ACID RAIN: Chemistry applied

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Overview

Acid rain generally refers to precipitation that has become acidic due to the development of acidic compounds in the atmosphere. Acid rain can be divided into two categories (*What is Acid Rain*, 2019). The first category is wet and the second category is dry. The wet category includes rain, snow, hail, or fog. The dry category occurs when certain particulates, such as dust, fall to the ground and have the potential to become acidic when they encounter water. This research report will cover the following topics: how acid rain is formed, the effects acid rain has on the environment, the damage acid rain can do to infrastructure, and how acid rain can be mitigated.

Although some acid rain can occur from natural sources, mainly volcanic eruptions, the largest contributor is the burning of fossil fuels (*What is Acid Rain*, 2019; *Acid Rain FQA*, 2013). The particulates that help form acid rain are sulfur dioxide (SO_2), carbon dioxide (CO_2), and nitrogen oxides (NOx). When these compounds come into contact with water, oxygen, or other chemicals in the atmosphere, they form an acid. Some of the acids that can form are carbonic acid, sulfuric acid, and nitric acid. Generally, these acids are weak because they are diluted, but over time, they can accumulate and cause damage.

Once acid rain starts to precipitate, it can affect both terrestrial and marine ecosystems. Acid rain has the potential to strip valuable nutrients and decrease the pH of soil. This will negatively impact the quality of soil and affect plants. The other way that acid rain impacts the ecosystem is through accumulation in the oceans. More acidic conditions can lead to decreased shell production, as in bivalves, as well as reduced growth rate in coral reefs (Hoegh-Guldberg et al., 2007).

Certain types of structures are susceptible to acid rain. Limestone is greatly affected by acid rain, as that stone is highly reactive (Ophradt, 2003). Loss of detail on monuments such as statues, tombstones, and building's exterior can occur. Not only does acid rain affect the decoration of a building, but it also impacts the structure of a building, leading to major damage over time.

There are some ways to mitigate acid rain, with the main purpose to combat the base components before they can form acid rain. Clean coal technologies, such as washing and scrubbing, aim to remove impurities so that the coal will produce fewer by-products when burned (Dowdey, 2007). Another form of mitigation is the catalytic converter in vehicles, which helps to reduce pollutants (Nice & Bryant 2000). Environmental protection policies can also help reduce the amount of acid rain. Government interventions and regulations can reduce the amount of pollutants, which in turn, would reduce the formation of acid rain.

Formation

Chemical Overview

Acid rain is the general term for any form of precipitation that can become acidic including rain, fog, and snow (Hill, 2019). Rain is normally slightly acidic with a pH of approximately 5.6 (Singh & Agrawal, 2008). This is due to the carbonic acid (H_2CO_3) present in the precipitation following the reaction of atmospheric carbon dioxide (CO_2) with water (H_2O). It is officially considered acid rain when the pH is less than 5.6. Acid rain is caused by the reaction of an acidic gas with a compound present in the atmosphere, such as oxygen or water (Shukla, Sundar, Shivangi, & Naresh, 2012). There are specifically three compounds that contribute to the formation of acid rain: sulfur dioxide, nitrogen oxides, and ozone (Singh & Agrawal, 2008).

Figure 1 depicts how sulfur dioxide (SO_2) can lead to the formation of sulfur trioxide (SO_3), which is another compound that is of concern for formation of acid rain (Belo, Elliott, Stanger, Spörl, Shah, Maier & Wall, 2014; Shukla et al., 2012). Sulfur trioxide is water soluble, so it will then react with the water present in the atmosphere to form sulfuric acid (H_2SO_4) (Belo et al., 2014). Nitric acid is formed though the reaction of nitrogen dioxide with a hydroxide ion present in the atmosphere (Shukla et al., 2012).

$$SO_2 + OH^\bullet \rightarrow HOSO_2^\bullet$$

$$HOSO_2^\bullet + O_2 \rightarrow HO_2^\bullet + SO_3$$

$$H_2O(l) + SO_3(g) \rightarrow H_2SO_4(l)(\text{Sulfuric acid})$$

$$NO_2 + OH^\bullet \rightarrow HNO_3(l)(\text{Nitric acid})$$

Figure 1. Reactions that form sulfuric acid and nitric acid in the atmosphere. (Shukla et al., 2012)

Human Causes

Vehicle Caused Emissions

Although one vehicle on the road would not have a large enough impact to produce acid rain, there are an increasing number of cars being driven, which can lead to increasing amounts of pollution in the air, and therefore increasing amounts of acid rain being produced (Nice & Bryant, 2000). The pollution occurs because of the release of gases into the air due to the combustion of fuel in an automobile (Light Duty Fuel Emissions, 2019). This pollution is what can lead to acid rain, smog, and general air quality issues.

