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Energy and the Environment:

A brief review of the phenomena, effects and solutions

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ABSTRACT

Evidentially, the different types of energy resources conversion and use into different forms affect the environment. These effects are primarily involved the main air pollutant caused by fossil fuel combustion and secondary emissions from automobiles. Since air pollutants causes the emission of particulate matter (PM), sulfur dioxide (SO_2), nitrogen oxides (NO_x), hydrocarbons (HC) and carbon monoxide (CO) to the environment, likewise, automobiles as the main source of air pollution and greenhouse gases cause the emission of volatile organic compounds (VOC), nitrogen oxides (NO_x), carbon monoxide (CO) and carbon soot (C) particles. Although fossil fuel use has made possible the industrial development and better modern life facilities, but as a major factor, it has also led to the undesirable health effects and still causes massive global climate changes and generally the global warming. The increase of environmental pollution at alarming rates and the rising awareness of its dangers made it necessary to control it by legislation and international treaties. Therefore, better use of different energy resources and its adapted technologies has become an essential issue, and in this field demands major studies and researches to counter reducing its environmental impacts. Hence, this study deals with energy and the environment, along with a brief review of their phenomena, effects and solutions, so that the different types of emissions and pollutants are first introduced, then its effects are elaborated and in continuance referred to its appropriate solutions. And finally, this article can be a good reference for engineers, researchers and users of various energy sources by providing adequate information and useful conclusions in the form of tables.

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1. Introduction

The conversion of energy from one form to another often affects the environment and the air we breathe in many ways. Fossil fuels such as coal, oil, and natural gas have been powering the industrial development and the amenities of modern life that we enjoy since the 1700s, but this has not been without any undesirable side effects. From the soil we farm and the water we drink to the air we breathe, the environment has often payed a heavy toll. Pollutants emitted during the combustion of fossil fuels contribute to smog, acid rain, and climate change. The environmental pollution has reached such high levels that it has become a serious threat to vegetation, wildlife, and human health. Air pollution has been the cause of numerous health problems including asthma and cancer. It is estimated that, over 60,000 people in the United States alone die each year due to heart and lung diseases related to air pollution [1].

Considerable amounts of pollutants are emitted as the chemical energy in fossil fuels is converted to thermal, mechanical, or electrical energy via combustion, and thus power plants, industrial processes, motor vehicles, residential and commercial energy consumption, and even stoves take the blame for air pollution. Hundreds of elements and compounds such as benzene and formaldehyde are known to be emitted during the combustion of coal, oil, natural gas, and wood in electric power plants, engines of vehicles [2], furnaces, and even fireplaces.

The largest sources of air pollution are the industrial activities and motor vehicles, and the pollutants released by them are usually grouped as hydrocarbons (HC), sulfur dioxide (SO_2), nitrogen oxides (NO_x), particulate matter (PM), and carbon monoxide (CO) [3–5]. The HC emissions are a large component of volatile organic compounds (VOCs) emissions, and the two terms are generally used interchangeably for motor vehicle emissions.

The increase of environmental pollution at alarming rates and the rising awareness of its dangers made it necessary to control it by legislation and international treaties. In the United States, the Clean Air Act of 1970 (whose passage was aided by the 14-day smog alert in Washington that year) set limits on pollutants emitted by large plants and vehicles. These early standards focused on emissions of HC, NO_x, and CO. The new cars were required to have catalytic converters in their exhaust systems to reduce HC, NO_x, and CO emissions [6,7]. As a side benefit, the removal of lead from gasoline to permit the use of catalytic converters led to a significant reduction in toxic lead emissions. Emission limits for SO_2, PM, HC, NO_x, and CO have been declining steadily since 1970. The Clean Air Act

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of 1990 made the requirements on emissions even tougher, primarily for ozone, CO, nitrogen dioxide, and PM. As a result, today's industrial facilities and vehicles emit a fraction of the pollutants they used to emit a few decades ago.

Another important issue is the greenhouse effect and relevant gases emissions that is always experienced on a larger scale on earth. The surface of the earth, which warms up during the day as a result of the absorption of solar energy, cools down at night by radiating part of its energy into deep space as infrared radiation. Carbon dioxide (CO_2), water vapor (H_2O), and trace amounts of some other gases such as methane (CH_2) and nitrous oxide (N_2O) act like a blanket and keep the earth warm at night by blocking the heat radiated from the earth Figure 1. Therefore, they are called greenhouse gases, with CO_2 being the primary component along with water vapor [8,9]. Water vapor is usually taken out of this list since it comes down as rain or snow as part of the water cycle and human activities in producing water (such as the burning of fossil fuels) do not make much difference on its concentration in the atmosphere. CO_2 is different, however, in that people's activities do make a difference in CO_2 concentration in the atmosphere.

The greenhouse effect makes life on earth possible by keeping the earth warm (about 30°C warmer). However, excessive amounts of these gases disturb the delicate balance by trapping too much energy, which causes the average temperature of the earth to rise and the climate at some localities to change. These undesirable consequences of the greenhouse effect are referred to as global warming or global climate change.

The global climate change is due in part to the excessive use of fossil fuels such as coal, petroleum products, and natural gas in electric power generation, transportation, buildings, and manufacturing, and it has been a concern in recent decades. The concentration of CO_2 in the atmosphere as of 2019 is about 410 ppm. This is 20 percent higher than the level a century ago, and it is projected to increase to over 700 ppm by the year 2100 [10].

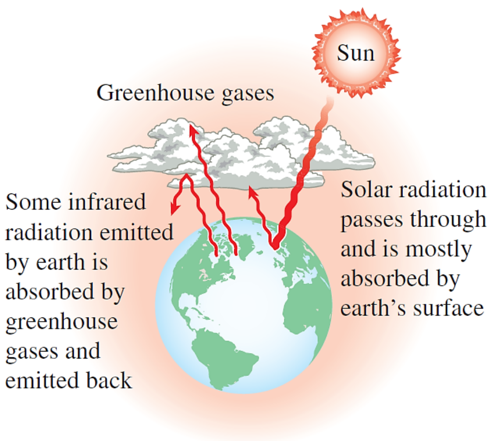

Figure 1. The greenhouse effect on the earth [11].

Under normal conditions, vegetation consumes CO_2 and releases O_2 during the photosynthesis process, and thus keeps the CO_2 concentration in the atmosphere in check, unfortunately, deforestation and the huge increase in the CO_2 production in recent decades have disturbed this balance.

