Acid Rain

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Contributor: Ille Gebeshuber

Acid rain has an acidity that is higher than that of normal rainwater. Normal rainwater is not neutral (which would be pH 7) but slightly acidic (it has a pH < 5.5), because some of the carbon dioxide CO_2 dissolved in the water is present as carbonic acid H_2CO_3. In acid rain, chemicals from pollution and natural causes such as volcanic eruptions and emissions from vegetation increase the acidity of the water to as low as pH 4.4 to 4 (as measured in the 1990s in various places). Such acidic rainwater is dangerous for people, vegetation, water bodies including the oceans and its inhabitants, buildings and soil. Since the pH scale is logarithmic, a change from 5.5 to 4.5 means a tenfold increase in acidity. The three main pollutants that cause acid rain are the nitric oxides NO and NO2 (summarized as NOx) and sulfur dioxide SO2. These substances react with water to nitric acid HNO3 and sulfuric acid H_2SO_4. In the 1980s, in nearly all of Northern Europe and in the Northern United States, suddenly and unexpectedly, whole forests began to die (this effect got to be known as forest dieback). German forests especially experienced severe damage: from 8% in 1982 it increased to 50% in 1984, and stayed as such till 1987. The damage occurred amongst various tree species. Researchers established connections of this damage to acid rain. The mandatory installment of sulfur filters in coal power plants and of catalytic converters in cars in various industrialized countries reduced air pollution with the chemicals related to the formation of acid rain, and, although the forests are still not in perfect shape (about 20% are heavily impaired) a complete death was prevented.

Keywords: acid rain ; environmental engineering ; pollution

1. History

Historically, already the Old Romans realized that trees were dying in areas next to factories that were processing galena (lead sulfide). The relation between air pollution and acid rain was first discovered 1852 in London (which was very polluted that time) by the Scottish chemist Robert Angus Smith (1870-1884) [1]. The British government in 1863 passed the Alkali Act to curb acidic emissions, and Smith was installed as the first Chief Inspector of the Alkali Inspectorate.

Forest dieback was first seen in Germany as well as in Middle, Eastern and Northern Europe[2], in the mid 1970s. Already then various stakeholders demanded cleaner air. At the end of the 1970s, large-scale forest dieback and sharply increased acidification of lakes was correlated with acid rain. Some lakes in Sweden looked crystal clear - they contained no more life anymore; their pH was equivalent to the pH of acetic acid (pH 3).

2. Pollutants cause acid rain

Various pollutants cause acid rain. Reasons for acid rain are anthropogenic and natural. Anthropogenic causes include volatile organic components (VOC) from industry, households, manufacturing, transport, etc., sulfur dioxide SO2 (a toxic gas), NOx and mercury (a potent neurotoxin). Burning coal, gas or oil that has impurities of sulfur results in SO2emissions to the atmosphere and subsequent transformation of SO_2 to in sulfuric acid in aqueous environments (such as raindrops, dew, fog, etc.). Another anthropogenic source of SO2 is from the roasting in the mining industry in the course of the extraction of metals from sulfide ores. In the roasting process, the ore is heated at high temperature in the presence of air, resulting in formation of metal oxides and SO_2 as waste gas. In some cars, especially in industrialized Western countries, flue-gas desulfurization is used to remove the sulfur from the exhaust gases. Natural VOC emissions come from terrestrial plants and marine organisms. Natural sources for SO2 comprise volcanoes and geothermal hot springs. NOx are generated whenever high temperature combustion processes take place in the presence of nitrogen. Since nitrogen makes up 78% of our atmosphere, this is always the case when something combusts in air at temperatures above 1800^{o}C. The very high local temperature at lightning is also conducive to NOx generation, as are geothermal springs and some decomposer bacteria that process organic nitrogenous material in the soil. The pollutants are transported in the air over wide distances and can cause effects in far away places.

