

CHAPTER 1

INTRODUCTION

1.1 Air Pollution

Air pollution is contamination of the indoor or outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere. Household combustion devices, motor vehicles, industrial facilities and forest fires are common sources of air pollution. Pollutants of major public health concern include particulate matter, carbon monoxide, ozone, nitrogen dioxide and sulfur dioxide. Outdoor and indoor air pollution cause respiratory and other diseases, which can be fatal. Air pollution is a major environmental risk to health i.e. disease from respiratory infections, heart disease, and lung cancer.

Air pollutants can be defined within primary pollutants and secondary pollutants. Primary pollutants are those released directly from the emission sources into the air in a harmful form. Secondary pollutants are modified to a hazardous form after they enter the air or are formed by chemical reactions with energy source from solar radiation. From the result, photochemical oxidants and atmospheric acid formed by these mechanisms are probably the most important secondary pollutants in terms of human health and ecosystem damage (Cunningham *et al.*, 2007).

Small particulate matter and other pollutants in indoor smoke inflame the airways and lungs, impairing immune response and reducing the oxygen-carrying capacity of the blood. There is also evidence of links between indoor air pollution and

low birth weight, ischaemic heart disease, nasopharyngeal and laryngeal cancers (WHO, 2011).

Indoor air pollution is estimated to cause approximately 2 million premature deaths mostly in developing countries. Almost half of these deaths are due to pneumonia in children under 5 years of age. Urban outdoor air pollution is estimated to cause 1.3 million deaths worldwide per year. Those living in middle-income countries disproportionately experience this burden. Exposure to air pollutants is largely beyond the control of individuals and requires action by public authorities at the national, regional and even international levels. The WHO estimates that emissions from cook stoves are one of the top five of threats to public health in poor, developing countries (Bruce *et al.*, 2000). Although biomass fuels are generally perceived to be a public health problem in developing countries, indoor combustion materials, including coal and wood are also used as primary or secondary heating fuels in many communities in the United States.

Around 3 billion people cook and heat their homes using open fires and leaky stoves burning biomass (wood, animal dung and crop waste) and coal. Among these deaths, 44% are due to pneumonia, 54% from chronic obstructive pulmonary disease (COPD), and 2% from lung cancer, pneumonia. Nearly half of deaths among children under five years old from acute lower respiratory infections (ALRI) are due to particulate matter inhaled from indoor air pollution from household solid fuels (WHO, 2010). Nearly 50% of pneumonia deaths among children under five are due to particulate matter inhaled from indoor air pollution. More than 1 million people a year die from chronic obstructive respiratory disease (COPD) that develops due to exposure to such indoor air pollution.

Both women and men exposed to heavy indoor smoke are 2-3 times more likely to develop COPD. Women exposed to heavy indoor smoke are three times as likely to suffer from chronic obstructive pulmonary disease (e.g. chronic bronchitis), than women who use cleaner fuels. Among men (who already have a heightened risk of chronic respiratory disease due to their higher rates of smoking), exposure to indoor smoke nearly doubles that risk. Approximately 1.5% of annual lung cancer deaths are attributable to exposure to carcinogens from indoor air pollution. As with bronchitis, the risk for women is higher, due to their role in food preparation as well as their comparatively lower rates of smoking. Women exposed to indoor smoke thus have double the risk of lung cancer in comparison with those not exposed.

In the other case many museums have been widely investigated in Europe, the effects of particulate matter and gaseous pollutants included NO_2 , SO_2 , O_3 , acetic acid, formic acid and BTEX in museums under tropical and subtropical climates and with different economic realities are still unclear then can be caused to the artwork by pollution in hot and humid environments, when air quality and microclimatic condition differences can cause deterioration (Godoi *et al.*, 2013).

1.2 Nitrogen Dioxide (NO_2)

Nitrogen dioxide (NO_2) is a major air pollution that causes the production of photo-oxidants such as ozone by a photochemical reaction with hydroxyl radical produced from volatile organic compounds in the atmosphere (Wellburn, 1994). It is considered the most toxic form of NO_x . It is both primary and secondary. Some is emitted by combustion processes, while some is formed in the atmosphere during chemical reactions (Colls, 2002). It is considered to be an important atmospheric trace

gas pollutant not only because its effects on health but also because it absorbs visible solar radiation and reduce atmospheric visibility (WHO, 2000). it is one of the major sources of acid rain and it plays a critical role in determining concentration of O₃, nitric acid (HNO₃), nitrous acid (HNO₂), organic nitrates such as PAN (CH₃C(O)O₂NO₂), nitrate aerosols and other species in the troposphere (WHO, 2000).

