ACID RAIN, CAUSES, EFFECTS AND CONTROL STRATEGIES

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Review

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Abstract

Acid rain is one of the major environmental threats since 19th century. This paper reviews the 2012 progress report of US EPA (2013) and summarizes the issue in various environmental aspects. Significant reduction in the SO_2, NO_x emission and deposition of acid have been occurred via the active implementation of Clean Air Interstate Rule (CAIR), Acid Rain Program (ARP) and NO_x budget training program(NBP). Cross state air pollution rule and litigation (CSAPR) implemented by US EPA since 2011, reduces the cross boundary movement of effluents between US and Canada. US national composite means of average SO_2 annual mean ambient concentration has been declined by 85% in the period between 1980 and 2012.

Keywords: Acid rain, acidification, acid deposition, effects of acid rain and acid rain control.

Introduction

The effect of acidification has been sighted all over the world such as deleterious ecological effects such as reduced reproduction of aquatic fish species, dieback and stunted growth in plants, accumulation of toxic aluminum and heavy metals in soil and water bodies, biodiversity loss including corals and shellfish, degrade to the manmade structures made up of marble and stone and corrosion of metal structures. According to 2012 progress report of US EPA (2013), The Impacts of major global environmental problems such as acid rain, acid deposition, depletion of ozone layer and health and environmental effects of particle matter are declining. Report further added though there is a significant reduction in the SO_2, NO_x emission and deposition of acid have been occurred via the active implementation of Clean Air Interstate Rule (CAIR), Acid Rain Program (ARP) and NO_x budget training program(NBP) the current emission levels are not sufficient to attain full recovery of acid –sensitive ecosystem. However, national composite means of average SO_2 annual mean ambient concentration has been declined by 85% in the period between 1980 and 2012 (see Figure 1&2).

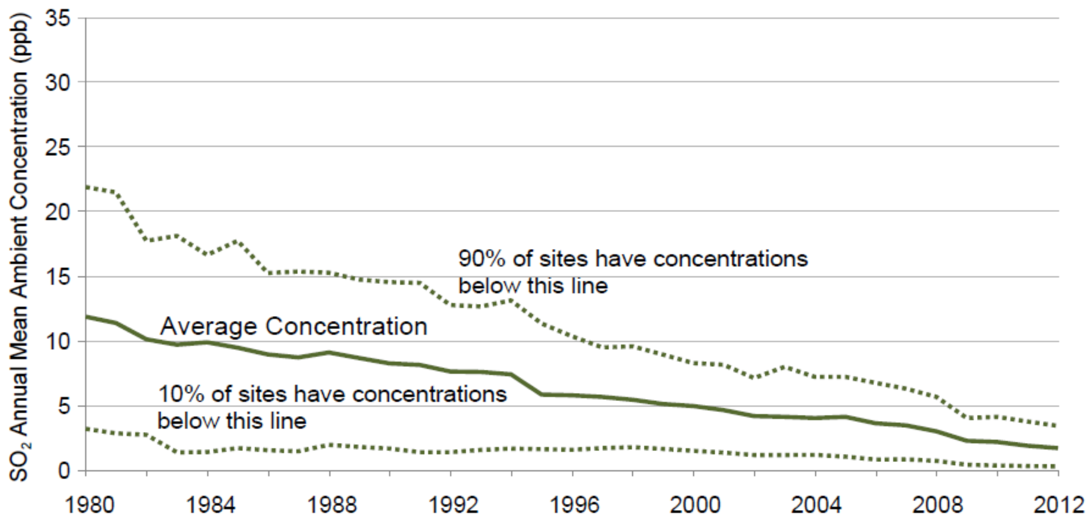


Figure 1. National SO_2 air quality USA (Source: US EPA, 2013).

