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ENVIRONMENTAL CHEMISTRY

CONTENTS

10. Acid Rain

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Introduction

Acid rain is a well known pollution phenomenon caused l atmospheric aqueous phases such as rainwater, cloud water, fog, mist etc. It had the effect of acidifying several lakes in Canada, damaging forest in United States and causing other ecological damages. These observations led to a public interest in the study of acid rain, identifying factors for acidification of water, and long-term planning to control it.

What is Acid Rain?

The term acid rain is often used as an overall expression for the wet deposition processes including rain, fog, dew and snow, although the actual meaning of acid rain is the wash out of trace substances by rain events (Brands and van Eldik, 1995). Its is better to use the term acid precipitation, which includes all kinds of wet depositions. Dry acid deposition is generally not noticed and monitored, but it is also responsible for the effects caused by acid rain phenomenon. Now, the term acid deposition is used to describe both wet and dry depositions (Brandt and van Eldik, 1995).

The term acid refers to an excess of H ions in water solution. Hydrogen ions are normally balanced by anions, SO_4^{2-}, NO_3^-, and to some extent by Cl^- and organic anions, e.g., acetate (CH_3COO^-) and formate $(HCOO^-)$.

Background pH of unpolluted water, which is buffered by atmospheric CO2 , is calculated as follows. Consider a dust free atmosphere, devoid of any manmade sources of acid rain precursors. In such an atmosphere, air contains about ~380 ppm CO2. The carbon dioxide will dissolve in the atmospheric water, which may be present as rainwater, cloud water, fog, mist or water film on surfaces. The dissolution of CO2 would be governed by the equilibria (1-2).

$$CO_2 + H_2O \xrightarrow{K_H} CO_2.H_2O \qquad (1)$$

$$CO_2.H_2O \rightleftharpoons HCO_3^- + H^+ \qquad (2)$$

KH is Henry's law constant and K1 is the first dissociation co

On the basis of equilibria (1-2), it can be shown that in atmospheric aqueous phase(s) the hydrogen ion concentration, [H+], would be given by Eq. (3).

$$[H^+] = (K_H K_1 p_{CO2})^{1/2} \quad (3)$$

On substituting in Eq. 3, $K_H = 3\times10^{-2}$ mol L^{-1} atm^{-1}, $K_1 = 4.3\times10^{-7}$ mol L^{-1} and p_{CO2} = 380 ppm = 3.8×10^{-4} atmosphere, we get,

$$[H^+] = (4\times10^{-2} \times 4.3 \times10^{-7} \times 3.8 \times 10^{-4})^{1/2} = 2.55\times 10^{-6} \text{ mol } L^{-1} \quad (4)$$

From the value of $[H^+]$, the pH is obtained as in following Eq.:

$$pH = -\log [H^+] = -\log 2.55\times 10^{-6} = 5.6$$

Thus, the pH of dust free and unpolluted atmosphere is 5.6, which is taken as the background or reference pH of rainwater. Now the term acid rain has come to mean the rainfall with pH less than 5.6. Thus, if the pH of rainwater is less than 5.6, it is termed as acid rain.

Regional pH Values

The unpolluted and dust free atmosphere is not found in the real world. So the pH value of 5.6 cannot be taken as the natural reference pH value of rain water at a given location. The dust, the major source of which is soil, is always present in atmosphere. It may be acidic, alkaline or neutral with reference to pH. Dust particles, when incorporated in atmospheric waters, neutralizes hydrogen ions and, therefore can, significantly change its pH value (Delmas and Gravenhorst, 1983). For example, in Western India, for example Rajasthan, the soil is alkaline. And the rain water pH values in unpolluted areas in Rajasthan often exceed 8.0 (Manoj et. at., 2000). Because of this, rainwater pH in Jaipur lies in the range 6.7-8.5. Obviously, the background pH values of different locations would be different. So for assessing any changes in rain water pH at a location, its background pH, based on local conditions, should be used as a reference.

Historical Perspective

Acidity problems were first recognised as early as 17th century in England. In a famous discussion entitled *Fumifigum*, Evelyn in 1661 commented on the damaging effects of atmoshperic sulfur and particulate levels near London (Bridgman, 1990). In 1842, Poggendorff reported about the acidification of rain by emission of the volcano, Vesuv, and he probably used the term acid rain for the first time in scientific literature (Brandt and van Eldik, 1995). In 1853, R.A. Smith published a report on the first detailed measurements of precipitation acidity in Scandinavia, and its possible effects on the environment. In the 1950's in Europe and in the 1960's in the North America, the continent wide precipitation chemistry networks were established. On the basis of research in England and Canada, E. Gorham showed as early as 1955 that most of the acidity of precipitation near industrial regions was due to combustion emissions, that progressive acidification of surface waters can be assiged to precipitation, and that the free acidity in soils receiving acid precipitation was due primarily to sulfuric acid.

