CHAPTER 1

Introduction

1.1 Atmospheric deposition

The major source of pollutants emitted from anthropogenic, for example combustion of fuel, industries, power station and biomass burning and other processes undergo chemical reactions in the atmosphere transport and then fall to the earth surface (Paode et al., 1996). Atmospheric deposition has traditionally been separated into two different mechanisms as wet deposition and dry deposition (Figure 1.1). Wet deposition is a deposition of all forms of precipitation through the earth such as rain, snow, cloud, fog. Dry deposition is deposition of dry particles and gases. It may become incorporate into dust and smoke (Porter, 2006; Xu et al., 2008). However, dry deposition can affect to human health in particular on respiratory system due to fine particulate matter in the air.

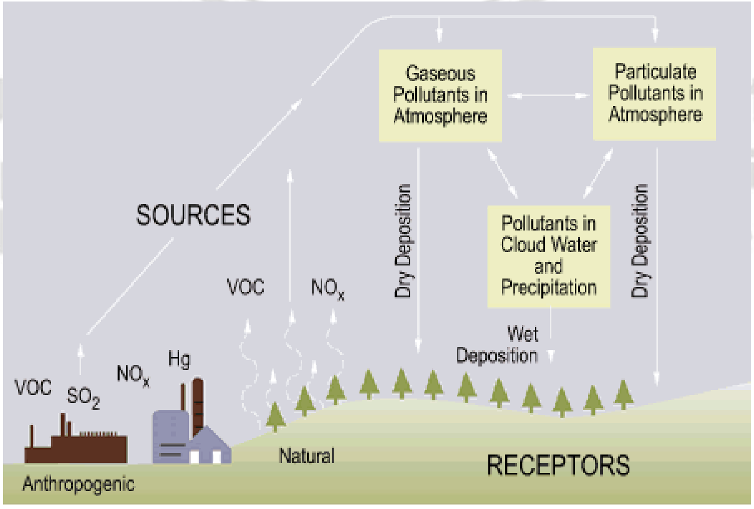

Figure 1.1 Atmospheric deposition process
(http://www.epa.gov/acidrain/what/index.html)

1.1.1 Wet deposition

Wet deposition is incorporation of atmospheric species into forms of precipitation such as rain, snow, cloud, fog and then removes from the atmosphere and deposition onto the earth's surface. The droplets in the forms of cloud, rain, snow, fog will be generally more or less acidified, which is the reason why the wet deposition is commonly known as acid rain or acid precipitation among the general public.

Atmospheric acids to formed acidify atmospheric water droplets including rain, where the acidity is commonly expressed in pH. The acidity of the solution will be decreased more or less, which would allow us to estimate acidification of atmospheric water by pH. The rainfall that has pH less than 5.6 may be considered as acid rain. The most important gasses which lead to acidification are sulfur dioxide (SO_2), nitrogen oxides (NO_x) and hydrogen chloride (HCl). Most of acids in the atmosphere are not emitted directly from sources but chemically formed during the course of the transport. In addition, atmospheric acid is to transport compounds by incorporating the bases through acid-base reactions. However, pH precipitation is associated with high concentration and low concentration of acids from atmosphere fall to the earth (Akimoto et al., 2011)

1.1.2 Dry deposition

Dry deposition is deposition of dry particles and gases from the atmosphere onto earth’s surfaces in the absence of precipitations, it may become incorporate into dust and smoke, and then fall to the ground and sticking to the buildings, homes, cars, trees and other surface (Porter, 2006).

The primary gases are SO_2, NO_x and NH_3, which is important in relation to the atmospheric deposition. Once emitted to the atmosphere, some of SO_2 and NO_x become oxidized to sulfate and nitrate through both gas and aqueous phase processes. The result of these reactions is the formation of acids in the gas phase such as HNO_3, HCl, HCOOH, CH_3COOH, etc. and in the aerosol phase for example sulfate, nitrate, chloride, organic acids, etc. Those primary gases and the aerosols formed by secondary reaction eventually will deposit onto surfaces. The rate of deposition depends on chemical and physical properties of the species, types of surfaces and meteorological.

Field studies on dry deposition fluxes of various chemical species have been done explicitly (Akimoto et al., 2011).

Sulfuric acid formed by oxidation of SO_2 may in turn neutralized by NH_3 to form ammonium sulfate. The conversion of H_2SO_4 to $(NH_4)_2SO_4$ changes the physical and chemical properties of the species changes in deposition characteristics. Gaseous nitric acid formed by oxidation of NO_2 may be neutralized by NH_3 to form ammonium nitrate solid aerosol. This equilibrium reaction between NH_3 and HNO_3 is particularly important from the point of dry deposition by converting to NH_4NO_3 (Erisman and Draaijers, 1995).

1.2 Sampling methods for atmospheric dry deposition

Amount of dry pollutants deposited on earth depends on many factors, including meteorological conditions, physical and chemical characteristics of the pollutants such as particle size, and characteristics of the surface on which deposition occurs (Patania et al., 2003; Wesely et al., 2006).