In a 1995 report, the world's leading climate scientists concluded that the earth has already warmed about 0.5°C during the last century, and they estimate that the earth's temperature will rise another 2°C by the year 2100. A rise of this magnitude is feared to cause severe changes in weather patterns with storms and heavy rains and flooding at some parts and drought in others, major floods due to the melting of ice at the poles, loss of wetlands and coastal areas due to rising sea levels, variations in water supply, changes in the ecosystem due to the inability of some animal and plant species to adjust to the changes, increases in epidemic diseases due to the warmer temperatures, and adverse side effects on human health and socioeconomic conditions in some areas.

The seriousness of these threats has moved the United Nations to establish a committee on climate change. A world summit in 1992 in Rio de Janeiro, Brazil, attracted world attention to the problem. The agreement prepared by the committee in 1992 to control greenhouse gas emissions was signed by 162 nations. In the 1997 meeting in Kyoto (Japan), the world's industrialized countries adopted the Kyoto Protocol and committed to reduce their CO_2 and other greenhouse gas emissions by 5 percent below the 1990 levels by 2008 to 2012. In December 2011, countries agreed in Durban, South Africa, to forge a new deal forcing the biggest polluting countries to limit greenhouse gas emissions. The Kyoto Protocol was extended to allow 5 more years to finalize a wider agreement. The goal was to produce a new, legally binding accord to cut greenhouse gas emissions that would be completed by 2015 and would come into force by 2020.

In 2015, the United Nations Climate Change Conference was held in Paris (France), resulting in the Paris Agreement on the reduction of climate change. The conference included participants from 196 nations. The main result of the conference was the establishment of a goal to limit global warming to less than 2°C compared to preindustrial times. According to the agreement, human-made (also called anthropogenic) greenhouse emissions should be eliminated during the second half of the 21st century.

Major sources of air pollution and greenhouse gas emissions are industrial sector and transportation [12,13], wich in the folloving, factors, effects and solutions are discussed in detail.

2. Air Pollutants

The minimum amount of air needed for the complete combustion of a fuel is called the stoichiometric or theoretical air [14]. When a fossil fuel such as coal, oil, or natural gas is burned completely with air, the combustion products do not contain any air pollutants. Natural gas is usually approximated by methane (CH_4), and the theoretical combustion of CH_4 with air which consists of nitrogen (N_2) and oxygen (O_2) is

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2 \quad (1)$$

Gasoline and diesel fuel used in automobile and vehicle engines are commonly approximated by octane (C_8H_{18}). If octane is burned completely with stoichiometric amount of air, the reaction is

$$C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + (12.5 \times 3.76)N_2 \quad (2)$$

If we consider the combustion of a particular composition or assay of coal (80 percent C, 5 percent H_2, 6 percent O_2, 2 percent N_2, 0.5 percent S, and 6.5 percent ash) with the theoretical amount of air, the complete reaction is

$$6.667C + 2.5H_2 + 0.1875O_2 + 0.07143N_2 + 0.01563S + 7.745(O_2 + 3.76N_2) \rightarrow 6.667CO_2 + 2.5H_2O + 0.01563SO_2 + 29.19N_2 \quad (3)$$

In this reaction, there will also be ash, which is nonreacting component. In actual combustion processes, it is common practice to use more air (called excess air) than the stoichiometric amount to increase the chances of complete combustion and/or to control the temperature of the combustion chamber. A combustion process is complete if all the carbon in the fuel burns to CO_2, all the hydrogen burns to H_2O, and all the sulfur (if any) burns to SO_2. That is, all the combustible components of a fuel are burned to completion during a complete combustion process. Conversely, the combustion process is incomplete if the combustion products contain any unburned fuel or components such as C, H_2, CO, or OH.

Insufficient oxygen is an obvious reason for incomplete combustion, but it is not the only one. Incomplete combustion occurs even when more oxygen is present in the combustion chamber than is needed for complete combustion. This may be attributed to insufficient mixing in the combustion chamber during the limited time that the fuel and the oxygen are in contact. This is particularly true for internal combustion engines. Another cause of incomplete combustion is dissociation, which becomes important at high combustion temperatures.

Oxygen has a much greater tendency to combine with hydrogen than it does with carbon. Therefore, the hydrogen in the fuel normally burns to completion, forming H_2O, even when there is less oxygen than needed for complete combustion. Some of the carbon, however, ends up as CO or just as plain C particles (soot) in the products.

Main air pollutants resulting from the combustion of fossil fuels [15–17] can be summarized as Figure 2:

- Particulate matter (PM)
- Sulfur dioxide (SO_2)
- Nitrogen oxides (NO_x)
- Hydrocarbons (HC) including carbon soot particles (C)
- Carbon monoxide (CO)

Note that HC , C, and CO emissions are mainly produced due to incomplete combustion which may be due to insufficient oxygen, insufficient mixing of fuel and air, etc. However, SO_2 is inevitably produced when the fuel contains sulfur [18]. Sulfur is a fuel which reacts with oxygen to form SO_2. NO_x generation is due to high temperature reactions between atomic nitrogen and oxygen. Particulate matter is commonly called ash and it is produced mostly when coal or oil is burned.

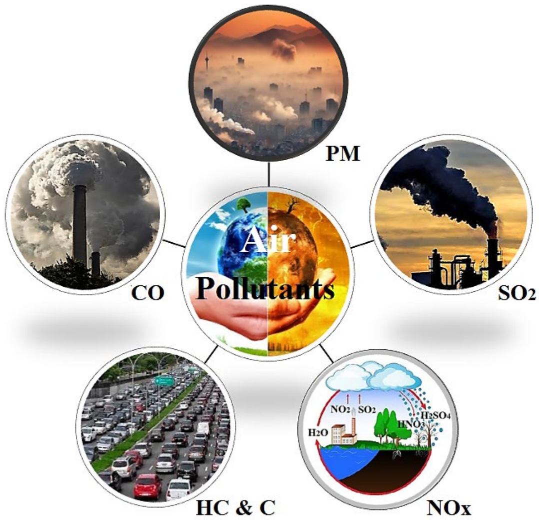

Figure 2. Main air pollutants resulting from the combustion of fossil fuels.

2.1. Particulate matter

Small solid and liquid particles suspended in air is generally referred to as particulate matter (PM). A primary group of PM is ash and soot particles generated from the combustion of coal and oil. Many manufacturing and other industrial processes are responsible for the production of various PMs [19]. Dust particles from roads and construction and agricultural activities as well as iron, silicon, soil, and materials of earth can also be considered as part of PM. Nitrates and sulfates are formed as a result of SO_2 and NO_x emissions, and referred to as secondary PM.

When the particles are less than 10 micrometers (10^{-6} m), they are called PM10 and classified as coarse. PM2.5 refers to particles less than 2.5 mm, and referred to as fine. Particulate matter is associated with significant health effects in particular respiratory diseases such as asthma and bronchitis, cardiovascular and lung diseases, lung tissue damage, visibility impairment, and cancer [20]. PM2.5 can penetrate deeply into the respiratory system, and therefore it is more dangerous to health than PM10. Coal contains considerable amounts of ash, which are noncombustible components of the fuel. The mass percentage of ash in coal greatly varies depending on the source. It is about 10 percent on average for bituminous coal (soft coal with high energy content) and about 5 percent for subbituminous coal (low energy content coal) [21].

