# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction to history of acid rain

The term "Acid rain," is the word used to describe all forms of acid precipitation (rain, snow, hail, fog etc.) that has a pH level less than 5.6. This form of air pollution is currently a subject of great controversy because of its worldwide environmental damages. Atmospheric pollutants, particularly oxides of sulfur and nitrogen, can cause precipitation to become more acidic when converted to sulfuric and nitric acids. These acids can be incorporated into the cloud and fall onto the ground which can make a serious environmental damage to aquatic and terrestrial ecosystems. For the last ten years, the effect of acid rain has brought destruction to thousands of lakes and streams in the United States, United Kingdom, Canada and parts of Europe (http://www.epa.gov). Acid rain is sometimes used more generally to include all forms of acid deposition and acid precipitation. The scientists generally use the term acid deposition but all three terms relate to the same issue.

Acid rain was first reported in Manchester, England, which was an important city during the industrial revolution. An English chemist, Augus Smith, working in Manchester as an early UK Inspector of Factories in the 1850s, was apparently the first to analyze in a systematic way the chemistry of rain near the industrial heartland of Britain. The term "acid rain" was used for the first time by him in 1872 (Cowling, 1980; Seinfeld and Pandis, 1998). The problem of acid rain is hence not a new one but the nature of the problem has changed from being a local problem for towns and cities to being an international problem. In Smith's time, acid rain fell both in towns and cities whilst today pollutants can be transported thousands of kilometers before washed out due to the introduction of tall chimneys dispersing pollutants high into the atmosphere.

Though acid rain was discovered in 1852, it wasn't until the late 1960s that scientists began widely observing and studying the phenomenon. Canadian Harold Harvey was among the first to research a "dead" lake. Public awareness of acid rain in the U.S increased in the 1990s after the New York Times promulgated reports from the Hubbard Brook Experimental Forest in New Hampshire of the myriad deleterious environmental effects demonstrated to result from it. Since the industrial revolution, emissions of sulfur and nitrogen oxides to the atmosphere have increased. Industrial and energy-generating facilities that burn fossil fuels, primarily coal, are the principal sources of increased sulfur oxides. Occasional pH readings of well below 2.4 (the acidity of vinegar) have been reported in industrialized areas. These sources, plus the transportation sector, are the major originators of increased nitrogen oxide. The problem of acid rain not only has increased with population and industrial growth, but has become more widespread. The use of tall smokestacks to reduce local pollution has contributed to the spread of acid rain by releasing gasses into regional atmospheric circulation. Often deposition occurs a considerable distance from its formation, with mountainous regions tending to receive the most (simply because of their higher rainfall). An example of this effect is the frequent low pH of rain which falls in Scandinavia compared to the local emissions. Industrial acid rain is a substantial problem in China, Eastern Europe, Russia and areas down-wind from them. Acid rain from power plants in the Midwest United States has also harmed the forests of upsets

New York and New England. These areas all burn sulfur-containing coal to generate heat and electricity (http://www. en.wikipedia.org).

## 1.2 Acidic pollutants

Actually, precipitation is naturally acidic because of carbon dioxide and water (20 degree Celsius at atmospheric pressure) in the air react together to from carbonic acid has a slightly acidic pH of 5.6. Therefore, 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).

### 1.2.1 Sulfur dioxide, $SO_2$

Sulfur dioxide is a colorless, non-flammable, non-explosive gas. This gas released as a byproduct of combusted fossil fuels containing sulfur. A variety of industrial processes, such as the production of iron and steel, utility factories, and crude oil processing produce this gas (e.g. reaction 1.1, 1.2 and 1.3).

Sulfur dioxide is obtained by burning sulfur;

$$S (s) + O_2 (g) \rightarrow SO_2 (g) \quad (1.1)$$

Roasting pyrite (iron sulfide) or other metal sulfides prior to smelting;

$$4 FeS (s) + 7 O_2 (g) \rightarrow 2 Fe_2O_3 (s) + 4 SO_2 (g) \quad (1.2)$$

Burning hydrogen sulfide from crude oil;

$$2 H_2S (g) + 3 O_2 (g) \rightarrow 2 SO_2 (g) + 2 H_2O (g) \quad (1.3)$$

After being released into the atmosphere, sulfur dioxide can either be deposited on the Earth's surface in the form of dry deposition or goes through several complex steps of chemical reactions before they become the acids found in acid rain. The steps are broken down into two phases, gas phase (photo-oxidation) which would produce a high oxidation rate during the middle of the day and aqueous phase oxidation which be independent of sunlight (Spedding, 1974; Mason, 1992). The rate at which oxidized determines its lifetime in the atmosphere provided that oxidation is the most important removal mechanism. A number of field experiments have been carried out to give the $SO_2$ oxidation rates summarized in Table 1.1.

**Table 1.1** Summary of $SO_2$ oxidation rate studies in the atmosphere (Sedding, 1974)

| Source of $SO_2$ | Concentration of $SO_2$ on release from source ($mg\ kg^{-1}$) | Relative humidity during measurement | Rate of $SO_2$ consumption in atmosphere ($\%\ ks^{-1}$) |
|---|---|---|---|
| Ni smelter | 0.1 – 1.0 | - | 0.6 |
| Smelter | 0.01 – 20.3 | 65-70% | 190 |
| Coal-fired power plant | 2200 | 70-100% | 1.7 |
| Coal-fired power plant | 2200 | 100% | 8.3 |

There are various potential reactions that can contribute to the oxidation of sulfur dioxide in the atmosphere each having varying degrees of success. One is photo-oxidation of sulfur dioxide by means of ultraviolet light. This process uses light form of the electromagnetic spectrum. The reactions are shown below;

$$OH\bullet + SO_2 \rightarrow HO.\ SO_2 \text{ adduct } (+ O_2, H_2O) \rightarrow H_2SO_4(aq) \qquad (1.4)$$

The gas phase oxidation of sulfur dioxide (reaction (1.4)) represents several steps. The rate-determining step is shown in reaction (1.4), and forms the HO.$SO_2$ adduct, which OH radical resulting from the photolytic decomposition of ozone and reaction with water vapor, i.e.

$$O_3 + hv \rightarrow O\bullet + O_2 \qquad (1.5)$$

$$O\bullet + H_2O \rightarrow 2HO\bullet \qquad (1.6)$$

The adduct reacts rapidly with $O_2$ to form $SO_3$ which in turn reacts with vapory water to form sulfuric acid aerosols (Castleman et al., 1975; Viggiano and Arnold, 1983; Khoder, 2002; Sanderson *et al.*, 2006). On the other hand, Wang *et al.* (1988) found that the reaction of $SO_3$ and vapory water is quite slow in the gas phase. A second and more common process is belonging to aqueous phase oxidation. The steps of reaction (Spedding, 1974; Sanderson *et al.*, 2006) are shown below.

$$SO_2\,(g) + H_2O \longleftrightarrow SO_2\,(aq) \qquad (1.7)$$

$$SO_2\,(aq) + H_2O \longleftrightarrow H_2SO_3^-\,(aq) \qquad (1.8)$$

$$H_2SO_3^-(aq) + H_2O \longleftrightarrow HSO_3^- + H^+ \qquad (1.9)$$

$SO_2$ reacts with moisture found in the atmosphere; $SO_2$ immediately oxidizes to form a sulfite and bisulfite ion, respectively. Afterwards, it becomes sulfuric acid by two main routes depending on the $SO_2$ concentration. At low $SO_2$ concentrations found in remote areas, the bisulfite is oxidized by hydrogen peroxide, i.e.

$$HSO_3^- + H_2O_2 \longleftrightarrow HSO_4^- + H_2O \qquad (1.10)$$

In more polluted regions, where the concentration of $SO_2$ is higher, the peroxide supply is inadequate. The oxidation by ozone becomes significant (Monn and Schaeppi, 1993; Colls, 2002). They added that $SO_2$ can be converted directly to $H_2SO_4$ after reaction with the OH radical.

### 1.2.2 Oxide of nitrogen, NOx

The other chemical that is also chiefly responsible for the make-up of acid rain is nitrogen oxides ($NO_x$). Oxides of nitrogen is a term used to describe any compound of nitrogen with any amount of oxygen atoms (Table 1.2). By the major proportion of emitted $NO_x$ is in the form of nitrogen monoxide or NO and nitrogen dioxide or $NO_2$ which most of the atmospheric burden is usually in this form (Harrison, 1996). Theses gasses are byproducts of firing processes of extreme high temperatures (automobiles, utility plants), and in chemical industries (fertilizer production) that some reactions are shown below. Natural processes such as bacterial action in soil, forest fires, volcanic action, and lightning make up five percent of nitrogen oxide emission. Transportation makes up 43 percent, and 32 percent belongs to industrial combustion (http://www.geocities.com).

**Table 1.2** Oxides of nitrogen (Spedding, 1974)

| Oxide | Formation | Stability in the atmosphere |
|---|---|---|
| Dinitrogen oxide | $N_2O$ | Stable gas |
| Nitrogen oxide | $NO$ | Stable gas |
| Dinitrogen trioxide | $N_2O_3$ | Unstable gas $N_2O_3 \longleftrightarrow NO + NO_2$ |
| Nitrogen dioxide | $NO_2$ | Stable gas |
| Dinitrogen tetroxide | $N_2O_4$ | Unstable gas $N_2O_4 \longleftrightarrow 2\,NO_2$ |
| Dinitrogen pentoxide | $N_2O_5$ | Unstable gas $N_2O_5 \longleftrightarrow N_2O_3 + O_2$ |
| Nitrogen trioxide | $NO_3$ | Unstable gas (never isolated) |

Nitrogen oxides rise into the atmosphere and are oxidized in clouds to form nitric or nitrous acid. These reactions are catalyzed in heavily polluted clouds where traces of iron, manganese, ammonia, and hydrogen peroxide are present. Nitrogen oxides rise into the atmosphere mainly from automobile exhaust. In the atmosphere it reacts with water to form nitric or nitrous acid follow the reaction (1.11) below.

$$NO_2\,(g) + H_2O\,(l) \longrightarrow HNO_3\,(aq) + HNO_2\,(aq) \qquad (1.11)$$

Richards (1983) and Russell *et al.* (1986) suggested that there are two different mechanisms for the formation of nitric acid which operate in the day and night. In the daytime, hydroxyl radical appears to be predominantly (reaction 1.12) whilst at night, $N_2O_5$ hydrolysis (reaction 1.13 to 1.15) is an important source of $HNO_3$ (Russell *et al.*, 1986, Rodhe *et al.*, 1988).

$$NO_2 + OH\bullet + M \longrightarrow HNO_3 + M \qquad (1.12)$$

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \qquad (1.13)$$

$$NO_3 + NO_2 \longleftrightarrow N_2O_5 \qquad (1.14)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \qquad (1.15)$$

In reaction 1.12 becomes much less important at night because the hydroxyl radical is primary formed photochemically. At night, ozone will reacts with $NO_2$ to form $NO_3$, which rapidly reacts with $NO_2$ to form $N_2O_5$. The $N_2O_5$ will react with water in droplets in the atmosphere and then convert to nitric acid. Richards (1983) suggested that this pathway is unimportant in the daytime because $N_2O_5$ is in equilibrium with $NO_3$, which is photolyzed as well as rapidly destroyed to NO. This reaction (1.16) is shown below.

$$NO_2 + h\nu \longrightarrow NO + O \qquad (1.16)$$

The $NO_2$ absorbs strongly in ultraviolet region, dissociating to NO and atomic oxygen. Consequently, $N_2O_5$ in reaction 1.15 (daytime) is less than in nighttime.

