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DEPOSITION OF FINE PARTICLES  
OVER A BOREAL FOREST

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Academic dissertation

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Tiia Helena Grönholm  
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## **Abstract**

Dry and wet deposition are removal mechanisms of atmospheric aerosol particles. Historically, there are very scarce scientific publications reporting experimentally determined dry deposition values for the ultra-fine size range. The physics of deposition is studied both using micrometeorological field measurements conducted at SMEAR II site in Hyytiälä, Southern Finland and by modeling approaches. Dry deposition velocity depends mainly on particle size and magnitude of the atmospheric surface layer turbulence. We present experimentally determined dry deposition velocity ( $v_d$ ) as a function of particle size for the ultra-fine aerosol size range (10 - 150 nm) using relaxed eddy accumulation and eddy-covariance (EC) methods accompanied by particle number size distribution measurements. The highest  $v_d$  was found for 10 nm particles and in all size classes  $v_d$  increased with increasing friction velocity.

By combining two-layer (above and sub-canopy) EC measurements and a new multi-layer canopy deposition model, we addressed how dry deposition is distributed within the forest canopy and between the canopy and the underlying ground. According to the measurements, about 20 - 30 % of particles penetrated the canopy and deposited on the forest floor. The model results showed that turbophoresis, when accounted for at the leaf scale in vertically resolved models, could increase  $v_d$  for 0.1 - 2  $\mu\text{m}$  particles and explain why the observations over forests generally do not support the pronounced minimum of deposition velocity for particles of that size. The developed multi-layer model was further used to study the effect of canopy structure (leaf-area shape and density) on  $v_d$ .

Scavenging coefficients for rain and snow deposition were calculated based on measurements of particle size distribution and precipitation. Parameterizations for both rain and snow wet deposition were derived for example to be applied in air quality and global models. Also a model including both in-cloud and below cloud wet deposition was developed and compared to the field measurements. Both snow and rain scavenging efficiency increased with increasing precipitation intensity. We also found, that the effectiveness of snow scavenging depends on the crystal or snow flake structure and the air relative humidity. Wet deposition was found to be an order of magnitude more effective "air cleaner" compared to dry deposition.

Keywords: aerosol particle removal, dry deposition, wet deposition, relaxed eddy accumulation, eddy covariance, turbulent flux, scavenging, multi-layer model

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## List of publications

This thesis consists of an introductory review, followed by eight research articles. In the introductory part, these papers are cited according to their roman numerals.

- I Grönholm, T., Haapanala, S., Launiainen, S., Rinne, J., Vesala, T. and Rannik, Ü.(2008). The dependence of  $\beta$  coefficient of REA system with dynamic deadband on atmospheric conditions, *Environ. Pollut.*, 152, 597–603.
- II Grönholm, T., Aalto, P. P., Hiltunen, V., Rannik, Ü, Rinne, J., Laakso, L., Hyvönen, S., Vesala, T. and Kulmala, M. (2007). Measurements of aerosol particle dry deposition velocity using the relaxed eddy accumulation technique, *Tellus*, 59B, 381–386.
- III Grönholm, T., Launiainen, S., Ahlm, L., Mårtensson, M., Kulmala, M., Vesala, T. and Nilsson, E. D. (2008). Aerosol particle dry deposition to canopy and forest floor measured by two-layer EC system, *J. Geophys. Res.*, 113, D04202.
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- V Katul, G. G., Grönholm, T., Launiainen, S. and Vesala, T. (2011). The effects of the canopy medium on dry deposition velocities of aerosol particles in the canopy sub-layer above forested ecosystems. *Atm. Environ.*, 45, 1203–1212.
- VI Laakso, L., Grönholm, T., Rannik, Ü., Kosmale, M., Fiedler, V. Vehkamäki, H. and Kulmala, M. (2003). Ultrafine particle scavenging coefficients calculated from six years field measurements . *Atm. Environ.*, 37:25, 3605–3613.
- VII Andronache, C., Grönholm, T., Laakso, L., Phillips, V. and Venäläinen, A. (2006). Ultrafine particles scavenging by rainfall at a boreal site: observations and model estimations. *Atmos. Chem. Phys.*, 6, 4739–4754.
- VIII Kyrö, E.-M., Grönholm, T., Vuollekoski, H., Virkkula, A., Kulmala, M. and Laakso, L. (2009). Snow scavenging of ultrafine particles: field measurements and parameterization. *Boreal Env. Res.*, 14, 527–538.

# 1 Introduction

The removal of aerosol particles from the atmosphere occurs through two different pathways, dry and wet deposition (*Seinfeld and Pandis, 1998*). Dry deposition is a direct transfer of particulate species to the Earth's surface without a help of precipitation. Dry deposition is highly dependent on the particle size, strength of atmospheric turbulence and the characteristics of the surface the deposition takes place. Deposition rate of aerosol particles are usually expressed as a deposition velocity, which is a local particle flux normalized by a local particle concentration. Sign reversal will result that the deposition velocity downwards is positive. Often, deposition velocity is also normalized with friction velocity to enable comparison of data measured over different surfaces.

Wet deposition is a process, where particles are removed from the air by aqueous scavengers. The main pathways are 1) activation of CCN to cloud or fog droplets and their subsequent removal by precipitation formation and 2) removal of particles by collision with a droplet or ice crystal in or below a cloud. Wet deposition is parameterized in terms of scavenging coefficient, which is the exponential constant in an exponential decay model for the physical removal of particles from the air by rainfall (*Slinn, 1977; Fenton et al., 1980; Scott, 1982*). A variety of the scavenging coefficients, expressed as a constant (bulk) value or as a function of precipitation intensity, are used to describe the wet removal of pollutants (*Mircea and Stefan, 1998*).

The interest towards aerosol particle deposition started already 1915 when O'Gara found that SO<sub>2</sub> particle emission induced crop damage (*Thomas, 1951*). The first atmospheric particle deposition models commenced 1930's when *Bosanquet and Pearson* (1936) presented a point source plume dispersion equation for smoke emitted from elevated chimneys, but this pioneering work did not consider surface effects. During the last century, interest on particle removal processes has increased because of the questions of air quality and impacts of aerosol particles on human health. The particle deposition to vegetated surfaces has influenced nutrient or toxic loading to ecosystems. During the last two decades, understanding the particle formation and removal has gained in importance also due to the need to understand the processes leading to and controlling the magnitude of the anthropogenic climate change. Hence, it is not surprising that the dry and wet deposition have been intensively studied by field experiments and modeling approaches. During the last decades, a large number of dry

and several wet deposition parameterizations have been proposed and developed for vegetated surfaces - ranging from bulk deposition rates (*Wesely et al.*, 1985; *Wesely and Hicks*, 2000) to particle size-resolved approaches (*Sehmel*, 1980; *Gallagher et al.*, 1997; *Pryor et al.*, 2007, 2008a).

This study, however, originates from a purely academic curiosity: to understand the physics behind the atmospheric deposition of fine (particle diameter  $< 2.5 \mu\text{m}$ ) and mainly ultrafine ( $< 0.1 \mu\text{m}$ ) particles above and below a boreal forest canopy. That thought gradually gelled into a reality. By novel measurement methods and modeling, our aims were to enlighten the common problems in the field of particle deposition over a forest:

1. To conduct size-segregated particle flux measurements in the size-range below few hundred nm due to lack of extensive data.
2. To understand partitioning of particle deposition between the vegetation and the underlying ground.
3. To find out why observations over forests generally do not support the models pronouncing a strong minimum of deposition velocity for particles  $0.1 - 2 \mu\text{m}$ .
4. To determine size-segregated scavenging coefficients for rain and snow from field measurements, and explain the results by a model.



## 2 Background and theory

### 2.1 Turbulent flow

Close the ground, surface friction decelerates the flow, the shear force exceeds molecular viscous force and a smooth laminar flow is perturbed generating random, irregular motions. The flow becomes turbulent. Turbulence is induced also in convective conditions via temperature and density differences (Figure 1).