The several techniques of measured deposited material have been made to estimate dry deposition in the atmosphere such as leaf-washing method, micrometeorological method, through fall method, watershed mass balance method, inferential and surface accumulation methods and four-stage filter pack method, etc. (Servant, 1976; Davidson et al., 1990; Gupta et al., 2004; Chirasathaworn, 2005; Wiriya, 2008; Chantara et al., 2012). This study has been focused on leaf-washing method in order to compare with the four-stage filter pack method, which is the standard method.

1.2.1 Four-stage filter pack

Four-stage filter pack method is widely used in Europe, North America and East Asia (EANET, 2003) because of high accuracy and no effect from environment. In addition, it has North America, the Clean Air Status and Trends Network (CASTNET, 2006), especially Japan Environmental Laboratories Association (JELA) and Republic of Korea also have experiences to carry out monitoring using the four-stage filter pack methods for air quality monitoring to provide data to assess trends of air quality, atmospheric dry deposition and ecological effects due to changes in air pollutant**.**

The four-stage filter pack is composed of four filters, which is using an air pump to pull the air through collecting filter and the dry deposition is adhered on the filter. The filter pack is normally set up at 3 m above ground level and flow rate of diaphragm pump at 1 L/min (EANET, 2003; Chantara et al., 2012). However, many disadvantages are existed such as air pump and electricity needed, high operating cost, immobile and complicated using.

1.2.2 Leaf-washing method

The leaf has been used to study the role of plants as biomonitoring for accumulation of particulates in the atmospheric (Aksoy et al., 1997; Ataabadi et al., 2012; Sæbø et al., 2012). Leaf-washing method is one popular method. This method has been applied in many researches for analysis of dry deposition in ambient air such as in India, Iran and Norway etc., which is easy method, low operating cost, no pump and electricity requirement, can be applied in wider areas. However, disadvantage of this method is affected by meteorological conditions i.e. amount of rain precipitation and wind speed as well as leaves characteristic such as smooth or roughness of leaves, arrangement of leaves and tree type (evergreen), but leaf-washing method is an alternative sampling method for atmospheric particulates deposition for many searches.

1.2.3 Comparison four-stage filter pack and leaf-washing methods

The summary of the comparative characteristic of leaf-washing and four-stage filter pack method to the qualitative for atmospheric dry deposition collection. Both methods have so many the differences such as method, equipment, cost and area etc., (Table 1.1).

Table 1.1 Comparison of characteristics for four-stage filter pack and leaf-washing methods

Features	Four-stage filter pack	Leaf-washing method
1. Complexity of laboratory deployment	High (-)	Low (+)
2. Laboratory/field maintenance cost	High (-)	Low (+)
3. Laboratory labor requirement	High (-)	Low (+)
4. Attendance for equipment	High (-)	Low (+)
5. Electricity requirement for field deployment	High (-)	Low (+)
6. Area for equipment installation	High (-)	Low (+)
7. Expert requirement	High (-)	Low (+)
8. Moving equipment	High (-)	Low (+)
9. Use for remote area	High (-)	Low (+)
10. Meteorological conditions	Low (+)	High (-)

Note; (+), advantage; (-), disadvantage

Source: Kotchabhakdi, 2007

Therefore, it can be seen that tree leaf used as bioaccumulation of air pollutants such as heavy metals, particle, ions, dust, aerosol, gases etc from the human activities. It has been applied in wide researches for analysis of atmospheric particulates deposition by leaf-washing method.

In 2004, Gupta and group studies that dry deposition of major ions on leaf between guava (*Psidium guyava*) and peepal (*Ficus religiosa*) leaves at the Rampur, a rural site of semi-arid region of India in summer, monsoon and winter season. Dry deposition samples (n = 85) were collected from eight leaves of guava and four leaves of peepal around tree canopy by randomly. The leaves attached to tree were washed with deionize water using a sprayer and air dried. The samples were collected after 72 hr, the leaf surface was washed into polyethylene (PE) bottle with 100 ml deionized at site. The major anions (F^-, Cl^-, NO_3^- and SO_4^{2-}) were analyzed by ion chromatograph (IC), while NH_4^+ was analyzed by UV-VIS spectrophotometer. The major cations (Na^+,

K^+, Ca^{2+} and Mg^{2+}) were analyzed by atomic absorption spectrophotometer (AAS). They found that dry deposition flux of ions on guava leaves in a descending order were $Ca^{2+} > K^+ > NH_4^+ > Mg^{2+} > SO_4^{2-} > Na^+ > Cl^- > NO_3^- > F^-$, while dry deposition flux on peepal leaves were $NH_4^+ > K^+ > Ca^{2+} > Na^+ > Mg^{2+} > SO_4^{2-} > Cl^- > F^- > NO_3^-$. The deposition flux of cations and anions were contribute to 66% and 76% of dry deposition on guava and peepal leaves, respectively, which soil is the major contribute towards of dry deposition flux at tropical region. The high correlation between $SO_4^{2-}$and NO_3^- indicates their likely origin from similar sources. Ca^{2+} and Mg^{2+} were probable origin from soil. Whereas, F^-, Cl^- and SO_4^{2-} may be attributed to biomass combustion, NO_3^- indicates that the contribution of atmospheric HNO_3 deposition. Overall dry deposition fluxes on guava leaves were higher than peepal leaves because the different of characteristic (rougher surface). In addition, dry deposition flux were highest in winter and lowest in monsoon season from guava and peepal leaves.