The combustion of coal produces large amounts of ash, which should be removed in a safe and effective manner. In coal-fired power plants, ash particles are carefully collected from the combustion gases. However, some ash and other particulates still remain in the combustion gases, and emitted to the atmosphere. It is estimated that about 1 g of PM is released to the environment for each kWh of electricity produced from a coal-fired power plant. The collection of ash from coal-fired plants involves some water pollution as water is used to transport ash in the plant. These ash particles are released to the environment when this water along with other water streams is discharged to the lakes or rivers.

In a coal-fired power plant, the flying ash particles (flash) in combustion gases can be removed and safely collected by various means. One common way is by using a device called an electrostatic precipitator (ESP) [22], as shown in Figure 3. This prevents flash particles from being emitted to the atmosphere. An ESP is very effective as it removes more than 99 percent of the ash in the combustion gases. In an ESP system, combustion gases flow between two collector plates. An electric field is applied between a discharge electrode wire and the two plates, creating electric field between the plates. As the combustion gases flow between the plates, ash particles are bombarded with negative ions. The charged particles are then moved toward positively charged plates as a result of electrostatic attraction. Ash particles are collected on the plates. This process is repeated in many plates for maximum removal of flash [23].

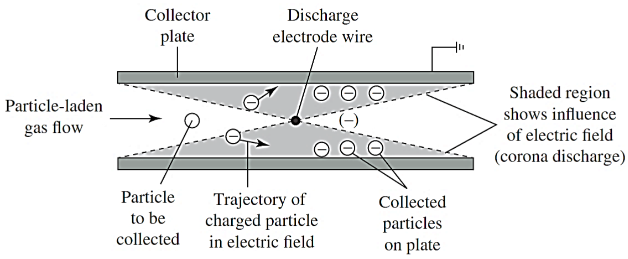

Figure 3. Operation of an electrostatic precipitator (EPS) [23].

2.2. Sulfur dioxide

Fossil fuels are mixtures of various chemicals, including some amounts of sulfur. The sulfur in the fuel reacts with oxygen to form sulfur dioxide (SO_2), which is an air pollutant:

$$S + O_2 \rightarrow SO_2 \quad (4)$$

Coal contains the most amount of sulfur among fossil fuels. Bituminous coal contains 0.5 to 4.0 percent sulfur by mass with an average value of 1.5 percent. Subbituminous coal typically contains much less sulfur with an average of 0.4 percent by mass. Low-sulfur coal is more desirable and has high monetary value. Mass percentage of sulfur in oil may range between 0.3 and 2.3 percent depending on the source and processing in oil refineries [21]. Natural gas also contains sulfur with varying amounts when extracted from the ground but it is removed in gas treatment plants. Therefore, natural gas combustion does not produce any SO_2.

The main source of SO_2 is the electric power plants that burn high-sulfur coal [24]. The Clean Air Act of 1970 has limited the SO_2 emissions severely, which forced the plants to install SO_2 scrubbers, to switch to low-sulfur coal, or to gasify the coal and recover the sulfur. Volcanic eruptions and hot springs also release sulfur oxides.

When coal is burned, more than 95 percent of sulfur is oxidized to SO_2. About 2 to 5 percent of sulfur in the coal does not get burned and ends up in the solid ash particles. Less than 1 percent of the SO_2 formed during combustion further reacts with O_2 to form SO_3. The resulting SO_3 react with water vapor in the combustion gases to form sulfuric acid (H_2SO4). SO_2 emitted from the combustion and other systems can react in the atmosphere to form sulfates which are components of acid rain [25,26].

Motor vehicles also contribute to SO_2 emissions since diesel fuel also contain small amounts of sulfur. Recent regulations have reduced the amount of sulfur in diesel fuel. In Europe the sulfur level in diesel fuel was limited to less than 50 ppm since 2005. The acceptable sulfur level in diesel fuel is dropped from 50 to 10 ppm in the United States in 1990s. Currently most diesel fuels in Europe and North America is ultra-low-sulfur diesel with a maximum of 10 ppm sulfur. The exhaust of a diesel engine can contain up to 20 ppm of SO_2.

The most effective method of reducing SO_2 emissions is to use low-sulfur coal in electricity generation plants and heating systems [27]. However, this may not be possible if low-sulfur coal is not available or expensive compared to high-sulfur coal. Also, installing a SO_2 removal system can be more cost-effective than using low-sulfur coal. Today, all coal-fired power plants must be equipped with flue gas desulfurization (FGD) systems, which are very effective in SO_2 removal [28]. In this process, a slurry of pulverized limestone (calcium carbonate - $CaCO_3$) mixed with water is used. The process takes place in a vessel called scrubber. A mixture of limestone and water is sprayed into the combustion gas containing SO_2 according to [23] the reaction:

$$SO_2 + (CaCO_3 + 2H_2O) + \tfrac{1}{2}O_2 \rightarrow CO_2 + (CaSO_4 \cdot 2H_2O) \quad (5)$$

The product gypsum ($CaSO_4 \cdot 2H_2O$) has commercial value as it is a main constituent in plaster, blackboard chalk, and wallboard. A modern flue gas desulfurization system utilizing limestone ($CaCO_3$) can remove more than 95 percent of SO_2 in combustion gases. Some systems may also use lime (CaO) which is more effective, and can remove up to 99 percent of SO_2.

Sulfur dioxide is a very toxic pollutant with serious health effects, as shown in Figure 4. It requires a shorter exposure time at higher SO_2 concentrations for significant health impact. Longer exposures at low concentrations and shorter exposures at high concentrations may result in the similar health effects. When SO_2 level in atmosphere is more than 1 ppm, it can lead to airway constriction. The health effects of SO_2 include respiratory, lung, and cardiovascular illnesses. Children and elderly with asthma and breathing problems are more sensitive to SO_2 exposure. It also negatively affects ecosystems of rivers, lakes, and forests.