In 1961, a Swedish soil scientist named Svante Odin established a Scandinavian network to measure surface water chemistry. On the basis of his measurements, Odin showed that acid precipitatiopn was a large scale regional phenomenon in much of the Eurpoe with well defined sources and sinks. He found the precipitations and surface waters becoming more acidic. He noticed the long distance (100-2000 km) transport of sulfur and nitrogen containing species taking place over Eurpoe and the seasonal trends in the deposition of major ions and acidity. Odin also hnypothesised the long term ecological effects of acid rain included decline of fish populations, leaching of toxic metals from soils into surface waters, and the decreased forest growth.

Real Rainwater pH Values

Much work has been done and continues to be done on sampling of rainwater to understand the region specific rainwater pHs. Some representative rain water pH value for different locations around the globe are given in Table 1. In India, the acid rain has been observed at quite a few places. In India, several groups in universities and institutes are active in the area of acid rain chemiatry. The acid rain has been observed at quite a few places. The rainwater pH values at selected locations are collected in Table 2.

Chemical analyses of rainwater with respect to the concentration of major anions(sulfate, SO42-, Nitrate, NO3-, carbonate/bicarbonate, CO32- /HCO3-, Cl-,

etc, cations(Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, etc.) and mass balanc the conclusion that in general the major cause of rainwater acidity are sulfuric acid, H_2SO_4 and nitric acid, HNO_3.

Table 1: Wet precipitation pH value at selected global and Indian locations (Brandt and van Eldik, 1995)

Area	pH	Year	Nature of Precipitation
Subarctic Tundra, Bethel, AK	4.69	1988	Rainwater
La Paragua, Venezuela	4.70	1985	Rainwater
Dharhan, Saudi Arabia	5.48	1987	Rainwater
Long Island, NY, USA	4.29	1983-1985	Rain+Snow Water
Los Angeles, USA	4.81	1985	Rain water
Pasadana, CA, USA	2.92-4.85	1981	Fog water
Southern California	2.25	1982	Fog water
Chembur, India	4.82	1976	Rain water
Jaipur	7.14-8.45	1996-98	Rain water
Kota	7.4-7.95	1996-1997	Rain water
ITP, Delhi	5.0	–	Rain water

Table 2: Rainwater pH value at selected Indian locations(Misra et al., 2013)

City	pH	Year
Jaipur	6.7 – 8.45	1996 – 2006
Delhi	6.7	1996
Agra	7.0	1991
Pune	6.5	1996
Kalyan	5.7	1989
Chembur	6.44	1994
Goa	6.3	1996
Roorkee	7.02	2006

The relative percentage contributions of different acids, taken from the col-

lection of Branst and van Eldik(1995), are in Table 3.. It can be s sulfuric and nitric acids, organic and other acids also contribute to rain water acidity and some times they dominate. At several locations in recent years the contributiojn of nitic acid has increaesd relatively due to huge increase in the number of automobiles and consequently much greater release of NOx.

There are many locations around the world, particularly, equatorial and tropical regions where organic acids have been found to contribute significantly to atmospheric acidity. The precursors for organic acids are mostly plants. Among organic acids formic and acetic acids are most important.

Table 3. Relative contributions of different acids(Brandt and van Eldik, 1995).

% H_2SO_4	%HNO_3	HX	Area
65	17	18 (HCl, H_3PO_4, RCOOH)	Alaska
43	18	52(RCOOH)	Bethel, AK
60	25-30	-	Germany
18	21	64(RCOOH)	North. Australia
33	26	41 (HCl, H_3PO_4, RCOOH)	North Australia
73	14	13 (HCl, H_3PO_4, RCOOH)	Amsterdam Island

Acid Rain Precursors

Main acid rain precursors responsible for acidification of rain water and other aqueous systems are sulfur dioxide, SO2 , nitrogen oxides, NO and NO2 and organic acids in particular formic and acetic acids. Other sulfur compouonds like, hydrogen sulfide, H2S, and dimethy sulfide, CH3SCH3, also contribute but through oxidation to SO2 first.

Rainwater Sampling and Chemical Analysis.

