CHAPTER 1

INTRODUCTION

1.1 GENERAL

The process of removing particles or gases from the atmosphere through the delivery of mass to the surface by non-precipitation is defined as dry deposition (Dolske and Gatz 1985). Dry deposition is an important pathway for the transfer of pollutants from the atmosphere to natural surfaces. Dry deposition process can be explained by three steps. The first step is aerodynamic transport. The second step is boundary layer transport and third one is reacting with receptor (Wu et al 1992). Interest in atmospheric deposition has increased over past decade due to concern about the effects of the deposition material entering the environment and its subsequent health effects. Dry deposition is important pathway for transfer of pollutants. The pollutants movement of this pathway in environment needs to be understood.

Atmospheric deposition results from the transport and accumulation of particle onto a surface during the periods of no precipitation. Dry deposition has gained a great deal of interest from researchers due to its effects on the environment and consequently there have been significant efforts to measure or estimate dry deposition using variety of techniques. Atmospheric deposition influences the fate of air borne toxics and often controls transfer of material form the atmosphere to natural surfaces. Dry deposition provides significant mechanism for the removal of particles from
the atmosphere and is an important pathway for the loading of toxic pollutants onto the environment.

1.2 BACKGROUND

Air Resource Laboratory (ARL) is a leader in the development and operation of dry deposition networks. Since 1984, the Atmospheric Turbulence and Diffusion Division in Oak Ridge has been operating a network specifically designed to get around the major problem confronting dry deposition monitoring activities as there is no existing method suitable for routine direct measurement. The nested network that was developed consisted of a small number of research sites supporting a larger array of stations making simpler but more routine observations. The Dry Deposition Inferential Method (DDIM) that was developed remains the central routine analytical tool of the ongoing National Oceanic Atmospheric Administrations (NOAA) dry deposition trial network. It is now identified as the dry deposition component of the Atmospheric Integrated Research Monitoring Network (AIRMoN). This network started with six sites; thirteen stations are now operating.

Then the National Dry Deposition Network (NDDN) was established in 1986 to document the magnitude, spatial variability, and trends in dry deposition across the United States. Currently, the network operates as a component of the Clean Air Status and Trends Network (CASTNet). Dry deposition is not measured directly in CASTNet, but is determined by an inferential approach (i.e. fluxes are calculated as the product of measured ambient concentration and a modeled deposition velocity). In CASTNet, Chemical species included were ozone, sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid. The temporal resolution for the ambient concentration
measurements and dry deposition flux calculations is hourly for ozone and weekly for the other species.

At the 2009 Fall Meeting in Saratoga Springs, the National Atmospheric Deposition program (NADP) Executive Committee accepted the Atmospheric Mercury Network as an official NADP network.

The Atmospheric Mercury Network (AMNet) established this network of monitoring stations for the purpose of measuring atmospheric mercury fractions which contribute to dry and total mercury deposition. Sites collect concentrations of atmospheric mercury species from automated, continuous measuring systems.

AMNet has specific objectives:

- To measure atmospheric mercury concentrations of gaseous oxidized, particulate-bound, and elemental mercury in select locations
- to offer high-quality measurement data to estimate dry and total deposition of atmospheric mercury to other researchers;
- to standardized operational methods so that instruments are being operated consistently
- to provide internal and external quality assurance
- to provide the data management capability and access and
- to provide field support through an experienced site liaison.

As with other networks, NADP welcomes the participation of other organizations and scientists. To truly understand the mercury problem, more monitoring information is needed. This section emphasizes the present status
of dry deposition research work around the world. ARL Headquarters develops and improves atmospheric dispersion and air quality models, which track the movement of potentially harmful substances. It collects air quality and deposition measurements of selected air quality parameters, provides climate-relevant datasets and assessments of climate variability and trends. It is operated from Silver Spring, Maryland 20910, USA. It is part of NOAA (www.arl.noaa.gov). As far as Indian context is concerned, no such dry deposition network has been operating to evaluate atmospheric dry deposition of pollutants. The present study could be the pioneer in India to establish such network. These networks are designed to reduce emissions of numerous polluting sources by significant amounts over large geographical area thereby improving environmental conditions. Based upon dry deposition network estimation, long term dry deposition distribution of various pollutants across the province can also be derived.

