. Lewellen and Sheng emphasized their model's omission of several potentially critical mechanisms, especially electrical migration, coagulation, evolution of particle size distributions, diffusiophoresis, and thermophoresis. *Slinn* [1974, 1982] assembled then-available information into a simulation of outdoor vegetated canopies. However, all of these models were acknowledged to be simplifications of what was recognized to be a complex process.

Atmospheric stability was an issue of immediate concern within the micrometeorological community, primarily because of its dominating influence on the diurnal cycle of V_d and also because of its influence on intermittency and gustiness within forest canopies. In simple concept, when a canopy is heated by insolation, pockets of warm air develop within it and eventually rise through it. In consequence, replacement air carries the particles of main interest here. This provides a mechanism for airborne pollutants to be entrained within a vegetation canopy and to remain there until they are deposited on one of the many available surfaces or "scavenged" by another rising bubble of warm air. This process is essentially turbulent, but it clearly bears little resemblance to any simple picture of high-frequency turbulent transfer to flat surfaces. Subcanopy velocities can be highly intermittent, the causes and consequences of which remain in study [*Baldocchi and Meyers*, 1988; *Katul et al*., 1997; *Belcher et al*., 2012].

In the 1970s, the predictions of then-existing models of dry deposition were increasingly viewed with caution by experimentalists, largely because of the natural complexity that was necessarily represented by simple parameterizations in the models. On the other hand, modelers favored the only experimental data that were then available—wind tunnel results. The matter came to a head when *Wesely et al*. [1977] reported an experimental determination of the deposition velocity of small particles over grassland, derived by application of eddy correlation methods. The results indicated daytime deposition velocities of about 1 cm s^{-1} for fine particles but without reliable indication of their size. Subsequent experiments over rough surfaces such as field crops and forests yielded similar daytime values [*Wesely and Hicks*, 1979; *Hicks*, 1980; *Wesely et al*., 1983]. At night considerably smaller values appeared typical. Some modelers considered the finding of upward fluxes of small particles to be indicative of an undetected flaw in the micrometeorological measurements, and

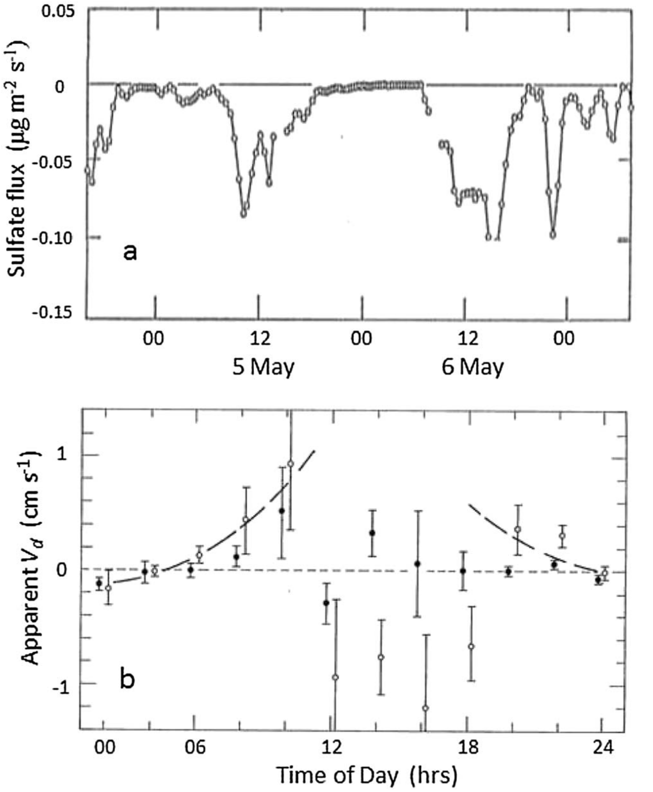

Figure 6. An example of accumulation-size particle deposition data, collected over a mixed deciduous forest in eastern Tennessee in 1983 [see *Hicks et al.*, 1985, 1989]. (a) The fluxes of sulfate particles measured by eddy correlation and coupled flame photometry. (b) The average deposition velocities (and standard deviation bars) during the same month, for 0.5 to 0.7 μm (open circles) and 0.7–1.2 μm (filled circles) particles measured optically.

hence, the results obtained in such experiments should be disregarded. On the other hand, experimentalists noted the inability of models to take all of the known processes fully into account, while at the same time representing known processes in ways that appeared limited by the small scales of the formative wind tunnel studies.