Kumar et al. (2006) investigated the dry deposition of atmospheric particles by using leaves of ashok (*Polyalthia longifolia*) and cassia (*Cassia siamea*) at an urban site in India from March 1999 to June 2001. Samples were collected from four leaves of ashok and cassia attached to the tree. Major ions were analyzed by using the same method with Gupta et al. (2004). The deposition flux was higher on cassia leaf than ashok leaf because the different of rougher surface. Dry deposition of cations varies from 0.46 to 12.16 mg/m^2/day while anions varies from 0.04 to 3.24 mg/m^2/day. Most dry deposition flux of cations were high in the monsoon season, while for anions were high in the winter season. For 37.9% of total variance, including F^-, Cl^-, NO_3^-, SO_4^{2-} and K^+ and has been contributed to combustion, which main source of K^+ is combustion and emissions from vegetation. F^- is mainly contributed from brick-kiln industries. In addition, for 26.1% of the total variance, consist of Ca^{2+}, Mg^{2+}, and NH_4^+ may be contributed in dust by road. For 18.9% of the total variance including Na^+ and F^- may be contributed to the brick-kiln industries.

Dry deposition flux on the different tree species including Japanese red pine (*Pinus densiflora*), Japanese cedar (*Cryptomeria japonica*), Japanese cypress (*Chamaecyparis obtusa*), and Japanese white oak (*Quercus myrsinaefolia*) were determined by Watanabe et al. (2008) at Tsukuba City, Ibaraki, Japan, which is a suburban area, using a modified leaf-washing technique. One set of leaves (test-leaves) was exposed to ambient air, while another set of leaves (control-leaves) was enclosed in a chamber (4 L transparent polyethylene bag) connected with a portable clean-air supply system. Dry deposition flux of NO_3^- and SO_4^{2-} to leaf surface were determined from the difference of accumulated on test and control leaf. Each of the leaf was washed with 40 ml de-ionized water and collected in polypropylene bottle. The washing solution was filtered and analyzed for NO_3^- and SO_4^{2-} by IC. Overall dry deposition flux of NO_3^- was higher than SO_4^{2-} for each tree species. The dry deposition flux of NO_3^- on pine, cedar, cypress and oak were 48.4±69.7, 14.9±10.7, 9.6±9.9 and 9.4±11.7 µmol/m^2/d, respectively while dry deposition flux of SO_4^{2-} were 8.8±8.9, 4.1±3.1, 1.8±1.6 and 2.0±2.3 µmol/m^2/d, respectively.

Ataabadi et al. (2012) assessed the washing effect with deionized water (DI) on several metal concentrations (aluminum, iron, nickel, manganese, zinc, copper and lead) in tree and shrub species in the vicinity of industrial zone for determination of metal contamination on leaves in botanic garden, Iran. They used six plant species which contain three tree species including *Pinus eldarica*, *Quercus brantii* and *Elaeagnus angustifolia*. And three shrub species including *Cercis siliquastrum*, *Nerium oleander* and *Thuja orientalis*. All of species ages were 15 years. The samples were divided into two groups. The first group was washed with deionized water to clean dust and deposited substances on leaves for 10 min while the second group was not washed. The leaves were dried at 70°C for 48 hr. One gram of each milled powder leave digested with 10 ml 2 N HCl and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results showed that the washed and unwashed samples had no significant effect on removing of metal.

Filter pack were used in many researches for sampling of dry deposition. Examples of the use of this equipment in Asia are measurement of ambient particulate species in Taiwan (Lin et al., 2006), Malaysia (Sumari et al., 2008) and Thailand (Chantara et al., 2012). The samples were extracted and analyzed by ion chromatograph (IC). At the city of Taichung, Taiwan, they found that concentrations of NO_3^- and NH_4^+ were 6.0 and 4.6 µg/m^3, respectively (Lin et al., 2006). At the Petaling Jaya, Malaysia, fluxes of of NH_4^+, SO_4^{2-} and NO_3^- were 13.7, 11.8 and 15.9 nmol/m^3 in 2004 and 111.9, 74.0 and 49.9 nmol/m^3 in 2005, respectively (Sumari et al., 2008). At Chiang Mai, Thailand, mean concentration of SO_4^{2-} was the highest 1.9 µg/m^3 during the period of

2005 to 2009 (Chantara et al., 2012). All particulates, which probably originated from the combustion process including transportation vehicles and biomass burning is closely linked to the production of air pollution.

Therefore, leaf-washing method is the possibility of using for atmospheric particulate deposition sampling.

1.3 Research Objectives

1. To compare ion composition of atmospheric particulate deposition collected by leaf-washing method and four-stage filter pack.
2. To compare seasonal variation of atmospheric particulate deposition by leaf-washing method and four-stage filter pack.