Turbulent flows can seldom be described analytically but instead by statistical properties. One statistical approach is Reynold's decomposition (e.g. *Stull, 1988*) where wind speed  $u_i$  and scalar  $s$  is presented as a mean ( $\bar{x}$ ) and fluctuating ( $x'$ ) part

$$u_i(t) = \bar{u}_i + u'_i \quad (1)$$

$$s(t) = \bar{s} + s'. \quad (2)$$

where  $\bar{u}_i$  is

$$\bar{u}_i(t) = \frac{1}{t} \int_{t-\bar{t}/2}^{t+\bar{t}/2} u_i(t') dt' \quad (3)$$



Figure 1: Turbulent transport during the prescribed burning in Juupajoki, Finland.

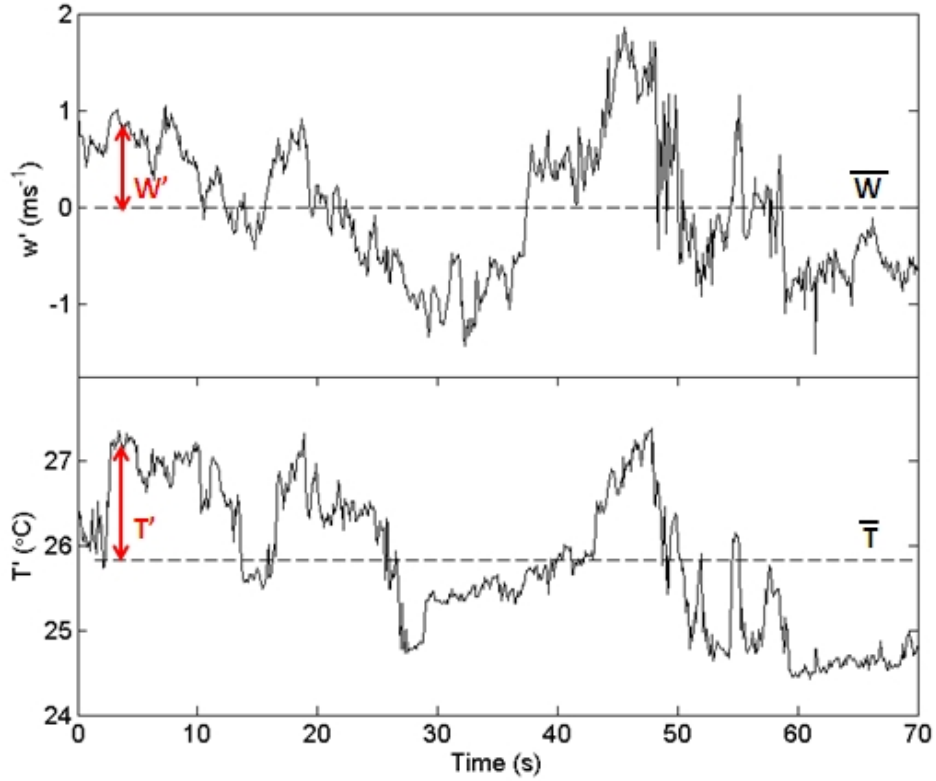


Figure 2: Mean (dash line) and fluctuation (difference between solid and dash line) parts of vertical wind ( $W$ ) and temperature ( $T$ ).

Figure 2 demonstrates the decomposition of wind and temperature. A mean value depends on the averaging time interval ( $\bar{t}$ ). Therefore,  $\bar{t}$  need to be large enough to include an adequate number of fluctuations, but not so large that important macroscopic features would be masked. The mean values are varying slowly (e.g. diurnal cycle) while fluctuations have extreme temporal and spatial variations. However, the viscosity of the fluid ensures that the smallest eddies are many orders of magnitude larger than molecular dimensions and continuum mechanics remains applicable. The largest scales of eddies are comparable with the dimensions of the flow and responsible for the most of the transport of momentum, heat and mass. Turbulent energy is transferred from larger to smaller eddies, although a part of it is dissipated as heat.

In turbulent flows the conservation of compound  $c$  in a unit volume is (*Finnigan, 2000*)

$$\frac{\partial \bar{c}}{\partial t} = \sum_{i=1}^3 \bar{u}_i \frac{\partial \bar{c}}{\partial x_i} + \sum_{i=1}^3 \frac{\partial \overline{u'_i c'}}{\partial x_i} + \sum S_c \quad (4)$$

where molecular and dispersive terms are neglected.  $u_{1,2,3}$  and  $x_{1,2,3}$  refer to wind  $u$ ,  $v$  and  $z$  and coordination directions  $x$ ,  $y$  and  $z$ , respectively.  $S_c$  is a source or sink of  $c$ . Assuming stationary conditions, horizontally homogeneous source or sink, flat topography and incompressible fluid, it is justified to neglect the time dependence, advection, and horizontal turbulent fluxes. Then, we have

$$\frac{\partial \overline{w'c'}}{\partial z} = - \sum S_c(z) \quad (5)$$

$$\Rightarrow \overline{w'c'}(z_{ref}) = - \int_0^{z_{ref}} S_c(z). \quad (6)$$

In **Paper IV** we have used a common meteorological K-theory to approximate turbulent transport

$$\overline{w'c'} = -K_c \frac{\partial \bar{c}}{\partial z}, \quad (7)$$

where  $K_c$  is a eddy diffusivity, a transport coefficient analogous to molecular diffusivity. The K-theory assumes that the characteristic eddy length scale is smaller than length scale of scalar concentration gradient, a valid assumption in the atmospheric surface layer turbulence, but not necessarily inside plant canopies.

## 2.2 Dry deposition

Dry deposition of aerosol particles is a process where aerosol particles are removed from the atmosphere. Thus, it reduces both mass and number concentration as well as total surface area of particles. Dry deposition flux ( $F$ ) is proportional to the local aerosol particle concentration ( $C$ ) at a reference height above the surface

$$F = -v_d C \quad (8)$$

where deposition velocity ( $v_d$ ), is a proportionality constant between  $F$  and  $C$ . By convention,  $F$  downward is defined negative. Because  $C$  is a function of height,  $v_d$  is related to a reference height where  $C$  is specified. In surface layer above the canopy  $F$  is assumed to be constant to the reference height.

Dry deposition of particles is usually described as a process consisting three steps: 1) turbulent transport through the atmospheric surface layer to a thin quasi-laminar sub-layer adjacent to the surface. Here, also gravitational settling plays a role with particles larger than a few micrometers; 2) transport across sub-layer by Brownian diffusion, interception (particle moving with the mean air flow and passing an obstacle sufficient close to contact with it) or inertial impaction (due to inertia, particle is not able to follow rapid changes of flow direction resulting collision with an obstacle); 3) uptake or bouncing off at the surface. Resuspension rate is, however, very small for sub-micrometer particles (e.g. *Ould-Data and Baghini*, 2001). Therefore, it is justified to assume that a particle hitting a surface is removed from atmosphere. Thus,  $v_d$  depends on the particle size, strength of atmospheric turbulence and the properties of the collecting surface. Figure 3 presents schematically the different deposition mechanisms.

### 2.2.1 Phoretic effects

In homogeneous fluid there is no preferential direction in the Brownian diffusion. When there are gradients in the fluid temperature, radiation energy, turbulence, aerosol particle concentration and so on, differences in momentum imparted to a particle will produce an external force. Next, five of these phoretic terms are discussed.