The difference in viewpoints was exacerbated by the finding [*Hicks and Wesely*, 1978] that the fluxes of particulate sulfur failed to display the small values indicated by wind tunnel experiments and theoretical studies. Particulate sulfur was known to be predominantly in the accumulation-size range, from 0.2 to 2.0 μm diameter. At that time, air quality models mostly assumed a deposition velocity of 0.1 cm s^{-1} to describe the rate of dry deposition of airborne particles in this particular size range, the origin of which assumption remains obscure. In the 1970s, the development of fast response flame photometric analyzers enabled eddy fluxes of sulfur to be measured. Using a filter in the air stream being sampled allowed the gaseous SO_2 to be measured, using a denuder system to remove the gaseous component left a sulfate particle ($SO_4^{=}$) signal. In daytime, deposition velocities for particulate sulfur were found to be of the order of 1 cm s^{-1}, but tending to follow a diurnal pattern like that of the surface heat energy cycle (small near dusk and dawn, and rising to a maximum near noon). This major departure from the expected value (of 0.1 cm s^{-1} or perhaps lower) was seen by some workers as further cause to distrust micrometeorological methods [e.g., *Slinn*, 1982].

At the same time as the North Carolina loblolly pine dry deposition experiment that yielded bidirectional eddy fluxes of small particles [*Hicks and Wesely*, 1982], independent studies were made of the emissions of terpenes from the pine trees at the same location. *Arnts et al.* [1978, 1982] report a flux of α-pinene ranging from 11 to 19 μg m^{-2} s^{-1}. The reaction with ozone is sufficiently rapid that submicrometer particles can be generated within the canopy, so that the instrumentation deployed above the canopy saw the net influence of a flux downward from the air aloft and upward from the subcanopy air space. To the satisfaction of experimentalists involved, the question of the bidirectional fluxes was then partially solved.

Figure 6 shows results from subsequent experiments over a mixed deciduous forest characteristic of the (aptly named) Great Smoky Mountains of the eastern USA [see *Hicks et al.*, 1985, 1989]. Measurements were made of particle fluxes for two size ranges, 0.5 to 0.7 μm diameter and 0.7 to 1.2 μm diameter, with separate measurements of sulfate fluxes, independent of particle size. Figure 6a shows that the fluxes of sulfur were from the air to the surface at all times, but the fluxes decreased to near zero at night. However, Figure 6b shows that the fluxes of small particles were highly scattered during the hottest parts of the day, often upward from the surface. Scrutiny of the data reveals that the sulfate fluxes often dropped at the time that upward particle fluxes were first observed, so the mechanism involved is more complicated than simple subcanopy air chemistry involving biologically generated organic chemicals and their reaction with ozone [*Hicks et al.*, 1985].