3. Effects of acid rain

Effects of acid rain are damages on the leaves and in the root system (death of fine roots, reduced reproductive capacity and less mycorrhization. Mycorrhiza denotes the symbiotic association of a fungus and the roots of higher plants that is necessary for nutrient uptake and therefore healthy growth [3]. Plants that are already damaged by acid rain are more sensitive for fungal infections, insect attacks and epidemics. Further effects of acid rain are acidification of soil and water bodies (rivers, streams, lakes, oceans), yielding alterations of sensitive ecological balances. Reaction products of neutralization reactions in the soil contain important potassium, magnesium and calcium minerals that can be washed out, decreasing the nutrient content of soil and loosing its important buffer capabilities, resulting in drastically reduced pH. At low pH, certain metals such as aluminum and irons ions are released from the rock part of the soil; this damages soil and plants, destructs roots, harms plant growth and yields higher disease susceptibility.

Acid rain has effects on soil, cultural heritage structures, water bodies, the sea (yielding a potential collapse of the marine ecosystem due to acidification) and plants, especially the leaves and the mycorrhiza of trees. Acid rain does not directly kill the trees, but rather long

term leaching of nutrients from the soil causes the death. The restoration of soil nutrients is very slow, since it mainly happens due to rock weathering. Acid rain causes weathering of limestone statues, carvings and facades to gypsum by sulfuric acid, which subsequently crumbles away, causing irreversible damage to cultural heritage; a similar effect takes place in sandstone artifacts.

4. Reactions and approaches for acid rain

The related chemical reactions that take place in rainwater are as follows:
Carbon dioxide plus water gives carbonic acid, $CO_2 + H_2O = H_2CO_3$; nitrogen dioxide plus water gives nitrous acid and nitric acid, $2\ NO_2 + H_2O = HNO_2 + HNO_3$; nitrogen oxide plus molecular oxygen plus water gives nitric acid, $4\ NO + 3\ O_2 + 2\ H_2O = 4\ HNO_3$; sulfur dioxide plus water gives sulfurous acid, $SO_2 + H_2O = H_2SO_3$; sulfurous acid plus water gives molecular hydrogen and sulfuric acid, $H_2SO_3 + H_2O = H_2 + H_2SO_4$; and sulfur trioxide plus water gives sulfuric acid, $SO_3 + H_2O = H_2SO_4$. These acids yield increased acidity of the rain, and subsequent damages to ecosystems and cultural heritage.

The US installed the Clean Air Act in 1970, and strengthened it in 1990. The United State's acid rain program resulted in a 33% decrease in sulfur dioxide emissions between 1983 and 2002. In the Northeastern United States, the soil is still too acidic, particularly in New York, Vermont, New Hampshire and Maine, but shows first signs of recovery [4]. Currently, China is the country with the highest SO2 emissions: since the year 2000 they have increased by 27%.

Major research approaches were undertaken as soon as the severe forest dieback started in Germany and the Northeastern United States. Exhaust gas desulfurization have been installed in German power plants (which were the main emitters of SO2) from the beginning of the 1980s.

Countermeasures against acid rain comprise liming of soils, desulfurization of exhaust gases, e.g. with filters in industrial facilities and catalytic converters in cars (in some Western industrial nations) and generally, resourceful energy management yielding lower emissions and longer preservation of resources. Desulfurization with filters is only possible in stationary applications. The gypsum that is produced from the desulfurization in industrial plants can be used for walls and construction materials, or be disposed safely. In aircraft, cars and other similar applications, sulfur has to be removed from the fuel before burning. However, mainly industrial countries apply such measures, and impose various thresholds while the developing countries still emit high amounts of chemicals polluting the air, resulting in smog and acid rain, also at places far away from the origin of the pollutant (pollution travels long distances in the atmosphere). Liming fertilizes and increases the pH of soil: helicopters and aircraft are used to release grounded limestone above forests and ground. Soil liming is expensive, and large amounts of limestone are needed. Furthermore, it only fights the effects and not the underlying causes; law in Switzerland prohibits calcification, because of potential adverse effects to the environment.

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