Thermophoresis arises from temperature gradients. A simplified description is that gas molecules in high-temperature region have higher kinetic energy than those in cold region. Therefore, the molecules hitting a particle from the hot side have greater

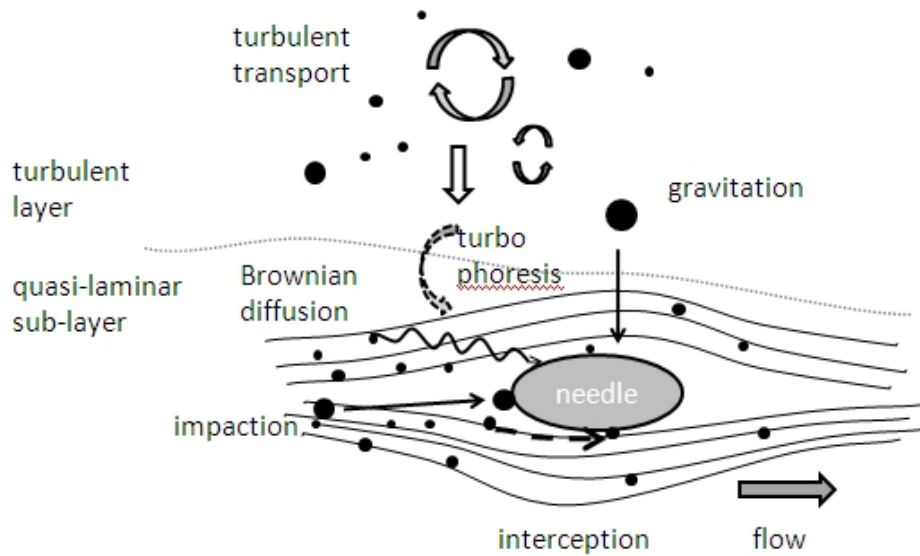


Figure 3: Dry deposition processes.

momentum than the molecules on the cold side. As a result, the particle will move toward colder region. This explanation applies directly to small aerosol particles (Knudsen number ( $Kn$ )  $\gg 1$ , see e.g. *Seinfeld and Pandis* (1998)). For larger particles ( $Kn \ll 1$ ) particle surface and a thin layer around it will develop temperature gradient which lead gas to move from the colder to the warmer regions along the surface of the particle (e.g. *Seinfeld and Pandis*, 1998). That results a force in the cold direction. For temperature gradients on the order of a few  $\text{K cm}^{-1}$ , the thermophoretic velocity for submicrometer particles is same order of magnitude than settling velocity for those (*Brock*, 1962). However, with the exception of very steep temperature gradients, thermophoresis can be neglected compared with the other forces on atmospheric aerosol particles.

Diffusiophoresis is a result of a gas molecule concentration gradient (*Lyklema*, 2005). Strong gradient causes that one side of the particle is towards the high concentration and the other towards the low concentration of gas molecules. Higher concentration of gas molecules are able to transmit more kinetic energy to the particle and therefore particle tends to move toward the lower concentration area. Diffusiophoresis is often neglected due to assumption of absence of significant gas molecule concentration gradients in the turbulent flow.

Photophoresis is a result of absorption or scattering of radiation from intense light

beam by a particle. Within the particle electromagnetic energy turns into thermal energy and causes uneven heat distribution of molecules around the particle (*Reed, 1977; Li et al., 2010*). The net force is either toward or away from the light depending on optical characteristics of the particle (*Li et al., 2010*). Photophoresis doesn't play a role in atmospheric aerosol dynamics and it is neglected (*Seinfeld and Pandis, 1998*).

Electrophoresis is the motion of particles under the influence of an electric field. This phenomenon is widely utilized in different equipment such as electrostatic filters and analyzers. In atmospheric conditions, the electric field is weak, and also the aerosol particles are weakly charged. Although electric forces might play a role in the particle size range of 10 - 200 nm during low wind conditions and around sharp structures like conifer needles (*Tamm et al., 2001*), electrophoresis related to particle deposition is generally neglected.

Turbophoresis refers to the tendency of particles to move in the direction of decreasing turbulent energy due the difference in momentum on the sides of a particle. Because near a surface, the vertical gradients of turbulent energy are large, turbophoresis is expected to enhance particle deposition rate onto the surface (*Caporali et al., 1975; Reeks, 1983; Guha, 1997; Young and Leeming, 1997, Paper IV*).

### 2.2.2 Models

Based on the fundamentals of electronics, deposition process could be interpreted in terms of an electrical resistance. There, aerodynamic transport ( $r_a = f(\frac{U}{u_*^2}, L)$ ), transfer across quasi-laminar surface layer ( $r_b = f(\frac{1}{u_*})$ ), and surface uptake ( $r_c = f(\text{surface properties})$ ) is assumed to be governed by resistances in series, and gravitational settling ( $v_g$ ) by resistance in parallel (e.g. *Zufall and Davidson, 1998*)

$$v_d(z) = \frac{1}{r_a(z) + r_b + r_c} + v_g. \quad (9)$$

Above,  $U$  refers to mean wind velocity,  $u_*$  to friction velocity and  $L$  is a transport length scale. Although very easy to follow, the resistance analogy is applicable only in 'a class-room use', due to its inconsistency with mass conservation (*Kramm et al., 1992; Venkatram and Pleim, 1999*).

In 1982, Slinn published an analytical model including semi-analytical descriptions of

particle collection efficiencies on vegetated surfaces (*Slinn*, 1982)

$$v_d = v_g + C_D U_r \left[ 1 + \frac{U_h}{U_r} \left( \frac{1 - \varepsilon}{\varepsilon + \sqrt{\varepsilon} \tanh \gamma \sqrt{\varepsilon}} \right) \right]^{-1} \quad (10)$$

$$C_D = \left( \frac{u_*^2}{U_r^2} \right) \quad (11)$$

$$\frac{U_h}{U_r} = \frac{u_*}{\kappa U_r} \ln \frac{1}{z_0}, \quad (12)$$

where  $C_D$  is canopy drag coefficient,  $U_h$  is  $U$  at canopy top ( $h$ ),  $U_r$  at a reference height above canopy,  $\varepsilon$  is particle collection efficiency,  $\kappa$  is von Karman constant and  $\gamma$  is a parameter characterizing the wind profile through the forest. However, although extensively used and probably the most cited dry deposition model, it is based upon a number of assumptions which may be frequently violated in practice (see e.g. *Pryor et al.*, 2008a).

Over the last three decades, number of dry deposition parameterizations and models have been published. Many of those are based on Slinn's formulation, but also new approaches have been developed. Roughly, dry deposition models could be classified into two groups. The first group includes models assuming similarity between deposition of particles on walls of pipes and on the canopy-soil system (e.g. *Chamberlain*, 1967; *Caporali et al.*, 1975; *Noll et al.*, 2001; *Feng*, 2008). The second group contains models proposed for vegetated surfaces ranging from bulk deposition rates (*Wesely et al.*, 1985; *Wesely and Hicks*, 2000) to size-resolved approaches (*Sehmel*, 1980; *Gallagher et al.*, 1997; *Pryor et al.*, 2007, 2008a; *Petroff et al.*, 2008b). *Petroff et al.* (2008a) and *Pryor et al.* (2008a) summarized and compared models and formulations mainly developed over the past 20 years.

In a multilayer model developed in **Paper IV**, a second order differential equation for the particle concentration is derived

$$\begin{aligned} & \frac{\partial}{\partial z} \left[ - (D_{p,m} + D_{p,t}(z)) \frac{\partial C(z)}{\partial z} + V_s C(z) \right] \\ & + \frac{a(z)}{\pi} \left[ \sqrt{-u'w'(z)} (\theta S c^{-2/3} + 10^{-3/St(z)}) + V_t \right] C(z) = 0 \end{aligned} \quad (13)$$

where the Brownian diffusion term ( $D_{p,m}$ ) is given as (*Seinfeld and Pandis*, 1998)

$$D_{p,m} = \frac{k_B T}{3\pi\mu d_p} C_c, \quad (14)$$

where  $k_B = 1.38 \times 10^{-23} J K^{-1}$  is the Boltzmann constant,  $T$  is the absolute temperature,  $d_p$  particle diameter, and  $\mu = \rho\nu$  is the dynamic viscosity of the air, where  $\rho$  and  $\nu$  are the air density and kinematic viscosity, respectively, and  $C_c$  is the Cunningham coefficient. The particle turbulent diffusivity is primarily dominated by the flow turbulent diffusivity and is given as

$$D_{p,t} = K_t \left(1 + \frac{\tau_p}{\tau}\right)^{-1}, \quad (15)$$

where  $K_t$  is the eddy viscosity of the flow,  $\tau_p$  is the particle time scale given by

$$\tau_p = \frac{\rho_p d_p^2}{18\mu} C_c, \quad (16)$$

where  $\rho_p$  is particle density. The Lagrangian turbulent time scale ( $\tau$ ) is given as

$$\tau = \frac{K_t}{\sigma_w^2}, \quad (17)$$

where  $\sigma_w$  is the turbulent vertical velocity standard deviation. For small aerosol particles in the  $\mu m$  diameter range,  $\tau_p/\tau \ll 1$ , and  $D_{p,t} \approx K_t$ .

