

Custom Essay

Toxic Substances

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Abstract

The present study investigated the emission of three toxic substances in North America: dioxins, inorganic nitrogen and mercury. The various aspects of each toxic substance explored include the source of the emission, its toxic effects and the industrial processes adopted to minimize the emission. Coal-fired electric power generation plants are responsible for the highest percentages of most of the toxic emissions released into the environment in North America. However, the recognition of the need to adopt better industrial processes to reduce toxic emissions and the development of regulatory frameworks to ensure industries adhere to environmental safety standards has helped to keep toxic emissions at low levels especially in the past three decades.

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Introduction

The environment is constantly under the threat of toxic emissions, the majority of which result from human activity. These toxic substances fall into different categories including organic, non-organic and metallic substances. While many of these toxic substances occur naturally, human activity is responsible for the increased concentrations of these substances. North America, Europe and other authorities across the world have recognized the growing need for greater control of human activities that emit pollutants to the environment and have developed regulations to ensure various industries adopt strategies to minimize the emission of toxic substances.

The United States Environmental Protection Agency (EPA) and the Canadian Council of Ministers of the Environment are examples of regulatory bodies created to provide standards for reducing environmental pollution in the North American continent. The present study examines three toxic substances—dioxins, inorganic nitrogen and mercury, their sources, effects on the environment and the industrial processes taken to minimize their release into the surrounding.

Dioxins

Dioxins are a class of organic compounds consisting primarily of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzofurans (PCDFs). The discovery of the toxic effects of 2,3,7,8-TCDD, a member of PCDDs sparked interest in the toxicity of dioxins and other related chemicals (Feng et al. 35).

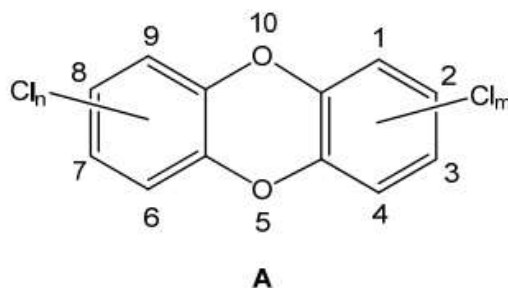


Figure 1. General Structure of Dioxins

Sources of Dioxins

The Canadian Council of Ministers of the Environment identified three main sources of dioxins: discharge from industries to the surrounding land, water and air, transportation by air from distant origins, and contamination from dioxins already present in the environment (2). Numerous industries in different parts of North America release dioxins into the surround soil and atmosphere through various processing including waste incineration, and wood burning. Paper and pulp industries in British Columbia burn salt-treated wood resulting in the production of dioxins. Electric arc furnace steel manufacturing and iron sintering industries in Newfoundland also produce dioxins. In addition, wood combustion in homes and incineration of municipal waste release considerable amounts of dioxins to the soil and air. Wood treatment procedures involving the use of creosote insecticides in many wood processing industries account for the release of dioxins in many parts of the United States (Feng et al. 34). Furthermore, the cement manufacture involves the combustion of fossil fuels and this produces dioxins. Dioxins from these industries accumulate in dust and soil and eventually find their way into water sources where animals and humans can ingest them.

Toxicity of Dioxins to Soils

Toxic equivalents (TEQs) are the conventional measures of the toxicity of chemicals. Dioxins are released in minute quantities such as parts per trillion but their persistence in the environment allow them to accumulate in levels that can harm living organisms. The chemicals adhere to sediments and soils and are immobile because they have low water solubility and do not vaporize easily. Dioxins occur in potentially toxic levels areas near wood treatment industries in various parts o Canada and the United States. For example, Feng et al. conducted an analysis of dust from areas near wood treatment plants in Pineville, Alexandria, Grenada, and Florala and found levels of dioxins significantly above the concentrations recommended by the U.S. Environmental Protection Agency for the general population (37). Dioxins occur in different concentrations in different types of soils depending mainly on the proximity of such soils to the point sources of the pollutants. For example, concentrations of dioxins ranging from 0.1 to 5.0 ppt TEQ have been reported in Washington soils (Washington State Department of Ecology 2). Concentrations of dioxins ranging from 72 ppt TEQ to 11200 ppt TEQ were reported in areas near Dow Chemical Company in Michigan (Demond et al. 1298). The concentrations of dioxins in urban soils are manifold higher than in rural soils in most part of North America.