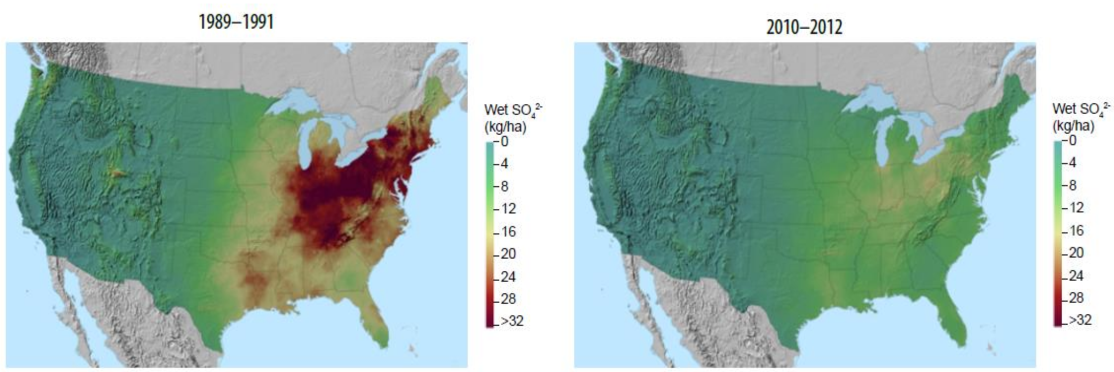


Figure 2. Three year mean of wet sulphate deposition in USA in different periods (Source: US EPA, 2013).

Acid rain History

First observation of acid rain was recorded in the mid-19th century in Europe. Signs of leaf deterioration were found in forest located downwind of large industrial areas. In 1872 an English scientist Robert Angus Smith introduced the term "acid rain" as he noticed that acid precipitation damages the leafs. First attempt to reduce the acid rain was took place in 1936 at Battersea plant in London, UK, however after 1970 the severity of the issue had been increased. Increased utilization of coal fuel has resulted in elevated levels of SO_2 concentrations in the atmosphere, thus, after 10 years of continuous National Acidic Precipitation Assessment Program (NAPAP), US congress has passed acid deposition act in 1980. This enlarged the monitoring site network for dry deposition and the effects of acid rain on monuments, fresh water, terrestrial ecosystem and buildings. Funded studies were carried out on atmospheric process and potential control programs. According to NAPAP's first assessment report in 1991 on acid rain, about 5% of New England's (in USA) lakes were acidic and issues such as changes biochemical pattern in soil, fresh water bodies and damages to the manmade structures were observed.

By 1990 US congress has passed amendments to the Clean Air Act. Title IV of the amendment consist control measures to SO_2 and NO_X. This was implemented in 2 phases aiming to decreases the total SO_2 emission by 10 million tons. Phase 1(from 1995) limited the SO_2 emission from 110 of the largest power plants; Phase II (since 2000) affects most of the other power plants in US. In the period of 2000 to 2006 SO_2 emission had declined by 54% (from 211,000 tons to 96, 500 tons). Similarly, several programs were carried out since 1999 to reduce NO_x from factories and automobiles. By March 2005 US EPA has issued Clean Air Interstate Rule (CAIR) this reduces the pollution from power plant emission from one state to another (Adapted from US EPA, 2014).

Acid rain

Acid rain caused by emission of SO_2 and NO_X from various sources to the atmosphere and they dissolve in atmospheric water and produce acids in the rain water. SO_2 does not react much in the atmospheric chemicals but it can travel quicker to long distances and when get contact with ozone or hydrogen peroxide it produces SO_3, which is highly soluble in water and form sulphuric acid. Sulphur dioxide is naturally produced by volcanic eruptions, sea spray, planktons, rotting vegetation and forest fires. Anthropogenic sources 69.4 % of Sulphur dioxide released from industrial combustion (point sources), house hold heating of fire wood and coal (area or non-point sources) and 3.7% from transportation (mobile sources). Coal burning sources such as coal power plants, coal powered engines in vehicles, smelting of metal ore, production of iron and steel, process pure metal (obtaining pure metals of Zn, Ni & Cu) oil refinery, domestic and industrial boilers, it also released from the manufacture of sulphuric acid during the production of disinfectants, bleaching agents and fumigants. NO_X is naturally produced by lightening, bacterial action, forest fire and volcanoes, manmade emission are by automobiles (43%) and fertilizer industries, utility plants and other industrial combustion (32%) ('Causes and Effects of Acid Rain', 2012).