The rainwater collection and its subsequent chemical analysis for pH and, if facilities exist, for major cations and anions can be done by students of chemistry/environmental science at all levels. The analytical treatment will de-

pend up on the facilities available. The process carried out in d described(Mishra et al., 2013, Dhayal et al. 2014). The samples can be collected at a suitable site in 10 L polyethylene bottles to which a polyethylene funnels of 30 cm diameter fitted. The sizes of bottle and funnel can vary depending up on availability. The funnels and bottles should be cleaned thoroughly every day before the sample collection in order to reduce the effect of dry deposition. The rainwater samples should be filtered through Whatman No. 41 filter paper (pore size, 20-25 µm) and be kept at 6oC in the refrigerator until the pH / metal ion analysis is complete.

pH in each sample can be measured using digital pH meter and conductance by using conductivity meter. Students at lower level may easily have an approximate idea of rainwater pH with help of pH-papers. The experiments can be continued during the rainy season and a pH profile of the specific location can be generated. For advanced studies, automatic rainwater samplers are available, which can collect rainwater at all times without there being any need of anyone being present near the sampling site. The samples can be analyzed using standard methods. The rain water pH profile of Jaipur city(1998-2006) is given in Fig. 1.

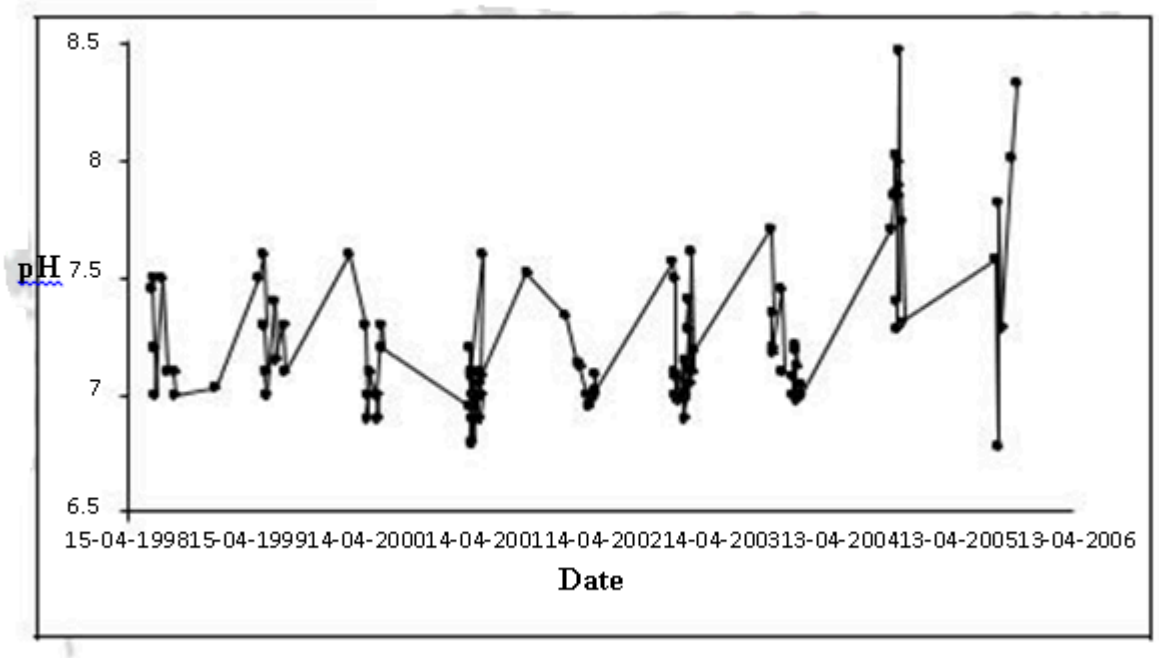

Fig. 1. Rainwater pH profile of Jaipur

Influence of Suspended Particulate Matter on Rainwater pH

Collection of sequential rainwater samples one after the other in a rain event

leads to some interesting information. This is possible if the few hours. In Jaipur, average rainfall is ~ 50 cm and such occasions are few and far between. However, few rain events provided opportunity for collection of sequential rain water samples. An examination of these results showed the pH, conductance, individual and total ion concentrations in sequential rainwater samples, pertaining to a particular continuous rain event, to decrease. This is due the following reason. Composition of initial part of rain fall is largely controlled by wash-out process through scavenging of gaseous constituents, and suspended particulate matter (SPM), which is largely alkaline. As the rainfall progresses, the amount of SPM available for wash out, decreases, and hence the pH also decreases.