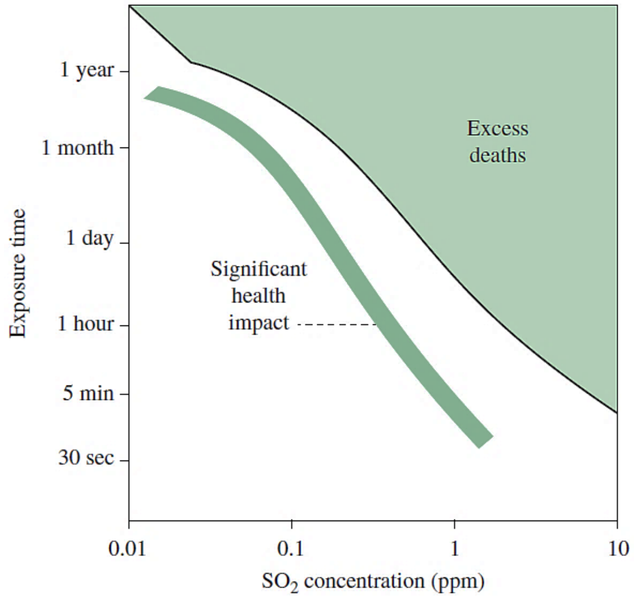

Figure 4. Health impact of SO_2 concentration as a function of exposure time [29].

Sulfur dioxide is not only a harmful emission but also poisons catalyst materials in catalytic converters. Particulate traps used in reducing carbon soot particles in diesel engines are negatively affected by sulfur components in the exhaust. Another reaction of sulfur is that it combines with hydrogen at high temperatures to form hydrogen sulfide (H_2S):

$$S + H_2 \rightarrow H_2S \tag{6}$$

H_2S is a colorless, poisonous, corrosive, flammable, and explosive gas with a rotten egg smell. Long-term exposure to H_2S is associated with nervous and respiratory system and eye effects.

2.3. Nitrogen oxides

Nitrogen oxide (NO_x) and nitrogen dioxide (NO_2) are produced during the combustion of fossil fuels such as coal, oil, and natural gas. Electrical power plants, automobiles, and other vehicles burning fossil fuels are responsible for nitric oxide (NO) and nitrogen dioxide (NO_2) emissions, which are combined with a name of nitrogen oxides or oxides of nitrogen (NO_x). Most of the NO_x emissions from a combustion system to the atmosphere are NO but it gradually turns into NO_2 by reacting with oxygen in air [30].

Nitrogen oxides are produced at high combustion temperatures when a fuel is burned with oxygen in air. A number of possible reactions can contribute the formation of NO and NO_2. Some of these reactions are as follows:

$$N_2 + O \rightarrow NO + N \tag{7}$$

$$N + O_2 \rightarrow NO + O \tag{8}$$

$$N + OH \rightarrow NO + H \tag{9}$$

$$NO + O_2 \rightarrow NO_2 + O \tag{10}$$

$$NO + H_2O \rightarrow NO_2 + H_2 \tag{11}$$

In above reactions, monatomic oxygen (O) reacts with N_2 and monatomic nitrogen (N) reacts with O_2 to form NO. Also, N and OH react to produce NO. Nitrogen is normally stable in air as diatomatic (N_2) and does not react with oxygen. However, some nitrogen breaks down at high combustion temperatures as a result of dissociation reaction

$$N_2 \rightarrow 2N \tag{12}$$

At high combustion temperatures, O_2 and H_2O also dissociates as follows:

$$O_2 \rightarrow 2O \tag{13}$$

$$H_2O \rightarrow OH + \frac{1}{2}H_2 \tag{14}$$

The monatomic nitrogen N can easily react with O_2 to form NO, N_2 reacts with O to form NO, and NO reacts with O_2 or H_2O to form NO_2.

NO_x can also be formed by the reactions of atomic nitrogen and oxygen particles in fuel. This is particularly the case for coal as it contains about 10 percent oxygen and 1 percent nitrogen by mass. Natural gas also contains small amounts of nitrogen and oxygen. For higher NO_x formation levels, the nitrogen in fuel usually has greater contribution to NO_x formation compared to that due to N_2 and O_2 in air.

In an internal combustion engine, the combustion temperatures can reach 2500 or 3000 K allowing some dissociation reactions, which result in NO_x formation. At higher combustion temperatures, more dissociation reactions cause greater amounts of NO_x production. Very little NO_x is formed at low temperatures.

Nitrogen oxide emissions are greatly reduced in gasoline burning automobiles by the use of catalytic converters. In diesel engines, catalytic converter is not much effective in reducing NO_x. Instead, exhaust gas recycling (EGR) is used effectively to control NO_x generation [31]. In EGR, some exhaust gases (up to 30 percent) are diverted back to the combustion chamber. These gases do not react with air, but absorb heat in the chamber, thus reducing the combustion temperature. In some large internal combustion engines such as those used in electricity production and in ships, tiny water droplets are injected into the combustion chamber. Water evaporates absorbing heat from the surroundings. This reduces combustion temperature and levels of NO_x formation.

An effective method of NO_x control involves design and optimum operation of combustion process in combustion chambers and burners. This includes controlling combustion temperature, combustion time, and some design characteristics of the burner. The burners specifically designed for controlling NO_x emission is called low- NO_x burners.

Another method of NO_x control involves a chemical treatment system to remove NO_x components in combustion gases [32]. In coal-fired power plants, a selective catalytic reduction (SCR) unit is installed into the combustion gas stream right after the boiler. The system uses a catalyst material to promote the conversion of NO_x components into non harmful molecular nitrogen N_2. Ammonia (NH_3) is also injected into the combustion gas stream during the following reactions:

$$NO + NH_3 + \frac{1}{4}O_2 \rightarrow N_2 + \frac{3}{2}H_2O \quad (15)$$

$$NO_2 + 2NH_3 + \frac{1}{2}O_2 \rightarrow \frac{3}{2}N_2 + 3H_2O \quad (16)$$

These reactions require a temperature of about 400°C, and this is the reason the SCR system is installed right after the boiler of the power plant. The SCR systems can typically remove 70 to 90 percent of NO_x in the combustion gases.

Nitrogen oxides react in the atmosphere to form ground-level ozone. It contributes to the photochemical smog and acidification of waters and soils. The emission of NO_x causes the formation of nitrates, which are considered as PM (mostly PM2.5). Nitrogen dioxide (NO_2) gas is toxic at high concentrations. The primary health effects of NO_2 are related to respiratory illnesses such as asthma and bronchitis.

2.4. Hydrocarbons

Fossil fuels (coal, oil, natural gas) are primarily made of hydrocarbons (HC). In a combustion reaction, some of the fuel cannot find oxygen to react with during the combustion period. As a result, some unburned or partially burned fuel particles leave the exhaust gases as HC components. This will certainly happen when there is deficiency of air (not enough air to burn all the fuel) during combustion. However, having sufficient (i.e., stoichiometric) or excess air does not guarantee that all fuel will be burned at the end of the combustion process. Insufficient mixing between fuel and air, nonhomogeneous mixture, and short time of reaction are some of the causes for incomplete combustion and resulting HC emission.