1.3 RESEARCH ACTIVITIES

The major goal of dry deposition research conducted by ARL scientists relates to the need to identify and understand the processes that cause dry deposition, in order to quantify dry deposition rates at locations where direct measurement is not possible. The focus is on the development and improvement of models, whether for site-specific application using local observations of key variables as input or for regional application using model "data" fields to drive the deposition routines. ARL presently focuses its attention on

- the development of systems for quantifying dry deposition,
- the measurement of dry deposition using micrometeorological methods,
• the development of techniques for assessing air-surface exchange in areas (such as specific watersheds) where intensive studies are not feasible, and

• the extension of local measurements and understanding to describe areal average exchange in numerical models.

1.4 ATMOSPHERIC DEPOSITION

Atmospheric deposition is an ensemble of environmental processes by which airborne pollutants from various sources are delivered to receptor systems at the earth’s surface. Atmospheric deposition is considered for two receptors such as forest ecosystems and lakes and impoundments, because research (conducted at Illinois Institute of Technology) has shown possible damage to these receptors from certain kinds and amounts of atmospheric deposition. The characteristics of atmospheric deposition in Illinois, and how it varies across the state and throughout the year are described in that research work, where there are data sufficiently available for analysis. Changes over several years are calculated and trends are inferred, if these changes are significant. Also shown are maps of deposition loadings, which together with the concentration data provide information necessary for assessments of the exposure of Illinois’ natural environment to atmospheric deposition. While an explicit description of the source receptor relationships for major pollutants, such as sulfur dioxide (SO₂) and nitrogen oxides (NOx), is not considered, the sources of these pollutants in Illinois and surrounding states are compared to their occurrence in atmospheric deposition. Finally, additional work is discussed that is needed to improve the assessment of atmospheric deposition in Illinois and over Lake Michigan.

Atmospheric deposition includes gases and aerosols that are solid, liquid, or mixed phase. It includes both primary pollutants, which retain their
chemical identity between source and receptor, and secondary pollutants, which undergo transformation during transport in the atmosphere. Deposition of pollutants from the atmosphere is a continuous process, though there are large temporal variations in the deposition rate or flux. These variations relate to the kind of deposition that is occurring and to surface and atmospheric conditions. There are two kinds of atmospheric deposition, wet and dry. Wet deposition is defined as the delivery of pollutants to the surface by precipitation. Dry deposition is the delivery of gases and aerosols to the surface by mass transfer processes other than precipitation. In principle, dry deposition occurs continuously, while wet deposition occurs episodically, e.g., when it rains.

Dry deposition includes the mass transfer of pollutants to the surface by a variety of physicochemical processes: turbulent diffusion, diffusion followed by surface sorption of gases, gravitational settling of large particles, impaction, and interception of solid and liquid particles. Dry deposition fluxes are strongly affected by atmospheric factors, which influence the rate at which pollutants are delivered to a receptor surface; and by surface factors, which influence the efficiency with which pollutants stick to a receptor surface. Among the atmospheric factors which affect dry deposition are wind speed and turbulence, air temperature, solar radiation, and relative humidity and the surface factors are roughness, wetness, surface-to-air temperature difference, and type of surface, which may animate or inanimate.

The relative importance of these factors in determining the dry deposition rate depends also on the physical and chemical nature of the pollutant. For example, factors that affect the mass transfer of carbonaceous soot, an unreactive, insoluble particle, are much different than the ones affecting nitric acid, a highly reactive, soluble gas. The dry deposition of
gases and submicron aerosols involves highly complex processes, and direct measurements are intractable on a spatial domain the size and complexity. For this reason, an indirect method is applied to infer, rather than measure, dry deposition fluxes (Lee 1991)

1.5 DIRECT METHOD

Direct methods are subdivided into surface analysis and atmospheric flux methods. Surface analysis includes foliar extraction, throughfall and stem flow, watershed mass balance, aerodynamically designed surface, isotopic tracers, snow sampling and cloud droplet collection. The atmospheric flux method includes eddy correlation (tower and aircraft based), gradient method, eddy accumulation, variance technique, aerometric mass balance and multiple artificial tracers (Fairall and Larsen 1982, Leiming Zhang and Robert Vet 2006). Throughfall and stemfall have been taken in many countries as a simple technique for the assessment of total deposition flux of oxides of sulphur to forests, although this method can be usually be used only during the warm season.