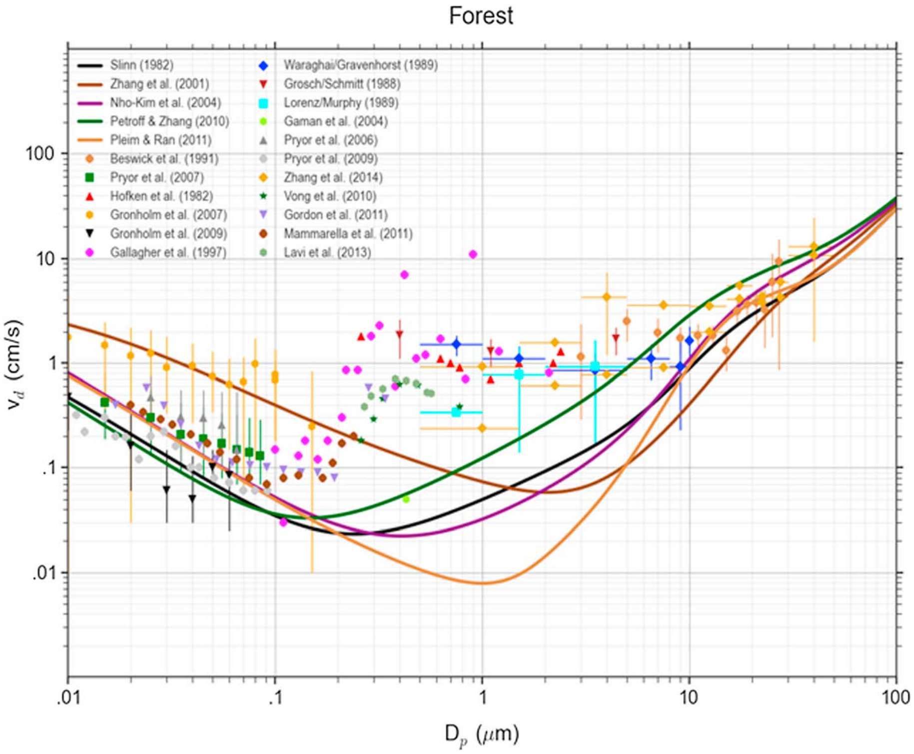

Figure 7. The dependence of the particle deposition velocity from the air to forest canopies, as predicted by several modeling schemes (the lines) and as determined by field experiments (the points). Note that the models seem to share the familiar "well" in the curve, whereas almost all of the experimental data do not.

However, many studies have failed to detect such upward fluxes of submicrometer particles; in this regard note the summation of results obtained over a variety of canopies, presented by *Gallagher et al*. [1997, 2002]. Hence, it appears that the occurrence of upward fluxes is related to site-specific circumstances, primary among which are the biological species of the plant cover and the environmental stresses affecting them [see *Rasmussen*, 1972; *Street et al*., 1997].

5. Relating V_d to Particle size

The dependence of deposition velocity on particle size is well known for the cases of pipe flow and wind tunnel/laboratory experiments using test surfaces. The outstanding problem is to consolidate this understanding in a way that accurately portrays the behavior of a natural landscape. This was the challenge addressed by *Slinn* [1982]. Figure 7 presents the results of many field studies conducted over forests and the predictions of several recent numerical simulations. The figure shows that the deposition velocities predicted for particles less than about 0.2 μm diameter are in fair agreement with observations, but this is not the case for particles in the range 0.3 to about 5 μm.

For the first of these two ranges, *Gallagher et al*. [2002] consolidate evidence from many field experiments and conclude that for daytime conditions the relevant deposition velocity is linearly related to the roughness length of the canopy involved, with a stability contribution such that the peak values of V_d are likely to occur when the atmosphere is most unstable. A similar conclusion was reached by *Wesely et al*. [1985] for the second of the two ranges. Both of these analyses start by relating V_d to the friction velocity, u_*, so that both propose a first-order dependence of V_d in daytime on the level of turbulence that prevails. The property V_d/u_* is sometimes referred to as B^{-1}.

Vong et al. [2010] present data obtained over a plantation of ~ 8 m *Pinus ponderosa*. For particles in the 0.2 to 0.8 μm diameter size range, there is a general dependence of V_d on u_*, but the relationship is not linear for any size range (although the departures might be of questionable statistical significance). Vong et al. compare regression results for their young pine plantation with the results presented by Wesely *et al*. [1985] (pasture) and Gallagher *et al*. [1997] (mature forest) and find the expected ordering: all other factors being equal, the average deposition velocities are largest for canopies with the largest leaf area index. Overall, the data indicate that scaling according to the leaf area index (LAI) might be an appropriate first-order assumption, after accounting for the apparent proportionality of V_d on the friction velocity, u_*.