Prior to 1975, car emissions had a much larger impact on the acidic composition of the air because they did not have a catalytic converter (Farrauto & Heck, 1999). Without the catalytic converter three gases were being emitted from cars and contributing to some of the ground level ozone increases that were causing smog and acid rain formation (Kahlon & Tang, 2013). These three types of gases are nitrogen oxides, carbon monoxide, and hydrocarbons (Nice & Bryant, 2000). Nitrogen oxides impact the environment because following release from cars, they are combined with atmospheric organic compounds through a sunlight driven reaction. The result of this combination is smog. Another reaction that can cause smog is the reaction of nitrogen oxides with ozone (Kahlon & Tang, 2013). Nitrogen oxides can also react with sulfur dioxide leading to acid rain. Another gas emitted from cars is carbon monoxide, which is odourless and colourless. Although carbon monoxide has a small environmental impact, it can be very harmful to humans because it binds to hemoglobin with a higher affinity than oxygen, therefore depleting the body of oxygen (Topacoglu, Katsakoglou, & Ipekci, 2014). In the presence of sunlight, hydrocarbons can be reacted with nitrogen oxides to produce smog (Kahlon & Tang, 2013). As well, like carbon monoxide it can have serious health effects on humans, including death.

Although the catalytic converter has reduced the emission of carbon monoxide, hydrocarbons, and nitrogen oxides, there is still a small amount of each that is released (Nice & Bryant 2000). The catalytic converter uses reduction and oxidation reactions to change carbon monoxide, hydrocarbons, and nitrogen oxides into carbon dioxide, nitrogen gas and water vapour, which have a much smaller impact on the atmosphere. However, when a vehicle is driven prior to the engine being hot these emissions are released in high amounts because the catalytic converter only works at hot temperatures. Therefore, it is recommended to let a vehicle warm up prior to driving to reduce greenhouse gas emissions.

Factory-caused emissions

Much of the sulfur dioxide created by human activities is the by-product of processing other materials that contain sulfur. Although coal is used as a fuel source because of the carbon it contains, combustion of coal often results in the production of sulfur dioxide, nitrogen oxide, and carbon dioxide, which are all significant pollutants.

One of the primary sources of nitrogen oxide pollution is manufacturing facilities. These facilities commonly use coal as fuel, which contains a significant amount of nitrogen. In 2015, the United States produced over two million metric tons of sulfur dioxide emissions from electricity production, with the vast majority of this coming from coal usage (Devilbiss & Suparna, 2017). During the combustion of coal, nitrogen is released as a free radical and can form nitrogen oxides by combining with the oxygen that is also present (Kumar, 2002). This is called thermal NOx. These fuel sources can also create nitrogen oxides through other means, as the air surrounding the combustion is still at a very high temperature. The high temperature leads to an increase in fuel NOx, which is when nitrogen bound in the fuel reacts with oxygen in a combustion reaction in the air. Gaseous fuels have lesser potential to form nitrogen oxide through fuel NOx, but oils and coal are more likely to produce large amounts of nitrogen dioxide if preventative measures are not taken (Kumar, 2002). A third type of formation, prompt NOx, can also occur. This process occurs separately from combustion of fuel sources. Prompt NOx is created when hydrocarbon radicals, released from combusting fuels, react with atmospheric nitrogen. This generally produces less NOx than the other sources. All three of these sources produce more NOx at higher temperatures, and thermal NOx has a much higher ceiling of production than other types (see Figure 2).

