ENVIS NEWSLETTER

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Indian Institute of Tropical Meteorology, Pune

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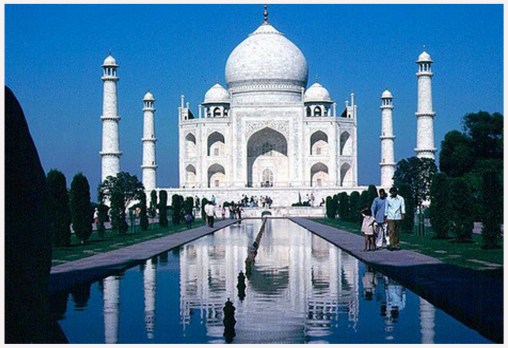
The Air Quality : A Global Challenge -1








In side this Issue

- Composition of normal rain drop
- What is acid
- Measure of acidity
- Components affecting acidity of rainwater
- Their sources
- Acid Rain formation : Chemistry
- Effect of Acid Rain

ENVIS NEWSLETTER

Editorial Team

Editorial

ENVIS-IITM centre deals with the very important and sensitive component of the environment ***"The Air we breathe"*** *and related challenges. In our last series of newsletters under the heading "Air Pollution Chemistry" we have taken a brief knowledge of Earth system, interdependence of different components of environment, the atmosphere, air pollution, criteria air pollutants etc. now it's a time to go deep in to the subject "Acid Rain and Atmospheric Pollution" and know much more about how the air quality has changed over the period of time resulting in to the very complex local, regional and global problems like urban heat Iceland, visibility reduction, smog formation, acid rain, global warming, climate change etc…We are very happy to introduce you with our new series of ENVIS newsletters* ***"The Air Quality: A Global Challenge"*** *which will give you detailed information of various striking problems in the field of Air Pollution and different scientific pathways involved. At the end of this series you will come to know what causes the smog, what is acid, how it damage our ecosystem, Is climate is changing with unsustainable rate, what is global warming so on and so forth… This will help you to take definite measures to improve air quality at your level.*

Present issue gives you information about normal composition of rain water, acidifying components, their sources, formation of acid rain and what it can damage. We hope our attempt to convey complicated scientific information in simple language will help to create awareness amongst the common public which is the first step towards safeguarding our environment

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WHAT IS THERE IN NORMAL UNPOLLUTED RAIN DROP

Pure Water H_2O

Some dissolved Carbon Dioxide (CO_2)

Some ammonia as NH_4^+

Small amount of cations (Ca^{++}, Mg^{++}, K^+, and Na^+)

Small amount of anions (CL^-, SO_4^{2-})

Ph: 7(for Pure Water) 5.6 (For Rain Water)

When pH of rain water goes below 5.6 it is considered as ACIDIC

WHAT IS ACID

The term acid refers to an excess of hydrogen ions (H^+) in water solution, which is normally balanced at least in part by the major acid anions SULPHATE (SO_4^{2-}) AND NITRATE (NO_3^-)

MEASURE OF ACIDITY

Acidity is usually measured by a pH scale

(pH= -log [H^+])

Where, [H^+] = The concentration of hydrogen ions expressed as mol L^{-1}

The pH scale is logarithmic and ranges from 0 to 14.

pH 7 is considered as neutral, Higher pH's basic and lower pH's acidic

Table-1 Major inorganic ions affecting rainwater quality and acidity

Atom or molecule	Symbol	Ion Type	Comments
Hydrogen	H^+	cation	Amount determines rainwater acidity
Sulphate	SO_4^{2-}	anion	Strong acid, gas and liquid reactions
itrate	NO_3^-	anion	Strong acid, gas and liquid reactions
Choride	Cl^-	anion	Acid, mainly gas interaction
Ammonium	NH_4^+	cation	Neutralization of anions
Calcium	Ca^{2+}	anion	In conjunction with carbonate acts to buffer acidity
Potassium	K^+	cation	In conjunction with carbonate acts to buffer acidity
Magnesium	Mg^{2+}	cation	In conjunction with carbonate acts to buffer acidity
Sodium	Na^+	cation	In conjunction with carbonate acts to buffer acidity