### 1.2.3 Hydrogen chloride, HCl

A third acidic pollutant associated with some fossil fuels and other industrial activities is hydrogen chloride or HCl. This is a highly soluble and reactive gas. In Western Europe, coal combustion is the major source, accounting for about 65 percent of total emissions being perhaps the next largest contributor. In the UK, coal combustion is estimated to contribute 93 percent to emissions of HCl.

## 1.3 Sources of ions in rainwater

Most rainwater has a pH of 5.6 to 5.8, simply due to the presences of carbonic acid ($H_2CO_3$). The latter is formed from dissolved $CO_2$ gas and $H_2O$. The source of the $CO_2$ is the atmosphere, which presently contains about 380 ppm $CO_2$.

$$CO_2\,(g) + H_2O \longleftrightarrow H_2CO_3\,(l) \qquad (1.17)$$

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \qquad (1.18)$$

If values of pH below 5.6 or above, it will show that something interferes in rainwater. As far as rain in concerned, abnormal acidity or bacidity is relative to $CO_2$-$H_2O$ equilibrium values of 5.6 to 5.8. There are both natural and non-natural sources of materials that cause rain pH to deviate from the $CO_2$-$H_2O$ equilibrium values.

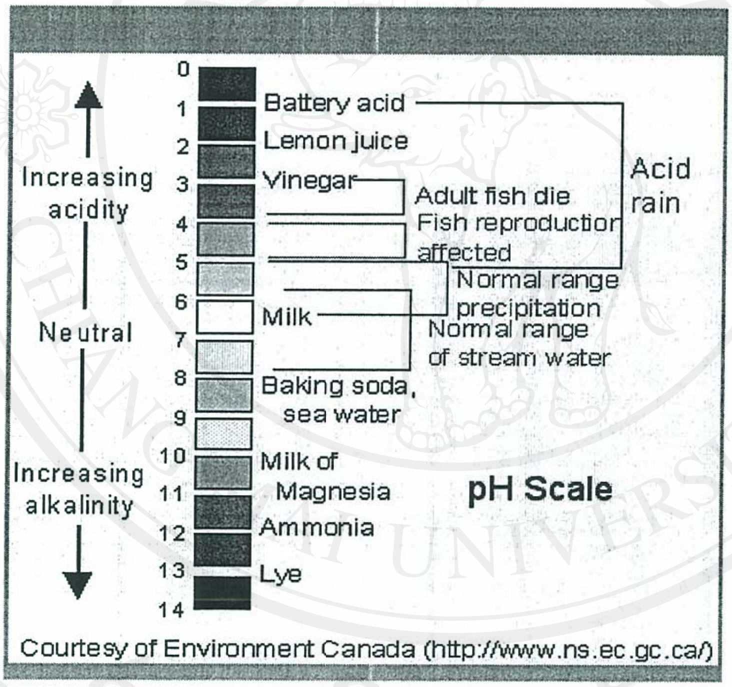
The rainwater has pH more than 5.8 because it has interacted with a basic substance at some point in their history. Probably this was in the soils or rocks. The most common one is calcium carbonate ($CaCO_3$). Calcium carbonate may be present as limestone or marble. Another possibility is the closely related material $Ca(Mg)CO_3$ (dolomite), which is calcium carbonate with some magnesium impurity in it. A second common base found in soils of either agricultural or heavily forested areas in ammonia ($NH_3$). Either of these bases may be the cause of the high pH. But the rain waters have pH less than 5.6 because they have interacted with acidic substance like $SO_2$ and $NO_x$ to form strong acid ($H_2SO_4$ and $HNO_3$). Some ions and sources of ions that contain in rainwater are shown in Table 1.3.

**Table 1.3** Sources of ions in rainwater (Berner, and Berner, 1987; Canter, 1986)

| Ion | Origin | | |
|---|---|---|---|
| | Marine Input | Terrestrial Input | Pollution Inputs |
| $Na^+$ | Sea Salt | Soil Dust | Burning Vegetation |
| $Mg^{2+}$ | Sea Salt | Soil Dust | Burning Vegetation |
| $K^+$ | Sea Salt | Biogenic aerosols, Soil Dust | Burning Vegetation, Fertilizer |
| $Ca^{2+}$ | Sea Salt | Soil Dust | Manufacture of Cement, Burning of Fossil Fuels |
| $Cl^-$ | Sea Salt | Volcanism | Industrial $Cl^-$ chemicals, Gas Release, Road Salt |
| $SO_4^{2-}$ | Sea Salt | $H_2S$ from Decay | Burning of Fossil Fuels, Marine Gases |
| $NO_3^-$ | - | Lightning, Decay of Organic Matter | Auto and Truck Emissions, Burning of Fossil Fuels |
| $NH_4^+$ | - | $NH_3$ from Bacterial Decay | Ammonia Fertilizer, Decomposition of Sewage, Combustion |
| $PO_4^{3-}$ | - | Soil Dust, Biogenic Aerosols, Absorbed on Sea Salt | Fertilizers, Burning Vegetation |
| $SiO_2$, Al, Fe | - | Soil Dust | Land Clearing |

## 1.4 Measuring acidity

The simply way to measure acidity of rainwater can be done by pH (potential hydrogen) measurement. The pH scale is used to measure the acidity or alkalinity of an aqueous solution and is determined by the hydrogen ion ($H^+$) content. This scale was invented by a Danish scientist, Sorenson, in 1909. A pH from 6.5 to 8 is considered the safe zone. Between these numbers, organisms are in very little or no harm. Figure 1.1 shows pH scale.



Courtesy of Environment Canada (http://www.ns.ec.gc.ca/)

**Figure 1.1** pH scale (http://www.ns.ac.gc.ca/)

The pH scale is logarithmic rather than linear (see Figure 1.2), and so there is a ten fold increase in acidity with each pH unit, such that rainfall with pH 5 is ten times more acidic than pH 6, rainfall with pH 4 is 100 times more acidic than pH 6 and rainfall with pH 3 is 1000 times more acidic than pH 6.

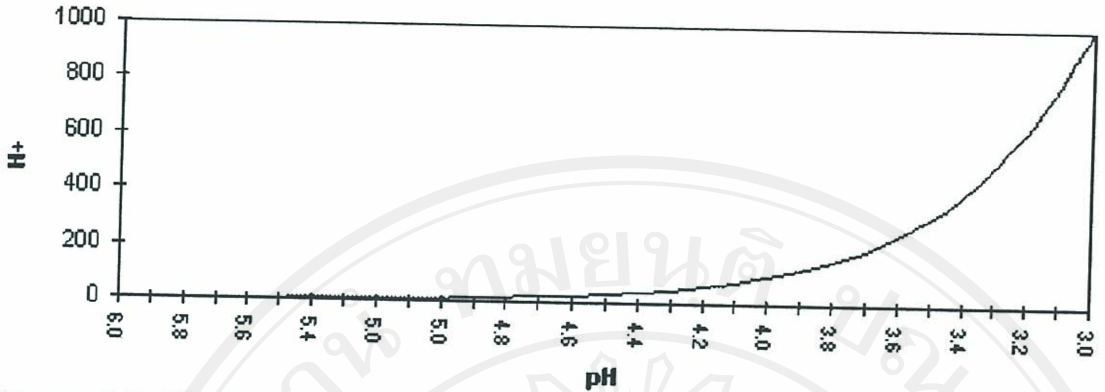


**Figure 1.2** The logarithmic pH scale for range pH 6.0 - pH 3.0 (http://www.ace.mmu.ac.uk/)

Rainfall acidity is measured in pH units. The individual pH readings may be converted to hydrogen ions to give a linear rather than a logarithmic representation of acidity. To convert the pH values to hydrogen ions, the following formula applies;

$$H^+ \ (\mu eq/L) \quad = \quad \ln(6.0 - pH) \qquad (1.19)$$

Where; $H^+$ (μeq/L) is the hydrogen ion content in micro equivalents per liter (a unit which measures the concentration of hydrogen ions in a liter of water).

The hydrogen ion content of various pH values is given in the Table 1.4 and illustrated on Figure 1.2.

**Table 1.4** Correlations between pH value and $H^+$ (http://www. ace.mmu.ac.uk/)

| pH value | $H^+$ (μeq/L) | pH value | $H^+$ (μeq/L) |
|---|---|---|---|
| 6.0 | < 1 | 4.0 | 100 |
| 5.5 | 3 | 3.5 | 316 |
| 5.0 | 10 | 3.0 | 1000 |
| 4.5 | 32 | 2.5 | 3162 |

## 1.5 Adverse effects of acid deposition

### 1.5.1 Effects of acid deposition on forests

Over the years, scientists have noticed that some forests have been growing more and more slowly without reason. Trees do not grow as fast as they did before. Leaves and pines needles turn brown and fall off when they are supposed to be green.

The problem of acidification was first observed by foresters in the 1960s and 1970s when individual spruces died and crown thinning of older trees became apparent. The damage is now spreading to the valleys and is also affecting deciduous trees. In the European countries, especially Norway, more resistant species of spruce such as *Picea pungens* (blue spruce) are being planted where trees have died and other areas are being replaced by grassy meadows (http://www. ace.mmu.ac.uk/).