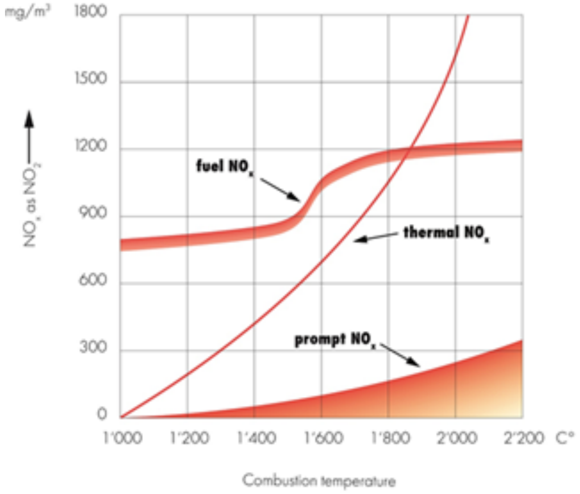

Figure 2. Types of NOx produced during combustion of fuel at different temperatures (Engineer Live, 2018).

Natural Effects on Acid Rain

Nitrogen cycle

Some naturally occurring processes also affect the formation of acid rain. Some organisms capture atmospheric nitrogen (Fowler, Roush & Wise, 2013). These organisms are referred to as nitrogen-fixing. The nitrogen is then converted to ammonia, which makes it more usable for biological processes. Nitrogen-fixing organisms can reduce the amount of acid rain that is formed, by reducing atmospheric nitrogen levels. However, nitrogen does not remain in these organisms forever. If they are consumed by predators, the nitrogen transfers to the predators. When an organism containing nitrogen dies and begins to decompose, bacteria use the nitrogen from that organism, and this continues the nitrogen cycle (see Figure 3). Ammonia is converted to nitrates and nitrites by nitrifying bacteria. The ammonia is later converted into nitrogen (N_2) gas before being released into the atmosphere by denitrifying bacteria (Fowler, Roush & Wise, 2013).

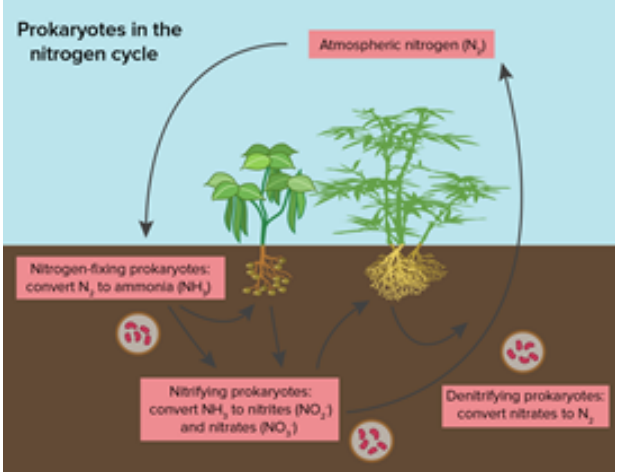

Figure 3. Prokaryote involvement in the nitrogen cycle (Fowler, Roush & Wise, 2013).

Fertilizer is also a major contributor to the amount of nitrogen oxide pollution. Fertilizer is commonly created using the Ostwald process (Gasmet, 2011). In this process, ammonia is oxidized to produce nitric oxide and nitrogen dioxide, and then the nitrogen dioxide is absorbed into water, forming nitric acid. This process also releases NOx emissions.

Other natural processes reduce concentrations of atmospheric nitrogen. After nitrogen fixation has occurred, some compounds found in terrestrial ecosystems get introduced to the ocean. They eventually fall to the ocean floor as sediment and get compressed into sedimentary rock (Fowler, Roush & Wise, 2013). However, this nitrogen will continue to be a part of the nitrogen cycle, as sedimentary rock is eventually lifted through geological processes, and when erosion occurs, this sediment can once again become a source of nitrogen for living organisms (Fowler, Roush & Wise, 2013). Volcanic eruptions also contribute to acid rain formation, as sulfur dioxide is a significant component of the gases released during these events (Husar, Lodge & Moore, 1978). This affects areas outside of the immediate vicinity of the volcano as well, as similarly to anthropogenic pollutants, gases emitted by volcanic eruption can travel far distances within the atmosphere.