An organization for Economic Co-operation and Development (OECD, 2012) estimates the input of the anthropogenic emission of NO_x, which includes nitric oxide (NO) and NO₂, at some 50 Tg per year (OECD, 2012). The main source of NO₂ resulting from human activities is the combustion of fossil fuels, motor vehicles and the indoor sources are combustion appliances such as smoking, gas heating and cooking.

Over half of the world's population relies on open burning of biomass fuels for cooking and heating (WRI, 1998). Elevated concentrations of NO₂ occur in homes where unvented gas appliances are used. NO₂ concentrations in the home depend also on source use, ventilation habits etc (Brunekreef *et al.*, 2012). As a consequence, there is considerable overlap between NO₂ concentrations found in homes with and without sources like gas stoves, unvented gas heats etc.

U.S. Environmental Protection Agency (USEPA) has developed guidelines for acceptable indoor air quality and recommends that the level of NO₂ should not exceed the National Ambient Air Quality Standards (NAAQS) of 0.05 ppm for 1 year period (ASHRAE, 2004) and World Health Organization has a guideline for indoor NO₂ level (1 hour and 1 year), which should not exceed 0.1 ppm and 0.004 ppm, respectively (WHO, 2010).

1.2.1 Nitrogen dioxide cycle

Gaseous nitrogen is the most abundant element in the atmosphere and its global circulation provides an inexhaustible reservoir for the nitrogen-fixing organisms which supply almost all of the nitrogen utilized by plants. The quantity of nitrogen combined in living or dead organic matter is small compared with the total capacity of the atmospheric reservoir, a characteristic in which nitrogen differs from carbon cycling. The nitrogen cycle may thus be divided into a simple gaseous reservoir of enormous capacity and a complex, soil-base cycle which is localized and of small magnitude (Figure 1.1 and 1.2). In most ecosystems the N-fixation step is rate-limiting and plants are in strong competition for soil-N. Under these circumstances the rate of N-recycling within the system is very important for example in some peat soils, a high percentage of the ecosystem-N is immobilized as organic matter in the soil thus limiting primary production and energy flow. By contrast many tropical rainforests have the majority of the available-N in the standing crop recycling from litterfall is extremely fast and the ecosystem has a high energy throughput.

The nitrogen cycle is geochemically stable and not easily disturbed by loss to some inaccessible pool such as the sedimentary deposits of insoluble compounds which disrupt the phosphorus cycle. The stability is mainly due to the buffering effect of the very large atmospheric reservoir but also the efficiency of the denitrifying process in most soil environments. (Etherington, 1975)

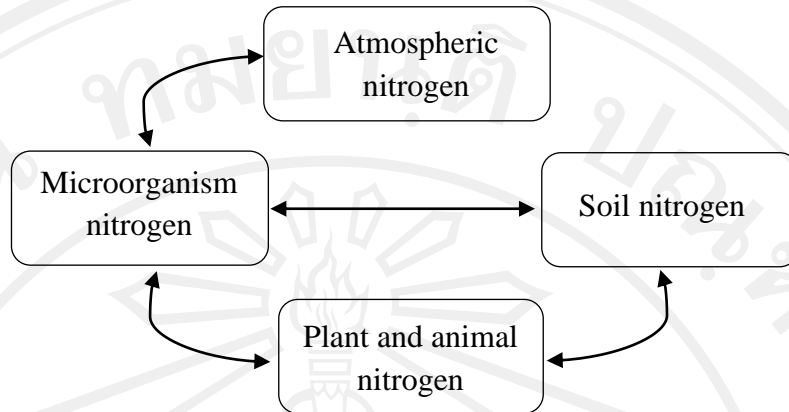


Figure 1.1 Major relationships between the very large atmosphere pool of gaseous nitrogen and the biosphere (adapted from Etherington, 1975)