Eventually, after several years of collecting and recording information on the chemistry and biology of the plant tissues, researchers have concluded that this was the work of acid rain (Krusche, *et al*., 2003). When acid rain washes the leaves of the branches and fall to the forest floor below, some of the water is absorbed into the soil. That soil may have neutralized some or all of the acidity of the acid rainwater. This ability of neutralization is call buffering capacity. Without buffering capacity, soil pH would change rapidly. Low pH levels in the soil will remove nutrients; know as base cations are critical in neutralizing acids. As forest soils lose nutrient cations, they become more vulnerable to further acidification, and, as a result, trees become more sensitive to disease and stress (Adams *et al.*, 2000, Adriano and Johnson, 1989). It also makes some toxic elements, for example aluminium, more soluble. High aluminium concentrations in soil can prevent the use of nutrients by plants. Acid rain does not kill trees immediately or directly. Instead, it is more likely to weaken the tree by destroying its leaves, thus limiting the nutrients available to it.

### 1.5.2 Effect of acid deposition on water

Acid rain does not only affect organisms on land, but also effect organisms in aquatic biomass. Most lakes and streams have a pH level between six and eight. Some lakes are naturally acidic even without the effects of acid rain. For example, Little Echo Pond in New York has a pH level of 4.2 (http://www.geocities.com).

There are several routes through which acid rain can enter the lakes. Some chemical substances exist as dry particles in the atmosphere, while others enter directly into the lake in a form of precipitation. Acid rain that has fallen on land can be drained through sewage systems leading to lakes. Another way acids can enter the lake is by spring acid shock (snow melts in the spring, the acids in the snow seeps into the ground).

It has been widely demonstrated that pH affects the survival of many fish species when the pH falls below about 5.0 (Haines and Backer, 1986). Aluminium released to lake and streams from acidified soils and sediments is also toxic to fish. The relative abundance of the various aluminium species, inorganic and organic, depends on the pH, temperature, and the presence of inorganic and organic ligands (Driscoll, 1984).

Evidence is accumulating that not only the fish, but other components of the freshwater biota change when pH levels are consistently below about pH 6.0. Some species such as mayfly, shrimp and mollusks tend to disappear and many species are less abundant (Fjellhiem and Raddum., 1990). These changes are due to a combination of direct toxicity effects on respiratory membranes and indirect ecosystem effects including reduced microbial and algal activity leading to reduce food chain. For example; as the water pH approaches 6.0, crustaceans, insects, and some plankton species start to disappear. As the pH approaches 5.0, major changes in the plankton community begin, less desirable kinds of mosses and planktons begin to take over, and a progressive loss of fish populations begins. Below pH 5.0, fish nearly disappear, decomposition of bottom material slows and frog populations decline steeply. In general, the eggs or young of most species are more sensitive to acidification than the adults (Mierle *et al.*, 1986). Thus, for example, the pH of a lake may still be high enough to support a population of adult fish for a time, but those fish will not be able to reproduce successfully. Eventually, the fish population will disappear. A detailed review of aquatic effects of acid deposition in Canadian has been presented by Schindler (2006).

### 1.5.3 Effect of acid deposition on structures and materials

Acid rain does not only damage the natural ecosystems, but also man-made materials and structures. Man-made materials slowly deteriorate even when exposed to unpolluted rain, but acid rain helps speed up the process since the mid 19th century. Marble, limestone, and sandstone which were commonly used in historic buildings and monuments can easily be dissolved by acid rain. Irreversible damage has also been caused to stained glass windows in historic churches (Harter 1986).

The effects of sulfur pollutions on various materials have been shown in extensive field tests and for some materials such as carbon steel, zinc, marble, bronze and copper response relationships have been established (Kim *et al.*, 2004, Meada *et al.*, 2001) While the influence of $NO_x$ on atmospheric corrosion is slight. Some reactions that can make corrosion are shown below.

In limestone, acidic water reacts with calcium to form calcium sulfate;

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2CO_3 \qquad (1.20)$$

The mass of $SO_2$ absorbed by limestone is increased as relative humidity increases. The absorbed gas is oxidized to sulfate and become part of the $CaCO_3$ matrix. The molecular volume of $CaSO_4$ is greater than that of $CaCO_3$ hence mechanical stresses on the molecular scale arise. The accumulated effect of these stresses is to cause flaking-off of the limestone. Further, $CaSO_4$ has a higher solubility in rain water than $CaCO_3$ and is thus readily leached out.

For iron and steel; the atmospheric corrosion may be explained by an electrochemical mechanism (equation 1.21-1.23). In the atmosphere iron and steel are always covered with a thin layer of $Fe_3O_4$ which itself is covered by a film of its oxidation product FeOOH.

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad (1.21)$$

$$Fe^{2+} + 8\,FeOOH + 2\,e^- \longrightarrow 3\,Fe_3O_4 + 4\,H_2O \quad (1.22)$$

$$3\,Fe_3O_4 + 0.75\,O_2 + 4.5\,H_2O \longrightarrow 9\,FeOOH \quad (1.23)$$

The overall effect is to increase the amount of rust, FeOOH, by one eight by transferring iron from the metal to the surface rust layer (Spedding, 1974).

Kim (2004) showed that the corrosion rates of the test materials in ambient air were found to be in the order: carbon steel > marble > bronze ≥ copper.

### 1.5.4 Effect of acid deposition on human health

Since the 1960s, air pollution has become an increasing problem affecting health. Acid rain can affect health of a human being. It can harm us through the atmosphere or through the soil from which our food is grown and eaten from. The impact of acidification on human health is both direct and indirect. Direct effects have been reported when acid sulphate aerosols come into contact with sensitive mucus membrane surfaces of the respiratory tract and lungs (Zelikoff *et al.*, 1997, Kenneth *et al.*, 1998, John *et al.*, 2002). The sulfur dioxide and nitrogen oxide emission gives risk to respiratory problems such as dry coughs, asthma, headaches, eye, nose, and throat irritation. Polluted rainfall is especially harmful to those who suffer from asthma or those who have hard time breathing. But even healthy people can have their lungs damaged by acid air pollutants. Acid rain can aggravate a person's ability to breathe and may increase disease which could lead to death. A detailed review of health effects of acid air has been presented by Spengler (1990) and James (1993). Table 1.5 summarizes of health effects of exposure to $NO_2$ at concentrations from 0.25 to 1 ppm.

**Table 1.5** Key human health effects of exposure to $NO_2$ from clinical studies (US.EPA., 1993).

| $NO_2$ in ppm (Exposure Duration) | Observed Effected |
|---|---|
| 0.2-0.3 (0.5-2.0 hr.) | Trend toward increased airway responsiveness to challenges in asthmatics. However, no significant effects observed by same of other investigators at $NO_2$ levels up to 4 ppm. Small (4-6%) decreases in $FEV_1$ or FVC in adult or adolescent asthmatics, in response to $NO_2$ alone |
| 0.3 (3.75 hr.) | Small decreases (5-9%) in FVC and $FEV_1$ in COPD patients with mild exercise. No effects seen by other investigators for COPD patients at 0.5-2.0 ppm $NO_2$ |
| 1.5-2.0 (2-3 hr.) | Increased airway responsiveness to bronchoconstrictor in health adults. However, effects not detected by other investigators at 2-4 ppm. |
| ≥ 2.0 (1-3 hr.) | Lung function changes (e.g. increased airway resistance) in healthy subjects. Effects not found by others at 2-4 ppm. |

$FEV_1$ = Forced expiratory volume in 1 sec.
FVC = Forced vital capacity
COPD = Chronic obstructive pulmonary disease

Acidic deposition may also affect human health indirectly by increasing metallo-solvency which results in the leaching of toxic metals and asbestos into drinking water from watersheds, sediments and plumbing (Batti *et al.*, 1990). In this way human exposure to elements such as Pb, Cd, Al and Cu can increase markedly. Increases theses toxic metals that might be absorbed by the drinking water, crops, or animal that human consume. Theses foods that are consumed could cause nerve damage to children or severe brain damage or death.

McDonald (1985) reviews the likely effects of raised metal levels in drinking water and concludes that there is strong evidence of increased risk due to Pb plumbling in soft water areas. Increased solubility of Cd, Al, and Cu levels are also cause for concern. He also notes that acid drinking waters can corrode asbestos cement which may also prove to be a health risk.

## 1.6 Further trends of emission

Since man-made (industrial) emissions are a significant source of constituents of rain, it is expected that changes in rain quality will parallel the growth of industry in developed and developing countries, especially in parts of Asia and the Pacific region where energy use has surged and the use of sulfur contaminating coal and oil. An estimated 34 million metric tons of $SO_2$ were emitted in the Asia region in 1990, over 40 percent more than in North America (Downing *et al.*, 1997). Acid deposition levels were particularly high in areas such as southeast China, northeast India, Thailand and the Republic of Korea due to high population and the consequent upward trend in agricultural production, industrialization, transportation, energy consumption, biomass burning, etc. (Hu *et al.*, 2003).

Rapid urbanization and continued reliance on coal as a primary fuel is likely to increase acid rain in developing countries, whereas in Western Europe emissions have decreased substantially since 1980 (Mason, 1992) especially, Asia as much as triple from 1990 to 2010 if current trends continue (see Figure 1.3). By 2000, $SO_2$ emission in Asia will be greater than those of North America and Europe combined. By 2020, Asian $SO_2$ emission could reach 110 million metric tons if no action is taken beyond current levels of control (Downing *et al.*, 1997).

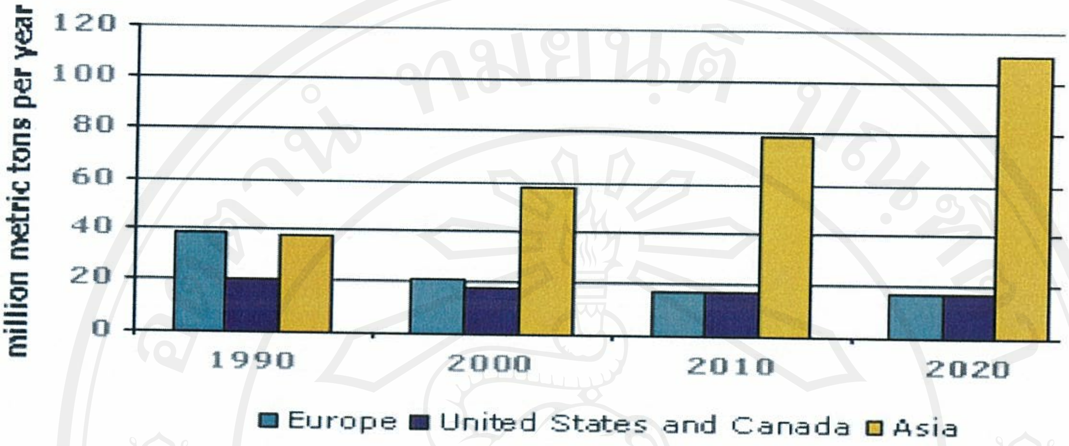


**Figure 1.3** Sulfur dioxide emissions among continents (Downing *et al.*, 1997)

In Asia, almost all of the countries are developing country with the heavy reliance on coal and oil. The largest increase in emissions of $SO_2$ and $NO_x$ would be seen in China, South Asia and South East Asia. The emission of acidic pollutants of these countries is shown in Tables 1.6 and 1.7.