Table-1 Major organic ions and catalyst affecting rainwater quality and acidity

Atom or molecule	Symbol	Ion Type	Comments
Organic			
Formic acid	HCOOH	Molecule	Weak acid
Acetic acid	CH_3COOH	Molecule	Weak acid
CATALYSTS			
Hydrogen Peroxide	H_2O_2		Major at all acidity level
Ozone	O_3		Minor
Iron	Fe^{3+}		Minor
Manganeze	Mn^{2+}		Minor
Mitrogen Dioxide	NO_2		Minor
			Minor

GENERAL SOURCES

Above mentioned organic, inorganic cation, anion, molecules and catalysts comes from verities of natural as well as anthropogenic i.e. man made sources some of them are given bellow.

Aqueous chemistry, fossil fuel burning, oceans, soil processes, agriculture, cars, industrial activities, decay processes, vegetation, atmospheric chemistry

NATURAL and ANTROPOGENIC SOURCES

Formation of ACID RAIN

Acid gases such as SO2 and NO2 gets transformed into dilute acid concentrations in rainwater by THREE different pathways.

- Homogeneous Gas Phase Reactions
- Homogeneous Aqueous Phase Reactions
- Heterogeneous Aqueous Phase Reactions

Homogeneous gas phase reactions occur in dry atmosphere and are associated with the photolytic oxidation process. Homogeneous aqueous phase reaction occurs between individual species in al liquid medium such as a cloud or rain drop whereas heterogeneous aqueous phase reaction occur during adsorption on sold surface and are not considered as important as the other two.

CRUTIAL COMPONENTS: METEOROLOGY

The relative importance of any process operating in the atmosphere depends strongly on the meteorological condition, such as presence of clouds, relative humidity, intensity of solar radiation, temperature etc..

Homogeneous gas phase chemistry

In the dry atmosphere most of the acid gas reaction leading to acid ions, such as sulphate, nitrate, involved exited molecules, atoms, free radicals and sunlight.

The OH radical is particularly important.

CHEMISTRY INVOLVED

HOMOGENEOUS GAS PHASE

A. Sulphur Dioxide

$2SO2 + O2 \rightarrow 2SO3$

(Very slow)

Or

$OH + SO2 + M \rightarrow HOSO2 + M$

(Unstable compound)

$HOSO2 + O2 \rightarrow HO2 + SO3$

$SO3 + H2O \rightarrow H2SO4$

(Very Fast)

B. Nitrogen Dioxide

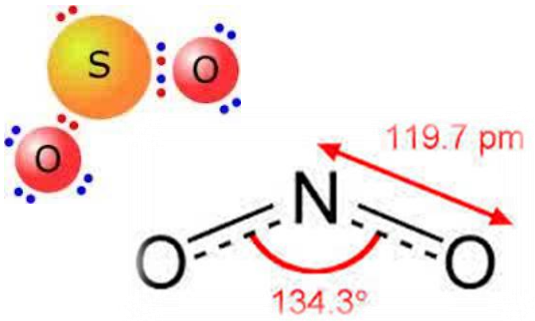
$2NO + O2 \rightarrow 2NO2$

Or

$HO2 + NO \rightarrow OH + NO2$

$2NO2 + H2O \rightarrow HNO3 + HONO$

M: Catalyst, often Fe^{3+} or Mn^{2+}



HOMOGENEOUS AQUEOUS PHASE

A. Sulphur Dioxide

$SO_2 + H_2O \leftrightarrow SO_2H_2O$

$SO_2H_2O \leftrightarrow H^+ + HSO_3^-$

$HSO_3^- \leftrightarrow H^+ + SO_3^-$

$O_2 + 2HSO_3^- \rightarrow 2H^+ + 2SO_4^{2-}$

(Slow W/O catalysts)