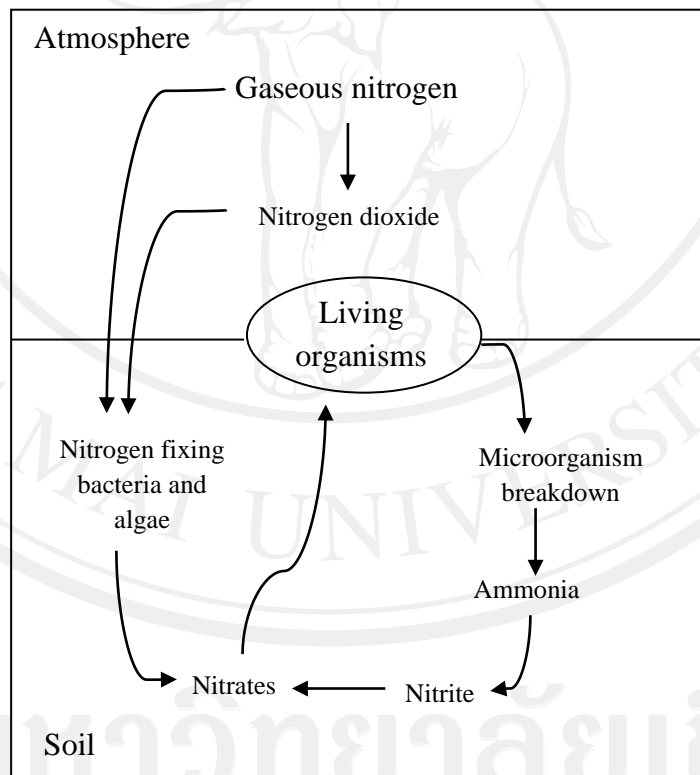


Figure 1.2 The complex interrelationships of the soil-base portion of the cycle (adapted from Etherington, 1975)

1.2.2 Effects of indoor NO₂ on human health

The quality of the indoor air environment has become a major health consideration in the developed world, since urban-dwellers generally spend 80-90% of their time indoor (Brunekreef and Holgate, 2002). Tightly sealed buildings are an additional concern for the health of those who live and work inside. Skolnick (1989) reported that a population living in the tight energy efficient buildings contracted upper respiratory diseases at rates 46% to 50% higher than a compared group living in better ventilated houses (Skolnick, 1989). The effects of air pollutions on human health are very complex. After inhalation, they affect human health severely damaging the lungs and respiratory system (Sather *et al.*, 2007). The United Nations estimated that over 600 million people worldwide in urban areas are exposed to dangerous from the traffic-generated air pollutants. From many epidemiological studies, it has been shown that this pollution causes respiratory diseases combined or not with other air pollution such as ozone, sulfur oxide, and particulate matters less than 2.5 μm (Wellburn, 1994).

1.2.3 Effects of NO₂ on plants

Plants are also affected by NO₂ exposure, such as reduction of net photosynthesis, respiration, stomatal conductance, enzyme activities, and growth. High concentrations of NO₂ can cause acute damage to plant leaves, probably through the accumulation of nitrite (Rogers *et al.*, 1979; Yoneyama and Sasakawa, 2008). Chronic exposure to lower concentrations of NO₂ usually reduces the growth of plants (Pandey *et al.*, 2005; Gibert *et al.*, 2007).

The leaves are the photosynthetic organs of a plant. The cells are packed with chloroplasts, which convert CO₂ gas from the atmosphere and water to glucose, using the energy of sunlight. The produced glucose is then both respired and used as an energy source, or it is converted to other organic substances needed for plant growth. The cells of a leaf also produce molecular oxygen (O₂ gas) as a waste product. This gas is either given off into the atmosphere, or stored inside the leaf for the night, to be used for cell respiration.

In order to provide the cells of the leaf with sufficient CO₂ and to allow for the escape of O₂, the bottom side of the leaves contain countless openings, the stomata. Each stoma can be opened and closed by the expanding and contracting action of two guard cells. The stomata open during the day to allow for the free movement of gases into and out of the leaf. At night, when photosynthesis does not take place, the guard cells close the stomata to minimize the loss of water. Exceptions do exist, such as the CAM (Crassulacean acid metabolism) plants, which grow in hot and dry environments. These plants close the stomata during the day to further reduce the water loss. These plants then open the stomata at night to allow CO₂ to enter the leaves. The CO₂ is fixed and the product is stored in vacuoles to be used for photosynthesis during day.

The stomata and associated guard cells can be made visible in several ways. Thin leaves can be placed directly on the slide for observations. The light intensity must be sufficiently high to pass through the leaf. The distinctive shape of the stomata and guard cells can then be seen, but the quality of the image is naturally not high. Carefully microtoming the leaf would be another possibility, but this can become a problem, especially when leaf observation is to be done with students or children,

when safety issues start to play a role. Making leaf impressions is probably one of the least complicated and easiest methods to make the surface texture of the leaves visible (Kim, 2008).

a) Leaf uptake and assimilation of NO_x

Figure 1.3 shows leaf uptake and assimilation of atmospheric NO and NO₂. The NO_x has diffused from the atmosphere through the stomata into the intercellular spaces of the leaf. Then NO and NO₂ were disunited into NO₂⁻ and NO₃⁻ in the aqueous layer surrounding each cell, the apoplast, which is mostly contained within the cell wall. The NO/NO₂ reaction is irreversible and dependent upon the concentration of NO₂⁻/NO₃⁻ in the apoplast (Sparks, 2009). The rate of NO₂ uptake must exceed that of NO because it is more reactive with water. Wellburn (1994) suggested that the solubility for two gasses were different and the subsequent conversion to nitrous (HNO₂) and nitric acid (HNO₃) greatly increases when the visible solubility of NO₂.