Acid deposition can be classified as wet deposition such as acid rain, snow, sleet and fog or dry deposition such as deposition as particulate matter even less then PM 2.5. Effects of acid rain can either chronic or episodic. Chronic acidification is a long term effect due to years of acid rain, Episodic acidification is due to heavy rain storms, it also occur in spring as concentrated nitrate and sulphate in lower layer of snow pack get released when snow get melts.

Acid rain increases nitrate levels in soil, leading to nitrogen saturation in soils. Nitrate ions remove additional calcium and magnesium from soil, excess nitrogen also leads to eutrophication in water bodies. Trees starve for aluminum and other minerals as aluminum of soil get converted to aluminum nitrate or sulphate when get absorbed by trees cause harmful effects. In dry deposition sulphate and nitrate ions fall as small particles without dissolving in water, about 20-60 % of the total deposition is dry deposition.

Effects on surface waters

Acid rain releases aluminum from the soil into lakes and streams which is toxic to many aquatic organisms. According to natural surface effects of deposition about 75% of the lakes and about 50% of the streams in U.S are acidified as the pH falls below 5. Similarly, in eastern Canada about 14,000 lakes were reported as acidic. Soft waters with low alkaline metal ions are more susceptible to acidification.

Acidification increases the release of aluminum from granite rocks. Aluminum gives chronic stress lower bodyweight or smaller the size thus fish become inefficient in competing for food and habitat. In addition, most of the eggs do not hutch, some adult fish may die, and partially sensitive species such as snails and clams cannot tolerate pH below 5.5. However, in case some species such as frog though it can tolerate lower pH but their prey species such as mayfly cannot and decrease in prey population subsequently lower the frog population as well. Interconnections and interdependencies in the food chain affect the ecosystem. Release of toxic heavy metal ions such as ions of copper, cadmium, nickel, chromium, cobalt, lead and zinc in the water body reduces the development and growth of the fish. Acidic condition together with toxicity of heavy metals reduced the growth of the fish and increases the stress, this make the fish less immune, thus become more susceptible to diseases, kills the eggs and larval stages, reduces spawning and reproductive success. Nitrogen dioxide deposition in water bodies is another major reason for episodic acidification, about 10- 45 % of the nitrogen dioxide reaching water bodies are airborne and they are released to atmosphere mainly from anthropogenic sources.

Acidification effects shell forming mollusks, shell fish, coral reefs, sea grass beds and juvenile stages of aquatic organisms. In case of shell fish and corals their calcareous shell or skeleton get dissolved in acidic environment. Reduced pH encourages the growth of acid tolerant forms such as some bacteria and protozoa. Acid rain is not the sole cause of acidification, some swamps, bogs and marshes naturally have low level of pH. In addition, acid water runoff from coal mines could reach the surface waters bodies e.g. fish kills in Pennsylvania, West Virginia and Virginia surface waters in US and Canada (see Figure 3).

a) 

b) 

Figure 3. a) A signpost in Nova Scotia, Canada proclaims effects of acid rain on salmon fishery (source: 'Water Encyclopedia', 2015) b) fish kill due to acidification of river ('Juliana Muna', n.d.) Adapted from 'Effects of Acid rain' US EPA (2012).

Effects on forest

Acid precipitation on vegetation reduces the photosynthesis and growth also increase the susceptibility to draught and disease, process called 'dieback' it causes browning of leaf and fall off (see figure 4), in addition, effects such as thinning of annual growth ring and reduction in biomass (due to reduced growth), it also damage the fine root system, affect root mycorrhiza (due to increase in Al and acidity) and decrease the lichens, reduction of soil fertility as potassium leached out of the soil, phosphorus is also reduced this reduces the fruit production, toxic metals such as zinc and aluminum accumulates, aluminum toxicity retard root growth and causes loss of chlorophyll (Sharma and Kaur, 1994). Young seed lings are more susceptible than older plants (Sthana and Asthana, 2001), Adapted from Verma *et al.* (2010). Soil acidity can be overcome by addition of lime, whereas alkalinity of limestone neutralizes the negative ions in acid.