Toxic Effects of Dioxins

Dioxins are hazardous to animals and humans in various ways. The acute effects of dioxins include the disruptions of the endocrine system leading to developmental defects. The endocrine system is responsible for the transmission of messages in the body through the activity of neurotransmitters to regulate various body functions

(Washington State Department of Ecology 3). Dioxins interfere with this system by inhibiting hormones, acting as synthetic hormones or altering the functions of the various components of the endocrine system. Disruption of the endocrine system can cause numerous abnormalities including prostate cancer, testicular cancer, breast cancer, infertility, immune suppression, and thyroid gland dysfunction. The unborn and infants are particularly vulnerable to dioxin poisoning because of their accelerated rate of growth and development. Breast milk contains traces of dioxins, which increases their risk of infants' exposure to dioxins. Prolonged exposure to dioxins weakens the immune system, paving way for other infections. Human and animal studies have shown 2,3,7,8-TCDD to be a potential cause of cancer in humans. Numerous globally recognized health agencies including the International Agency for Research on Cancer and the US Department of Health and Human Services categorize characterize dioxins as human carcinogens (Washington State Department of Ecology 4).

Dioxins disrupt the endocrine systems of animals leading to various defects such as lower fertility in mammals, fish, and birds (Demond et al. 1295). For animals that lay eggs, dioxins reduce hatching success and offspring survival rates. In addition, affected animals may experience behavioral abnormalities and increased vulnerability to infections. Dioxins pass from animals to humans easily through contaminated animal food products. For example, Demond et al. found that people who ate eggs and meat obtained from animals that were raised in a contaminated area had higher amounts of dioxins in their blood compared to those who consumed similar products from animals raised far from contaminated areas (1298).

Industrial Processes that Emit Dioxins

The main industrial process that produces dioxins is the combustion of organic compounds containing chlorine. Indeed, dioxins are unwanted products of these processes. Wood treated with salt produces dioxins when burned in paper and pulp factories (Feng et al., 34). Similarly, combustion of fossil fuels in cement manufacturing industries may release dioxins depending on the kiln temperatures and the chemical nature of the fuel used. It is believed that lower temperatures (about 250°C) favor the production of dioxins.

Industrial Methods to Reduce Dioxins Emission

One of the industrial processes used to reduce dioxins emission is temperature control. Lower kiln exit temperatures reduce the exit of dioxins (Gossman para 4). Temperature control is an issue of kiln design. Lower temperatures can be achieved by air quenching and water spray and slurry spray systems. Another process for reducing dioxins is the use of catalytic filter systems such as the Gore bags, which cleans exhaust gases of all particles including dioxins. However, this technique is very expensive. In addition, preheater kilns have been used to destroy organic matter in alternative raw materials and thus reduce the amount of dioxins produced. The pulp industry uses a number of industrial processes to reduce dioxin emission. First, pulp plants are turning to chlorine-free methods of pulp bleaching. Since dioxins contain chlorine, eliminating the use of chlorine compounds would prevent the release of dioxins. One of the ways to reduce over-reliance on chlorine is to use chlorine dioxide or replace chlorine with hydrogen peroxide. However, chlorine is much more effective than hydrogen peroxide in bleaching. Another process for reducing the emission of dioxins in

paper industries is the treatment of effluents. The focus of this process is to displace chlorine ions with hydrogen ions in anaerobic settings. Removal of chlorine ions encourages biodegradation of the residue (Gossman para 8).

Inorganic Nitrogen

Inorganic nitrogen is one of the main toxic substances affecting aquatic ecosystems in North America. Inorganic nitrogen becomes toxic once its abundance in nature exceeds levels that the natural ecosystem can assimilate fully (Camargo & Alonso 835). Dissolved inorganic nitrogen forms three main reactive ions: nitrite ion (NO_2^-), ammonium (NH_4^+) ion and nitrate (NO_3^-) ion. These ions may result from human activity and natural processes. Initially, natural processes primarily determined the amount of inorganic nitrogen in ecosystems through bacterial nitrogen fixation, atmospheric deposition, dissolution of naturally occurring nitrogen in ground water and the decomposition of organic matter. However, the abundance of nitrogen has grown tremendously during the past two centuries due to human activities such as the production of nitrogenous fertilizers for agricultural use.