As a result, damage to natural ecosystems and crops is likely to increase dramatically. Large regions of southern and eastern China, northern and central Thailand, and much of the Korean peninsula could experience damaging sulfur and nitrogen deposition levels (Downing *et al.*, 1997).

**Table 1.6** Total sulfur dioxide emissions by country (Foell and Green, 1990)

All figures in million tones of $SO_2$

| **Country** | **1986** | **2000** | | | **2001** | | | |
|---|---|---|---|---|---|---|---|---|
| | **Actual** | **S1** | **S2** | **S4** | **S1** | **S2** | **S3** | **S4** |
| **Group A** | | | | | | | | |
| China | 18.972 | 34.036 | 28.552 | 32.882 | 48.802 | 38.861 | 37.152 | 41.933 |
| India | 3.181 | 5.386 | 4.761 | 5.035 | 8.796 | 6.656 | 6.294 | 7.112 |
| Indonesia | 0.780 | 1.850 | 1.669 | 1.687 | 3.184 | 2.485 | 2.395 | 2.411 |
| Korea, DPR | 0.587 | 0.920 | 0.735 | 0.920 | 1.275 | 0.892 | 0.794 | 1.275 |
| Korea | 1.224 | 2.721 | 2.455 | 2.641 | 3.308 | 2.781 | 2.456 | 3.162 |
| Rep. of Taiwan, Province of China | 0.850 | 1.738 | 1.398 | 1.563 | 2.217 | 1.676 | 1.500 | 1.797 |
| **Group B** | | | | | | | | |
| Bangladesh | 0.150 | 0.204 | 0.173 | 0.202 | 0.270 | 0.202 | 0.171 | 0.245 |
| Hong Kong | 0.274 | 0.397 | 0.343 | 0.377 | 0.588 | 0.480 | 0.318 | 0.532 |
| Malaysia | 0.298 | 0.441 | 0.404 | 0.435 | 0.753 | 0.596 | 0.595 | 0.705 |
| Pakistan | 0.748 | 1.675 | 1.426 | 1.617 | 2.486 | 1.892 | 1.592 | 2.295 |
| Philippines | 0.403 | 0.815 | 0.727 | 0.742 | 1.339 | 0.988 | 0.973 | 1.036 |
| Singapore | 0.061 | 0.107 | 0.093 | 0.085 | 0.151 | 0.110 | 0.094 | 0.088 |
| Thailand | 0.627 | 2.616 | 2.349 | 1.979 | 2.999 | 2.313 | 1.994 | 1.866 |
| ***Total (A+B)*** | **28.155** | **52.904** | **45.085** | **50.165** | **76.167** | **59.932** | **56.327** | **64.457** |

| | |
|---|---|
| S1 | Base Case Scenario (all countries) |
| S2 | Energy Efficiency Scenario (all countries) |
| S3 | Low Carbon Scenario (all countries) |
| S4 | Control Scenario |

**Table 1.7** Total nitrogen oxides emissions by country (Foell and Green, 1990)

All figures in million tones of $NO_x$

| **Country** | **1986** | **2000** | | **2001** | | |
|---|---|---|---|---|---|---|
| | **Actual** | **S1** | **S2** | **S1** | **S2** | **S3** |
| **Group A** | | | | | | |
| China | 7.671 | 15.316 | 12.748 | 21.864 | 17.221 | 16.279 |
| India | 2.830 | 5.516 | 4.813 | 9.252 | 6.924 | 6.358 |
| Indonesia | 0.712 | 1.701 | 1.474 | 3.131 | 2.359 | 2.262 |
| Korea, DPR | 0.628 | 0.938 | 0.751 | 1.249 | 0.874 | 0.753 |
| Korea, Rep. of | 0.663 | 1.302 | 1.173 | 1.641 | 1.360 | 1.098 |
| Taiwan, Province of China | 0.298 | 0.648 | 0.520 | 0.828 | 0.612 | 0.515 |
| **Group B** | | | | | | |
| Bangladesh | 0.025 | 0.039 | 0.032 | 0.052 | 0.039 | 0.035 |
| Hong Kong | 0.111 | 0.162 | 0.139 | 0.249 | 0.201 | 0.122 |
| Malaysia | 0.296 | 0.582 | 0.501 | 0.982 | 0.741 | 0.704 |
| Pakistan | 0.119 | 0.274 | 0.232 | 0.405 | 0.309 | 0.260 |
| Philippines | 0.202 | 0.438 | 0.377 | 0.734 | 0.546 | 0.534 |
| Singapore | 0.166 | 0.252 | 0.216 | 0.338 | 0.252 | 0.247 |
| Thailand | 0.495 | 1.508 | 1.292 | 3.523 | 2.66 | 2.482 |
| ***Total(A+B)*** | **14.216** | **28.676** | **24.268** | **44.249** | **34.101** | **31.649** |

S1 Base Case Scenario (all countries)
S2 Energy Efficiency Scenario (all countries)
S3 Low Carbon Scenario (all countries)

## 1.7 The acid deposition monitoring program in Thailand

Acid precipitation had been recognized as one of the environmental problems that might result from the rapid development of energy consumption in Thailand. Very large increases in both $SO_2$ and $NO_x$ emissions are projected over the next twenty years. These increases would come primarily from expansion of lignite-based power sector supporting the rapidly expanding industrial base. Repowering and cogeneration is some sectors, especially cement, may also be based on the high sulfur lignite resource due to its significantly lower fuel cost (Kritiporn, 1990).

Since year 1992, Thailand had an experience about harmful of acid deposition due to $SO_2$ emitted from the Mae Moh lignite-fired power plant in Lampang province. Therefore, Thai government was starting to reduce the acid deposition problems. In 1998, they set up an acid deposition monitoring network in Thailand to monitor acid deposition around country. In January 2001, they are joining with other Asian countries including Russia, Mongolia, China, Korea, Japan, Philippines, Indonesia, Malaysia and Vietnam to establish the Acid Deposition Monitoring Network in East Asia aimed to observe and solve this problem in the region. This network monitors acidic pollutants in both, wet and dry form to asses the risk of its effect and changing on ecosystem. The monitoring stations are spread out to many of our country and the government still has a plan to set up more stations in the future (Chirasathaworn, 2005).

## 1.8 Acid depositions

Wet deposition is defined as the process by which atmospheric compounds are attached to and dissolved in cloud and precipitation droplets and delivered to the earth's surface by rain, snow, hail or mist. There are several sampling equipments to measure wet deposition. In theory, wet deposition is best measured using wet-only or wet and dry collectors. But wet-only collectors have the drawback of being expensive and requiring a power supply. Consequently, continuously open funnels or bulk collectors are often used to collect precipitation in studies. Detail of the collectors are as follow:

### 1.8.1 Types of collector

#### a) Wet-only collectors

Deposition of atmospheric compounds by rain (wet deposition) is theoretically best measured with specially designed collectors, which are closed by a lid during dry periods and open whenever raindrops are detected by a sensor. Such a system prevents the deposition of particles and gases on the walls of the collector during dry period.

The rain sensor can be an electrical or an optical device (Plaisance *et al*., 1998) that recognizes rain when it is already falling. Of the two types, electrical sensors are the ones in frequent use. These sensors keep the collector lid open whenever the flux of precipitation exceeds the evaporation from the heated sensor. Thus, the amounts of rain collected in the wet-only samplers are generally smaller than the bulk samplers (Stedman *et al*., 1990) However, Marendic-Miljkovic *et al*. (2000) developed an improved precipitation sensor with a response time of <30 s at a minimum precipitation intensity of 0.1 mm $h^{-1}$.

#### b) Wet and dry collectors

These collectors are just different from wet-only collectors that have two buckets. Therefore, these collectors allow the collection of both wet and dry (dust) deposition as separate fractions (CANSAP, 1982; NADP, 1990). Here the rain collector lid is either opened or closed as appropriate by a signal from a rain-sensing device (Figure 1.4). Because the open and close positions are triggered by the rain sensor, individual rain events can be sampled.

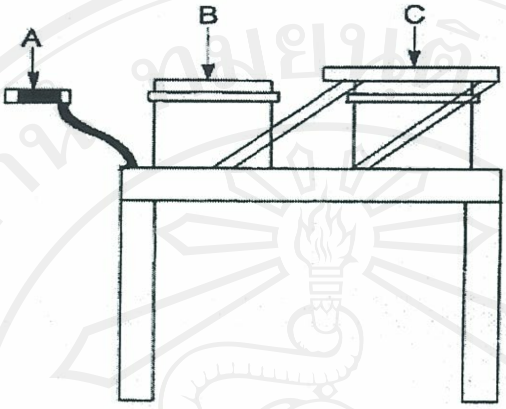


**Figure 1.4** A schematic diagram showing a bucket type wet and dry deposition sampler (A) Rain sensor; (B) dustfall collector; and (C) wet deposition collector