The terms HC and volatile organic compounds (VOC) are usually used interchangeably [33]. However, some of VOCs found in an automobile exhaust also contain components other than HCs such as aldehydes.

A significant portion of the VOC or HC emissions in vehicles are caused by the evaporation of fuels during refueling or spillage during spit back or by evaporation from gas tanks with faulty caps that do not close tightly. The solvents, propellants, and household cleaning products that contain benzene, butane, or other HC products are also significant sources of HC emissions. Additional sources of HC emissions include venting of crankcase, petroleum refineries, chemical plants, gasoline and diesel fuel distribution and storage facilities, dry cleaners, and other processes involving chemical solvents.

When diesel fuel is burned in an internal combustion engine, combustion gases contain unburned carbon (C) soot particles, which are sometimes seen as a black smog. Carbon soot particles are usually in the form of spheres with diameters between 10 and 80 nm (10×10^{-9} to 80×10^{-9} m). The particles are essentially solid carbon with some HC on the surface.

Carbon particles are generated during combustion of an HC fuel in the fuel-rich zones with insufficient air:

$$C_mH_n + w(O_2 + 3.76N_2) \rightarrow a\,CO_2 + b\,H_2O + \quad (17)$$

$$c\,CO + d\,N_2 + e\,C(solid)$$

These soot particles may find oxygen to react with by the time the combustion is finished:

$$C(solid) + O_2 \rightarrow CO_2 \quad (18)$$

Therefore, most of carbon particles generated initially in the combustion chamber will be burned into CO_2, and never get exhausted to the atmosphere. Most diesel automotive engines are equipped with particulate traps to collect soot particles. The traps are cleaned/regenerated periodically by burning the collected particles.

In a gasoline automotive engine, up to 6000 ppm of HC components exist in the exhaust after the combustion chamber. This represents 1 to 1.5 percent of the fuel. About half of these are unburned fuel components while the rest are partially burned. Fortunately, most of these components are treated in the catalytic converter of the engine before exhaust gases end up in the atmosphere.

Compared to gasoline engines, much less HC is found in the engine exhaust of a diesel engine. The reason is that the air-fuel ratio in diesel engines (between 18 and 70) is typically much higher than those in gasoline engines (between 12 and 18). If diesel engines did not use considerable amounts of excess air for combustion, the carbon soot particle emissions would be higher than most legal limits.

Hydrocarbon components and carbon soot particles in air act as irritants and odorants. Some of them are believed to be carcinogenic. Nitrogen oxides and HC are two main sources for the formation of ground level ozone. Except for CH_4, HC components react in atmosphere to form photochemical smog.

2.5. Carbon monoxide

Carbon monoxide (CO) is a colorless, odorless, poisonous gas [34]. It is mostly emitted by industry and motor vehicles, and it can build to dangerous levels in areas with heavy congested traffic. CO is produced during combustion when there is fuel-rich mixture (not enough air or oxygen in the air-fuel mixture). During the combustion of an HC fuel, carbon reacts with oxygen according to the reaction:

$$C + \frac{1}{2}O_2 \rightarrow CO \quad (19)$$

The resulting CO is also a fuel with energy content (HV = 10100 kJ/kg). It further reacts with oxygen again to form CO_2 to complete the reaction:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad (20)$$

If CO cannot find oxygen after the first reaction due to deficiency of oxygen or insufficient mixing, some CO will be part of the exhaust. CO emission can be minimized by avoiding fuel-rich mixtures, better mixing of fuel and air, and increasing combustion time.

In a gasoline automobile, most CO is produced at engine start-up and acceleration during which engine runs with fuel-rich mixtures. The percentage of CO in the exhaust of a gasoline engine can be as low as 0.1 percent and as high as 5 percent. Diesel engines generate very small amounts of CO since they use excess air in fuel-air mixtures.

Carbon monoxide deprives the body's organs from getting enough oxygen by binding with the red blood cells that would otherwise carry oxygen [35]. At low levels, CO decreases the amount of oxygen supplied to the brain and other organs and muscles, slows body reactions and reflexes, and impairs judgment. It poses a serious threat to people with heart disease because of the fragile condition of the circulatory system and to fetuses because of the oxygen needs of the developing brain. At high levels, it can be fatal, as evidenced by numerous deaths caused by cars that are warmed up in closed garages or by exhaust gases leaking into the cars.

Hemoglobin is the protein molecule in red blood cells that carries oxygen from the lungs to the body's tissues and returns carbon dioxide from the tissues back to the lungs. Carbon monoxide absorbed in hemoglobin is called carboxyhemoglobin (COHb). Negative physiological effects on the body are observed when the levels of COHb is above 100 ppm or 0.01 percent, Figure 5. Serious effects including coma take place after 300 ppm, and long-term exposure above 600 ppm is fatal.

3. Ozone, smog, and acid rain

If you live in a metropolitan area, you are probably familiar with urban smog (smoke + fog = smog) - the dark yellow or brown haze that builds up in a large stagnant air mass and hangs over populated areas on calm hot summer days. Smog (also called photochemical smog) is made up mostly of ground-level ozone (O_3), but it also contains numerous other chemicals, including CO, PM such as soot and dust, volatile organic compounds (VOCs) such as benzene, butane, and other HC.

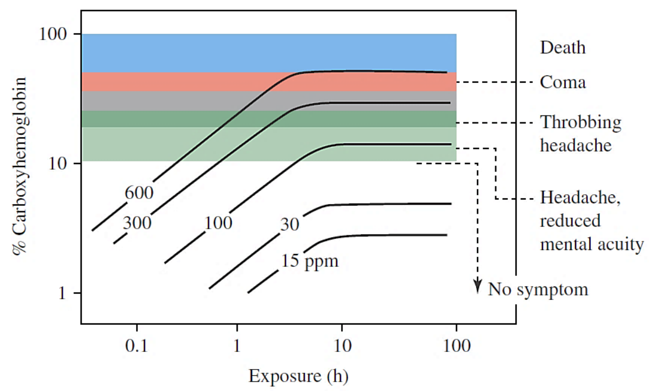

Figure 5. Effect of carboxyhemoglobin (COHb: CO absorbed in hemoglobin) on the human body [36].

The harmful ground-level ozone should not be confused with the useful ozone layer high in the stratosphere that protects the earth from the sun's harmful ultraviolet (UV) rays [37]. Ozone at ground level is a pollutant with several adverse health effects. It is harmful to lungs, other biological tissue, and trees. It can react with rubber, plastics, and other materials with serious damage.