Sources of Inorganic Nitrogen

Point sources of nitrogen include wastewater from livestock farming, untreated sewage effluents, and wastewater from nitrogen manufacturing industries. The fertilizer manufacturing industry in the United States and Canada is one of the main sources of toxic inorganic nitrogen. Between 1960 and 2005, the annual production and use of nitrogen fertilizers in the United States grew over 450 percent (McDonald para 3). The demand for nitrogenous fertilizers continues to grow worldwide and North America alone accounts for 13 percent of the global demand. The United States produces

ammonia in large quantities to meet its demand for nitrogenous fertilizers (see fig. 1). In addition, the automobile industry accounts for a significant percentage of all inorganic nitrogen emissions in north America, and more than half of nitrogen oxides emitted in the United States (Knight 7). Furthermore, electric generating plants and other activities involving fossil fuel burning release nitrogen compounds in to the atmosphere while the byproducts of industrial processes account for a small percentage of the emissions.

Fig.1 U.S. ammonia production plants, 2005-06



Figure 2. U.S. Ammonia Production Plants (Source: <http://www.bigpictureagriculture.com>)

Toxicity of Inorganic Nitrogen to Aquatic Life

Ammonia

Elevated amounts of dissolved inorganic nitrogen are toxic to aquatic animals and plants. Ammonia (NH_3) and aqueous ammonia (NH_4^+) exist in equilibrium in water (Camargo & Alonso 835). Ammonia concentration increases with temperature and pH. Ammonia is highly toxic to fish and other aquatic animals. In addition, ammonia kills

Nitrobacter and *Nitrosomonas* bacteria responsible for the nitrification process.

Increased concentration of ammonia affects fish in different ways including suppressing the immune system, damaging the respiratory system, inhibition of energy production and disruption of osmoregulation (Bernhard 25). Freshwater fish and mollusks are most vulnerable to ammonia toxicity with acute effects occurring after 4 days in 0.6 mg NH₃-N/L and chronic effects at 0.05 mg NH₃-N/L for two to three months. The recommended maximum concentrations of ammonia required to ensure the safety of aquatic animals should be 0.35 mg NH₃-N/L and 0.02 mg NH₃-N/L for acute and chronic toxicity respectively.

Nitrites

The nitrite ion exists in equilibrium with the nitrous acid ($\text{NO}_2^- + \text{H}^+ \leftrightarrow \text{HNO}_2$). The relative concentrations of the nitrite and the nitrous acid depend on the pH and temperature, but both compounds are toxic to aquatic life (Camargo & Alonso 835). Nitrous acid inhibits nitrogen fixation by killing *Nitrobacter* and *Nitrosomonas* bacteria, which further increases the concentration of both the nitrous acid and the nitrite leading to increased toxicity. However, the nitrite is much more abundant than nitrous acid and thus is more toxic than nitrous acid. Nitrite alters oxygen-carrying cells in fish rendering them unable to carry sufficient oxygen, which cause hypoxia and death. Nitrite catalyzes the conversion of iron II to iron III and consequently the transformation of the oxygen carrying hemoglobin to the less functional methemoglobin.

In addition, nitrite toxicity oxidizes copper I to Copper II, which produces compounds that are poorly adapted to oxygen, transport (Bernhard 25). Other effects of increased nitrite levels on aquatic animals include lowering of chloride concentration

leading to electrolyte imbalance, interference with potassium balance, which interferes with transportation, heart function and neurotransmission, formation of carcinogenic *N*-nitroso compounds, and suppression of the immune system. Some of the most vulnerable aquatic animals to nitrite toxicity include cyprinids, salmonids, amphipods, and ephemeropterans. Acute toxicities occur at 3 mg NO₂-N/L compared to the recommended maximum concentration of 0.35 mg NO₂-N/L (Camargo & Alonso 835).

Nitrate

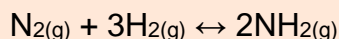
Nitrate exists in aquatic habitats in fully ionized form (NO₃⁻) and (H⁺). Nitrate toxicity is associated with the (NO₃⁻) species. Nitrate causes poisoning in fish and other aquatic plants by catalyzing the conversion of hemoglobin to methemoglobin (Camargo & Alonso 835). The latter compound does not release oxygen easily. However, nitrate is the least toxic on its own compared to ammonia and nitrite. Indeed, nitrate is not considered a significant threat to aquatic life. Nevertheless, prolonged exposure to high concentrations of nitrate (more than 5 mg NO₃-N/L) can cause problems for sensitive freshwater aquatic animals such as amphipods, salmonids and caddis flies (Camargo & Alonso 836). Amphibians are particularly vulnerable to inorganic nitrogen toxicity and the continued use of nitrogenous fertilizers may account for the gradual decline of amphibians in aquatic ecosystems located within agricultural areas. The Canadian Council of Ministers of the Environment now recommends maximum nitrate level of 2mg NO₃-N/L to protect marine and freshwater animals.