Biological and Environmental Effects

Amongst the other negative effects of acid rain are the impacts on the natural environment and biology. This can be broadly separated into two categories: impact on terrestrial systems and impact on marine or aquatic systems. In terrestrial systems, acid rain can affect the erosion and acidity of soils and have consequences for natural geological processes. These both have direct roles in the mobilization of certain elements like magnesium and aluminum (*Effects of Acid Rain—Forests | Acid Rain | US EPA*, n.d.). In terms of terrestrial biology, the two most impacted organisms are the bacteria and archaea living in the soil, and plants. The microorganisms are severely impacted because of the denaturation of proteins due to lower than usual pH, and often microbial communities are less diverse (Chodak et al., 2013). In regard to plants, acidification of soils can lead to nutrient leaching that impacts availability of essential nutrients as well as defoliation (leaf loss) resulting from exposure to acid rain (Wang et al., 2007). When it comes to marine systems, the biggest impact of acid rain is the acidification of the body of water in question ("The Oceans Feel Impacts from Acid Rain," n.d.). This has grave implications for many organisms, especially those that form calcium carbonate ($CaCO_3$) shells because it affects the availability of the necessary minerals in solution (Kurihara, 2008).

Terrestrial

When acid rain occurs over soils, the soils have the potential to acidify. However, many soils have the ability to resist this acidification, which is known as the ability to buffer. The buffering capability is dependent on the composition of the soil as well as the bedrock that is underneath it, and has the potential to slow pH change in the soil (Bowman et al., 2008). However, no matter how high the buffering capability of the soil, eventually it can be depleted by sufficient acidification from rain or other sources. In soils with a pH of 4.0 or lower, there has been a decrease in both calcium and magnesium ions, which has negative effects on trees that require those cations for growth (Tomlinson, 2003). Acidified soils can also result in an increased presence of aluminum and manganese in the soil, both of which cause toxicity to plants in high concentrations (Xu et al., 2012). Both the decrease of necessary nutrients and the introduction of potentially harmful elements have negative impacts on agriculture, forestry and the state of natural ecosystems.

A recent study estimated that there were over 25,000 phylotypes (a proxy for species in microbial biology) found in the soils of the world (Delgado-Baquerizo et al., 2018). The pH of the soil is the environmental factor that has the strongest influence on the composition of the microbial community (Romanowicz et al., 2016). Both relative abundance and diversity of microbial species increased when researchers increased the pH from 4 to 8 (Rousk et al., 2010). Therefore, any modification to the pH of the soil would have a strong influence on the microbial community in that area, even if it were localized to the region that received acid rain. Certain bacteria have irreplaceable roles in plant growth, and some have even been shown to be able to breakdown hydrocarbons for spill remediation (Babalola, 2010; Khan et al., 2013). These organisms have far reaching impacts and the acidification of their environment is detrimental to their health, and therefore the ecosystem as a whole.

As previously mentioned, the acidification of soils will have negative impacts on the nutrient availability and may introduce toxic compounds, both of which affect plant health. However, a more acute concern for many plants exposed to acid rain is defoliation. High SO_2 levels around cities in China has been shown to cause needle loss and early mortality of pine trees (Wang et al., 2007). Acid rain also has the potential to damage the outer cuticle of plant cells and diffuse acidic water into them, causing discoloration and disruption of normal functioning (Tamm & Cowling, 1977). These acute impacts on trees and other plants have negative ramifications for forestry and agriculture, especially when they are close to cities or industrial areas that produce high amounts of SOx and NOx.

Marine

As in soil, oceans and lake systems have the ability to buffer their pH to counteract rapid change and acidification. It is estimated that up to one third of the anthropogenic output of CO_2 is taken up by the ocean (Doney et al., 2009). This may cause ocean acidification via the following formula:

$$CO_{2\ (aq)} + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^{-} + H^{+} \rightleftharpoons CO_3^{2-} + 2\ H^{+}$$

Because of the unprecedented input of CO_2 into the atmosphere and the subsequent acidification of the ocean, the buffering capability is reduced from its usual baseline. Due to atmospheric transport of weather systems, areas that may not be close to a source of SOx and NOx may be still impacted by acid rain such as struggling Caribbean reef systems (Albright et al., 2010; Church et al., 1982). This could mean that sensitive areas that have already been compromised by large-scale acidification could be further damaged by the offshore transport of acidic precipitation from areas of heavy industry or large cities.