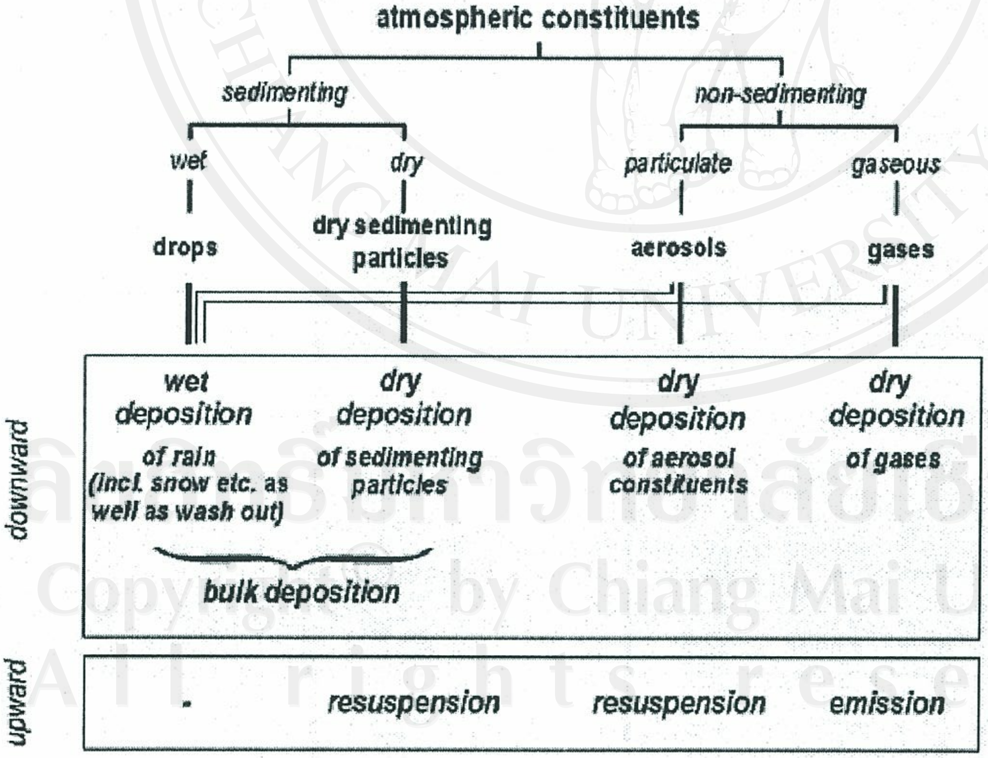
### c) Bulk collectors

Bulk collector is used for bulk deposition. In principle, bulk deposition is defined as the sum of wet-only deposition and of sedimenting (dry) particles to a sample collector in ambient air (Figure 1.5)

In practice, this sum can be biased by simultaneous deposition of gases and fine aerosols to the collector. Consequently, bulk deposition is often defined operationally as the total deposition of material to a continuously-open collector. From Figure 1.5, bulk deposition may also include a contribution from sedimenting particles that have been resuspended by the wind from the surrounding soil and vegetable. These resuspended particles do not represent a net input to the ecosystem, so sampling has to be designed by careful consideration of sampler location and height above ground.

Although, this collector has more problem than wet collector but, if this one is such that sampling of gases and fine aerosols is minimized, and sampling artifacts can be excluded, bulk collector provides a quantitative measure of the deposition of sedimenting particles (both solid and liquid) (Dammgen *et al*., 2005). Furthermore, bulk sampling does not require a power supply, sensors and movable lids. It thus allows for the cost-effective operation of large networks.

**Figure 1.5** (Conceptual) differentiation of air constituents with respect to their deposition properties (particle size and mass, state) in order to derive flux detection methods (Grunhage *et al*., 1993)



The bulk collector, as a rule, bucket type and bottle-with-funnel are used which constructed from inert material with respect to the chemical species to be determined. For bucket type collectors, it has wide diameter so, there is a risk of blow-out of material collected if the sampled solution evaporates. Conversely, the exposed liquid surface can act as a sink for reactive and water soluble gases such as $NH_3$ and $SO_2$. Theses disadvantages are minimized if the sample is separated from ambient air as in a bottle-with-funnel collector are shown in figure 1.6. As a consequence, bucket collectors are to be avoided (e.g. Galloway and Likens, 1978; WMO, 1971) whenever blow-out or gas deposition are likely to alter the quantification process.

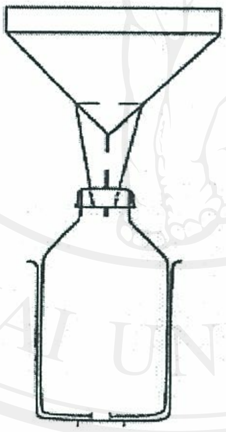


**Figure 1.6** Bulk collector designed (Thimonier, 1998)

Besides of bulk collector that told before, it still has difference designs e.g. three different research groups have employed linked collection vessels (Robertson *et al.*, 1980). All these samplers consist of a series of bottles linked together by tubing. When one bottle is full, the rainwater flows into the next in line (Figure 1.7).

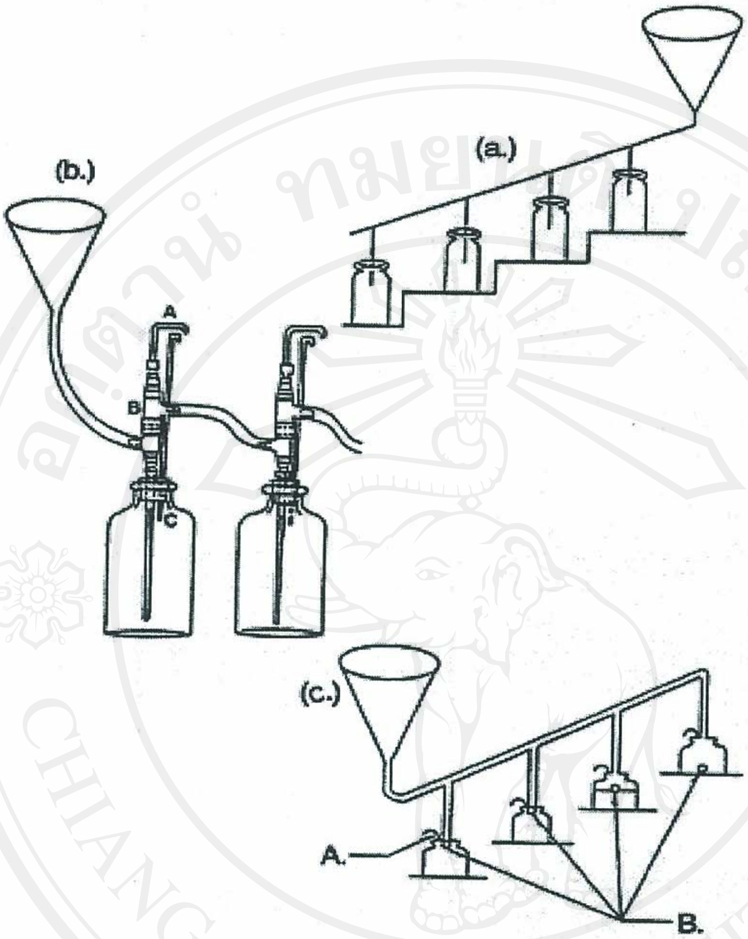


**Figure 1.7** A schematic diagram showing three different types of linked bottle samplers: (a) Cooper et *al.*, 1976; (b) Kennedy *et al.*, 1976; (c) Liljestrand and Morgan (Robertson *et al.*, 1980).

### 1.8.2 Characterization of collector properties

### a) Factor affecting the amount of precipitation collected

In 1953, Kurtyka estimated the potential errors in the determination of precipitation amount (Table 1.8). Of those, the error resulting from flow distortion is the highest from other sources.

**Table 1.8** Estimate of potential errors for the determination of precipitation

| | Potential error (%) |
|---|---|
| Evaporation | -1 |
| Adhesion | -0.5 |
| Colour of sample | -0.5 |
| Aperture not horizontal | -0.5 |
| Splash | 1 |
| Flow distortion | -0.5 to -80 |

## b) Flow distortion correction for precipitation measurements

One potential solution of the flow distortion problem is to expose the aperture at a height (increasing with height above ground). Therefore, particles with small diameters will follow the distorted airflow and do not enter the aperture quantitatively as can be deduced from Figure 1.8

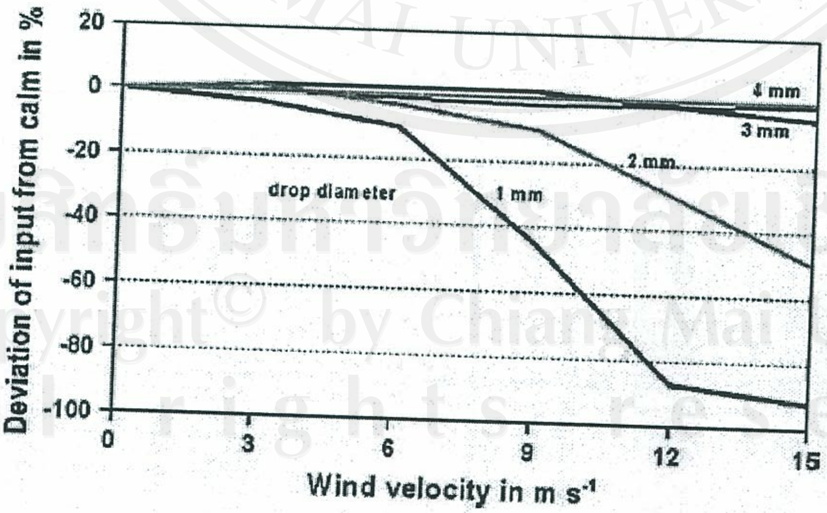


**Figure 1.8** The influence of wind velocity on the deposition of droplets with different diameters (Mueller and Kidder, 1972)

To avoid error resulting by flow distortion the collector must be set at low height, but it then creates an obstacle by wind raised material (decreasing with height above ground) from the ground (Rodda and Smith, 1986; Sevruk *et al*., 1994). Actually, a precipitation collector mounted with its aperture level with ground and surrounded by an anti-splash grid is therefore considered (Suvruk and Hamon, 1984) because wind velocity almost become to zero, but it can be contaminated by resuspended particles and by insects etc or problem with deposition of dew. Therefore a practical compromise between minimal flow distortion and minimal contamination, combined with simple operation of the collectors, is an exposure height of the aperture should be between 1.0 to 1.5 meters (EANET 2000; Draaijers *et al*., 2001; Erisman *et al*., 2003).

### c) Evaporation from collector surfaces

Potential error in the deposition estimates is due to wetting (adhesion of water on the walls of the sampling funnel) and evaporation, accounting for 2-10% and 0-4% water losses, respectively (Thimonier, 1998). Evaporative losses are likely to be higher for collectors due to their larger surface area. For wet-only collectors, especially those with a PTFE surface coating, several ml of water can be retained on the surface at the end of rain event.

### d) Diameter of the opening

The effective collecting area of a collector, it is aperture of funnel. It often recommend rather large diameter of apertures (20-40 cm). When the sampling interval is short, large diameters of aperture have the advantage of providing enough solution for analysis (Lewis and Grant, 1978). Conversely, when the collection frequency is low and when rainfall is potentially high over the defined sampling interval, small diameters are more fit.

WMO (1971) also recommends that precipitation gauges should comply with the following;

- The area of the aperture should be known to the nearest 0.5% and the construction should be such that this area remains constant.
- The rim of the collector should have a sharp edge and should fall away vertically inside and should be steeply bevelled outside.
- The vertical wall of the collector should be sufficiently deep and the slope steep enough (at least 45°) to prevent loss by splashing and to allow good drainage.
- The receiver should have a narrow neck and should be sufficiently protected from radiation to prevent loss of water by evaporation.