Inorganic nitrogen compounds also affect humans. Nitrites and nitrates in drinking water can interfere with human respiratory process by inhibiting oxygen transfer and increasing the levels of blood methemoglobin. Symptoms of nitrate and nitrite

poisoning include fatigue, headache, coma, asphyxia, cyanosis and stupor (Bernhard 25). Infants have a higher susceptibility to nitrogen poisoning because of their overreliance on fluids, higher gastric pH, and the reduced body capacity for mitigating the activity of methemoglobin. Cases of methemoglobin poisoning are common in areas with high concentrations of dissolved nitrate in drinking water.

Industrial Processes that Emit Inorganic Nitrogen

One of the industrial processes that increase the amount of inorganic nitrogen in ecosystems is the combustion of fossil fuels. The Haber process for producing ammonia involves the combustion of methane in presence of nitrogen gas.



The ammonia produced through the Haber process finds its way into the soil and aquatic ecosystems through its use in making nitrogenous fertilizers (Bernhard 25). It is estimated that the manufacture of synthetic fertilizers through the Haber-Bosch process accounts for 80 percent of the nitrogen ingested by humans through contaminated water. Another industrial process that generates nitrogen oxides is combustion of fossil fuels in electric power generation plants, which yields significant amounts of nitrogen monoxide (Vallero 88). The resulting nitrogen monoxide is further converted to the more reactive nitrogen dioxide. Furthermore, the industrial production of nitric acid releases nitrogen oxides into the environment.

Industrial Methods for Reducing Inorganic Nitrogen Emission

The most common industrial process for scrubbing nitrogen compounds emitted in energy and automobile industries is selective catalytic reduction (SCR) (see fig. 2).

Fig. 2. Selective catalytic reduction equipment

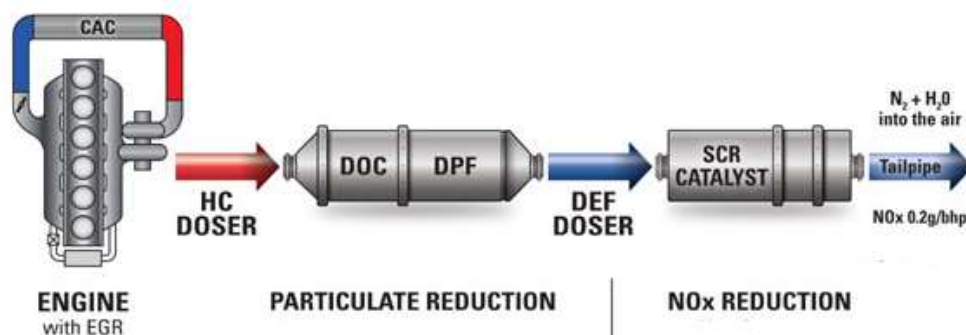


Figure 3. Source: <http://www.factsaboutscr.com/scr/>

In SCR, ammonia is used to reduce nitrogen oxides in the presence of a catalyst.

The pollutants are converted to less harmful products mainly water, nitrogen and carbon IV oxide (Nakamoto & Neidig 1). The ammonia used as a reductant is obtained by hydrolyzing diesel exhaust fluid, which contains mainly urea. SCR reduces nitrogen oxides by more than 90 percent. Some of the manufacturing companies in North America already using SCR include the Detroit Diesel, Isuzu Commercial Trucks and Mack (factsaboutscr.com para 3).

Nitrogen oxides emitted through burning of fossil fuels in industries can also be reduced through using alternative fuels or upgrading existing fuels (EPA para 3). The energy industry and the automobile industries are adopting newer production technologies that can convert nitrogen compounds into less harmful products. However, the production of nitrogenous fertilizers will continue to contribute to nitrogen levels in soil and water sources since there is no indication that the existing fertilizers factories will close down. Nevertheless, farmers should use such fertilizers efficiently.

Mercury as Air Pollutant

Mercury occurs naturally in soil, air and water in various forms including metallic mercury, organic and inorganic mercury compounds (EPA para 2). The metallic mercury is liquid at room temperature. Its high volatility renders it an important air pollutant.

Mercury occurs naturally in rocks and coal.

Industries that Emit Mercury

The combustion of coal releases mercury into the atmosphere. Indeed, coal-burning electric power plants account for over 50% of all the mercury emitted to the atmosphere in the United States, as well as significant proportions of other pollutants (see fig. 3).