Rainwater Acidity: Indian Scene

The acid rain in India ia not widespread and is at the most a local phenomenon, usually observed within a distance of 2 km from the industrial units. The probabilty of occurrence of acid rain in India is ~2% (Verma, 1989). At most places the rainwater has alkaline pH(>6)(Brandt and van Eldik, 1995). Local factors may play an important role . For example, acid rain recorded in Chembur(Mumbai)(pH = 4) during 1970 -1980) turned alkaline in 1990.The acid rain was caused by the release of large amount of SO2 and NOx by the industrail units located in Chembur.. When these units were relocated or closed down, the acid rain too disappeared. Owing to massive industrialization, Delhi and Agra saw decline in rainwater pH from 9.1-7.0 in 1963-1965 to 6.3-6.1 in 1984. In Jaipur city too, the studies during 1996- 2006 indicated a 3% decline in average pH. This is most probably due to increase in concntrations of acid rain precursors notably by automobiles and construction boom.

Ecological and other Damaging Effects of Acid Rain

The acids and acid rain precursors reach the ground level by the following two processes.

1. **Wet Deposition Processes.** These include the delivery of the pollutants to the Earth's surface through rain, snow and fog.
2. ***Dry Deposition Processes.*** These processes deposit the acids and acid rain precursors onto solid and liquid surfaces, when these come in contact with air.

The damaging effect \both the dry and wet depositions are same.

Weathering of Rocks: Soil Acidification

The amount of acid in rainwater decides its effect of weathering of rocks. When natural rain water(pH = 5.6) falls on limestone derived rocks, as in Rajasthan, etc., the reaction with limestone neutralize the acid and limestone dissolves. The alkaline soil acts as a buffer.

$$CaCO_3 + H^+ \quad Ca^{2+} + HCO_3^- \qquad (5)$$

So if the soil is underlain by sedimentary rocks then the acid is neutralized and the soil is buffered. Buffering is high, if the rock contains alkaline material like limestone or chalk. This acid- base reaction is very slow, even then during the past millennia huge quantities of rocks have dissolved. If the rock is igneous, composed of SiO_2 and Al_2O_3, it has little buffering capacity. So the soil, which contains igneous rocks such as granite, quartz sandstone, shale etc., are not easily weathered and so have a poor buffering, i. e., acid neutralizing ability. The lack of buffering leads to the acidification of the ecosystem. Several areas in North America, South East Canada and northern part of South America have poorly buffered soil and, therefore, prone to acidification.

The following are the consequences of soil acidification.

1. Leaching of plant nutrients.

The nutrients, particularly the base cations, such as magnesium, calcium and potassium are leached out. These are replaced by hydrogen ions owing to ion exchange. The increased acidity combined with nutrient deficiency leads to decrease in soil fertility. The girth size, foliage and yield may decrease. In many countries, the forest decline has been attributed to acidification of ecosystem.

2. Mobilization of Toxic Metals

An increase in acidification of soil, results in the leaching of potentially toxic metal ions such as aluminum, cadmium, manganese, copper, iron, etc. The aluminum is mobilized as Al^{3+} ions, which are potentially toxic to root systems of plants. Aluminum ion is believed to interfere with the uptake of nutrients by trees and plants. An increase in metal ion concentrations also affects the microorganisms living in soil negatively. So under conditions of high acid, that is low pH, the biodegradation in the soil is slowed down.

3. Inaccessibility of Phosphates and Micronutrients

The vital nutrient phosphorus is available in soil as phosphate. The aluminum ions, Al^{3+}, are able to bind the phosphate very strongly and so the latter becomes

unavailable to plants. Likewise, micronutrients such as bo molybdenum also become less accessible.

Effect on Plant Life

The tree growth is affected in the following ways.

1. A13+ ions damage the root fibers and lead to forest decline. Acidity coupled with presence of tropospheric ozone and other oxidants cause stress, which when combined with drought, temperature extremes and disease and insect attack, leads to forest decline.
2. The forests at high altitude are more susceptible to damage due to their exposure to the base of low level clouds, where the acidity may be high.
3. Fogs and mist are more acidic than clouds due to much less water than clouds and hence the trees may suffer from *dieback* in regions of acid fogs.
4. The effect of acid rain on deciduous trees is gradual. The outermost leaves dry and fall prematurely and are not replenished in the spring. The trees become weaker affecting the growth.
5. Acidification is also affects the ability of some plants to grow including those in fresh water.