### e) Sensing rainfall for wet-only collectors

With wet-only collectors, the aperture is covered by a removable lid, the movement of which is governed by a rain sensor. Therefore, collection efficiency for rain depends on the sensitivity of the sensor, the speed with which the lid responds and the ability of the sensor to detect the end of the rain event. The sensor should have a minimum detection capability of 0.05 mm/h rainfall intensity and of 0.5 mm raindrop diameter (EANET 2000). Plaisance and his researchers (1998) studied and compared two type of sensors; resistivity and optical sensors. The results were rather similar, but with optical sensor being inferior to the resistivity sensors.

### 1.8.3 Material of collector

The type of material which chosen, all components should be made from material that are inert with respect to the chemical species to be determined. Quality Teflon (with smooth surface) is ideal but it's expensive. Alternatively, polyethylene is recommended for analysis of macro-ions in most monitoring manuals, and has been extensively. But the disadvantage of this material is retains dry deposition (including aerosols and pollen) more efficiently than Teflon surface because of electrostatic properties of polyethylene. Consequently, the composition of bulk precipitation may thus be more influenced by dry deposition when polyethylene surface are used, but adsorption of gaseous $SO_2$, $NO_2$ and $HNO_3$ on polyethylene surface is insignificant (Dasch, 1985).

### 1.8.4 Sources of sample contamination

Wet-only collector has less contamination than bulk collector, because it has a lid to cover water sample during dry period. On the other hand, sample collected by bulk collectors can be contaminated due to leaves, insects, bird droppings and human fingerprints. Normally, a few leaves or small insects in the collectors will not cause significant interference with the rainwater sample, if the rainwater sample is protected by placing (rinsed) quartz wool, small glass (not-soda glass) beads (Brechtel, 1989) or filter nets (Dammgen *et al.*, 2005) into or above the funnel. Normally, small glass beads have been used because quartz wool has the disadvantage of presenting a large surface area which could adsorb dissolved substances (Lewis and Grant, 1978) and nets may have the drawback of algae which may influence nitrogen transformations (Ferm, 1993). Dammgen and his researchers (2005) are also suggested that to avoid or minimized contamination, the collectors should be placed in a way that leaf capture is unlikely and used perches nearby the collectors to avoid fouling from bigger birds.

## 1.9 Stability of the composition of rainwater samples

Natural samples will always be contaminated with micro-organisms e.g. algae and bacteria (Slanina *et al.*, 1979) if rainwater samples are sampling for a long time. Consequently, the concentration of some compounds can vary over time due to biochemical reactions in the samples which are likely to convert potential nutrients, in particular N species (Draaijers *et al.*, 1996, Dammgen *et al.*, 2005). Chen *et al* (2001) and Krupa *et al* (2002) showed ammonium can be partly converted to nitrate. Consequently, ammonium concentrations were decreased over time, but Van der Maas and Valent (1989) observed increased ammonium concentrations in their samples which they related to ammonification.

Reactions of the rainwater sample with the collector surface or walls are also likely to change the sample composition e.g. glass bottles will interfere with $NH_4^+$ concentrations due to exchange processes with $K^+$ in glass. Therefore, it is necessary to select collector bottles which material is inert for the species to be determined e.g. Teflon or glass should be used for studying organic components (EMEP, 1977), for glass, it is not suitable for elements as the glass surface can act as an ion exchanger (Galloway and Likens, 1976; 1978). So, polyethylene surface should be used instead, but it can be contaminated by dry deposition cause of electrostatic properties (Dammgen *et al.*, 2005). Therefore, the collectors should be washed in acid and thoroughly rinsed with deionised water after each sampling (Galloway and Likens,

1978) especially, when the collector bottle has a small capacity, as the error due to contamination by any remaining solution in the container is then proportionally higher.

pH also varies with storage time in the field. Liechty and Mroz (1991) observed a decrease in pH in their samples, which they attributed to the production of protons ($H^+$) associated with ammonium transformations. Conversely, some publications showed the opposite trends e.g. Camuffo *et al.* (1998), Sisterson *et al.* (1985), de Pena *et al.* (1985). Several possible causes for this pH increase may be from slow dissolution of alkaline (Ca, Mg, K) soil or dust particles (Peden and Skowron, 1978, Camuffo *et al.* (1998) or transformation of organic acids by micro-organisms in the sample before analysis in laboratory (Keene and Galloway, 1984).

Of those, when sampling has to cover longer period, chemical reactions within the sample or microbial degradation are likely occur. Therefore, sampling intervals have to be adjusted in a way that these processed do not significantly interfere, or samples have to be stabilized to have defined properties e.g. biological activity in the rainwater sample can then be reduced by shielding the collector from sunlight and preventing warming (e.g. Granut *et al.*, 1996) or storage the collectors in the ground, but the collecting surfaces must be raised to avoid contamination by splashing (Thimonier, 1998). The other choice is adding non-volatile chemical preservatives (biocide), but they should not interfere with elements being measured. Galloway and Likens (1978) tested a variety of preservatives including $CuSO_4$, $Na_2SO_3$, $NaS_2O_5$, HCHO, $CH_3OH$, $CHCl_3$, $C_6H_5CH_3$, $Hg(Ac)_2$. All these biocides had disadvantages because of contamination with impurities in the reagent, or interference with the analytical method, especially harmful to human health. Gillett and Ayers, (1991) suggested larger than 200 ppm of thymol (2-isopropyl-5-methyl phenol) as biocide in preventing biological degradation of $HCO_2H$ in rainwater. As thymol is a solid, and hence nonvolatile. Hadi and Cape (1995) showed that chloroform and thymol could maintained the pH, conductivity and $NH_4^+$ for 50 days in the cold room (2°C in the dark) while only thymol could maintain these concentrations beyond 14 days in the greenhouse (about 20°C) and not more than a week in rainwater samples without thymol even in the cold room. In 1998, Ayers and his co-workers also studied rainwater samples with and without thymol as biocide in that collected in Niigata, Japan. The results showed that rainwater samples without thymol exhibited lowered elctro-conductivity, loss of the cations $H^+$ and $NH_4^+$, and loss of the anions $HCO_2^-$, $CH_3CO_2^-$, $CH_3SO_3^-$ and $PO_4^{3-}$. Nitrate showed no change in rainwater with and without thymol (Ayers *et al.*, 1991, Granat *et al.*, 1996). Thymol can however have an influence on the chromatograms for anions depending on column and eluent, especially for chloride (Granat *et al.*, 1996) and $NH_4^+$ is not also recommended for spectrophotometry (Indophenol blue) when samples are preserved by thymol (The second Interim Scientific Advisory Group Meeting, 2000).

## 1.10 Ion chromatography for analysis of acid deposition

Ion Chromatography (IC) was introduced in 1975 by Small, Stevens, and Bauman (Frank and Richard, 1983) as a new analytical method. Within a short period of time, ion chromatography evolved from a new detection scheme for a few selected inorganic anions and cations to a versatile analytical technique for ionic species in general. For a sensitive detection of ions via their electrical conductance, the separator column effluent was passed through a second column. This second column, "stripper", later called the "suppressor" column. This suppressor column chemically reduces the eluent background conductance, while at the same time increasing the electrical conductance of the analyte ions (Small *et al.*, 1975).

At the end of the 1970s, ion chromatographic techniques were used to analyze organic ions for the first time. The requirement for a quantitative analysis of organic acids brought about an ion chromatographic method based on the ion-exclusion process that was first described by Wheaton and Bauman in 1953. The 1980s witnessed the development of high efficiency separator columns with particle diameters between 5 μm and 8 μm, which resulted in a significant reduction of analysis time. In addition, separation methods based on the ion-pair process were introduced as an alternative to ion-exchange chromatography, because they allow the separation and determination of both anions and cations (Weiss, 2004).

The 1980s witnessed the development of high efficiency separator columns with particle diameters between 5 μm and 8 μm, which resulted in a significant reduction of analysis time. In addition, separation methods based on the ion-pair process were introduced as an alternative to ion-exchange chromatography, because they allow the separation and determination of both anions and cations. Since the beginning of the 1990s column development has aimed to provide stationary phases with special selectivities. In inorganic anion analysis, stationary phases were developed that allow the separation of fluoride from the system void and the analysis of the most important mineral acids as well as oxyhalides such as chlorite, chlorate, and bromate in the same run. Moreover, high capacity anion exchangers are under development that will enable analysis of, for example, trace anionic impurities in concentrated acids and salinary samples. Problem solutions of this kind are especially important for the semiconductor industry, sea water analysis, and clinical chemistry. In inorganic cation analysis, simultaneous analysis of alkali- and alkaline-earth metals is of vital importance, and can only be realized within an acceptable time frame of 15 minutes by using weak acid cation exchangers. Of increasing importance is the analysis of aliphatic amines, which can be carried out on similar stationary phases by adding organic solvents to the acid eluent (Weiss, 2004).

Today the chromatographic analysis of ionic materials is widely applied and rapidly expanding. The number of species that may be determined continues to grow, as does the number of areas of science and technology where IC plays an important role. Application of ion chromatography at the present time can be seen through type of sample such as acid rain, pharmaceuticals, pesticides, wastewater and drinking water (Small, 1989).

### 1.10.1 Types of ion chromatography (Weiss, 2004)

Modern ion chromatography as an element of liquid chromatography is based on three different separation mechanisms, which also provide the basis for the nomenclature in use.

#### a) High performance ion chromatography, HPIC

This separation method is based on ion-exchange processes occurring between the mobile phase and ion-exchange groups bonded to the support material. In highly polarizable ions, additional non-ionic adsorption processes contribute to the separation mechanism. The stationary phase consists of polystyrene, ethylvinylbenzene, or methacrylate resins co-polymerized with divinylbenzene and modified with ion-exchange groups. Ion-exchange chromatography is used for the separation of both inorganic and organic anions and cations. Separation of anions is accomplished with quaternary ammonium groups attached to the polymer, whereas sulfonate-, carboxyl-, or phosphonate groups are used as ion exchange sites for the separation of cations.

### b) High performance ion chromatography exclusion, HPICE

The separation mechanism in ion-exclusion chromatography is governed by Donnan exclusion, steric exclusion, sorption processes and, depending on the type of separator column, by hydrogen bonding. A high-capacity, totally sulfonated cation exchange material based on polystyrene/divinylbenzene is employed as the stationary phase. In case hydrogen bonding should determine selectivity, significant amounts of methacrylate are added to the styrene polymer. Ion-exclusion chromatography is particularly useful for the separation of weak inorganic and organic acids from completely dissociated acids which elute as one peak within the void volume of the column. In combination with suitable detection systems, this separation method is also useful for determining amino acids, aldehydes, and alcohols.