One of the most consequential impacts of ocean acidification is the effect on shell-forming organisms. This is done primarily by decreasing the availability of $CaCO_3$ for uptake and disrupting the natural pH of the organisms (Doney et al., 2009). Multiple studies have shown that the predicted ocean pH (primarily due to CO_2) will reduce coral growth by 40%, as they require $CaCO_3$ to create the skeleton within which they live (Hoegh-Guldberg et al., 2007). However, although the majority of species seem to have negatively impacted shell formation, certain organisms like crabs, shrimp and lobsters actually were shown to have increased shell formation under more acidic conditions (Ries et al., 2009). Ocean acidification may also have an impact on phytoplankton, the base of marine food chains. A lower pH in the ocean may decrease the availability of iron(III) for both diatoms and coccolithophores (Shi et al., 2010). Iron is already a limiting nutrient for phytoplankton growth in much of the world's oceans so decreasing it further may have negative impacts for entire marine food webs. Marine pteropods, an often undiscussed but foundational species in marine systems in the arctic, show both shell degradation (see Figure 4) and increased rates of mortality in more acidic conditions (Lischka et al., 2011).

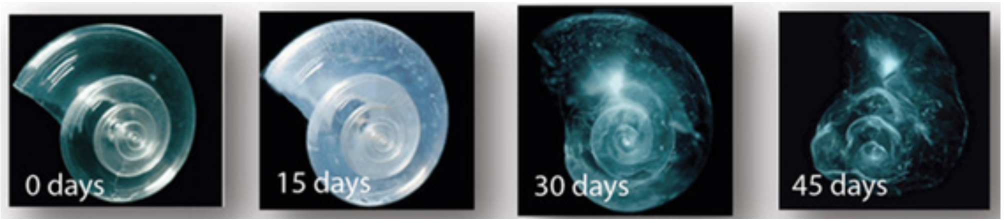

Figure 4. Degradation of a pteropod shell over 45 day when placed in sea water with pH and carbonate levels projected for the year 2100 (*What is Ocean Acidification?*, n.d.).

Infrastructure Effects

The negative affects of acid rain are not limited to our natural environment but extend to human-made structures as well. Many historic buildings such as statues, monuments, and tombstones are made of materials vulnerable to the corrosive effects of acid rain. The damage caused on these structures can lead to costly consequences; the materials damaged often need to be repaired or replaced to maintain structural integrity, the cost of maintenance increases, and there can be loss of detail on stone and metal statues, monuments, and tombstones (US EPA, n.d.). In the following sections, the chemistry responsible for the decay of certain structures will be presented, as well as examples of the affects acid rain has on these vulnerable structures.

Stone Chemistry and Vulnerability to Acid Rain

The monuments, buildings, and statues primarily affected by acid rain are those made of stones vulnerable to acidic solutions. Limestone and marble are made up of compounds that react readily with the sulfuric acid in acid rain (Ophradt, 2003). The neutralization reaction for limestone is presented here:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3$$

$$H_2CO_3 \rightarrow CO_2\ (g) + H_2O$$

The calcium sulfate ($CaSO_4$) produced in this reaction is water soluble, forming an aqueous solution on the limestone that washes away. The carbonic acid (H_2CO_3) generated in this reaction decomposes into carbon dioxide gas and water. This process of breaking down calcium carbonate ($CaCO_3$) causes the surface of statues, monuments, and other structures to dissolve, which creates ghostly statues lacking surface features and blank tombstones.

Unlike limestone, marble is made up of calcite crystals, which have a whitish colour, and some coloured grains of mica (McGee, 1995). When marble is exposed to the sulfuric acid in acid rain it produces gypsum, a white porous crystal, on top of the marble (see Figures 5 and 6). The gypsum is water-soluble so it washes away with consistent rainfall, but in sheltered areas it will collect pollutants in the air and create cracks in the marble.

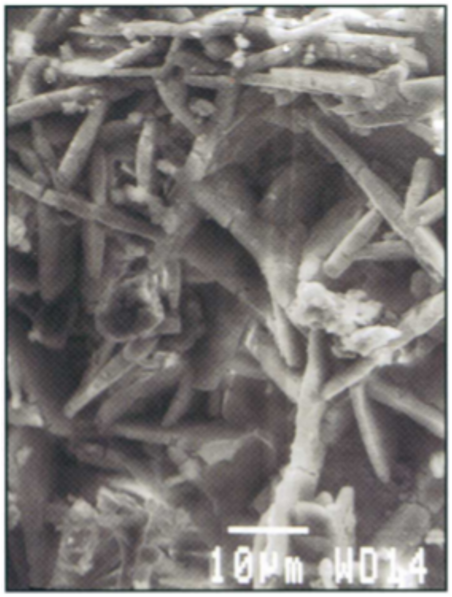

Figure 5. Formation of gypsum crystal structures in marble under shelter. Pollutants captured in the crystals create a blackish colouration, and cracking allows for plant life to grow through structures (McGee, 1995).