The models represented in Figure 7 are mainly diagnostic simulations intended to help understand how the various processes contribute to the gross canopy capture of particles. With some exceptions, the dependence on particle size is introduced through adjustment to the way in which transport occurs across the shallow layer of air in immediate contact with any of the surfaces populating the subcanopy airspace or in practice by adjusting similarly the overall canopy characteristics. For a receptor surface within a canopy, the eventual deposition of a particle will depend on its size, expressed through its Brownian diffusivity, D_p, and its gravitational fall speed, v_g. For a small particle such that v_g can be ignored, the determining factors associated with the layer of air immediately in contact with the surface are the kinematic viscosity of the air (ν) and the thickness (and longevity) of any laminar layer that might develop. Therefore, any allowance for the role of the air layer in close contact with a receptor surface must account for the difference between D_p and ν. On the scale of individual receptor surfaces, the relevant formulations relate the surface-specific deposition velocity v_d to the surface-specific scale velocity u_* via the dimensionless relationship

$$B^{-1} \equiv v_d/u_* = a.Sc^b \tag{1}$$

where a is a surface-specific constant to be determined empirically, and Sc is the Schmidt number ($\equiv D_p/\nu$). On the basis of wind tunnel studies [*Harriott and Hamilton*, 1965; *Hubbard and Lightfoot*, 1966; *Mizushina et al*., 1971], b is usually taken to be $-2/3$, and equation (1) is applicable for particle sizes less than about 0.5 μm diameter [see *Friedlander*, 1977; *Hicks*, 1984].

There are several alternative ways to utilize equation (1) as means to derive a whole-canopy relationship. At one extreme, the contributions of the individual contributing surfaces can be combined by integration through a vertical column of the entire canopy. At the opposite extreme, the whole canopy can be viewed as a single entity sharing the characteristics of the individual surfaces—the "big leaf" approach of *Monteith* [1963, 1965]. Summaries of many canopy models are presented by *Katul et al*. [2010], *Pleim and Ran* [2011], and *Huang et al*. [2014].

The need for a specified subcanopy velocity profile permeates all multilayer simulations and presents a continuing challenge. There have been many studies of subcanopy velocity profiles (extending back to times when the studies related to gas warfare), but these often depict gross wind speed profiles with little information regarding turbulence or intermittency [see *Cionco*, 1972, 1985]. Recent subcanopy velocity models (as discussed by *Katul and Albertson* [1998] and *Belcher et al*. [2012]) yield adequate information, but the dependence on canopy structure and its species dependence remain a problem confounding extension to situations beyond a uniform and homogeneous forest.

6. Discussion

Early bulk canopy models were intended to yield estimates of particle dry deposition at specific locations where the formulations involved could be tested in short-term field studies. In particular, they are currently used to estimate dry deposition at locations where selected relevant surface and atmospheric observations are routinely measured. This approach (the "inferential method," see *Hicks et al*. [1987]) is in recognition of the lack of a direct dry deposition measurement system ready to be deployed at this time. The inferential method has been adopted to analyze data collected in the U.S. Clean Air Status and Trends Network (CASTNet) [see *Clarke et al*., 1997; *Wu et al*., 2003]. It is now in routine use for deriving dry deposition estimates from field data, in both multiple-level and big leaf forms. Air chemistry measurements obtained in the CASTNet program are presently analyzed using a multilayer model evolved from *Meyers and Paw U* [1987], later expanded by *Meyers et al*. [1998] (a third-order closure scheme) and *Wu et al*. [2003]. Several diagnostic models [e.g., *Katul and Albertson*, 1998] make use of alternative multilevel subcanopy closure schemes [*Wilson and Shaw*, 1977] to provide requisite subcanopy velocity estimates. In practice, describing the flow field within and below a forest canopy and formulating its coupling with flow aloft remain a challenge, one that certainly limits the ability to simulate the deposition of particles with generality. Incorporating contemporary understanding of plant species-dependent biochemical factors complicates the problem considerably [*Wu et al*., 2003].