### c) Mobile phase ion chromatography, MPIC

The dominating separation mechanism in ion-pair chromatography is adsorption. The stationary phase consists of a neutral porous divinylbenzene resin of low polarity and high specific surface area. Alternatively, chemically bonded octadecyl silica phases with even lower polarity can be used. The selectivity of the separator column is determined by the mobile phase. Besides an organic modifier, an ion-pair reagent is added to the eluant (water, aqueous buffer solution, etc.) depending on the chemical nature of the analytes. Ion-pair chromatography is particularly suited for the separation of surface-active anions and cations, sulfur compounds, amines, and transition metal complexes.

### 1.10.2 Ion chromatographic system (Weiss, 2004).

The basic components of an ion chromatograph are shown in Figure 1.9. It resembles the setup of conventional HPLC systems.

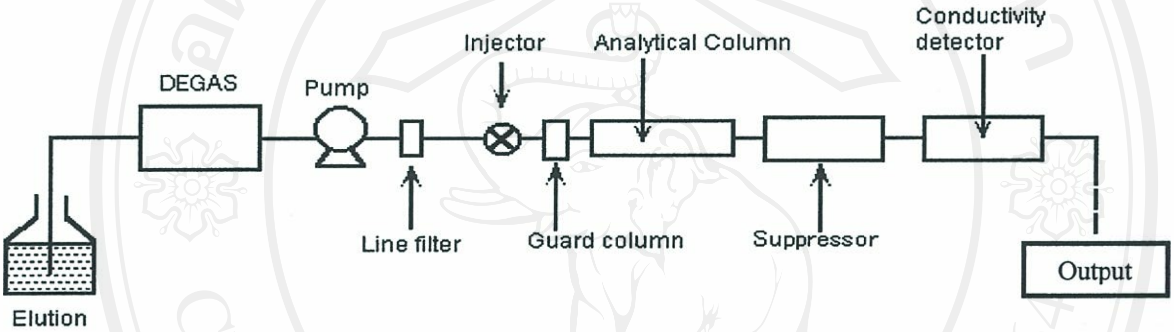


**Figure 1.9** Basic components of an ion chromatograph

A pump delivers the mobile phase through the chromatographic system. In general, either single-piston or dual-piston pumps are employed. A pulse-free flow of the eluent is necessary for employing sensitive UV/Vis and amperometric detectors. Therefore, pulse dampers are used with single-piston pumps and a sophisticated electronic circuitry with dual-piston pumps. The sample is injected into the system via a loop injector, as schematically shown in Figure 2.7. A three-way valve is required, with two ports being connected to the sample loop. The sample loading is carried out at atmospheric pressure. After switching the injection valve, the sample is transported to the separator column by the mobile phase. Typical injection volumes are between 5 μL and 100 μL.

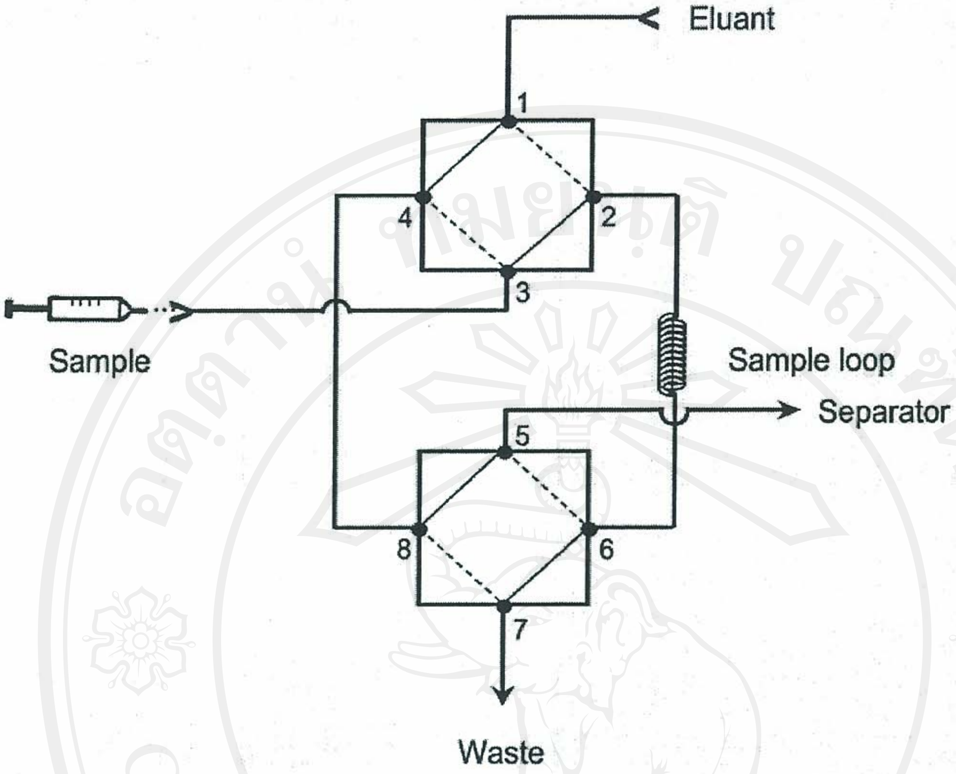


**Figure 1.10** Schematic representation of a loop injector

The most important part of the chromatographic system is the separator column. The choice of a suitable stationary phase and the chromatographic conditions determine the quality of the analysis. The column tubes are manufactured from inert material such as Tefzec, epoxy resins, or PEEK (polyether ether ketone).

The analytes are detected and quantified by a detection system. The performance of any detector is evaluated according to the following criteria:

- Sensitivity
- Linearity
- Resolution (detector cell volume)
- Noise (detection limit)

The most commonly employed detector in ion chromatography is the conductivity detector, which is used with or without a suppressor system. The main function of the suppressor system as part of the detection unit is to chemically reduce the high background conductivity of the electrolytes in the eluent, and to convert the sample ions into a more conductive form. In addition to conductivity detectors, UV/Vis, amperometric, and fluorescence detectors are used.

The chromatographic signals can be displayed on a recorder. Quantitative results are obtained by evaluating peak areas or peak heights, both of which are proportional to the analyte concentration over a wide range. This was traditionally performed using digital integrators which are connected directly to the analog signal output of the detector. Due to low computer prices and lack of GLP/GLAP conformity, digital integrators are hardly used anymore. Modern detectors feature an additional parallel interface that enables the connection to a personal computer or a host computer with suitable chromatography software. Computers also take over control functions, thus allowing a fully automated operation of the chromatographic system.

Because corrosive eluents such as diluted acids and bases are often used in ion chromatography, all parts of the chromatographic system being exposed to these liquids should be made of inert, metal-free materials. Conventional HPLC systems with tubings and pump heads made of stainless steel are only partially suited for ion chromatography, because even stainless steel is eventually corroded by aggressive eluents. Considerable contamination problems would result, because metal ions exhibit a high affinity towards the stationary phase of ion exchangers, leading to a significant loss of separation efficiency. Moreover, metal parts in the chromatographic fluid path would make the analysis of orthophosphate, complexing agents, and transition metals more difficult.

The determination of ionic species in solution is a classical analytical problem with a variety of solutions. Whereas in the field of cation analysis both fast and sensitive analytical methods (AAS, ICP, polarography, and others) have been available for a long time, the lack of corresponding, highly sensitive methods for anion analysis is noteworthy. Conventional wet-chemical methods such as titration, photometry, gravimetry, turbidimetry, and colorimetry are all labor-intensive, time-consuming, and occasionally troublesome. In contrast, ion chromatography offers the following advantages;

- Speed
- Sensitivity
- Selectivity
- Simultaneous detection
- Stability of the separator columns

## 1.11 Data analysis

### 1.11.1 Neutralization of acidity

The acidity (pH) of precipitation is determined by the relative proportion of acids and bases in solution or rainwater sample. Major ions typically present in rainwater are hydrogen ($H^+$), sodium ($Na^+$), ammonium ($NH_4^+$), potassium ($K^+$), calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), chloride ($Cl^-$), nitrate ($NO_3^-$), sulfate ($SO_4^{2-}$) and phosphate ($PO_3^{2-}$). Squeira (1982) pointed out that sulfate and nitrate are not quantitative indicators of acid deposition unless the relative alkali deposition is negligible or corrected for neutralization. In principle, changes in pH can be brought about as well by changes in the concentrations of neutralizing substances as by changes in the concentrations of the strong acids. Substances which are recognized for their abilities to neutralize the atmospheric acidic load are fine wind-blow soil particles (Ca and Mg), K and $NH_3$ (Bubenick, 1984, Das *et al.*, 2005). Neutralization of the acids by these base cations are validated by calculation of the neutralization factors (NF) by following equations (Possanzini *et al.*, 1988).

$$NF = \frac{[X_i]}{[SO_4^{2-}] + [NO_3^-]} \qquad (1.24)$$

where $X_i$ is the chemical component of interest, with all the ions expressed in μeq/L

When the NF value of one specific component, it means that the component plays major roll in acid neutralization. Normally, $NH_4^+$ and $Ca^{2+}$ are the dominant neutralization substances depend on the sampling site. On the other hand, neutralization by $Mg^{2+}$ and $K^+$ is negligible i.e. Kulshrestha *et al.*, 1996; Hu *et al.*, 2003; Tehpanondh *et al.*, 2005 and Das *et al.*, 2005.

### 1.11.2 Marine and non-marine contribution

Normally, the ionic components in rainwater such as $Cl^-$, $SO_4^{2-}$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$can be come from earth crust, volcanoes, anthropogenic or even ocean (Das *et al.*, 2005). Therefore, in order to estimate the marine and non-marine contribution to different ionic species in rainwater, enrichment factor (EF) and sea salt fraction (SSF) have been calculated.