$H_2O_2 + HSO_3^- \rightarrow H^+ + SO_4^{2-} + H_2O$

$O_3 + HSO_3^- \rightarrow H^+ + SO_4^{2-} + O_2$

(Rapid if Ph > 4.5)

B. Nitrogen Dioxide

$NO_2 + O_3 \rightarrow O_2 + NO_3$

$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M$

$N_2O_5 + H_2O \rightarrow 2H+ + 2NO_3-$

$2NO_2 + H_2O \rightarrow 2H+ + NO_3- - NO_2$

The oxidation of SO_2 and NO_2 in the atmosphere is a relatively slow process and several other reactions are possible along the same. The reactions between SO_2 and NO_2 with O_3 in the dry atmosphere are considered to be very slow without catalyst that the eventual output of acid is very minor. Reactions including the addition of catalysts and free radicals are the main sources of ions leading to acidity in rainwater.

The rates of oxidation of both SO_2 and NOx in a cloud free environment are highly variable and strongly dependant on the concentration of the OH radical. The conversion of NO_2 to $HONO_2$ is much more rapid. There is a reduction in conversion rate with lower OH concentrations. At night when OH concentrations are the minimum conversion rates diminish sharply.

Homogeneous aqueous- phase chemistry

Sulphur species and nitrogen species can be incorporated into liquid droplets in several different ways.

- Dissolve in water
- Diffusion process
- Impaction and collision Acid aerosol species can act as nuclei for water droplet formation

In liquid water, catalysts are important to the rate of the conversion process. The impact of catalysts is generally dependant on the level of acidity in the water.

Importance of Hydrogen Peroxide (H_2O_2) in the aqueous phase reaction

H_2O_2 is the important molecule which enhances the conversion rate of SO_2 to SO_4^{2-} independently of acid levels in water droplets. After H_2O_2, O_3 becomes the important catalyst. In areas where neither H_2O_2 or O_3 exist in significant concentrations, NO_3^- formation can control the production of sulphuric acid. H2O2 is not important in NO_3^- formation. Not much known about NOx conversion in an aqueous environment. It is likely that N_2O_5 plays an important role, probably with NO_3^- forming directly from the molecule, depending on the relative concentrations of NOx and NO_3^- . Reaction of NOx with O_3 at night can produce considerable amounts of NO_3^- because there is no photochemical destruction. Cations in solution, particularly ammonia may alter the formation rates of SO_4^{2-} and NO_3^-, and can increase the oxidation of SO_2. Ammonium enhances SO_4^{2-} formation in spring, when the concentrations of both ions are the highest.

Effects of ACID RAIN

Acid rain has impact on

- **Vegetation**
- **Surface Waters**
- **Forests**
- **Materials**

Symptoms of damage may be subtle, highly variable and hard to distinguish from natural stresses. The strongest evidence for the acid deposition is fish kills in a number of lakes in Scandinavia and northen America. Toxicity from acid precipitation adds to the natural stresses created by climate variation, competition of species, and biotic and chemical changes. There is enough overall evidence to suggest that damage from increasing acidity in precipitation over the past few decades is real and is serious, and may cause changes which may not be reversible. And hence need to be addressed with proper planning.

DO YOU KNOW?

- Acid Rain was first described by Robert Smith, UK's first alkali inspector, in 1872.
- H2O2 dominates the aqueous chemistry process and in the presence of H2O2 conversion rates can reach 100% h^{-1} depending on cloud type and other meteorological parameters, until the H2O2 is exhausted.
- Ammonia can dissolve as a gas in water droplet, thus directly acting to reduce rainwater acidity.
- In areas of the world where soil particles rich in cations such as Ca2+ and Mg2+ dominate air quality, rainwater tends towards alkalinity rather than acidity.
- In India, during 1974- 1984, although the strong acid ions exist, especially around urban areas, the highest pH was recorded as 6.5 to 7, are heavily neutralized.

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