The primary sources of NO_x and HC are motor vehicles and power plants. Hydrocarbons and NO_x react in the presence of sunlight on hot calm days to form ground-level ozone, which is the primary component of smog. Possible reactions to produce smog and ozone are:

$$NO_2 + \text{energy from sunlight} \rightarrow NO + O + \text{smog} \quad (21)$$

$$O + O_2 \rightarrow O_3 \quad (22)$$

The smog formation usually peaks in late afternoons when the temperatures are highest and there is plenty of sunlight. Although ground-level smog and ozone form in urban areas with heavy traffic or industry, the prevailing winds can transport them several hundred miles to other cities. This shows that pollution knows of no boundaries, and it is a global problem.

Ozone irritates eyes and damages the air sacs in the lungs where oxygen and carbon dioxide are exchanged, causing eventual hardening of this soft and spongy tissue. It also causes shortness of breath, wheezing, fatigue, headaches, and nausea, and aggravates respiratory problems such as asthma. Every exposure to ozone does a little damage to the lungs, just like cigarette smoke, eventually reducing the individual's lung capacity. Staying indoors and minimizing physical activity during heavy smog minimizes damage. Ozone also harms vegetation by damaging leaf tissues. To improve the air quality in areas with the worst ozone problems, reformulated gasoline (RFG) that contains at least 2 percent oxygen was introduced. The use of RFG has resulted in significant reduction in the emission of ozone and other pollutants, and its use is mandatory in many smog-prone areas.

The most effective method of reducing ground-level ozone involves minimizing NO_x and HC emissions. Large reductions of HC emissions from motor vehicles in recent decades contributed this cause. However, significant reductions in NO_x and further reductions in HC emissions are needed to deal with the challenges to control ozone levels in atmosphere.

The other serious pollutant in smog is CO. Smog also contains suspended PM such as dust and soot emitted by vehicles and industrial facilities. Such particles irritate the eyes and the lungs since they may carry compounds such as acids and metals.

The sulfur oxides and nitric oxides react with water vapor and other chemicals high in the atmosphere in the presence of sunlight to form sulfuric and nitric acids. The acids formed usually dissolve in the suspended water droplets in clouds or fog. These acid-laden droplets, which can be as acidic as lemon juice, are washed from the air on to the soil by rain or snow. This is known as acid rain.

Sulfur dioxide reacts with water and dissolved oxygen to produce sulfuric acid (H_2SO_4):

$$H_2O + SO_2 + \tfrac{1}{2}O_2 \rightarrow H_2SO_4 \quad (23)$$

Another reaction of SO_2 produces sulfurous acid (H_2SO_3):

$$H_2O + SO_2 \rightarrow H_2SO_3 \quad (24)$$

Both sulfuric acid and sulfurous acid are components of acid rain. Acid droplets can penetrate deeply into lungs during respiration. When SO_2 produced from power plants are transported through long distances due to winds, it may be transformed into sulfate particles and other acidic species. Also, NO_x emissions cause the formation of nitrate species. Sulfates, nitrates and other acidic species contribute acid rain.

The soil is capable of neutralizing a certain amount of acid, but the amounts produced by the power plants using inexpensive high-sulfur coal has exceeded this capability. The magnitude of the problem was not recognized until the early 1970s, and serious measures have been taken since then to reduce the SO_2 emissions drastically by installing scrubbers in plants and by desulfurizing coal before combustion.

4. Emissions from automobiles

Automobiles are most noticeable source of air pollution and greenhouse gas emissions [38]. Pollutant emissions from automobiles and other internal combustion engine powered vehicles and machines have decreased by more than 90 percent since 1970s. However, the number of automobiles has multiplied many times over the same period resulting in a significant increase in pollutant and greenhouse gas emissions.

There are four major pollutant emissions from automobiles powered by internal combustion engines burning gasoline or diesel fuel:

- Hydrocarbons (HC). Also called volatile organic compounds (VOC).
- Nitrogen oxides (NO_x)
- Carbon monoxide (CO)
- Carbon soot (C) particles. Primarily emitted from diesel fuel vehicles.

Table 1, gives average emissions from different type of motor vehicles in the United States. For passenger cars, HC, CO, and NO_x emissions are 0.79, 8.73, and 0.56 g/mi, as shown in Table 1. The corresponding emission values were 4.0, 42.9, and 2.7 g/mi in 1990 [11]. These values indicate that HC, CO, and NO_x emissions from automobiles were decreased by about 80 percent over a 20-year period.

Environmental impacts of automobiles are not limited to pollutant and greenhouse gas emissions with the exhaust. For example, disposal of cars with minimum impact on the environment remains a challenge. In the United States, about 75 percent of car materials are recycled and reused. The remaining 25 percent is buried in a landfill. Lead emissions from the use of leaded gasoline in some parts of the world, chlorofluorocarbon (CFC) emissions from automobile air-conditioning, and waste motor oil are among other environmental issues related to automobiles.

Table 1: Average Emissions from Automobiles in the United States [11].

Setup	Average Emission (g/mi)	Annual Emission (kg/yr)
Light-duty vehicles (passenger cars)		
HC	0.79	10700
CO	8.73	117900
NO_x	0.56	7560
PM10	0.0044	59
PM2.5	0.0041	55
CO_2	368	4968000
Gasoline consumption	0.04149 gal/mi	560 gal/yr
Light-duty trucks		
HC	1.01	13600
CO	11.02	148800
NO_x	0.81	10900
PM2.5	0.0049	66
PM2.5	0.0045	61
CO_2	514	6939000
Gasoline consumption	0.05780 gal/mi	780 gal/yr
Heavy-duty vehicles		
HC	1.14	
CO	9.42	
NO_x	2.25	
Motorcycles		
HC	2.29	
CO	14.59	
NO_x	1.25	
Diesel, light-duty vehicle		
HC	0.18	
CO	0.90	
NO_x	0.42	
Diesel, light duty trucks		

HC	0.44	
CO	0.76	
NO_x	0.72	
Diesel, heavy-duty vehicles		
HC	0.39	
CO	1.75	
NO_x	6.87	
Average, gasoline and diesel		
HC	0.89	12000
CO	9.37	126500
NO_x	1.30	17600

Notes:
• Annual emissions data is based on an average 13,500 mi of travel per year.
• Vehicles types are defined as follows: light-duty vehicles (passenger cars up to 6000 lbm); light-duty trucks (pickups and minivans up to 8500 lbm); heavy-duty vehicles (8501 lbm or more); motorcycle (highway only).
• Emissions factors are national averages based on the following assumptions: ambient temperature 75°F, daily temperature range 60 to 84°F, average traffic speed 27.6 mph (representative of overall traffic in urban areas).