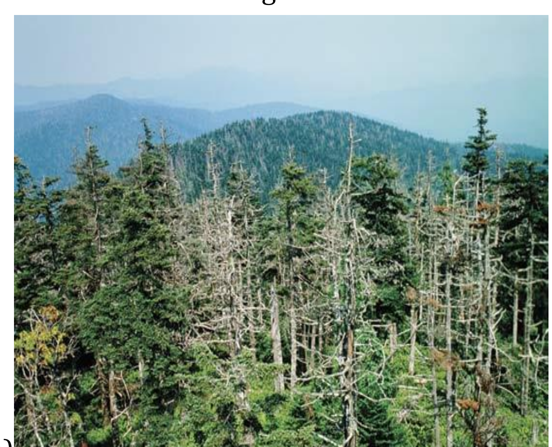
a) 
b) 

Figure 4. a) Branches of trees in Germanys Black forest showed needle lose and yellowed boughs (branch on left) b) Affected trees in the Great Smoky Mountains (Source: Butler, 2014).

Effects to manmade structures

Nitric acid, sulphurus and sulphuric acid concentrated in dew or rain deposited on automotive coating causes fading of the paint, thus the modern vehicle manufactures are coating with acid resistant top paint and modern buildings are painted with acid resistant exterior wall paints. Metal such as bronze and alloy structures get corrode, acid also degrade marble (limestone) architectures see figure 5.

a)  b) 

Figure 5. Affected a) monument -statue on left taken in 1908 and right taken in 1968; b) affected building (Butler, 2014).

Visibility impairment

Acid fog particularly particles of suphur dioxide and sulphur trioxide reduces the visibility by 50-70% in eastern U.S.A.

Health effects

The causing agents of acid rain SO_2, SO_3 and NO_x may affect the health particularly SO_2 & SO_3 effect on asthma and emphysema patients and increase the incidence (Phamornsuwana, n.d.). Particulate deposition of particles less than PM 2.5 can even reach the blood stream via lungs and cause harmful effects such as lung cancer (Particulates, n.d.).

Liming

Lime stone is added to neutralize the acid in the water body; it also facilitates the release of locked nutrients of the acidified mud bottoms by neutralizing the ions. Essential nutrients such as phosphorus and other limiting minerals get released and thereby planktons and plant productivity get increased. In addition it also reduces the toxic effect of heavy metals which are normally high in acidified waters. Thus, bring back the aquatic life in its norm level. Furthermore, calcium in lime supports the mollusks population in developing their calcareous exoskeleton. As calcium and phosphorus are essential plant nutrients, liming enhance the primary production and subsequently the entire community of the water system, increase in rooted plants also elevates the quality of breeding and nursery ground, thus increases the chances of survival of the juvenile forms. It was observed liming improved the sport fishery in US. However, liming is not recommended at all, particularly in portable waters, as it increase turbidity and cloudiness of the water temporarily, increases algal blooms and alters the taste and mineral content of the water. Liming process can either be protective (preventive) liming or mitigatory liming; preventive liming is applied on sensitive soft water lakes to increase their buffering capacity to acidification, on the other hand mitigatory liming used to bring the acidified lakes and ponds back to the normal condition by neutralizing the acidity. Agricultural lime ($CaCO_3$) is recommended type generally in use, Dolomite lime ($MgCO_3$) is impure substance, Quicklime (CaO) and Hydrated lime ($Ca(OH)_2$) are caustic, used in acidified lakes in little quantities and if applied in high amount results fish kill and Soda ash (Na_2CO_3) also usable but it is less preferred due to its high cost. In addition factors such as hardness of the water, existing ph, alkalinity, chemistry and acidity of bottom mud, temperature and water quality, density and type of aquatic plants, targeted pH, type, type of limestone (purity and particle size) amount and flushing rate to be considered in liming applications. Treatment can be extended in several additional applications if required, limestone is applied by boat or barge (flushing lime at high pressure), by snow mobile tractor or spreader on ice covered lakes (lime dissolved on surface ice and subsequently reaches the waters), shore land tractor, feeder stream application and by air (plane or helicopter) for huge area of application (Helfrich *et al.*, 2009).