Based on K-theory for momentum transfer,

$$K_t = - \frac{\overline{u'w'}}{\left|\frac{\partial \bar{U}}{\partial z}\right|}, \quad (18)$$

where  $\bar{U}$  is the mean longitudinal velocity, and  $\overline{u'w'}$  is the turbulent stress. The modelling of the vertical variation of flow statistics is described in **Paper IV**.

Settling velocity  $V_s$  for particles with Reynolds number  $\leq 1$  is

$$V_s = C_c \frac{(\rho_p - \rho) g d_p^2}{\rho 18\nu}, \quad (19)$$

where  $\rho_p$  is the particle density, and  $g$  is the gravitational acceleration.

The role of turbo-phoresis, recognized and listed along with other phoretic terms, was absent in virtually all atmospheric aerosol deposition models over vegetated surface and was not explicitly treated in any of the data-model inter-comparisons reviewed in *Petroff et al.* (2008a) and *Pryor et al.* (2008a). Turbophoresis ( $V_t$ ) plays a role via vegetation collection mechanisms ( $S_c(z)$ ) within a quasi-laminar boundary layer close to the leaf surface

$$S_c(z) = \frac{a(z)}{\pi} \frac{(C(z) - C_L)}{r_b(z)}, \quad (20)$$



where  $a(z)$  is the total leaf area density, the  $\pi$  adjusts for the single-side projected leaf area to total surface area of leaves (assuming the cylinder shape for needles),  $C_L$  ( $\approx 0$ ) is the mean particle concentration at the leaf surface, and  $r_b$  is the local quasi-laminar boundary layer resistance for particles (*Seinfeld and Pandis, 1998*):

$$r_b(z) = \left( \sqrt{-\overline{u'w'}(z)} (\theta Sc^{-2/3} + 10^{-3/St}) + V_t \right)^{-1}, \quad (21)$$

where  $Sc = \nu/D_{p,m}$  is the Schmidt number and  $St = V_s(-\overline{u'w'}(z))/(g\nu)$  is a turbulent Stokes number.  $\theta = (\pi/2)(c_v/c_d)$ , where  $c_v/c_d$  is the ratio of the viscous to form drag coefficient of the leaf. Moreover, the inertial impaction term in  $r_b$  is parameterized as  $10^{-3/St}$ , which is based on *Slinn and Slinn (1980)* formulation for water or smooth surfaces (see *Aluko and Noll, 2006*). Sedimentation, interception, and rebound are all ignored in equation though those can be readily added into  $r_b$  if known. Note here, that the  $r_b$  and the  $St$  vary with the local turbulent flux of momentum ( $= -\overline{u'w'}$ ) rather than some of the common formulations that adopt the local mean velocity (e.g. see review by *Pryor et al., 2008a*).

The turbo-phoretic velocity can be approximated by (*Caporali et al., 1975; Reeks, 1983; Guha, 1997; Young and Leeming, 1997; Zhao and Wu, 2006*)

$$V_t = -\tau_p \frac{d\sigma_{w,p}^2}{dz}, \quad (22)$$

where,

$$\frac{\sigma_{w,p}^2}{\sigma_w^2} = \left( 1 + \frac{\tau_p}{\tau} \right)^{-1}. \quad (23)$$

and the main 'driving force' for turbo-phoresis is given (see details in **Paper IV**) as

$$\frac{\partial \sigma_w^2}{\partial z} \approx \frac{\sigma_w^2 \sqrt{-\overline{u'w'}}}{b\nu}. \quad (24)$$

## 2.3 Wet deposition

Wet deposition is a major removal mechanism for atmospheric aerosol particles. Precipitation scavenging can occur both in- and below-cloud (Figure 4). At cloud base, in a supersaturated conditions, aerosol particle can act as a cloud condensation nucleus (CCN) providing the surface on which water vapor can condense and form cloud droplets. In-cloud aerosol particles can also be scavenged by coagulation with cloud droplets and by collection onto falling raindrops.

Below-cloud scavenging is a process where aerosol particles are collected by a falling raindrop. The object lesson of *Seinfeld and Pandis* (1998) is, that when a raindrop (diameter  $D_p$ ) falls, it collides with aerosol particles (diameter  $d_p$ ) collecting them. As a first thought, one could think that the raindrop sweeps the volume of  $\pi(D_p - d_p)^2(U_t(D_p) - u_t(d_p))/4$  per unit time, where  $U_t$  is raindrop's and  $u_t$  particle's terminal falling velocity. However, falling drop perturbs the air around it and creates the flow field which streamlines diverge around the drop causing a force on particle modifying its trajectory. The possible collision depends on the sizes and relative locations of the drop and the particle. A complicated fluid mechanics problem has arisen.

The below-cloud scavenging by precipitation is an important aerosol particle removal mechanism. While  $v_d$  is an important parameter related to dry deposition, a scavenging coefficient ( $\lambda$ ) is that for wet deposition.  $\lambda$  represents a fractional amount of aerosol particles of certain size which are removed from atmosphere by precipitation per time unit

$$\frac{\partial c(d_p)}{\partial t} = -\lambda(d_p)c(d_p) \quad (25)$$

where  $c(d_p)$  is concentration of particles with a diameter  $d_p$ .

Although many theoretical and experimental studies have been carried out in the last few years, below-cloud  $\lambda$  still has large uncertainties. Assuming that  $U(t) \gg u(t)$ ,  $\lambda$  is

$$\lambda(d_p) = \int_0^\infty \frac{\pi}{4}(D_p)^2 U_t(D_p) E(D_p, d_p) N(D_p) dD_p \quad (26)$$

where  $N(D_p)$  is number concentration of raindrops of the size  $D_p$  and  $E(D_p, d_p)$  is the collection efficiency between raindrops and particles. Raindrop-aerosol collision efficiency takes into account the contribution of Brownian diffusion, interception and

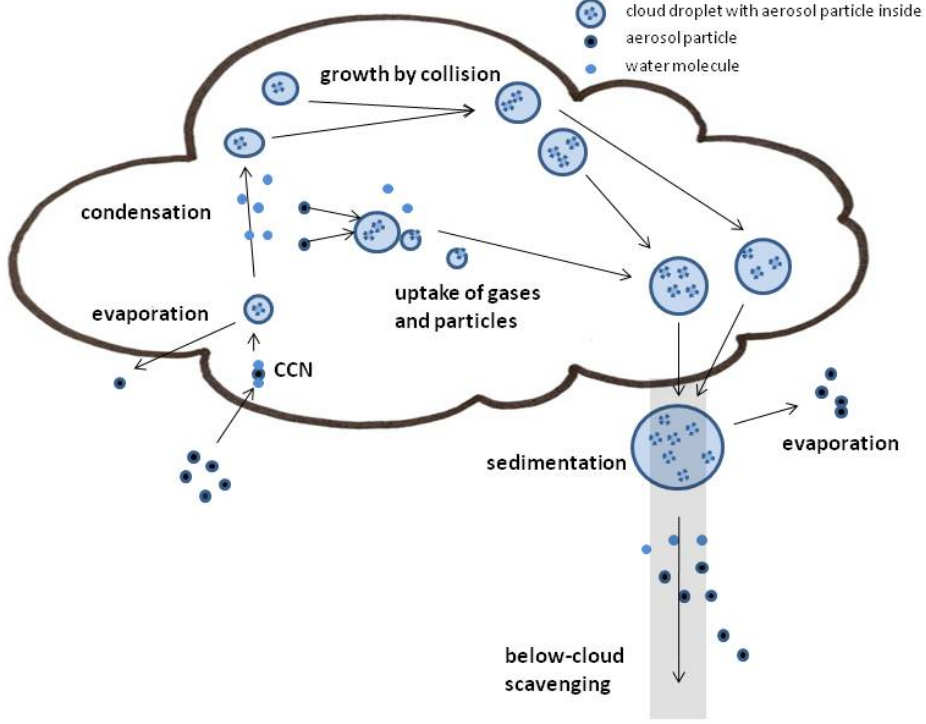


Figure 4: In- and below-cloud scavenging of particles.