The consequences of different species-specific leaf behaviors have yet to be fully addressed, although some initial probing examinations in wind tunnel experiments have been reported. *Miller and Lin* [1985], for example, give details of the structure of a red maple canopy in the eastern USA—leaves at the top of a canopy are oriented more vertically than elsewhere in the canopy. Flutter is most evident in the case of broadleaf trees (e.g., poplars, oaks, and maples). In the case of conifers, needle length seems to be a key factor, but the whole leafed structure sways in accord with gustiness. Moreover, visual observation of the foliage in a forest canopy gives immediate evidence that the leaves respond to turbulence, especially during intermittent gusts associated with the exchange of subcanopy air with the air above the canopy. This gustiness (causing "surface renewal") has been the subject of extensive examination (reviewed, for example, by *Katul et al.* [2006]), and the corresponding flutter of leaves could give rise to a modification of the usual expressions describing the interception and impaction mechanisms that underlie simulations of the kind developed by *Friedlander and Johnstone* [1957] and *Slinn* [1982]. The influence of leaves that respond to wind gusts was explored by *Finnigan* [1985], who concluded that the single-leaf resistances in *Monteith's* [1963] scheme cannot be used directly in a subcanopy multilayer model of a canopy with moving leaves.

The chemical sensors available for measuring the deposition of sulfate particles in early field studies did not permit investigation of how V_d varied with the size of the contributing particles. The available data were formulated empirically in expressions that described how V_d varied with stability but without allowance for particle size [*Wesely et al.*, 1985; *Ruijgrok et al.*, 1997]. The resulting empirical expressions were used in models addressing the issue of acid rain (in the 1980s and 1990s, e.g., the Regional Atmospheric Deposition Model [*Chang et al.*, 1987]).

Enhancements of the basic interception and impaction framework presented by *Slinn* [1982] are the foundations of the dry deposition modules included in many contemporary air chemistry models, including the U.S. Environmental Protection Agency's Community Multiscale Air Quality modeling system [*Byun and Schere*, 2006], Environment Canada's Global Environmental Multiscale Modeling Air quality and CHemistry forecast model (GEM-MACH [*Talbot et al.*, 2008]), and Harvard University's GEOS-Chem global model [*Fiore et al.*, 2003]. Some models permit the alternative use of the formulation developed by *Wesely et al.* [1985] which expresses the deposition velocity for sulfate aerosol particles in terms of the friction velocity, with no allowance for a change in the appropriate particle size spectrum. This illustrates a dichotomy in the applications—one focuses on the deposition of particles of specified size, the other on a particular chemical species carried by a broad band of particle sizes.

The data now becoming available suggest an enticing ordering. On the one hand, *Gallagher et al.* [2002] indicate that differences among areas dominated by different vegetation species can be ordered by the roughness length, z_0. On the other hand, *Vong et al.* [2010] find that leaf area index (LAI) is a dominant factor. These two surface features are obviously related, with the former being dependent on the wind profile above the surface and the latter by the canopy itself. All formulations taking such matters into account start with the initial dominant dependence of V_d on the friction velocity, u_*. Then, the diurnal cycle in data records like that shown in Figure 6a is accounted for by formulating the ratio V_d/u_* as

$$V_d/u_* = F_1(z_0,\ \mathrm{LAI},\ \text{species},\ \text{etc.}).(1 + (-b/L)^c) \tag{2}$$

for unstable conditions ($L < 0$) and

$$V_d/u_* = F_2(z_0,\ \mathrm{LAI},\ \text{species},\ \text{etc.}) \tag{3}$$

for stable ($L > 0$) [see *Wesely et al.*, 1985; *Pryor et al.*, 2008], where the empirical function F expresses the fundamental differences among different plant canopies. Depending on the source, b is either a constant (with units of length), proportional to the height of measurement above the canopy or proportional to the height of the daytime mixed layer. The exponent c is another empirical constant (typically two/thirds, based on similarity with other micrometeorological properties), and L is the Monin-Obukhov length scale of turbulence. So far, most attention has been given to single-species uniform canopies. The experimental values of F_1 and F_2 are typically in the range 0.001 to 0.005. The quantity b is often taken to be about 300. The case of a mixed species surface in terrain other than flat and homogeneous remains a challenge.