The source of NO₃⁻ in the leaf can come from leaf uptake from the atmosphere or root transport from the soil. However, NO₂ was absorbed most efficiently by foliage near tops of plant where both light intensities and metabolic rate are highest (Wallburn, 1990). NO₂ from the atmosphere can be quickly incorporated into amino compounds, glutamine in the shoots and subsequently transferred to the roots. Amino compounds transported from shoots to roots through phloem act as control signal of nitrate uptake by the roots (Rennenberg *et al.*, 1998).

will be near the peak of its activity level. Focusing on NR, there are two protein components were required to convert active NR to inactive state. When photosynthesis is active, NR is dephosphorylated and active. In the dark, NR becomes phosphorylated by an NR kinase. The phosphorelated NR is inactivated by binding to NIP (NR-inhibitor protein). Reactivation of NR occurs by dephosphorelation of NR and dissociation of NIP. Rowland *et al.* (1987) found that fumigating barley plant with NO₂ caused an increase in NR activity later confirmed by Weber *et al.*, (1995). They found an increase of about 30% in NR in the wheat leaves when exposed to 60 ppbv NO₂.

1.3 Literature review; effects of air pollutants on plants

Uptake of pollutants into plant foliage varies with plants and chemical, and can be greatly influenced by adjuvant and environmental conditions. Bhaskar *et al.* (2004) studied about impact of frond age from arsenic. It was found that the young fronds with immature sori absorbed more arsenic than the fertile mature fronds. When internal combustion engines with improved efficiency and reduced hydrocarbon emissions are manufactured, some types of air pollutants will diminish but not the oxide of nitrogen. Nitric oxide (NO), nitrogen dioxide (NO₂) and nitrogen tetroxide (N₂O₄) will all remain as significant contributors air pollution. Any combustion process which produces high temperatures in the presence of nitrogen and oxygen will yield nitrogen oxide as combustion products. Over 70 percent of the NO₂ in the atmosphere originates from automobile exhausts but significant contributions are also added by combustion of fuels used in heat and power generating and in domestic operations.

Hari and Douglas (1984) study about effect of NO₂ growth and pigment are strongly influenced by nutrient nitrogen level. Although NO₂ is assimilated by bean leaves, it can serve as an alternate source of nitrogen to a limited extent only. Taylor and Eaton (1970) attempted to learn the response of *Nicotiana glutinosa* and Pinto bean (*Phaseolus vulgaris*) seeding (3 days or less) to high concentration of NO₂ (2-10 ppm). They found that physiological age leaf tissue were necrotic lesions and bleaching of leaves. Nevertheless Pinto bean and Pearson improved tomato (*Lycopersion esculentum*) seeding were continuously exposed for 10-20 days, to low concentrations of NO₂ (less than 1.03 mg/m³). These exposure increase in green color and distortion of leaves.

Marie and Ormrod (1984) studied about tomato plants exposed continuously to 0.11 µl/L SO₂ or 0.11 µl/L NO₂ solutions. They found no significant difference of those plants from control plants in leaf, stem or root fresh or dry weights or leaf area. Exposure to a mixture of SO₂ and NO₂ at these concentrations resulted in significant decreases in leaf fresh weights and area after 14 days and significant decreases in root fresh weight and stem and root dry weight after 28 days. Leaf water concentrations decreased markedly in mixture-treated plants while leaf dry weight and stem and root water concentrations were unchanged. The leaves/stem and leaves/root fresh weight ratios decreased in mixture-treated plants while leaves/stem and leaves/root dry weight ratios increased.

Yanbo *et al.* (2011) described NO₂ uptake by plants. Plants in nature show species-specific NO₂ uptake and a wide variation in NO₂ assimilation. This specific NO₂ uptake or assimilation is affected not only by the structural, physiological and genetic makeup of leaves, but also by various environmental factors. Leaf

morphological and physiological genetic features contribute to species-specific NO₂ uptake. A primary role of stoma is to regulate leaf gas exchange, in particularly maximizing the uptake of CO₂ for photosynthesis and minimize transpiration water loss (Nejad, 2007; Shimazaki *et al.*, 2007).