Reduce acid rain

This can be done either fuel switching or scrubbing. Fuel switching includes limiting the use of Sulphur containing fuels such as coal or switching to low sulphur containing coal or oil, switching to alternative energy sources such as using gas boilers instead of coal or oil boilers, nuclear power generation, using renewable energy sources such as wind, air, wave and geothermal energy. Use solar batteries, fuel cells, natural gas and electric motor vehicles. EPAs energy star program, reduce carpool by using public transportation, maintain the vehicle for low NO_x emission and factory boilers such as clean the stacks and exhaust pipes. Use energy efficient boilers and using filters or scrubbers to catch the oxides of sulphur and Nitrogen in industrial effluents and vehicles, defining the right stack height, in 1970s average stack height was 150-300m common in smelters and thermal electric generating plants in Europe and North America, however later 400m super stacks are introduced which reduces the local pollution by emitting pollutants outside the boundary layer (Kemp, 2004).

Scrubbing includes use of electrostatic precipitators where positively charged sulphur particles are get attracted by negatively charged plate or chemical means either wet scrubbing such as injecting water or chemical solution such as flue gas desulphurization (FGS) which has the SO_2 removal rate between 80-95% or dry scrubbers such as lime injection multi stage burning (LIMB) or fluidized bed combustion (FBC or circulation dry scrubber) that react with sulphur in the absence of water medium. To reduce NO_x methods such as selective catalytic reduction process (SCR) which has the NO_x reduction rate up to 80% where injection of reactive chemicals such as ammonia reacts with NO_x and convert into N_2 and O_2, changing air to fuel ratio and changing the combustion temperature. In automobile NO_x reduction, catalytic converters are used e.g. three way catalytic converters (1. conversion of NO_x into N_2 and O_2, 2. conversion of CO into CO_2 3. conversion of hydrocarbons into CO_2 and water) ('Reducing Acid Rain' US EPA, 2012). Title IV of the 1990 clean air act amendments of the EPA's acid rain program has set a cap for the volume of SO_2 emitted by power plants, it also take measures to reduce the NO_x emission. Program also used continuous emission monitors (CEMs) which monitor the sulphur content of the fuel, amount of fuel used, and the rate of SO_2 emission.

Each plant was given a number of "allowances" based on annual emission of SO2 in the period of 1985 to 1987 program also encouraged the use of renewable energy and conservation of energy. Allowances are also given for solar, wind and geothermal plants. Title V acid rain permit program made the plant or industrial owners to get legal permission via applying to the appropriate agency. Acid rain program was geld in two phases, Phase I held in the period of 1995 to 2000 and phase II is being conducted since year 2009 (see figure 6 and 7 for overall trends in SO2 and NO_x emission respectively in New England). Similar program is being done in Asia, Regional Acidification Information and Simulation programme, where the threat is increasing in developing countries as their energy need is now increased (Hunt, 1992 as cited in Kemp, 2004). NO_x Budget Trading program (NBP) operated from 2003 to 2008 this cap and trade programmes where NO_x reduction is required by the industries in eastern US in the summer season (see figure 7& 8).

To reduce the effects of trans boundary acid deposition US and Canada have signed in a bilateral air quality agreement in 1991 and an integrated atmospheric deposition network (IADN) was established to collect and manage data on the same. Similarly, Cross state air pollution rule and litigation (CSAPR) implemented by US EPA since 2011, which reduces the emissions that cross state boundaries significantly.