5. Catalytic Converters

Catalytic converters are commonly used in automobile engines for after treatment, and located in the exhaust system [39]. Hot exhaust gases leaving the combustion chamber are forced to flow in the converter which is a chemical chamber. Some catalyst materials are used in the chamber to promote treatment reactions. HC and CO O that exist in the combustion gases react with O_2 in the converter to form H_2O and CO_2:

$$C_mH_n + wO_2 \rightarrow a\,H_2O + b\,CO_2 \tag{25}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{26}$$

Here, m, n, w, a, b, and c are some suitable constants and are needed to balance the chemical equation. Another possible reaction is called water-gas shift, which uses water instead of oxygen as the oxidant:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{27}$$

Several reactions are possible to convert NOx to acceptable components [40] such as:

$$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2 \tag{28}$$

$$2NO + CO \rightarrow N_2O + CO_2 \tag{29}$$

$$NO + H_2 \rightarrow \frac{1}{2}N_2 + H_2O \tag{30}$$

$$2NO + H_2 \rightarrow N_2O + H_2O \tag{31}$$

$$2NO + 5CO + 3H_2O \rightarrow 2NH_3 + 5CO_2 \tag{32}$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \tag{33}$$

The above reactions readily take place in the converter at chamber temperatures of 600 to 700°C. However, due to the existence of catalyst materials in the converter, these reactions can occur 250 to 300°C. Since exhaust temperatures found in automobile and other transport engines are normally between 300 and 500°C, catalytic converters are very effective in reducing harmful emissions.

A well-working catalytic converter reduces HC, CO, and NO_x components by more than 90 percent when the converter temperature is 400°C or above. Converter effectiveness reduces when the temperature goes down. For a converter to effectively treat HC and CO components, the air-fuel mixture should have some excess air. Therefore, the converter is most effective for lean air-fuel mixtures. Sometimes gasoline engines operate with rich mixtures especially during start-up and acceleration, and the catalytic converter becomes very ineffective during these periods. On the other hand, the converter is most effective in NO_x conversion when the mixture is close to stoichiometric (theoretical). At lean mixtures, the converter becomes ineffective for treating NO_x components.

Diesel engines also use catalytic converters but their design should also include the conversion of carbon soot particles. This is done by using larger flow passages in the converter. Since diesel engines generally use lean mixtures, their converter is not effective in treating NO_x components. The solution for diesel engines is to use exhaust gas recycling (EGR).

Catalytic converters are called three-way converters as they mainly work on reducing three major automobile related pollutants: HC, CO, and NO_x. Some catalytic converters are basically a stainless steel container mounted in the exhaust system, but close to the engine. The inside of the container is a porous ceramic structure with packed spheres. A more common type is a single honeycomb structure in which there are multiple flow passages for the exhaust.

Catalyst materials are located on the surface of ceramic passages. Their task is to accelerate chemical reactions for the treatment of the pollutants. The most common material used as the ceramic material of the converter is aluminum oxide (alumina). Platinum, rhodium, palladium, iridium are commonly used as catalyst materials. Platinum is particularly effective in HC reaction, palladium with CO reaction, and rhodium with NO_x reactions.

Some components that may exist in fuel such as lead and sulfur and other components coming from engine oil additives such as zinc, phosphorus, antimony, calcium, and magnesium can seriously harm catalytic converter by poisoning catalyst materials. Lead is particularly to be avoided as it poisons catalyst materials fast. An engine with catalytic converter must not use leaded gasoline. Leaded gasoline has been phased out in gasoline engines since 1990s as lead is a poisonous pollutant with significant adverse effects on liver and kidney. It also accumulates in blood, bone, and soft tissues when ingested. About 0.15 g of lead was present in leaded gasoline with 10 to 50 percent ending up in the engine exhaust.

Diesel fuel contains some sulfur, which is converted to SO_2 after the combustion process. When the combustion gases containing some SO_2 flow through the catalytic converter, it may react with O_2 forming SO_3 with the help of some catalyst materials. SO_3 is then converted to H_2SO_4, an ingredient of acid rain. This process degrades the catalytic converter.

6. CO_2 production

When a fuel containing carbon is burned, carbon is first converted to CO by the reaction $C + \frac{1}{2}O_2 \rightarrow CO$ and then to CO_2 by the reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$. When there is a deficiency of O_2 in the combustion process, some CO cannot find O_2 to form into CO_2 and leaves the combustion chamber as CO. CO is a very undesirable and poisonous emission. CO_2 is not a pollutant. It is undesirable because it is the primary greenhouse gas of concern regarding global warming.

All fossil fuels (coal, oil, natural gas) contain carbon, and burning more of these fuels corresponds to more CO_2 production. The CO_2 emissions can be minimized by replacing fossil fuels by renewable energy sources such as solar, wind, biomass, hydro, and geothermal [41]. The consumption of fossil fuels can also be reduced by energy efficiency measures. The combustion of fuels with a greater carbon percentage by mass produces a greater amount of CO_2 emission.

Assuming complete combustion with air with no CO in the products, when 1 kmol of HC fuel (CmHn) is burned, m kmol of CO_2 is produced. For example, if octane is burned completely with stoichiometric amount of air, the complete combustion reaction is:

$$C_8H_{18} + 12.5(O_2 + 3.76N_2)$$
$$\rightarrow 8CO_2 + 9H_2O + (12.5 \times 3.76)N_2 \tag{34}$$

That is, when 1 kmol of C_8H_{18} is burned, 8 kmol of CO_2 is produced. In general, the amount of CO_2 production per unit mass of fuel burned can be determined from:

$$\frac{m_{CO_2}}{m_{fuel}} = \frac{N_{CO_2}M_{CO_2}}{N_{fuel}M_{fuel}} \tag{35}$$

where N is the mole number and M is the molar mass. For example, if pentane (C_5H_{10}) is burned, the amount of CO_2 production will be:

$$\frac{m_{CO_2}}{m_{fuel}} = \frac{N_{CO_2}M_{CO_2}}{N_{C_5H_{10}}M_{C_5H_{10}}} = \frac{(5\text{ kmol})(44\text{ kg/kmol})}{(1\text{ kmol})(70\text{ kg/kmol})} = \frac{220\text{ kg}}{70\text{ kg}}$$
$$= 3.14\text{ kg }CO_2/\text{kg pentane}$$

Table 2, gives the amount of CO_2 production per unit mass of fuel burned for common fuels. When 1 kg of natural gas (approximated as CH_4) is burned, 2.75 kg of CO_2 is produced, as shown in Table 2. It appears that the combustion of natural gas involves the least amount of CO_2 production among all fuels. For example, 11 percent less CO_2 is produced per unit mass of fuel when natural gas is burned instead of gasoline (approximated as octane, C_8H_{18}) in a car.

Table 2: The Amount of CO_2 Emission per Unit Mass of Fuel Burned for Common Fuels [11].