Stomata open or close in response to a wide range of environmental factors such as light, air temperature, atmospheric CO₂ concentration, air humidity and internal hormone such as abscisic acid (Nejad, 2007; Shimazaki *et al.*, 2007). In most plants, in the absence of stresses, stomata open in response to light and close in response in darkness. Many studies suggested that NO₂ uptake through leaf stomata depended on stomatal opening or stomatal conductance (Geßler *et al.*, 2000, 2002; Neubert *et al.*, 1993; Rondon and Granat, 1994).

Effect of varied level of atmospheric NO₂ on plants, for example sunflower, found that the lower rate of NO₂ absorption in the nitrate-deficient plant was not due to the changes in stomatal resistance or stomatal density of the leaves, but could have been due to an increase in mesophyll resistance resulting from accumulation of high levels of nitrite in the leaf tissue (Okano and Totsuka, 1986). In other hand, the ¹⁵N dilution method was used for the quantitative estimation of NO₂ absorbed by plants during a relatively long period. Okano *et al.* (1988) studied about absorption of NO₂ by eight herbaceous species was determined by the ¹⁵N dilution method. Among the tested species, sunflower showed the highest rate of NO₂ absorption per unit leaf area. A proportion of the NO₂ accumulated in the plant might be absorbed via the air, soil and root route respectively. Sunflower and radish which had higher rates of NO₂ absorption than other species were more susceptible to NO₂. On the contrary, sorghum and maize which showed a lower rate of NO₂ absorption were tolerant. Consequently,

the higher susceptibility to NO₂ of radish and sunflower is considered to be directly related to their superior ability to absorb NO₂.

Okano and Totsuka (1986) found that the total amount of NO₂ absorbed by the plants over two weeks increased with increasing concentrations of NO₂. The rate of absorption of NO₂ per unit leaf area also increased. This means the diffusive resistances of stomata of mesophyll tissues were not changed by continuous exposure to NO₂ for two weeks. These results demonstrated that the values estimated by the quantitative determination of NO₂ absorbed by plants during a long period.

Morikawa *et al.* (1998) studied about the production of a novel NO₂ philic plant that can grow with atmospheric NO₂ as its only nitrogen source, by analysis of NO₂ assimilation in response to fumigation with ¹⁵N-labelled NO₂ in 217 taxa of the higher plants. They found nine species NO₂ utilization indices greater than 10%, including *Erechtites hieracifolia*, *Crassocephalum crepidioides*, *Nicotiana tabacum*, *Eucalyptus viminalis*, *Solidago altissima*, *Rumex acetosella*, *Plantago lanceolata*, *Magnolia kobus* and *Erechtites hieracifolia*. These plants can be considered as NO₂ philic plants.

In 2005, Shuji and team studied the examination of the air purification capabilities through urban planting. NO₂ and CO₂ were selected as experimental gaseous contaminants. A measurement system using a chamber having an atmospheric environment was developed. To verify the NO₂ plant removal effect, *Conferta* was used in the experiment. The decrease of NO₂ sorption by plant is influenced by a rise in the surrounding temperature, illuminance. Therefore, the removal effect by plants should be considered for not only absorption but also adsorption.

Farrelly (2011) reported that ambient NO₂ uptake by bullet wood and queen's flower at high polluted area (Chiang Mai Moat) were 6.2-46.1 and 0.4-18.3 ppbv, respectively. Whereas, those at low polluted area (Chiang Mai University) were 3.2-10.3 and 0.7-13.3 ppbv, respectively. Size of stomata is the main factor influenced on gas absorption. Bullet wood's stomata are larger than Queen's flower's stoma, thus allowing increased NO₂ uptake. From the studies refer, plant absolutely absorbed NO₂ and capacity varies from species. Some plant species have a capacity for NO₂ phytoremediation that occurs from the atmosphere (Gilbert and Goldberg, 2007; Talor and Eaton, 1966) and can assimilate its nitrogen into organic nitrogenous compounds through the primary nitrate assimilation pathway (Thomson *et al.*, 1970; Ashenden and Mansfield, 1987). The capability of plants to take up and assimilate NO₂ depends on the plant species (Lucas *et al.*, 1991) and the NO₂ concentration levels in the atmosphere. Even though they are many research studies that have been conducted using plants to absorb pollutants, this is the first study that has used dumb cane and little prayer plant for NO₂ absorption.

1.4 Research Objectives

1. To determine capability of some ornamental plants on NO₂ absorption from air.
2. To observe effect of NO₂ on morphology and anatomy of the selected plants.
3. To determine and compare ion content in plant leaves with and without NO₂ uptake.