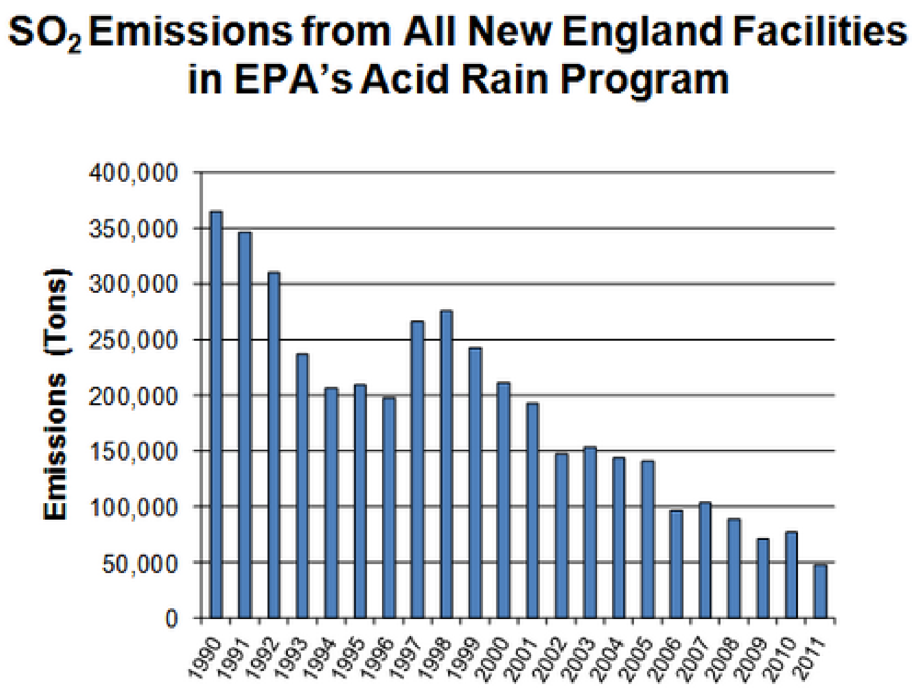


Figure 6. SO_2 Emissions in the period of 1990-2011 in New England, USA. (Source : 'Trends', 2014)

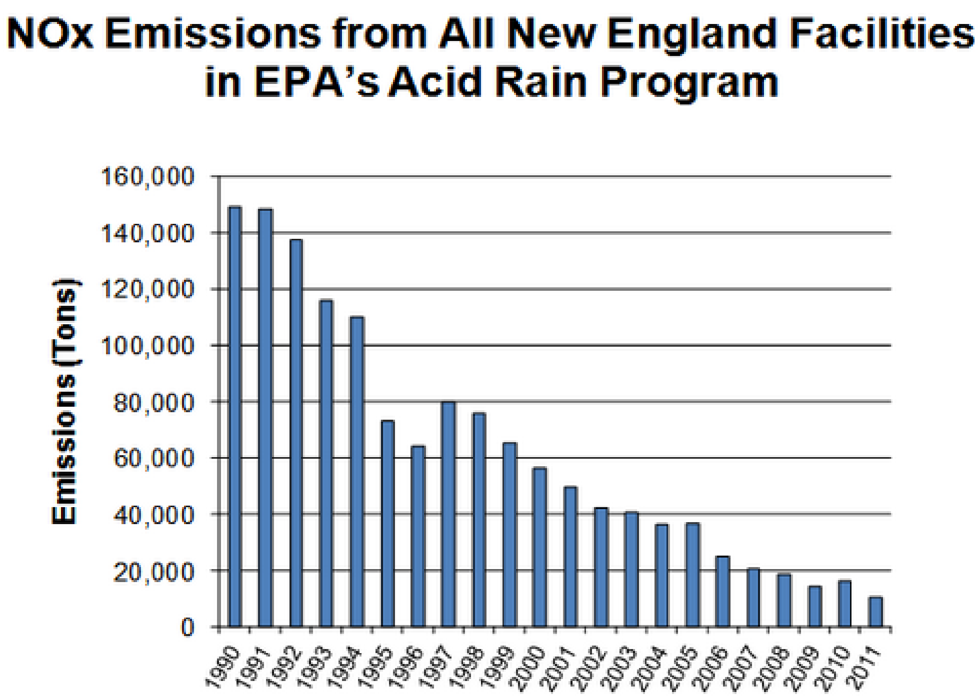


Figure 7. NO_x emission in the period of 1990-2011 in New England, USA (Source: 'Trends', 2014).