The matter of subcanopy particle generation remains a topic for research, especially since both deciduous and coniferous forests are known to be involved. It is accepted that reactions involving ozone and a variety of organic chemicals exuded from foliage are a major reason for visibility impairment in many otherwise pristine environments [see *Kahlil and Rasmussen*, 1992; *Simon et al.*, 1994; *Tolocka et al.*, 2006]. The central factors appear to be the biological species involved and the stress under which the foliage is transpiring. It seems unlikely that the subcanopy generation of small particles could have hindered the downward transport of larger sulfate particles (see Figure 6), and hence, an additional influential mechanism is suspected—likely one that depends on surface temperature. There have been many determinations of particle deposition velocities over forests, many of which have been in far more benign conditions than the southern USA. For example, extensive measurements of particle concentration gradients over the Speulder forest in the Netherlands enabled *Wyers and Duyzer* [1997] and *Erisman et al.* [1997] to confirm the prevalence of daytime deposition velocities exceeding 1 cm s^{-1} for particles from 0.1 to 1.0 μm diameter, but with relatively little evidence of particle emission from the canopy.

Studies of particle fluxes above forests continue [e.g., *Pryor et al.*, 2009; *Copeland et al.*, 2014] with slowly accumulating evidence of upward (and often episodic) small-particle fluxes from both coniferous and deciduous forests and with new understanding of the chemical and biological complexities of the mechanisms involved [*Kahlil and Rasmussen*, 1992; *Tolocka et al.*, 2006; *Pryor et al.*, 2008, 2014]. The number of chemical species involved continues to grow, but it is now well recognized that the bidirectionality of small-particle fluxes over forests is, at least partially, due to gas-to-particle reactions within the subcanopy airspace and depends on the plant species distribution and the related response to environmental stress.

7. Conclusions

The matter of the accumulation-mode size range deposition velocity discrepancy has now been contentious for decades. The cause of the discrepancy is still not known convincingly. Some researchers initially dismissed the micrometeorological (eddy correlation and gradient) results because such methods yielded unexpected results. It has further been argued that micrometeorological measurements made above a surface are not indicative of the surface values themselves. The counter argument that if there is a difference then there must be a source or a sink of particles in the intermediate region has not always been received favorably. However, consideration of the air chemistry regime near the surface and of the role of biologically generated chemicals, such as isoprene, and their reactions with oxidants (particularly with ozone) has led to the understanding that there is indeed a flux divergence in some circumstances. Estimating and accounting for this divergence is now a major task for the surface chemistry aspects of modern air quality models.

It remains to be argued as to which of the available approaches offers a preferred pathway to better descriptions of particle deposition. Such questions are likely to remain unanswered until the appropriate measurement methods and model capabilities can be brought together in a series of studies of particle deposition conducted simultaneously over different vegetated surfaces. Measurement capabilities have improved markedly over the 40 years since the first field micrometeorological studies of particle deposition. At the same time, micrometeorological instrumentation has evolved considerably. Given the persistence of aged formulations, and the wide acceptance of basic data sets that now appear to be of questionable relevance to the case of a model grid cell (e.g., many laboratory and wind tunnel studies), it is surely time to combine the new and highly advanced measurement capabilities in field studies to provide solutions, convincing to all.

The challenge is not unique to the dry deposition community. The same issue of assembling biological, physical, and chemical factors into a coherent simulation of a vegetative canopy confronts workers studying forest meteorology in general. The dominant problem is shared by all such endeavors—to combine what is known about the interaction of many surfaces of various textures and orientations into an ordered and formulated description of the canopy in question. To accomplish this in the case of a natural landscape with a distribution of vegetative species in complex terrain will require spatial sampling of both concentrations and fluxes, with statistical analysis to identify and formulate the appropriate median quantities such as V_d for a model grid cell.

Acknowledgments
Data used in this presentation are available in the publications referenced or by contact with the corresponding author. Random numbers were derived from the standard spreadsheet algorithm of Lotus 123. The basic understanding of dry deposition of particles owes more to Arthur Chamberlain than to any other individual. He took the first steps to extend the limited understanding derived from studies of radioactive fallout so that modern-day pollution aspects could be discussed. He was the originator of the chamber and wind tunnel studies that led to the initial formulations. Moreover, it was Arthur Chamberlain who first studied deposition to real vegetation in real situations, showing that particles were captured upon deposition and that the microscale roughness of the surface (such as the hairiness of foliage) was important. In the early years, the development of understanding was also led by the "Hanford Georges"—Sehmel and Slinn. The extension into the real world and the development of micrometeorological methods brings to mind a fourth name to be remembered—Marv Wesely.

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