Fig. 3: contribution of power plants to U.S. air pollution

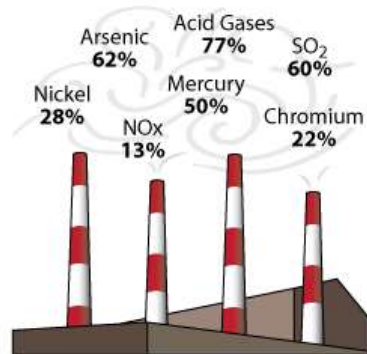


Figure 4. Source: <http://www.epa.gov/mats/powerplants.html>

Other industries that generate significant mercury emissions include mineral refineries, cement manufacturing and waste management systems involving burning (EPA para 2). Mercury first enters the atmosphere where it can be blown by wind to places further away from its point source. Mercury vapor is toxic to animals and humans when inhaled. Eventually, mercury settles on land and water and poses danger to

ecosystems. For example, some microorganisms convert elemental mercury to more toxic methyl mercury, which is later consumed by fish and fish predators. Eventually, methyl mercury enters the human body through the consumption of contaminated fish.

Toxicity of Mercury

Mercury exists in different chemical forms including elemental mercury, methyl mercury and other mercury compounds. The toxicity of mercury varies according to its chemical form, abundance, period of exposure, mode of contamination, and the personal risk factors such as age and health (EPA para 1). Once inhaled, elementary mercury vapor enter the blood stream via the lungs where it is converted into other toxic forms that affect the nervous system. Metallic mercury is mildly toxic when ingested because of its poor absorption in the gastrointestinal tract. Inorganic mercury occurs in three states: elemental mercury (Hg), mercuric mercury (Hg^{2+}) and mercurous mercury (Hg^+) (EPA para 2). This form of mercury is corrosive and can enter the body through oral or dermal inlets. Toxicity may result after long durations of exposure. Organic mercury has high lipid solubility and thus it can be absorbed into the gastrointestinal tract from which it enters other parts of the body including the kidney, brain, skin and liver. The risk of mercury poisoning is significant in North America. For example, 1700 cases of mercury exposure were reported in 2011 but most of them involved minor effects (EPA para 2).

Effects of Mercury

Metallic mercury enters the body through inhalation of contaminated air. Mercury poisoning is associated with numerous symptoms such as emotional instability, tremors, headache, neuromuscular changes, insomnia, and cognitive dysfunction. Higher doses

may cause respiratory failure, kidney dysfunction and death. Methyl mercury impairs neurological developments in fetuses and young children. Exposure to fetuses results from the mothers' consumption of contaminated fish. Early exposure to methyl mercury affects critical functions such as attention, fine motor skills, cognitive thinking, language and memory (US Environmental Protection Agency para 15). Such children may be born with severe disabilities regardless of the mother's health history. Other effects of methyl mercury include sensational disturbances; poor motor coordination, muscle weakness, speech and hearing impairment. Although many studies have investigated the carcinogenic potential of mercury, the available data indicates that mercury cannot cause cancer except in abnormally high doses. Inorganic and organic mercury compounds usually enter the human body via the gastrointestinal tract and cause various symptoms including mental disturbances, memory loss, skin problems and muscle weakness.

Industrial Processes that Emit Mercury

Coal combustion in coal-powered energy plants releases elemental mercury into the atmosphere especially when the combustion occurs at high temperatures. Coal-fired power plants are the leading sources of mercury in North America (EPA para 3). Mercury may also find itself in the environment through the disposal of untreated industrial waste from mineral refineries and municipal waste (Liu, Chai & O'Driscoll 3). In addition, refining processes including smelting, use of hydrocarbons and purification of minerals emit mercury. The main source of mercury emissions in mining and mineral refining is the burning of fossil fuels. Copper, alumina, gold, zinc, and lead refineries

contribute significantly to mercury pollution. Mercury may also be released through mercury extraction processes.

In refineries, the process of roasting, often conducted at temperatures above 1000° C, yields significant amounts of mercury vapor (Liu, Chai & O'Driscoll 4). Roasting is an essential process in iron and steel manufacturing industries and thus this industry plays a significant role in mercury emission. Furthermore, various manufacturing processes such as cement production and caustic soda manufacture release mercury. In cement manufacture, mercury emissions occur as part of the kiln exhaust gases produced when the combustion of fuel in presence of raw materials increases the temperature of the kiln to nearly 1500° C. At these temperatures, significant amount of mercury vapor is generated. The most common raw materials used to produce cement include calcium, alumina, silicon, magnesium oxides and ferric oxides. Part of the mercury comes from the fuels burnt in cement kilns including coal, natural gas, petroleum coke and alternative fuels. However, the combustion of hazardous waste in cement kilns produces much of the industrial mercury pollutants.