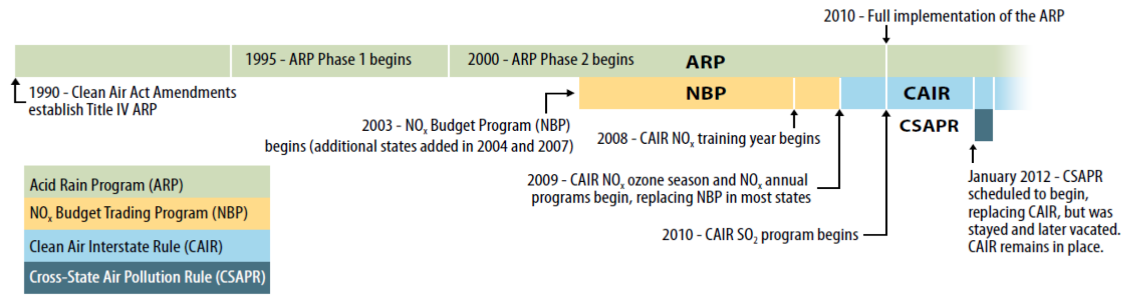


Figure 8. Important milestones of acid rain control mission (Source US EPA, 2013).

Monitoring Acid rain

During monitoring Wet and dry deposition collectors are used in monitoring of the acid deposition by the national acid deposition Program (NADP) see Figure 1, container on the left collects rain water and the right container to measure the dry deposition (see figure 9). Though it is the traditional method, nowadays sensors based on electrical resistance are used worldwide.

Figure 9. Wet and Dry deposition collector (Source: NADP, n.d.).

Other related pollution problems

Sulphur and nitrate effluents forms small particles PM 2.5, they can irritate eyes and nasal cavity, also particle matters of PM2.5 do reach the blood and adversely affect the heart and lungs. Formation of Smog due to the effluents of coal burning affect London in 1952 (Great smog) which killed about 4000 people and injured more than 100 thousand due to its affect to the respiratory system such as hypoxia, pneumonia and bronchitis 'Great smog', n.d.). Particles in smog affects visibility as it scatter the light. In 2013 cities of Beijing, Tianjin and Hebei experienced the hazardous effects of PM2.5. Smog affects severely in cities where coal combustion is increasingly high. (Zhang, 2014) (See Figure 10).