inertial impaction (*Slinn, 1983*)

$$E(D_p, d_p) = \frac{4}{ReSc} (1 + 0.4Re^{1/2}Sc^{1/3} + 0.16Re^{1/2}Sc^{1/2}) + \quad (27)$$

$$4 \frac{d_p}{D_p} \left[ \frac{\mu_a}{\mu_w} + (1 + 2Re^{1/2}) \frac{d_p}{D_p} \right] + E_e \quad (28)$$

where  $Re$  and  $Sc$  are particle Reynolds and Schmidt numbers,  $\mu$  is air viscosity and indexes  $a$  and  $w$  refer to aerosol and water. Raindrop size distribution is usually described by exponential (e.g. *Marshall and Palmer, 1948*), gamma (e.g. *Ulbrich, 1983*) or lognormal distribution (e.g. *Cerro et al., 1997*).

The electric term  $E_e$  is (*Pruppacher and Klett, 1998; Andronache, 2004*)

$$E_e = \frac{16KC_c a^2 \alpha^2 d_p}{3\pi \mu_a U} \quad (29)$$

where  $K = 9e^9 \text{ Nm}^2\text{C}^{-2}\text{s}^{-1}$ ,  $a = 0.83e^{-6}$  and  $\alpha$  is an empirical parameter varying from 0 (neutral particles) to 7 (highly electrified clouds during thunderstorms).  $C_c$  is

the Cunningham slip correction factor to account for non-continuum effects associated with small particles.

While *Slinn* (1983) included Brownian diffusion, interception and inertial impaction in  $E(D_p, d_p)$ , the recent parameterizations add also phoretic terms (thermo-, diffusio- and electrophoresis), which increase  $E(D_p, d_p)$  especially in sub-micrometer particles. However, theoretical values for  $\lambda$  are still usually order of magnitude smaller than those based on observations. Therefore, more scavenging measurements and theoretical studies are needed to improve the existing models. This is especially true for the below  $3 \mu\text{m}$  aerosol particles where the discrepancy between the models and measurements is largest (*Wang et al.*, 2010). The most uncertain terms of the scavenging equation are  $E(D_p, d_p)$  and the  $D_p$  distribution (*Wang et al.*, 2010). In contrast to *Mircea et al.* (2000), *Wang et al.* (2010) found that the various  $D_p$  distributions can yield 3 to 5 fold difference to  $\lambda$  values depending on rainfall intensity and  $d_p$ . Also, the uncertainty related to  $U_t$  exists, but is generally smaller than factor of 2.

Snow scavenging is even more complicated process due to large variety of frozen precipitation: snow flakes, ice grains, ice pellets and so on. Different shapes, sizes and densities result differences in terminal settling velocities and cross-sectional areas. The process is not well understood and only a few studies exist (e.g. *Graedel and Franey*, 1975; *Jylhä*, 2000; *Ying et al.*, 2004; *Paramonov et al.*, 2011, **Paper VIII**). *Pruppacher and Klett* (1998) found that aerosol particles are scavenged at the rim of ice crystals due to a strong horizontal flow underneath the falling crystal. Snowflakes are better collectors than ice crystals because of the filtering effect; collection efficiency is dependent on the flow through the aggregates rather than on the flow around the crystal (*Mitra et al.*, 1990).

### 3 Experimental methods and measurements

Measurement set-ups and detailed description of data processing are given in papers followed this introductory part. Therefore, only a common description about site and the methods used in the studies are given in this chapter.

The main particle measurement device was condensation particle counter (CPC), which measures particles from 0.01 to 1.0  $\mu\text{m}$  (TSI-3010) or from 0.003 to 1.0  $\mu\text{m}$  (TSI-3025) in diameter. Inside a CPC the sample flow goes through a saturator and becomes saturated with alcohol vapor. The flow continues into a cooled condenser where the alcohol supersaturates and condenses onto particles forming droplets. Droplets pass through a thin ribbon of laser light which scatters by the droplets. The light signal is focused onto a photodetector and converted to an electrical pulse which is counted.

Aerosol particle size distribution measurements were performed with two differential mobility particle sizers (DMPS). A DMPS consisted of a neutralizer, Hauke-type differential mobility analyzer (DMA) and a condensation particle counter (CPC). The first DMPS measured particle size spectrum between 3 - 40 nm and the second between 10 - 1000 nm with a time resolution of 10 minutes. *Aalto et al.* (2001) describe this twin-DMPS system used at SMEAR II station. Figure 5 shows a mean aerosol size distribution at SMEAR II during the spring 2005.

#### 3.1 SMEAR II measurement site

All the measurements were carried out at the SMEAR II station in southern Finland (61°51'N, 24°17'E, 181 m above sea level). The Scots pine stand (*Pinus sylvestris* L.) around the station is a rather homogeneous, established in 1962 through direct sowing after clear felling and prescribed burning. The height of the dominant trees were about 14 - 16 m. The homogeneous fetch in the prevailing wind direction (230°) is 250 m (*Vesala et al.*, 1998). The soil is podzolic and composed of sandy and coarse silty glacial till, and the terrain is subject to modest height variations. The annual mean temperature in 1961 - 1990 was +2.9 °C and the annual mean precipitation 700 mm. Part of the stand was thinned between January and March 2002, and total LAI in the thinned area dropped from 8 to 6 (*Vesala et al.*, 2005). *Hari and Kulmala* (2005) give more information about atmospheric measurements at the site.

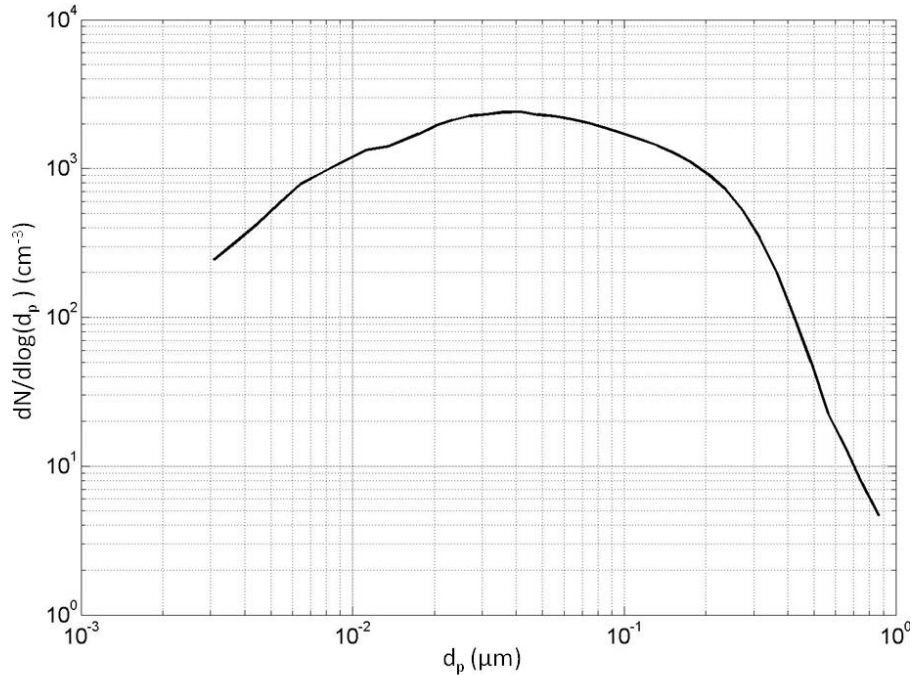


Figure 5: Mean size (diameter,  $d_p$ ) distribution for aerosol number ( $N$ ) measured with twin-DMPS at SMEAR II between March 1st to May 31st, 2005. Mean particle concentration was  $2880 \text{ cm}^{-3}$ .