Fuel	Chemical Formula	Molar Mass M, kg/kmol	CO_2 Production, kg CO_2/kg fuel
Carbon	C	12	3.67
Methane	CH_2	16	2.75
Ethane	C_2H_6	30	2.93
Propane	C_3H_8	44	3.00
Butane	C_4H_{10}	58	3.03
Pentene	C_5H_{10}	70	3.14
Isopentane	C_5H_{12}	72	3.06
Benzene	C_6H_6	78	3.38
Hexene	C_6H_{12}	84	3.14
Hexane	C_6H_{14}	86	3.06
Toluene	C_7H_8	92	3.34
Heptane	C_7H_{16}	100	3.08
Octane	C_8H_{18}	114	3.09
Decane	$C_{10}H_{22}$	142	3.10

When coal, oil, and natural gas are burned in a combustion unit to provide thermal energy as in a space heating system or boiler of a power plant, the amount of CO_2 produced by natural gas is about 40 percent less than that by coal. This is due to much higher energy content of natural gas (50,000 kJ/kg) per unit mass of the fuel compared to coal (usually between 20,000 and 30,000 kJ/kg). Natural gas also emits less NO_x and PM and no SO_2 compared to coal and gasoline. Thermal and environmental benefits of natural gas compared to coal and oil has made it an attractive fuel for electric power generation and space heating. For these reasons, many consider natural gas as a clean fuel. However, natural gas is still a fossil fuel and its combustion results in considerable amount of CO_2 and pollutant emissions.

Methane and N_2O are other notable greenhouse gas emissions as well as air pollutants even though their emission rates are much lower than carbon dioxide. The energy sector (coal mining, natural gas systems, oil systems, combustion systems), agriculture, industrial activities, and waste management are major sources of CH_4 emissions. N_2O is mostly emitted due to agricultural activities (nitrogen fertilization of soils and management of animal waste). Energy use and industrial processes are other sources of N_2O.

Methane and N_2O emissions can also be expressed as CO_2 equivalent in terms of their effect on global warming. Global warming potential (GWP) is defined as the ratio of the global warming effect of a given mass of a substance to that caused by the same mass of CO_2. Carbon dioxide is the reference gas used in measuring GWP, and, by definition, has a GWP of 1. CH_4 is estimated to have a GWP of 28 to 36, and N_2O has a GWP of 265 to 298 [42].

Other greenhouse gases include CFCs such as $R-11$, $R-12$, and $R-113$, which also cause stratospheric ozone depletion, hydrochlorofluorocarbons (such as $HCFC-22$), hydrofluorocarbons (HFCs), perfluorocarbons (HFCs), and sulfur hexafluoride (SF_6).

7. Conclusion

In this article, the air pollutants and other emissions that result from fossil fuel combustion and vehicles are comprehensively presented. The main sources of air pollutants and greenhouse gases emission have been highlighted in the preliminary section of this study, which continues to explain and analysis the effects of air pollutants and its relationship with climate change and global warming. In the next section, the emissions from Automobiles along with its factors and effects has been taken into account. Since it is important to counter the reduction of energy environmental impacts and the use of its adapted technology, the most effective solutions and practical approaches have been suggested in accordance with the latest and most up to date references. Table 3 shows the different types of pollutants and emissions, so that it is briefly presented in the relevant columns, the factors, effects, and its reasonable solutions as well.

Table 3: Environmental pollution's phenomena, effects and solutions.

No	Compound	Effects	Main source of production	Solutions
1	Particulate Matter (PM)	Particulate matter is associated with significant health effects in particular respiratory diseases such as asthma and bronchitis, cardiovascular and lung diseases, lung tissue damage, visibility impairment, and cancer.	Small solid and liquid particles suspended in air Ash and soot particles generated from the combustion of coal and oil Dust particles from roads and construction and agricultural activities Iron, Silicon, Soil, and materials of earth can also be considered as part of PM	Using a device called *Electrostatic Precipitator* (ESP)
2	Sulfur Dioxide (SO_2)	It can lead to airway constriction and include respiratory, lung, and cardiovascular illnesses.	Electric power plants that burn high-sulfur coal Volcanic eruptions and hot springs Motor vehicles	Using low-sulfur coal in electricity generation Using *flue gas desulfurization* (FGD) systems
3	Nitrogen oxide (NO_x)	Nitrogen oxides react in the atmosphere to form ground-level ozone and it contributes to the photochemical smog and acidification of waters and soils. Nitrogen dioxide (NO_2) gas is toxic at high concentrations. The primary health effects of NO_2 are related to respiratory illnesses such as asthma and bronchitis.	Combustion of fossil fuels such as coal, oil, and natural gas	In gasoline burning automobiles, using catalytic converters In diesel engines, using exhaust gas recycling (EGR) Chemical treatment system to remove NO_x components in combustion gases Selective catalytic reduction (SCR) unit in coal-fired power plants
4	Hydrocarbons (HC)	Hydrocarbon components and carbon soot particles in air act as irritants and odorants. Some of them are believed to be carcinogenic. Nitrogen oxides and HC are two main sources for the formation of ground level ozone. Except for CH_4, HC components react in atmosphere to form photochemical smog.	HC emissions in vehicles are caused by the evaporation of fuels during refueling or spillage during spit back or by evaporation from gas tanks with faulty caps that do not close tightly. The solvents, propellants, and household cleaning products that contain benzene, butane, or other HC products Additional sources of HC emissions include venting of crankcase, petroleum refineries and chemical plants	Most diesel automotive engines are equipped with *particulate traps* to collect soot particles. In gasoline burning automobiles, using catalytic converters
5	Carbon Monoxide (CO)	Carbon monoxide deprives the body's organs from getting enough oxygen by binding with the red blood cells that would otherwise carry oxygen. At low levels, CO decreases the amount of oxygen supplied to the brain and other organs and muscles, slows body reactions and reflexes, and impairs judgment.	It is mostly emitted by industry and motor vehicles During the combustion of HC fuel	CO emission can be minimized by avoiding fuel-rich mixtures, better mixing of fuel and air, and increasing combustion time.
6	The harmful ground-level Ozone (O_3)	Ozone irritates eyes and damages the air sacs in the lungs where oxygen and carbon dioxide are exchanged, causing eventual hardening of this soft and spongy tissue. It also causes shortness of breath, wheezing, fatigue, headaches, and nausea, and aggravates respiratory problems such as asthma.	Hydrocarbons and NO_x react in the presence of sunlight on hot calm days to form ground-level ozone, which is the primary component of smog.	To improve the air quality, reformulated gasoline (RFG) that contains at least 2 percent oxygen was introduced, and its use is mandatory in many smog-prone areas.
7	Carbon dioxide (CO_2)	As a major greenhouse gas causing global warming.	When a fuel containing carbon is burned, carbon is first converted to CO and then to CO_2	The CO_2 emissions can be minimized by replacing fossil fuels by renewable energy sources.

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