ACID RAIN



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WHAT IS ACID RAIN?

The term "acid rain" refers to the various ways in which the acids formed in the atmosphere condense and fall on the earth. It is a rain or any other form of precipitation that is usually acidic, meaning that it has elevated levels of hydrogen ions (low pH). It is the deposition of a mixture from wet (such as rain, snow, sleet, fog, cloud water, dew, etc.) and dry (acidifying particles and gases) acidic components. Distilled water, once carbon dioxide is removed, has a neutral pH of 7. Liquids with a pH less than 7 are acidic, and those with a pH greater than 7 are alkaline. "Clean" or unpolluted rain has an acidic pH, but usually no lower than 5.7, because carbon dioxide and water in the air react together to form carbonic acid, a weak acid.

Carbonic acid then can ionize in water forming low concentrations of carbonate and hydronium ions. Unpolluted rain can also contain other chemicals which affect its pH (acidity level). A common example is nitric acid produced by electric discharge in the atmosphere such as lightning. Acid deposition as an environmental issue would include additional acids other than carbonic acid. The main pollutants responsible for the occurrence of acid rain are the oxides of sulphur and the oxides of nitrogen.

FORMATION OF ACID RAIN

Acid rain can be formed due to the following:

Natural sources such as bacterial decomposition, forest fires, volcanic eruptions and *man-made sources* such as power, industrial and smelting plants and automobile exhausts, produce oxides of sulphur and nitrogen which interact with water vapours in the presence of sunlight in the atmosphere to form sulphuric acid and nitric acid mist. The mist remains as vapours at high temperatures and condenses at low temperatures. The acids mix with rain (or snow, fog, etc.) and fall down on the earth resulting in "acid rain".



CHEMICAL PROCESSES INVOLVED IN FORMATION OF ACID RAIN

SULPHUR OXIDES

1) Sulphur dioxide $(S0_2)$ is produced industrially from the combustion of sulphurcontaining fossil fuels and smelting of sulphide ores.

 $\mathrm{S}(s) + \mathrm{O}_2(g) o \mathrm{SO}_2(g)$

2) Sulphur dioxide (S02) is then oxidized by sunlight to form sulphur trioxide (S03)

 $2\mathrm{SO}_2(g) + \mathrm{O}_2(g)
ightarrow 2\mathrm{SO}_3(g)$

3) The oxides react with water to form acids

S02(g) +H20(Z)
$$-t$$

H2S03(aq)S03(g)
+H20(Z) $-t$ H2S04(aq)

NITROGEN OXIDES

1) Nitrogen monoxide (NO) is produced from internal combustion of engines

 $\mathrm{N}_2(g) + \mathrm{O}_2(g) o 2\mathrm{NO}(g)$

2) Nitrogen monoxide (NO) oxidizes to form nitrogen dioxide

 $2\mathrm{NO}(g) + \mathrm{O}_2(g)
ightarrow 2\mathrm{NO}_2(g)$

3) Nitrogen dioxide reacts with water to form nitric acid (HNO_3) and nitrous acid (HNO_2)

$$egin{aligned} &2\mathrm{NO}_2(g)+\mathrm{H}_2\mathrm{O}(l)
ightarrow\mathrm{HNO}_3(aq)\ &+\mathrm{HNO}_2(aq) \end{aligned}$$

or it reacts with oxygen and water and becomes nitric acid

 $4\mathrm{NO2}_g + \mathrm{O_2}(g) + \mathrm{H_2O}(l)
ightarrow 4\mathrm{HNO_3}(aq)$