### 3.2 Eddy covariance

Eddy covariance method (EC) is the most direct way to measure vertical turbulent fluxes of atmospheric constituents. The principle of EC is simple: in horizontally homogenous and stationary conditions the vertical flux equals all sources and sinks in the source area, the footprint. In EC, the flux ( $F_c$ ) is calculated as a covariance between the vertical wind velocity ( $w$ ) and concentration of the compound ( $c$ )

$$F_c = \overline{c'w'} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} ((c(t) - \bar{c})(w(t) - \bar{w})) dt \quad (30)$$

where overlines denote time averages. Due to significant portion of vertical flux carried by less than few seconds time scale eddies, the  $w$  and  $c$  should be measured with a fast response time. *Wesely et al. (1977)* was the first one who published the results of particle flux measurements performed with EC. Since then, the EC has become the most common tool for particle flux measurements above the surface (e.g. *Wesely and Hicks, 2000; Fairall, 1984; Lamaud et al., 1994; Buzorius et al., 1998, 2000; Rannik*

*et al.*, 2001, 2003; *Held et al.*, 2006; *Pryor et al.*, 2007). EC has also been used within a canopy to measure mainly energy and CO<sub>2</sub> exchange (e.g. *Baldocchi et al.*, 1986; *Blanken et al.*, 1998; *Launiainen et al.*, 2005; *Misson et al.*, 2006). To my knowledge, **Paper III** presents the first measurements of particle fluxes to forest floor by using EC.

A footprint area depends on the measurement height, topography, wind speed and surface layer stability. According to *Sogachev et al.* (2004), at SMEAR II when near-neutral conditions, 80% of fluxes measured at 23 m height has a footprint extending 200 - 300 m upwind from the measurement tower.

The EC methodology assumes stationarity and horizontal homogeneity of sinks, sources and transport phenomena. By using linear de-trending the weak non-stationary concentration changes (linear trend) can be corrected to stationary. Typically data post-processing include co-ordinate rotation of the wind speed components to remove advective part from the flux. Also, the delay time due to air traveling in the sampling tube (time lag) is taken into account. That is calculated from searching for the largest correlation between the vertical wind speed and concentration measurements inside a certain, theoretically estimated time window.

Data processing could include corrections related to EC measurement. WPL correction is taking into account variation of particle concentration due to density variations caused by heat or water vapor fluxes. The errors due to imperfect frequency response of an analyzer can be estimated and accounted by using the spectral models based on Fourier transformed auto- and cross-correlation functions producing power and cross spectrum, respectively. In atmospheric studies, usually the one-sided (frequencies from zero to plus infinity) power spectrum and real part of the cross-spectrum (co-spectrum) are used (e.g. *Kaimal and Finnigan*, 1994). Sometimes also a correction for the influence of deliquescence causing condensation or evaporation and therefore variation in the detection of particles is applied.

### 3.3 Relaxed eddy accumulation

Despite the importance of size-resolved particle flux and deposition velocity determination, only few studies have sought to quantify the size dependence of sub-micron particle  $v_d$ . At the time that was mainly due to requirement of fast analyzers in EC

applications. Therefore, a relaxed eddy accumulation (REA) collection system with DMPS was build up at SMEAR II site (**Paper II** and *Gaman et al.*, 2003).

The history of accumulation methods begin on 1972, when *Desjardins* (1972) presented an eddy accumulation (EA) method where instantaneous air samples are collected by two separate reservoirs. One reservoir opens when air flow is upward ( $w^+$ ) and the other when the flow is downward ( $w^-$ ). After a sufficiently long sampling period the total air mass collected and measured in the two reservoirs represents the total vertical flux

$$\overline{w^+c} + \overline{w^-c} = \overline{w^+(\bar{c} + c')} + \overline{w^-(\bar{c} + c')} \quad (31)$$

$$= (\overline{w^+w^-})\bar{c} + \overline{w^+c'} + \overline{w^-c'} \quad (32)$$

$$= \overline{w^+c'} + \overline{w^-c'} \quad (33)$$

$$= \overline{w'c'} \quad (34)$$

where one assumes  $\overline{w^+} + \overline{w^-} = \bar{w} = 0$ . The disadvantage with EA is that the sample flow rate has to be adjusted instantaneously according to magnitude of  $w$ . To simplify the problem, *Businger and Oncley* (1990) suggested a REA method in which the vertical flux is determined as the product of the standard deviation of  $w$  ( $\sigma_w$ ) and the mean concentration difference of the air sampled upwards and downwards multiplied by an empirical constant  $\beta$  (Businger coefficient):

$$\overline{w'c'} = \beta\sigma_w(\bar{c}^+ - \bar{c}^-) \quad (35)$$

To maximize signal-to-noise ratio (the ratio of the concentration difference between the  $c^+$  and  $c^-$  to the uncertainty in the concentration measurement) the samples are collected only when  $|w| > \text{deadband}$  (a threshold value  $w_0$ ). The signal increases with increasing  $w_0$ , but at the same time decreases the effective sampling time resulting the larger noise. Thus, to minimize the total uncertainty, an optimal compromise should be found. Usually, the deadband proportional to  $\sigma_w$  is used. To avoid dependence of  $\beta$  on stability, we applied a dynamic deadband proportional to the 5 minutes running mean of  $\sigma_w$ . Then, the constant value for  $\beta$  can be used and it depends only on deadband width (**Paper I**). It is recommended to determinate the value  $\beta$  by using fast analyzers and assuming scalar similarity (**Papers I and II**)

$$\beta = \frac{\overline{w'c'}}{\sigma_w(c^+ - c^-)}. \quad (36)$$



### 3.4 Scavenging coefficient determination

Both rain and snow scavenging studies (**Papers VI and VIII**) are based on semi-empirical approach similar to *Mircea and Stefan* (1998). The scavenging coefficient is calculated by integrating Eq. 25 from  $t_0$  to  $t_1$  resulting

$$\lambda(d_p) = -\frac{1}{t_1 - t_0} \ln \left( \frac{c_1(d_p)}{c_0(d_p)} \right), \quad (37)$$

where  $c_0(d_p)$  and  $c_1(d_p)$  are particle size distributions at the time  $t_0$  and  $t_1$ , respectively.  $\lambda$  can be determined as an average value or as a slope of the logarithm as a function of  $t$ . This applies if scavenging is the only process affecting to aerosol particle size distribution. However, many other processes exist: condensation, coagulation, advection, etc. (see **papers VI, VII and VIII**). Therefore, a large data set and a careful data selection is needed to minimize the effect of other mechanisms than precipitation scavenging.

In **Paper VI**, precipitation was measured with tipping bucket ARG100 rain gauge. It collects liquid precipitation by a funnel to one of the two buckets. When the first is full, the balance arm tips, empties the bucket, and moves the second one under the funnel. The number of tips are counted and saved with time resolution of 15 minutes. Disadvantage of the device is that it is not able to measure frozen precipitation and the flow field around the funnel tends to divert droplets past the funnel.

In **Paper VIII**, snow and rain precipitation was measured with Vaisala FD12P weather sensor. It includes optical forward scattering sensor and capacitive precipitation sensor and is able to measure both precipitation type and amount as well as visibility. The wavelength of light is 875 nm and sample volume is about 0.1 dm<sup>3</sup> located at the intersection of transmitter and receiver beams.

## 4 Results and discussion

An overview of the results obtained in the following peer-reviewed studies is given here. However, the reader is encouraged to read through the original studies (**Papers I-VIII**) to get a full understanding about the research and the results.

Starting from the measurements, **Paper I** presents the effect of deadband width and atmospheric stability on the numerical value of empirical  $\beta$  coefficient used to invert measured REA data to flux. Our simulations show that by using dynamic deadband, only a weak dependence between  $\beta$  and atmospheric stability appears. Therefore, the use of a constant  $\beta$  is justified. In agreement with previous studies (**Paper I**, Table 4), the median value obtained for a system with dynamic deadband proportional to 0.5 times the running mean of  $\sigma_w$  was  $\beta = 0.42 \pm 0.03$ .