Except in special circumstances, however, most of these direct methods are sufficiently complicated that routine application in a monitoring network is not yet practical. Moreover, routine applicability does not appear likely in the foreseeable future because: a) the chemical sensors necessary are not suitable for routine unattended use, b) the cost is prohibitive, c) the requirement of skilled operators is unavoidable, d) sites for suitable homogeneity are not available. Air pollution concentrations will also be monitored in this method.
1.6 BACKGROUND OF INFERENTIAL METHOD

This inferential method employs a conceptual model that estimates an atmosphere-to-surface coupling parameter known as the "deposition velocity" ($V_d$). The dry deposition flux is the product of $V_d$ and the measured air concentration of a particular pollutant. Model inputs, including the atmospheric and surface factors discussed earlier, are measured at sampling sites. Land-use and vegetation type and status are also reported at these sites, along with the airborne concentrations of Cl, SO$_4^{2-}$, particulate NO$_3$, nitric acid vapor (HNO$_3$), and SO$_2$. The NOAA sampling system is especially designed to exclude large particles, since the inferential method of calculating dry deposition applies specifically to gases and submicron aerosols.

The dry deposition of large particles, which have an aerodynamic diameter greater than 1 micrometer ($\mu$m), is typically estimated from an analysis of the mass of a pollutant accumulated on a surrogate surface. Dry falls (sedimentation of large particles) are measured in samples taken from the same collector used for precipitation. A wet/dry collector has been used to quantify deposition. This device (wet/dry collector), has two identical containers; it discriminates between wet and dry conditions, exposing the wet deposition container during precipitation and the dryfall container at all other times. Dryfall samples are sent for analysis of the same analytes measured in precipitation.

Dry deposition in Illinois tends to be somewhat higher in the Chicago area, both due to higher airborne concentrations of most pollutants and higher deposition velocities. For sulfate, nitrate, sulfur dioxide, ozone, arsenic, and manganese, the differences are in the order of 10 to 30 percent. For cadmium, chromium, iron, nickel, lead, and total suspended particles, dry deposition in the Chicago area exceeds the rest of the state by 200 to 400 percent, which is primarily caused by the differences in air quality. Temporal
trends in dry deposition generally follow air quality trends, although additional variability is introduced into the time series data by interannual variation in deposition velocities. More important for ecological impacts is the seasonal nature of dry deposition loadings, with higher deposition velocities for many pollutants occurring during the warm season, when biological impacts may also be the prevalent.

The total deposition of sulfur in the Chicago area is about 15 percent higher than in the rest of the state. For sulfur (sulfate plus sulfur dioxide), the ratio of wet to dry deposition is about 1 part wet to 1.5 parts dry. The deposition of nitrogen in the Chicago area is about 30 percent higher than in the rest of the state. For nitrogen (nitrate plus ammonium plus nitric acid vapor), the ratio of wet to dry deposition is about 1 part wet to 3 parts dry.

The spatial and temporal variation information is most useful in describing the coupling of the atmosphere to receptors that are also distributed in space and have temporally-varying sensitivity to the depositing pollutants. Acid deposition to forests for example, is most likely to have an effect during the growing season, and much less likely to be harmful in the dormant season. Toxic deposition to forests, however, may act through a cumulative effect, where the temporal variation is less important to understanding the impact on the receptor system.

Acid deposition to Lake Michigan presents a special difficulty in this analysis, since neither wet nor dry deposition is measured over the lake, although the refinement of estimates based on shoreline measurements which are an ongoing research topic.