Figure 6. Electron microscope imaging of gypsum crystals with dirt and other pollutants embedded in the crystal lattice (McGee, 1995)

Some metals are susceptible to the corrosive effects of acid rain as well. Bronze, copper, iron, some types of steel, and zinc structures corrode more rapidly in the presence of the acids in acid rain (Dolske, 1995). This causes discolouration, and the weakening of support structures where corrosion is especially heavy.

Examples of Damage to Statues and Monuments

The loss of details in statues and other monuments due to acid rain can severely alter the appearance of the structure (Ophradt, 2003), as shown in Figure 7. The loss of detail can be to such a high level that refurbishment is no longer possible, or the cost of repairing the structures would exceed the cost of commissioning a new one. Tombstones can have their etchings completely erased, and statues lose distinguishing features such creating smooth structures. The effects can be mitigated, as the smoothing and corrosions of many of these structures can take decades. But those monuments affected remain marked by the effect of acid rain to this day.

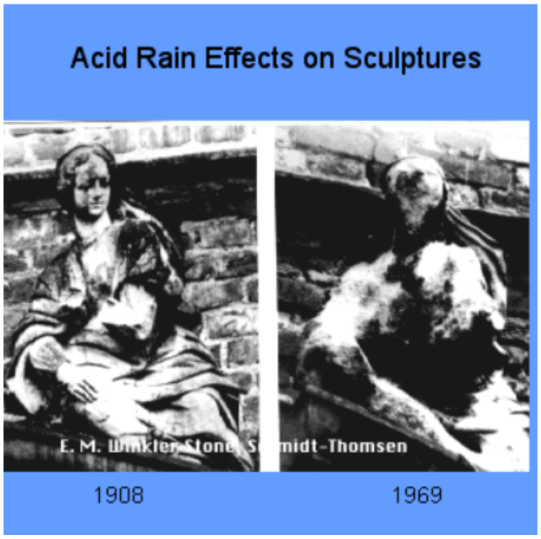

Figure 7. Loss of detail on a limestone statue. Facial features are "smoothed" leaving behind a mannequin-like figure (Ophradt, 2003)

Mitigation

Treatment and Prevention: Before and After We Burn Fuel

Clean coal technologies include treatments before and after coal is combusted (Dowdey, 2007). The following section will examine some of the major types of clean coal technologies used in industry. These technologies are not all aimed to reduce acid rain, but they each help address major pollutants in coal that result in acid rain.

Coal washing is a treatment performed on coal prior to burning. This pre-emptive treatment is done by mixing powdered coal and a specific solvent which allows for separation of impurities and pollutants (Dowdey, 2007). The washing process can help remove some sulfur that would have ended up as sulfur dioxide had it combusted.

Low nitrogen oxide burners (Low-NOx) are controlled environments that allow for combustion to be manipulated reducing nitrogen oxide product (Low NOx Burners—Bloom

Engineering, n.d.). Nitrogen oxides are created by the high temperature condition of combustion, thus Low-NOx burners control the temperature. These systems are also held in oxygen deficient environments to minimize the reaction of nitrogen with oxygen that results in nitrogen oxides.

Scrubbing is a post-combustion treatment (Afework et al., 2018a, 2018b; Hanania et al., 2018). Chemical scrubbers are used in industry to remove major chemicals and particulate from exhaust gas, or the resulting gas from combustion. The process of scrubbing includes spraying the gas to be emitted with a liquid or a powder solid, referred to as wet scrubbing and dry scrubbing, respectively. In general, the scrubbing reagent, liquid or powder, contains a base, often calcium carbonate, that will react with SO_2 to produce a precipitate that is collected as waste. First, the gas must be cooled and diluted. Next the reagent is added to remove the pollutants. Finally, the gas passes through a very fine filter to remove all solid powder waste. The solid waste can be decontaminated and then reused but this is rarely done because it is expensive and inefficient. Dry scrubbers are presently used more often in industry due to the reduced waste compared to wet scrubbers. Although both types of scrubbers efficiently reduce acid rain by removing acidic components from exhaust, the waste products are hazardous, the operation is expensive, and it is energy intensive. These processes are not completely effective, so there are still pollutants in the released gas.