By REA system we were able to measure size segregated particle fluxes (**Paper II**). Particles in the size range of 80 – 100 nm had the lowest  $v_d$ , about 0.4 – 0.5 cm s<sup>-1</sup>. From 80 – 100 nm size,  $v_d$  increased with decreasing or increasing particle diameter. At the larger end, our results agree with those obtained by *Gallagher et al.* (1997). Compared to indirect results from EC (*Rannik et al.*, 2001, 2003, **Paper III**),  $v_d$  measured with REA are higher. The reason for that is not understood although some hypothesis could be presented.

Measurements allowed us also to study the effect of increasing turbulence on  $v_d$ . Figure 6 shows mean deposition velocities of 15 – 80 nm particles as a function of  $u^*$ . Size classes 15, 20, 25 and 40 nm and size classes 50, 60, 70 and 80 nm were combined to get enough data for statistical analysis. For 30 nm particles, enough (12 months) data was available. Although the uncertainty is large, a clear dependence of  $v_d$  on  $u^*$  exists, especially for high  $u^*$  values. This is consistent with other flux studies.

To proceed from a bulk deposition studies to multi-layer approach, we installed EC measurement set-up below the canopy (**Paper III**). Spectral analysis showed that the method could be used to study ground deposition in a forest, which was the main advantage of the work. Also, we observed that approximately 20% of the particles penetrated the canopy and deposited on the forest floor. The promising results let us to continue the measurements and after a year we had enough data to build up and verify a multi-layer particle deposition model (MLM) presented in **Paper IV**.

With the MLM we were able to show that turbo-phoresis, excluded from the most of

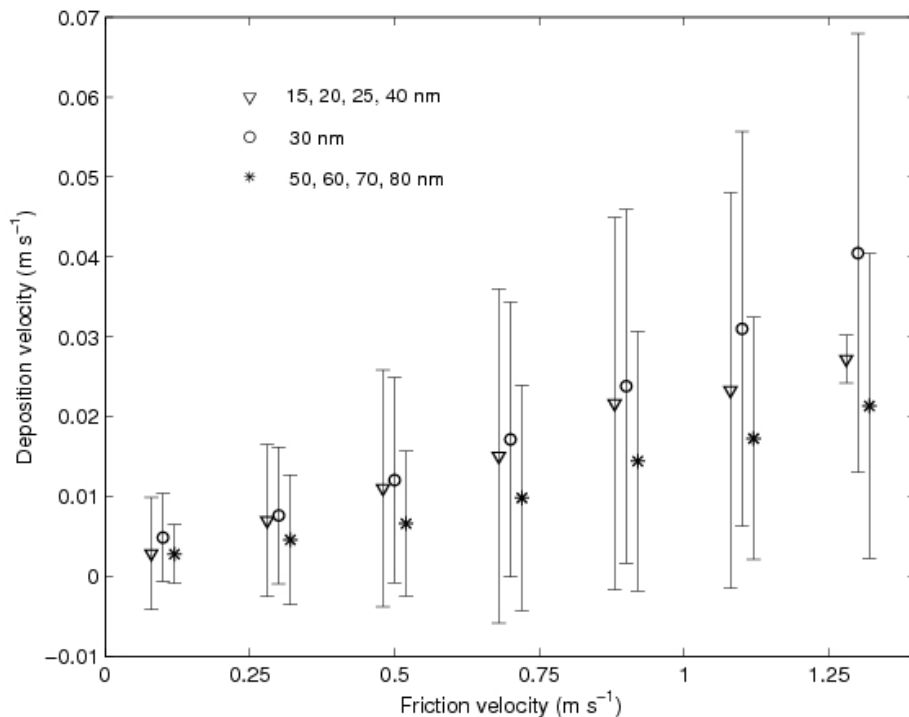


Figure 6: Deposition velocities measured with REA (**Paper II**). Vertical bars denotes standard deviations.

the existing models, provides a coherent explanation why  $v_d$  measured over tall forests do not support a clearly defined minimum for particle sizes in the range of 0.1-2  $\mu\text{m}$ . Turbo-phoresis is also likely to explain why particle dry deposition velocities observed over tall forests behave differently in the inertial-impaction regime than data from many laboratory and short-canopy crop experiments. The latter have indicated that when  $v_d$  is normalized by  $u^*$  ( $V_d^+$ ) and presented as a function of  $\tau_p$  normalized by  $\nu$  ( $\tau_p^+$ ), a power-law scaling in the form of  $V_d^+ \sim (\tau_p^+)^2$  emerges in the inertial-impaction regime. Over forest canopies, turbo-phoresis was found to increase  $v_d$  especially in that particular size range (**Paper IV**).

The MLM was also used to study the influence of vertical leaf area shape and total LAI on  $v_d$  (Fig. 7). At SMEAR II, thinning was performed during the winter 2002, which provided a nice set of experimental data to compare the MLM results. Both MLM and the measurements (**Paper V**) showed that after thinning  $v_d$  diminished about 25 %, which was comparable with the reduction of single-sided LAI. Besides of the value of LAI,  $v_d$  depends also on the location of leaves: 1) at a given LAI a constant leaf area

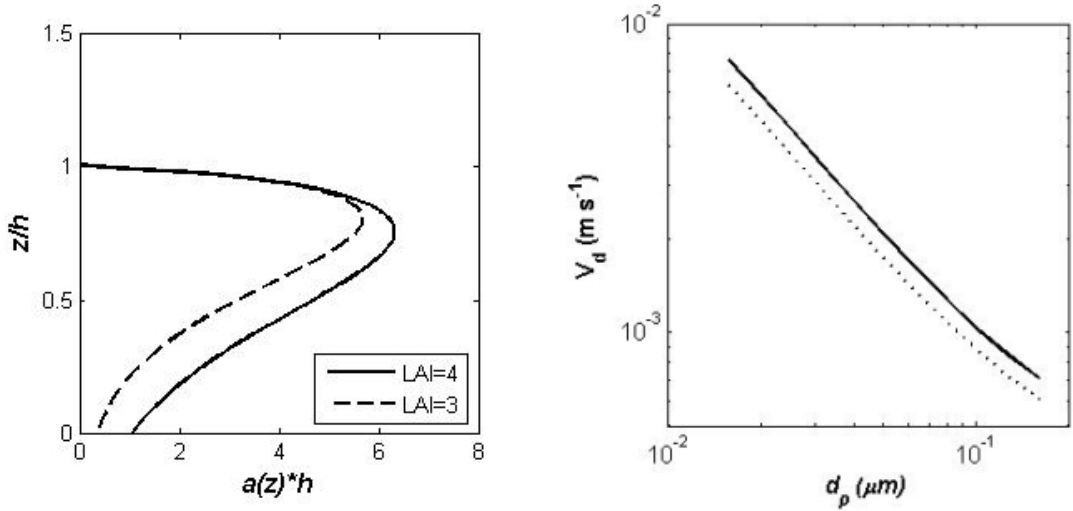


Figure 7: The effect of LAI reduction from  $4 \text{ m}^2\text{m}^{-2}$  (solid line) to  $3 \text{ m}^2\text{m}^{-2}$  (dashed line) to deposition velocity ( $V_d$ ) as a function of particle size ( $d_p$ ).

density distribution results in the lowest  $v_d$  when compared to skewed profiles and 2) When foliage is concentrated in the upper layers of the canopy, increase in LAI at first leads to increasing  $v_d$ , but the effect saturates at high LAI.

Despite careful observations, there are several possible processes which can affect the dry deposition results, especially when a full year measurement period is used (**Paper II**). One of the causes of uncertainty is seasonal variation of the boreal forest total surface area and type. During the winter (November-March) ground and occasionally also canopy are covered by snow. In contrast, during the summer broad-leaved trees can affect the deposition rates by increasing leaf area. It is noticed that above the canopy  $v_d$  tends to be higher during the winter (not shown). In below canopy measurements this phenomenon is not observable (data not shown). In spite of numerous attempts, the reason for the larger winter  $v_d$  remains unknown.