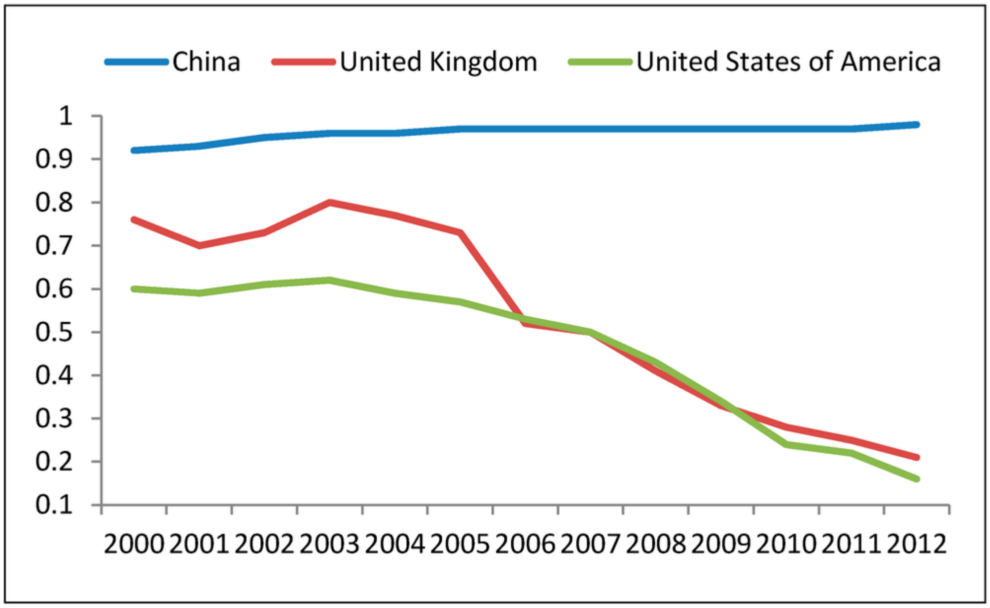


Figure 10. Proportion of population expose to PM2.5 concentration of 10 µg/ m^3

(Source: Hsu *et al.,* 2014 as cited in Zhang, 2014).

Similarly, brown cloud of Asia affected the northern Indian Ocean closed to India and Pakistan in 1999, 2004 and 2007 formed due to particle dust form industrial, transport and wood fire emission ('Asian brown cloud', 2015) and Artic haze consists of reddish brown clouds which mostly consist sulphur (90%) and carbon, this occurs in the arctic region due to limited amount of snow or rain precipitation or turbulent wind flow for dispersal of pollutant in the spring and stays more than a month. Ground level Ozone is another issue, which is a secondary pollutant result from the reaction between NO_x and volatile organic compounds in the atmosphere. Ground level Ozone reduces the function of lungs and inflame the lining of lung tissue, it also worsen the effects of Asthma, bronchitis and emphysema. (Adapted from 'Ground level Ozone' US EPA, 2014)

Coal plants and other fossil fuels also emits mercury and cadmium which are a hazardous heavy metals can accumulate in living cells and undergo bio magnification and affect the top level carnivores including man. In addition several hazardous compounds such as benzenes and formaldehyde are also found in smoke. Large amount of greenhouse gases such as NO_x and CO_2 are released by industries and vehicle effluents, which causes global warming and climatic change.

Conclusion

Acid rain is one of the world's major environmental problems since 19th century. Coal burning is the major cause of SO_2 production and also vehicle emission and various fossil fuel based power generation emits NO_x. Both SO_2 and NO_x produces suplhuric and nitric acid respectively by reacting with atmospheric water vapour and precipitate as wet deposition such as rain, snow, sleet and fog and dry deposition including hazardous particles of PM 2.5. Acid rain affects forest trees causes yellowing and leaf fall, acidified rivers and lakes causes fish death, loss of calcareous shell forming species (mollusks), it also affects soil microorganisms causes increased nitrification which also leads to eutrophication in water bodies and changes in the biodiversity. Acid rain also destroys the coral reefs. It causes leaching of metal ions including toxic Aluminum and heavy metals such as chromium, cadmium and nickel, which adversely affects the soil micro flora and aquatic biota. Acid rain deteriorates the marble, stone monuments and architectures, corrode metal structures and fading paints. Liming is used to neutralize the acidity in soil and aquatic bodies. Several methods are used to reduce the emission of SO_2 and NO_x such as reducing the sulphur content in fuels, using scrubbers such as flue gas desulphurization (FGS) lime injection multi stage burning (LIMB) or fluidized bed combustion (FBC or circulation dry scrubber). To reduce NO_x methods such as selective catalytic reduction process (SCR) where injection of reactive chemicals such as ammonia reacts with NO_x and convert into N_2 and O_2, changing air to fuel ratio and changing the combustion temperature. In automobile three way catalytic converters are used to get rid of NO_x. By 1990 US congress has passed amendments to the Clean Air Act. Title IV of the amendment consist control measures to SO_2 and NO_x, implemented in 2 phases. In Asia, regional acidification information and simulation programme is conducted. NO_x Budget Trading program (NBP) operated from 2003 to 2008, For trans boundary acid deposition issue US and Canada have signed in a bilateral air quality agreement in 1991, an integrated atmospheric deposition network (IADN) was established and in 2011cross state air pollution rule and litigation (CSAPR) implemented by US EPA for the same.

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