Agricultural systems have been shown to be relatively insensitive to current levels of acid deposition, but the impact of toxic deposition and dry deposition of many pollutants is unknown. Ozone has been demonstrated to
have negative impacts on yield and quality of cash crops in several areas of the United States. The role of wet and dry toxics deposition as a contributor to nonpoint source pollution in surface and ground-water supplies for human consumption is also unknown at this time. The impact of atmospheric deposition (acid rain, toxic pollutants, and biological nutrients) to lakes and streams in Illinois (i.e., other than Lake Michigan waters) has not been documented, although consideration of the magnitude of deposition for many chemicals would indicate that significant impacts are possible. Finally, the impacts of $\text{SO}_4^{2-}$, $\text{SO}_2$, acids, and $\text{NO}_3^-$ deposition, both in precipitation and dry deposition, has been demonstrated in recent federally sponsored research in many areas of the United States. Materials impacts in Illinois are as yet unquantified, but they are potentially large.

### 1.7 DEPOSITION OF PARTICLES

The mechanism of deposition of particles depends on the particle size. Large particles with diameter greater than 10 $\mu$m fall slowly by gravitational settlement. The larger the particles, the more rapid they fall.

Particles larger than 150 $\mu$m diameter, having settling velocity 1 m/s remain airborne for a very short time and need not be considered. Particles less than 5 $\mu$m have sedimentation velocities, which are so slow that their movement is determined by the natural turbulence of air, just as for gases.

Intermediate particles, between 1 and 10 $\mu$m diameter, can be removed by impaction onto leaves and other obstacles. Particles in the 0.1 to 1 $\mu$m range, which include most of nitrates and sulphates, are only removed very slowly by dry deposition. The deposition velocities in order of 1 mm/sec, much lower than for $\text{SO}_2$. The most likely route for their removal is rain-out followed by water vapor condensation and droplet growth in clouds. Wash out
is not very efficient for these fine particles although it becomes more significant for larger particles such as coarse dust (Roy Harrison 2006).

Air borne particles are produced by both natural and anthropogenic sources. They can be produced either by direct emission to atmosphere (primary aerosols) or by physical and chemical process within the atmosphere (secondary aerosols) (note that aerosol and particle are used interchangeably here). Fine particles are mainly contributed by industrial and residential emission or by vegetation fires (Leiming Zhang and Robert Vet 2006). Coarse particles includes soil dust and salt particles (Kaufman et al 2002). Different aerosol species from the same continent may have different transport pathways associated with the continental outflow and aerosol vertical profiles (Sataka et al 2004). Atmospheric particles have strong impacts on climatic and environmental issues. These particles have direct (Scattering or absorption of solar radiation) and indirect (increasing cloud condensation nuclei) effects on climate. Atmospheric deposition of particles delivers atmospheric loads of many compounds (eg., sulphate, nitrate, ammonium, base cations and heavy metals) to eco systems (Ruijgrok et al 1995). Atmospheric particles are also responsible for many urban air pollution related problems (eg., decreased visibility and human problems such as respiratory illnesses (USEPA 1996).

To understand thoroughly the above mentioned problems, particles emission, transport, transformation and removal mechanisms have to be quantified at multiple scales. Dry and wet depositions are the two major removal mechanisms for atmospheric particles. Dry deposition is the removal process though which particles are taken up by the earth’s surface. In the process of wet deposition, particles are delivered to the surface via precipitation. Both mechanisms are strongly size-dependent with removal
rates of particles from the atmosphere differing by several orders of magnitude for different particle sizes (Seinfeld and Pandis 1997).

Most of the emission sources in urban area are fugitive dust, which can arise from a wide variety of sources including paved and unpaved roads, industrial areas, construction and agricultural activities. Fugitive dust is usually associated with coarse fraction (>2.5 μm) of atmospheric aerosol (Sait Sofuoglu et al 1998). The process of dry deposition of air borne pollutants is influenced by various physical, chemical, and biological factors that can cause large variations in deposition on both small and large scales of time and space (Zitouni Ould-Dada et al 2002).