Catalytic converters are added onto the exhaust systems of combustion engine vehicles (Kahlon & Tang, 2013). These devices have ceramic structures and use metallic catalysts that are sites for reduction and oxidation. Nitrogen oxides are reduced to elementary nitrogen and oxygen. Some common precious metals in catalytic converters are platinum, rhodium and palladium. These metals can be very expensive so there are economic implications for individuals.

Policies: National and International Acts and Accords

The Canadian Environmental Protection Act, signed in 1999, aims to work in accordance with scientific findings, management strategies and public well-being. This act covers more than just air pollution and acid rain prevention (Canada, 2009). It is a federal law that works to reduce emissions of criteria air contaminants (CAC) by 2030 to at least 30 per cent of the emissions.

CAC include compounds such as nitrogen oxides and sulfur dioxide. The Environmental and Climate Change Canada (ECCC) and Transport Canada (TC) agencies are the legal departments that are responsible for overseeing emissions from internal combustion engines (Ahmad, 2018). Canada also enabled the 1985 Eastern Canada Acid Rain Program, which specifically worked to reduce acid rain. In addition to a 2.3-ton sulfur dioxide emission cap in Eastern Canada programs for scientific research and monitoring on the federal and provincial levels were implemented. Canada sought the insight and support of the governments of European countries and the United States because of the long-range transboundary nature of these types of air pollutants. This corroboration with governments eventually led Canada to sign the 1979 United Nations Economic Commission for Europe Convention on Long-Range Transboundary Air Pollution (UNECE LRTAP), which later included agreements on sulfur and nitrogen oxide compounds (Canada, 2013). This convention includes eight protocols dating from 1984 to 1999. Canada has signed onto all of the protocols. For the purposes of acid rain prevention, there are four main protocols that aim to reduce sulfur and nitrogen emissions: the 1985 Helsinki Protocol on the Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30 per cent, the 1988 Sofia Protocol concerning the Control of Emissions of Nitrogen Oxides or their Transboundary Fluxes, the 1994 Oslo Protocol on Further Reduction of Sulphur Emissions, and the 1999 Gothenburg Protocol to Abate Acidification, Eutrophication, and Ground-Level Ozone (Convention on Long-Range Transboundary Air Pollution, n.d.; Grennfelt et al., 2019).

Outcomes: Current Data and Our Next Steps

Figure 8 shows that countries, such as Europe and North America, that signed the UNECE LRTAP and implemented national protocols, saw improvements in their emissions of sulfur dioxide and nitrogen oxides (Grennfelt et al., 2019). However, countries such as China, Japan, and Korea, that did not sign the UNECE LRTAP did not show any improvements, on the contrary they showed an increase in emissions (Duan et al., 2016). Duan and colleagues (2016) suggest that this increase of emissions is due to rapid economic growth. This has become a major concern in Eastern Asia and the situation requires immediate action. The implementation of clean coal technologies in the major contributors, such as industrial and commercial process, is an important step in the reduction of acid rain causing emissions in Eastern Asia. On the other hand, the recently established, Asia Pacific Clean Air Partnership (2015), gives a hopeful outlook into the future (Clean Air Week, n.d.; Environment, 2017).

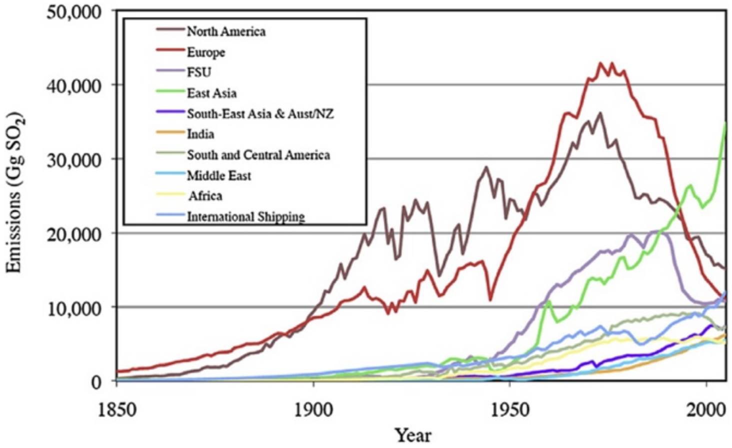

Figure 8. Global SO_2 emissions (Duan et al., 2016)

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