EMISSIONS OF CHEMICALS LEADING TO ACIDIFICATION

- The most important gas which leads to acidification is sulphur dioxide. Emissions of nitrogen oxides which are oxidised to form nitric acid are of increasing importance due to stricter controls on emissions of sulphur compounds. 70 Tg(s) per year in the form of sulphur dioxide comes from fossil fuel combustion and industry, 2.8 Tg(s) from wildfires and 7-8 Tg(s) per year from volcanoes.
- The principle natural phenomena that contribute acid- producing gases to the atmosphere are emissions from volcanoes. Thus, for example, fumaroles from the Laguna Caliente crater of Poas Volcano create extremely high amounts of acid rain and fog, with acidity as high as a pH of 2, clearing an area of any vegetation and frequently causing irritation to the eyes and lungs of inhabitants in nearby settlements. Acid-producing gases are also created by biological processes that occur on the land, in wetlands, and in the oceans. The major biological source of sulphur compounds is dimethyl sulphide.
- Acid deposits have been detected in glacial ice thousands of years old in remote parts of the globe.

- Nitric acid in rain water is an important source of fixed nitrogen for plant life, and is also produced by electrical activity in the atmosphere such as lightning.
- Soils of coniferous forests are naturally very acidic due to the shedding of needles, and the results of this phenomenon should not be confused with acid rain.
- The principle cause of acid rain is sulphur and nitrogen compounds from human sources, such as electricity generation, animal agriculture, factories, and motor vehicles. Electric power generation using coal is among the greatest contributors to gaseous pollution responsible for acidic rain.

 In the past, factories had short funnels to let out smoke but this caused many problems locally; thus, factories now have taller smoke funnels. However, dispersal from these taller stacks causes pollutants to be carried farther, causing



ACID DEPOSITION

WET DEPOSITION-

Wet deposition of acids occurs when any form of precipitation (rain, snow, and so on) removes acids from the atmosphere and delivers it to the Earth's surface. This can result from the deposition of acids produced in the raindrops or by the precipitation removing the acids either in clouds or below clouds. Wet removal of both gases and aerosols are of importance for wet deposition.

DRY DEPOSITION-

Acid deposition also occurs via dry deposition in the absence of precipitation. This can be responsible for as much as 20 to 60% of the total acid deposition. This occurs when particles and gases stick to the ground, plants or other surfaces.

CAUSES OF ACID RAIN

Acid rain is caused by the formation of nitric and sulphuric acids in our atmosphere. These compounds are strong acids and they are highly soluble in water and they dissolve in the water droplets within clouds. Sulphur and nitrogen oxides are lost from the atmosphere through dry deposition of sulphate and nitrate containing particulate matter and through the precipitation of solutions of sulphuric and nitric acids.

Rotting vegetation and erupting volcanoes release some chemicals that can cause acid rain, but mostly acid rain is a product of human activities. The biggest sources are coalburning power plants, factories and automobiles. When humans burn fossil fuels, sulphur dioxide and nitrogen oxides are released into the atmosphere. Those air pollutants react with water, oxygen and other substances to form airborne sulphuric and nitric acid. Winds may spread these acidic compounds through the atmosphere and over hundreds of miles. When acid rain reaches Earth, it flows across the surface in the runoff water, enters water systems, and sinks into the soil.

Causes Of Acid Rain

NATURAL CAUSES:Volcanic emissions.
Biological processes.
Lightning.

ANTHROPOGENIC CAUSES:Factories (industrialization)
Motor vehicles, automobile exhaust.
Coal based power plants.
Domestic fires.
Smelters.



EMISSION, DEPOSITION AND THE OCCURRENCE OF ACID RAIN

ADVERSE AFFECTS OF ACID RAIN

Acid rain has been shown to have adverse impacts on forests, freshwaters and soils, killing insect and aquatic life-forms as well as causing damage to buildings and having impacts on human health.

Surface waters and aquatic animals

- Not all fish, shellfish, or the insects that they eat can tolerate the same amount of acid; for example, frogs can tolerate water that is more acidic (i.e., has a lower pH) than trout.
- Both the lower pH and higher aluminium concentrations in surface water that occur as a result of acid rain can cause damage to fish and other aquatic animals. At pH lower than 5 most fish eggs will not hatch and lower pH can kill adult fish. As lakes and rivers become more acidic biodiversity is reduced. Acid rain has eliminated insect life and some fish species, including the brook trout in some lakes, streams, and creeks in geographically sensitive areas, such as the Adirondack Mountains of the United States.