Dry deposition of atmospheric pollutants especially mercury impose considerable impact into terrestrial and aquatic ecosystems. It is well known that vapor phase Hg constitutes the vast majority of atmospheric Hg burden but particulate phase Hg may actually play a disproportionately large role in the amount of Hg in the various environment compartments (Fengman Fang et al 2001). Dry deposition of ambient particles is thought to be an important pathway for the introduction of toxic trace elements and heavy metals into aquatic ecosystem (Hui-Jung Yun et al 2002).

There were many different types of surfaces that have been used for collection of atmospheric particles including filter papers, petri dishes, microscopic slides, Teflon plates etc., (Cheng-Nan Chang et al 1994). However, there is still no generally acceptable technology for sampling and analyzing dry deposition flux. The quantification of dry deposition flux is difficult because of large spatial and temporal variations. The use of surrogate surface to collect dry deposition is a technique that allows a comparison to be made of measured and modeled data because it can be used to directly access deposited material (Thomas Holsen and Kenneth Noll 1992).
Current dry deposition estimation methods often use measured air concentrations and modeled dry deposition velocities. Since the model used to predict dry deposition velocities are complex and require information that is difficult to obtain. Hence Dry deposition fluxes are often estimated using particulate concentration and assumed dry deposition velocities. However there has been no consensus on the appropriate dry deposition velocity. The use of surrogate surface is one approach to directly measure dry deposition (Mustafa Odabassi et al 2002).

1.8 DRY DEPOSITION MODEL

A variety of models have been developed to predict deposition velocities. For example, Slinn and Slinn (1980, 1981) developed a model for particles deposited on a water surface that describes delivery from the free atmosphere by eddy diffusion and sedimentation, followed by transport across the viscous layer by Brownian diffusion, inertial impaction and sedimentation. Williams (1982) developed a similar model that includes separate expressions for smooth and rough areas of water surface. Both of these models assumed the water is a perfect sink. Subsequent researchers added the effects of a non-perfect sink surface by including a surface resistance term.

Since these types of models are complex and require information that is often difficult to obtain, dry deposition is often estimated using total or partially size segregated particle concentrations and average or overall deposition velocities. These deposition velocities are difficult to predict because they vary with atmospheric conditions, location and size distribution of the depositing species. It is common to have one order of magnitude variations in calculated overall deposition velocities due to differences in methods. All these methods have employed particle size distribution to calculate dry deposition velocity (Van Aalst 1988). The number of steps used
to discretize the particle’s size range has a large influence on the computed dry deposition velocity (Dullac et al 1989) due to the non-linear dependence of the calculated deposition velocity on particle diameter and shape of the size distribution curve. For these reasons, the use of an overall deposition velocity, in combination with measured ambient concentrations, to estimate dry deposition, often greatly underestimates the contribution of coarse particles, particularly those > 10μm, to dry deposition (Holsen et al 1991, 1992).

1.9 DRY DEPOSITION VELOCITY

Dry deposition is characterized by dry deposition velocity, which is the relation between dry deposition flux and contaminant particle phase concentration (Yucel Tas demir et al 2004).

Strictly speaking dry deposition velocity is not a real velocity; however, it is referred to as velocity because of its units (Zannetti 1990). The one situation where dry deposition velocity may be considered a real velocity is when gravitational settling controls deposition as is the case for large particles. Impaction and interception were also important for larger size particles (Dp = 5μm) (Zhang et al 2001). For very small particles (Dp < 0.1μm) Brownian movement dominates the deposition velocity (Holsen et al 1991, Zannetti 1990). Particles in intermediate size range have the lowest predicted deposition velocities because of the relative weakness of their Brownian motion and gravitational settling effects.

In the literature, reported deposition velocities vary a lot possibly due to the spatial fluctuations (urban and non urban areas), temporal changes (winter and summer months), diurnal variations, surface type differences and micrometeorological conditions (such as wind velocity and direction, atmospheric stability) as well as experimental uncertainties (Finlayson-Pitts and Pitts 1986).