The enrichment factor is a ratio used to discriminate aerosol sources (Ahmed *et al*., 1990, Singer *et al*., 1993, Akkoyunlu and Tayanc, 2003). This calculation is based on the element ratio found between ions collected in the atmosphere or in precipitation compared with a similar ratio for a reference material, provides important information on the sources of the elements of concern, enrichment factors for component $X$ is calculated by using the following equation;

$$\mathrm{EF}(X) = \frac{(X / \mathrm{C})_{\textbf{precipitation}}}{(X / \mathrm{C})_{\textbf{reference material}}} \tag{1.25}$$

where, $X$ is the concentration of the ion of interest and 'C' is the concentrations of the reference ion (Bayraktar and Turalioglu, 2005, Das *et al*., 2005). In soil material, $Ca^{2+}$ is chosen as the reference ion (e.g. Bayraktar and Turalioglu, 2005), while $Na^{+}$ is chosen in seawater contribution (Kulshrestha *et al*., 1996). However, the above reference ions may not be strictly for a typical site.

In the event that the EF value is much smaller than 1 or much greater than 1, it will be considered as concentrated or diluted relative to the reference source (Okay *et al*., 2002).

The sea-salt fractions (SSF) or non sea-salt fractions (NSSF) of any component can be calculated using the following equation (Das *et al*., 2005, Akkoyunlu and Tayanc, 2003).

$$\mathrm{SSF}(X) = [\mathrm{Na}_{\textbf{rain}}][X/\mathrm{Na}]_{\textbf{seawater}} \tag{1.26}$$

$$\mathrm{NSSF}(X) = [X_{\mathbf{rain}}] - [\mathrm{Na}_{\mathbf{rain}}][X/\mathrm{Na}]_{\mathbf{seawater}} \quad (1.27)$$

where $X_{\mathbf{rain}}$ is the concentration of component *X* in rainwater.

The recommended sea water ratio of $[X/\mathrm{Na}]_{\mathbf{seawater}}$ is shown in table 1.9 (Akkoyunlu and Tayanc, 2003).

**Table 1.9** The recommended sea water ratio (ratio are mol/mol)

| | Cl | $SO_4$ | Mg | K | Ca |
|---|---|---|---|---|---|
| Sea water ratio[a] | 1.166 | 0.0603 | 0.1137 | 0.0218 | 0.0219 |

[a] With respect to $Na^+$

If sea salt fraction value of *X* is higher than sea water, it can be deduced that the component *X* is not from marine origin.

### 1.11.3 Comparison of bulk and wet concentration

Normally, wet-only collector is recommended to be used as precipitation collector for monitoring of acid deposition in form of rain. However, the collector is costly to operate. So another choice, collector, is brought into consideration. Consequently, the chosen collector is depended on objecting of the study. In 2005, Staelens reviewed differences in the chemical composition of precipitation collected by wet-only and bulk collectors as shown in Table 1.10.

Table 1.10 shows that most of ion concentrations are higher in precipitation samples than those collected by wet-only collector, because of the deposition of soil-derived particles on the walls of the collectors during dry periods, while different of $SO_4^{2-}$ and $NO_3^-$ are usually smaller e.g. Kulshrestha *et al.*, 1996, Tanner, 1999, but local and regional sources of emissions can significantly influence the composition of bulk samples (Stedman *et al.*, 1990).

Beside of ratio between bulk and wet-only concentration that is used to compare, it still has the other methods to compare. First, scatter plots of bulk against wet-only which plot between bulk and wet-only concentration for each ion e.g. Granat *et al.*, 1996 that has sampling site in Thailand. Second, remainder between bulk and wet-only (bulk – wet-only concentration) for each ion e.g. Das *et al.*, 2005 and Granat *et al.*, 1996. Third, statistic tests, they can show significantly different between collector types. The chosen of the statistic test depend on distribution of the dataset that is to say, in the event that the variances between two groups of the dataset are difference, non-parametric test is chosen. On the other hand, if the variances between two groups of the dataset are not difference, parametric test is chosen.

Up to now a comparison of the chemical composition of precipitation by bulk and wet-only collectors in Southeast Asia was quite limited, especially in Thailand. Only one paper was published in 1996. It was a joint Thai – Swedish project that was set up to start such measurements at a few remote sites in Thailand for investigation of rainwater composition and wet deposition in Thailand (Granat *et al.*, 1996). The sampling site was located in Srinakarin Dam and Num Pung Dam. That result showed that the percent significance difference of $Mg^{2+}$ and $Ca^{2+}$ were the highest concentrations in bulk - wet-only collector, respectively. The minor was $Na^+$, $SO_4^{2-}$ and $Cl^-$.

**Table 1.10** Ratio of volume-weighted mean bulk and wet-only concentrations in precipitation, as measured at several locations throughout the world (from Staelens *et al.*, 2005).

| Location | Reference | SI[a] | $H^+$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $NH_4^+$ | $NO_3^-$ | $SO_4^{2-}$ | $Cl^-$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Leadville. USA | Ranalli et al. (1997) | w | 0.65 | 2.03 | 1.67 | 1.64 | 2.55 | 1.26 | 1.29 | 1.51 | 1.57 |
| Oak Ridge. USA | Richter and Lindberg (1988) | 5-w | 1.04 |  | 4.41 | 2.44 | - |  | 0.68 | 1.15 |  |
| Hong Kong China | lanner (1999) | d | 0.86 | 1.03 | 1.09 | 1.57 | 1.06 |  | 0.99 | 1.01 | 1.01 |
| Kobe. Japan | Aikawa et al. (2003) | w | 0.29 |  |  | $3.96^b$ |  | 1.56 | 1.84 | $1.48^b$ |  |
| loyo-oka. Japan | Aikawa et al. (2003) | w | 0.53 |  |  | $1.73^b$ |  | 0.36 | 1.19 | $1.16^b$ |  |
| Kaibara. Japan | Aikawa et al. (2003) | w | 0.79 |  |  | $1.87^b$ |  | 1.24 | 1.20 | $1.19^b$ |  |
| Delhi. India | Kulshrestha et al. (1995) | d | $0.63^c$ | $1.01^c$ | $1.30^c$ | $2.03^c$ | $2.06^c$ | $0.93^c$ | $1.08^c$ | $1.02^c$ | $1.16^c$ |
| Istanbul. Turkey | Akkoyunlu and Tayance (2003) | w | $0.52^d$ | $1.63^d$ | $2.82^d$ | $2.60^d$ | $2.15^d$ | $1.36^d$ | $1.26^d$ | $4.39^d$ | $1.64^d$ |
| Palanza. Italy | Mosello et al. (1998) | w | 0.98 | 1.10 | 1.50 | 1.32 | 1.29 | 1.06 | 1.12 | 1.08 | 1.08 |
| Manchester. UK | Lee and Longhurst (1992) | w | 0.50 |  |  | 1.87 |  | 1.10 | 1.17 | 1.18 |  |
| Eskdalem | Stedman et al. (1990) | w | 1.00 | 0.97 | 0.89 | 1.14 | 0.90 | 0.87 | 1.00 | 0.98 | 0.93 |
| Stoke Ferry. UK | Stedman et al. (1990) | w | 1.28 | 1.41 | 1.00 | 1.45 | 1.42 | 0.84 | 1.10 | 1.05 | 1.39 |
| Ludlow. UK | Stedman et al. (1990) | w | 1.09 | 1.93 | 1.33 | 1.86 | 1.88 | 1.12 | 1.36 | 1.23 | 1.88 |
| Lough Navar. UK | Stedman et al. (1990) | w | 0.83 | 0.99 | 0.94 | 1.18 | 0.99 | 0.60 | 0.85 | 0.94 | 1.01 |
| Barcombe Mills. UK | Stedman et al. (1990) | w | 1.22 | 1.35 | 1.53 | 1.76 | 1.29 | 1.00 | 1.30 | 1.36 | 1.33 |
| Yarner Wood. UK | Stedman et al. (1990) | w | 1.07 | 0.85 | 0.85 | 1.05 | 0.83 | 0.72 | 1.00 | 0.95 | 0.84 |
| High Mufles. UK | Stedman et al. (1990) | w | 0.97 | 1.14 | 1.22 | 1.37 | 1.13 | 0.92 | 1.04 | 0.99 | 1.10 |
| Strathvench Dam.UK | Stedman et al. (1990) | w | 1.23 | 1.29 | 1.00 | 0.73 | 1.17 | 0.55 | 0.92 | 1.03 | 1.29 |
| Glen Dye. UK | Stedman et al. (1990) | w | 1.02 | 1.38 | 1.22 | 1.16 | 1.29 | 0.88 | 0.98 | 1.01 | 1.29 |

Values in italic indicate a non-significant ($p > 0:05$) difference between bulk and wet-only ion concentration.
[a] Sampling interval of bulk precipitation measurements: d: daily, w: weekly.
[b] Non-marine fraction.
[c] Significance of the difference between bulk and wet-only concentrations was not tested.
[d] Ratio of arithmetic mean concentration of bulk and wet-only precipitation.

### 1.11.4 Identification sources of acid deposition in rainwater samples

During the last decade, a number of studies on statistic which used to identify source of acid deposition in rainwater have been carried out in the world (e.g. Thepanondh *et al.*, 2005, Akkoyunlu and Tayanc, 2003, Bravo *et al.*, 2000, Bayraktar and Turalioglu, 2005, Saxena *et al.*, 1996). These statistics are Pearson correlation ($r$) and principle component analysis (PCA). Pearson correlation is the statistic value to identify possible relationships between the various ionic species in wet deposition. Strong correlation value between two ionic species can suggest that these ions are potentially important compounds in wet precipitation and can be assessed that this ions are come from same origin.

Principle Component Analysis (PCA) or factor analysis is the statistical test for determination the factors underlying the inter-correlations between the measured species. Initial factors are extracted from a matrix of correlations derived from standardized variables. Each variable were also evaluated for its KMO value (Kaiser-Meyer-Olkin) and was included in the matrix only if it had a KMO value greater than 0.6. Finally, factors with eigenvalues greater than one were considered for varimax rotation to obtain the final factor matrix (Saxena *et al.*, 1996). Factor analysis assumes that the inter-correlations among the original variables are generated by some smaller number of unobserved factors (Kessler *et al.*, 1992). Comray (1973) explained that data loading more than 0.5 are deemed to be statistically significant. If ether of factor has data of ($Na^+$ and $Cl^-$), ($NO_3^-$ and $SO_4^{2-}$), ($Mg^{2+}$, $Ca^{2+}$ and $SO_4^{2-}$), $H^+$, $NH_4^+$, $K^+$ loading more than 0.5, it can be deduced that source of wet deposition are from marine origin, combustion process, soil resuspension, power plant, biogenic, biomass burning (Thepanondh *et al.*, 2005, Hu *et al.*, 2003, Saxena *et al.*, 1996).

## 1.12 Research Objectives

1) To compare rainwater sampling methods; wet-only and bulk collectors.
2) To analyze chemical composition of rainwater samples.