However, the extent to which acid rain contributes directly or indirectly via runoff from the catchment to lake and river acidity (i.e., depending on characteristics of the surrounding watershed) is variable. The United States Environmental Protection Agency's (EPA) website states: "Of the lakes and streams surveyed, acid rain caused acidity in 75% of the acidic lakes and about 50% of the acidic streams".



Soils

- Soil biology and chemistry can be seriously damaged by acid rain. Some microbes are unable to tolerate changes to low pH and are killed. The enzymes of these microbes are denatured (changed in shape so they no longer function) by the acid. The hydronium ions of acid rain also mobilize toxins, such as aluminium, and leach away essential nutrients and minerals such as magnesium.
- 2 H⁺ (aq) + Mg²⁺ (clay) ⇒ 2 H⁺ (clay) + Mg²⁺ (aq)Soil chemistry can be dramatically changed when base cations, such as calcium and magnesium, are leached by acid rain thereby affecting sensitive species, such as sugar maple (Acer saccharum).

Forests and other vegetation

 Adverse effects may be indirectly related to acid rain, like the acid's effects on soil (see above) or high concentration of gaseous precursors to acid rain. High altitude forests are especially vulnerable as they are often surrounded by clouds and fog which are more acidic than the rain.

Other plants can also be damaged by acid rain, but the effect on food crops is minimized by the application of lime and fertilizers to replace lost nutrients. In cultivated areas, limestone may also be added to increase the ability of the soil to keep the pH stable, but this tactic is largely unusable in the case of wilderness lands. When calcium is leached from the needles of red spruce, these trees become less cold tolerant and exhibit winter injury and even death.



Ocean acidification

- Acid rain has a much less harmful effect on the oceans. Acid rain can cause the ocean's pH to fall, making it more difficult for different coastal species to create their exoskeletons that they need to survive. These coastal species link together as part of the ocean's food chain and without them being a source for other marine life to feed off of more marine life will die.
- Coral's limestone skeletal is sensitive to pH drop, because the calcium carbonate, core component of the limestone dissolves in acidic (low pH) solutions.

Human health effects

 Acid rain does not directly affect human health. The acid in the rainwater is too dilute to have direct adverse effects. The particulates responsible for acid rain (sulphur dioxide and nitrogen oxides) do have an adverse effect. Increased amounts of fine particulate matter in the air contribute to heart and lung problems including asthma and bronchitis.

Other adverse effects

 Acid rain can damage buildings, historic monuments, and statues, especially those made of rocks, such

as limestone and marble, that contain large amounts of calcium carbonate. Acids in the rain react with the calcium compounds in the stones to create gypsum, which then flakes off.

 CaCO₃ (s) + H₂SO₄ (aq) ⇒ CaSO₄ (s) + CO₂ (g) + H₂O (I)The effects of this are commonly seen on old gravestones, where acid rain can cause the inscriptions to become completely illegible. Acid rain also increases the corrosion rate of metals, in particular iron, steel, copper and bronze.

Acid Rain Effects on Buildings

- Acids have a corrosive effect on limestone or marble buildings or sculptures. It is well established that either wet or dry deposition of sulfur dioxide significantly increases the rate of corrosion on limestone, sandstone, and marble.
- sulfur dioxide plus water makes sulfurous acid

 $SO_2 + H_2O --> H_2SO_3$

sulfur trioxide plus water makes sulfuric acid $SO_3 + H_2O --> H_2SO_4$

- The sulfuric acid then further reacts with the limestone in a neutralization reaction. Limestone: $CaCO_3 + H_2SO_4 --> CaSO_4 + H_2CO_3$ $H_2CO_3 --> CO_2 gas + H_2O$
- The calcium sulfate is soluble in water and hence the limestone dissolves and crumbles.