Wet deposition induced both by rain was studied in **Papers VI** and **VII** for particle size range  $10 - 510 \text{ nm}$ . Measured rain scavenging coefficients  $7 \cdot 10^{-6} - 4 \cdot 10^{-5} \text{ s}^{-1}$  (**Paper VI**) were higher than existing model calculations based only on below-cloud processes, but comparable with results from similar experiments for the same rainfall rates. In **Paper VII** we used a model including below-cloud scavenging process, mixing of ultrafine particles from boundary-layer into cloud followed by CCN activation, and in-cloud removal. The model showed reasonable agreement with observed values.

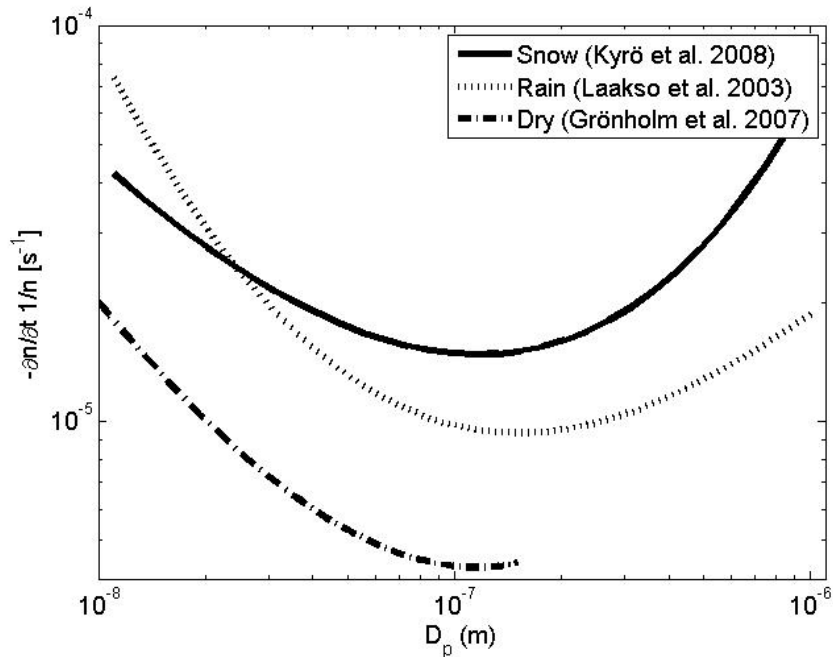


Figure 8: Scavenging coefficients ( $dn/dt1/n$ ) for snow and rain precipitation and virtual scavenging coefficient for dry deposition as a function of particle size ( $D_p$ ) calculated assuming well-mixed situation in boundary-layer with height 1000 m.

According to the model, ultrafine particle removal by rain depends on particle size, rainfall intensity, mixing processes between boundary-layer and cloud elements, the in-cloud collection efficiency and coagulation with droplets. Also chemical composition of particles can impact the growth factor and affect the scavenged fraction of particles in supersaturated conditions. Electric charge may play a role in scavenging by increasing the collection efficiency.

By using similar approach than for rain, we determined snow scavenging coefficients in **Paper VIII** for particles between (10 – 1000 nm). Scavenging coefficients varied from  $8.7 \cdot 10^{-6}$  to  $5.2 \cdot 10^{-5} \text{ s}^{-1}$  depending on particle size and precipitation intensity. This study was afterwards repeated in an urban area and compared to radar measurements (*Paramonov et al.*, 2011).

To compare dry and wet deposition, a 'virtual' scavenging coefficient can be determined for dry deposition (REA data, **Paper II**) using measured  $v_d$  and assuming well-mixed boundary layer with a height of, say, 1000 m. Figure 8 illustrates the scavenging coefficients determined for rain and snow as well as for dry deposition. For the size-

segregated data, a parametrization presented in **Paper VI** is used. To summarize, wet deposition is an order of magnitude more effective 'air cleaner' than dry deposition.

## 5 Review of papers and author's contribution

**Paper I** presents simulations to determinate a magnitude of the factor  $\beta$  related to REA data inversion to fluxes. Also deadband width is studied to optimize signal to noise ratio and statistics. I am responsible for simulations, data analysis and writing.

**Paper II** is a clear continuum to **Paper I** although published before that. It presents, to my knowledge, the first size-segregated  $v_d$  measurements covering particle sizes from 10 to 150 nm. Also the dependence of  $v_d$  on  $u^*$  was reported. I am responsible for data analysis and writing this paper.

**Paper III** is written to show that particle flux measurement with EC is possible to carry out successfully also below canopy. Related to **Paper II**, size-segregated  $v_d$  are derived and below canopy data set is compared to above canopy flux data. I did the most of the data analysis and about a half of writing.

**Paper IV** presents a new multi-layer deposition model for a forest canopy and floor. The experience gained in **Paper III** enabled to continue the below canopy flux measurements and get an extensive data set to verify the model. With the model we studied turbophoresis and found that it at least partly explained distinctions between the measurements and existing models. I was partly responsible for planning, installing and running the measurements and made data-analysis. I partly developed the model and wrote some chapters of the article.

**Paper V** takes advantage of the MLM developed in **Paper IV** and studies the effect of canopy structure and magnitude of LAI on  $v_d$ . I am responsible for data analysis, planning, and partly for writing.

**Paper VI** was the first published paper in this thesis. It reports size-segregated scavenging coefficients for ultrafine particles determined from DMPS measurements accounting of precipitation intensity. I did about half of the data analysis and writing of this paper.

**Paper VII** is a modeling study which shows that including in-cloud scavenging in addition to below-cloud wet deposition was necessary to reproduce the field observations presented in **Paper VI**. I am responsible for data analysis, parametrization, and partly for writing.

**Paper VIII** attacks snow scavenging. As in **Paper VI**, size-segregated scavenging coefficients and a parametrization for ultrafine particles is presented. I supervised this work and am responsible for parametrization and codes to process the data.



## 6 Conclusions

The open questions in the field of particle deposition were presented in the beginning of this book. The first one was lack of measurement data of size-segregated particle fluxes, especially in the size-range below few hundred nm. As mentioned, dry deposition velocity depends on particle size and turbulence. In **Paper II** we measured deposition velocities ( $v_d$ ) of 10 - 150 nm using REA system and studied the friction velocity ( $u^*$ ) dependence. As expected, the highest  $v_d$  was measured for the smallest particles and the  $v_d$  decreased with increasing particle diameter.  $v_d$  was duly dependent on  $u^*$ . The dependence was strongest for the smallest particles. The results of **Paper I** improve REA data inversion.

The second aim was to study partitioning of particle deposition between vegetation and the underlying ground. We grab this task by setting a particle EC measurement unit below canopy and showed by spectral analysis that the measurements are robust (**Paper III**). The main result of the short measurement period was that about 20 % of particles penetrated the canopy and deposited on the ground. This work was continued in **Paper IV**, where the sub-canopy particle flux measurements over one year were analyzed and used to verify a multilayer deposition model. The model was further used to study the effect of canopy structure on  $v_d$  (**Paper V**).

Third problem was to find out why the observations over forests generally do not support the pronounced minimum of deposition velocity for particles 0.1 - 2  $\mu\text{m}$ . In **Paper IV** we show that turbophoresis, when accounted for at the leaf scale in vertically resolved models, provide a plausible explanation for the discrepancy. It also explains why a power law scaling in the form of  $v_d$  normalized by  $u^* \sim$  particle time scale normalized by air viscosity to the power of 2 emerges in the inertial-impaction regime for laboratory experiments but not in the forest measurements.

The fourth issue concern lack of size-segregated scavenging coefficient data. In **Paper VI**, **VII** and **VIII** we present scavenging coefficients and parametrization both for rain and snow scavenging. Together with dry deposition velocities at the same site, we were able also to compare these removal mechanisms to each other. The importance of particle dry deposition relative to wet deposition depends on the solubility of the species in water, the amount of precipitation in the region and the surface properties. Effectiveness of snow scavenging depends on the crystal or snow flake structure and air relative humidity.

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