Industrial Processes for Reducing Mercury Emission

Most of the industries that emit mercury have adopted industrial processes for reducing emissions. The main processes currently in use include activated carbon injection (ACI) with electrostatic precipitators (ESP) or fabric filter (FF), selective catalytic reduction (SCR) with flue-gas desulfurization (FGD) and activated carbon injection (ACI) (EPA para 4). Selective catalytic reduction (SCR) for scrubbing nitrogen oxides and sulfur oxides also reduces mercury emissions. The SCR catalyst converts elemental mercury (Hg) to oxidized mercury vapor (Hg²⁺). The oxidized mercury is then

removed downstream as mercury chloride (Nakamoto & Neidig 1) (see fig 4). The current focus in technology development is to increase the capability of SCR to remove mercury emissions by developing better SCR catalysts.

Fig 4: mercury removal using SCR

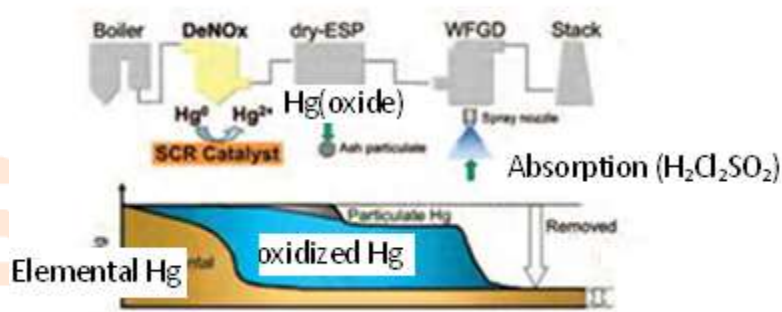


Figure 5. Source: www.apcmag.net

Another industrial process for reducing mercury emissions in coal-burning plants is activated carbon injection (ACI) (Sasmaz 12). Unlike SCR, this technology is specifically aimed at reducing mercury emissions. Two processes are employed depending on the point of injection—fixed-bed granular activated carbon (GAC) or powdered activated carbon (PAC). In the GAC system, the activated carbon is placed downstream of the flue-gas desulfurization unit such that mercury removal is a final purification process. PAC injection involves passing activated carbon via the flue gas and capturing mercury precipitate using electrostatic precipitators (ESP) or fabric filter (FF). The injection site varies depending on the equipment design. GAC is rarely used in coal burning industries. Instead, PAC is the most effective process for removing mercury emissions in coal-fired plants. Activated carbon is quite effective in capturing both oxidized and elemental mercury especially in bituminous coal.

Furthermore, flue-gas desulfurization systems (FGD) employed in removing sulfur emissions are also capable of removing traces of mercury. Wet FGD is able to trap oxidized mercury as an added benefit. Calcium-based FGD systems are able to capture nearly 90 percent of oxidized mercury (Sasmaz 16). Particulate matter (PM) control devices are also used to remove mercury pollutants. PM devices capture particulate matter, leaving the gases to escape. These devices adsorb traces of mercury on their surfaces upon interaction with gases containing mercury vapor. PM devices are quite effective in removing mercury from both bituminous and sub-bituminous coals.

Conclusion

The three types of toxic substances discussed seem to have common sources. The combustion of fossil fuel is the main source of dioxins, inorganic nitrogen and mercury emissions. This renders coal-burning industries especially electric power generation plants the largest source of toxic emission affecting land, water and the atmosphere. The automobile industry also contributes significantly to the emission and the distribution of gaseous emissions especially nitrogen oxides. Other industries including cement manufacturing, nitric acid manufacturing, synthetic fertilizer industry, and mining and mineral refineries are significant contributors to the burden of toxic substances in the environment. However, nearly all of these industries are embracing new technologies for reducing toxic emissions such as selective catalytic reduction and activated carbon injection, which have proved to be quite effective in reducing nitrogen oxides and mercury. The continuous process of developing regulations throughout the united states and Canada requiring industries to reduce toxic emissions through the

adoption of new technologies and alternative fuels will go a long way towards protecting the environment from these and other toxic substances.

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