Effects on Sculptures:

There are many examples in both the U. S. and Europe of the corrosive effects of acid rain on sculptures. Many sculptures have been destroyed, a few have been preserved by bringing them inside.

DEMONSTRATION-

The above reactions can be simulated in a demonstration by putting an egg in vinegar. The eggshell is made from the same material as limestone - calcium carbonate. The acetic acid produces an immediate bubbling as the carbonate converts first to carbonic acid and then to carbon dioxide bubbling. Within an hour the egg shell will be dissolved.



PREVENTIVE MEASURES

Technical solutions

Many coal-firing power stations use fluegas desulphurization (FGD) to remove sulphur-containing gases from their stack gases. For a typical coal-fired power station, FGD will remove 95% or more of the SO₂ in the flue gases. An example of FGD is the wet scrubber which is commonly used. A wet scrubber is basically a reaction tower equipped with a fan that extracts hot smoke stack gases from a power plant into the tower. Lime or limestone in slurry form is also injected into the tower to mix with the stack gases and combine with the sulfur dioxide present. The calcium carbonate of the limestone produces pH-neutral calcium sulphate that is physically removed from the scrubber. That is, the scrubber turns sulphur pollution into industrial sulphates.



- In some areas the sulphates are sold to chemical companies as gypsum when the purity of calcium sulphate is high. In others, they are placed in landfill. The effects of acid rain can last for generations, as the effects of pH level change can stimulate the continued leaching of undesirable chemicals into otherwise pristine water sources, killing off vulnerable insect and fish species and blocking efforts to restore native life.
- Fluidized bed combustion also reduces the amount of sulphur emitted by power production.
- Vehicle emissions control reduces emissions of nitrogen oxides from motor vehicles.

International treaties

 International treaties on the long-range transport of atmospheric pollutants have been agreed. for example, the 1985 Helsinki Protocol on the Reduction of Sulphur Emissions under the Convention on Long-Range Transboundary Air Pollution. Canada and the US signed the Air Quality Agreement in 1991. Most European countries and Canada have signed the treaties.

Emissions trading

 In this regulatory scheme, every current polluting facility is given or may purchase on an open market an emissions allowance for each unit of a designated pollutant it emits. Operators can then install pollution control equipment, and sell portions of their emissions allowances they no longer need for their own operations, thereby recovering some of the capital cost of their investment in such equipment. The intention is to give operators economic incentives to install pollution controls.

- The first emissions trading market ٠ was established in the United States by enactment of the Clean Air Act Amendments of 1990. The overall goal of the Acid Rain Program established by the Act is to achieve significant environmental and public health benefits through reductions in emissions of sulfur dioxide (SO₂) and nitrogen oxides (NO_x), the primary causes of acid rain. To achieve this goal at the lowest cost to society, the program employs both regulatory and market based approaches for controlling air pollution.
- Using alternative energy sources, such as alternatives to burning of fossil fuels like compressed natural gas (CNG) or use of cleaner energy sources such as hydro power or wind energy to minimise pollution.
- Usage of technical devices such as catalytic convertors, which can reduce nitrogen oxide emissions from automobiles. Usage of electrostatic precipitators in industries can also prove to be highly beneficial.



Drive Less

Limit long drives

Car-pool

Use low-energy light bulbs

Reduce, Re-use, Recycle Don't use air-con as much



Use a pool cover

What can be done to prevent acid rain?

Lakes with acid in them can be treated by putting large amounts of alkaline substances into them. This process is called liming. You can also use coal with low sulphur content to reduce the amount of chemicals going into the atmosphere. Reducing the amount of all chemicals going into the air will also

Preventing Acid Rain

- Using low sulphur fuels, such as natural gas or low- sulphur coal can reduce acid precipitation
 - -These are less plentiful and more costly to use
- Smoke stacks that remove sulphur dioxide Before it enters the air are also effective
- Reducing automobile use and keeping cars properly tuned can help, too

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