Aquatic Life

Acidification of lakes and rivers has serious consequence for aquatic life (Bridgman, 1990). Acidification of lakes has occurred in Canada, the Adriondacks, and Scandinavia. The acid has serious damaging effect on the living organism. Below pH = 5, many fish species, such as trout and bass cannot survive and disappear and in general the population of living organisms decreases. If the pH of lake/river water falls below 4.7, the lake/river becomes virtually sterile and unable to support aquatic life. And dead lakes occur at pH below 3.5. This is due to the mobilization of toxic metals, particularly aluminum as Al3+. Soil contains aluminum compounds, such as feldspar. These react with natural water as in Eq.:

$$2KAlSi_3O_8(\text{Feldspar}) + 2H^+ + H_2O \longrightarrow Al_2Si_2O_5(OH)_4\ (\text{kaolinite, clay}) + 4SiO_2 + 2K^+ \quad (6)$$

When the pH of rainwater is low, clay dissolves and the toxic Al3+ is mobilized. The r e p r o d u c t i v e capacity of fish is affected badly.

Buildings

Limestone and marble buildings are highly susceptible to rain (Spedding, 1974). Both SO2 and O2 are absorbed on to the wet surface. Amount of gases absorbed on stone surface increases with increase in relative humidity. The absorbed gas is oxidized to sulfate, which becomes a part of CaCO3 matrix and CaCO3 is converted into CaSO4

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O \quad (7)$$

CaSO4 has higher molecular volume than that of CaCO3. This causes stress on molecular level. The accumulated effect of this stress is to cause flaking off of the limestone. Moreover, CaSO4 has a higher solubility in rain water than CaCO3 and the former is thus easily leached out. For the same reason, works of art, especially frescoes, are damaged as true frescoes are a pigmented lime plaster. The degradation of timber takes place due to reaction of sulfite, i.e., absorbed SO2 in aqueous phase.

$$CaCO_3 + 2H^+ \longrightarrow Ca(HCO_3)_2 \quad (8)$$

The calcium bicarbonate, $Ca(HCO_3)_2$ is a powdery substance. It is easily leached by rainwater and the buildings/monuments are eroded /damaged.

The reaction of nitric acid with $CaCO_3$ produces calcium nitrate, which is highly soluble in water, so it is easily leached out and causes a severe damage to stone buildings.

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2 \quad (9)$$

Paper and Leather

The absorption of SO2 by paper in humid atmosphere is responsible for yellowing and loss of mechanical strength of paper (Spedding, 1974). The trace metal ions present as impurity catalyze the oxidation of SO2 into H2SO4 in the presence of moisture. The acid hydrolyses cellulose, and SO2 reacts with lignin on surface moisture to form lignosulfonic acid. In a similar manner, the hydrolysis of leather proteins deteriorates the leather goods.

Rusting of Iron and Other Damaging Effects

Acid rain is known to accelerate the rusting of iron. It painted surfaces, and damages glass articles. It accelerates the decay of building materials and paints, including buildings, statues, and sculptures and irreplaceable monuments like Taj Mahal.

Human Health

Acid rain is not reported to effect human health adversely. According to US EPA, acid rain does not affects the human health directly. It does not have an acidic enough pH to burn human skin. According to this agency, "Swimming in an acidic lake or walking in an acidic puddle is no more harmful to people than swimming or walking in clean water."

However, rain precursors, viz., SO2 and NOx may have deleterious effect on human health. On long exposure to SO2, the cases of bronchitis increase. Sulfur dioxide together with particulate matter causes respiratory problems. The reactions of these gases in the atmosphere produce fine sulfate and nitrate particles that can be transported long distances by winds and inhaled deep into human lungs. Fine particles can also penetrate indoors. A relationship between elevated levels of fine particles and increased illness and premature death from heart and lung disorders, such as asthma and bronchitis has been found.

Some Centres Engaged in Acid Rains Study in India

1. Centre for Atmospheric Sciences, IIT, New Delhi.
2. Atmospheric Chemistry Lab, Department of Chemistry, University of Rajasthan, Jaipur
3. Department of Chemistry, Dayalbag Education Institute, Agra (U.P.)
4. Indian Institute of Tropical Meterology, Pune
5. Centre for Environmental Science and Engineering, IIT, Mumbai.
6. Department of Chemstry, Pt. Ravi Shankar Shukla University Raipur, (Chhattisgarh)
7. Bhabha Atomic Research Centre, Mumbai
8. Physical Research Laboratory, Navrangpura, Ahemdabad
9. National Physsical Laboratory, New Delhi
10. School of Environmental Sciences, JNU, New Delhi

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you can view video on Acid Rain

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