CHAPTER 2
Energy and the Environment

As with many human activities, the conversion of energy from one form to another has a significant impact on the environment. Fossil fuels such as coal, oil, and natural gas have been powering the development of industrial countries since the Industrial Revolution. However, it is only recently that the impact of relying on fossil fuels has become a major concern. Pollutants emitted during the combustion of fossil fuels contribute to smog, acid rain, climate change, and pollution of soils, water, and the air we breathe. This significantly impacts vegetation, wildlife, and human health. Air pollution alone is considered responsible for the deaths of more than 600,000 people in the U.S. each year due to heart and lung diseases related to air pollution.
The sources of pollutants come from the chemical reactions that convert fossil fuels to thermal energy via combustion, as well as additives in liquid fuels to improve their performance. For example, MTBE (Methyl Tertiary-Butyl Ether) is added to raise the octane number of fuel and to oxygenate it during winter months to reduce urban smog.
The largest sources of air pollution are industrial activities and motor vehicles. The most important pollutants released are hydrocarbons (HC), sulfur dioxide (SO_2), nitrogen oxides (NO_x), particulate matter (PM), and carbon monoxide (CO).
Recent regulations and international treaties have placed limits on pollutants emitted by large plants and vehicles. As a result, current industrial facilities and vehicles emit only a fraction of the pollutants they did a few decades ago.

2.1. Air Pollutants

The minimum amount of air needed for the complete combustion of the fuel is called the stoichiometric or theoretical air:

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

Gasoline and diesel fuels used in automobile are commonly approximated by octane C8H18 then for a complete combustion:

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

And if we consider the combustion of an assay of coal including 80% C, 5% H_2, 6% O_2, 2% N_2, 0.5% S, and 6.5% ash, a complete combustion of 100 grams leads to:

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

In this reaction, we disregard ash, which is a non-reacting component. In practice, it is common to use more air than required to increase the chances of achieving complete combustion and to control the temperature. Combustion is considered complete if all the carbon in the fuel burns to CO_2, all the hydrogen burns to H_2O, and all the sulfur, if present, burns to SO_2.
If the analysis of the combustion products shows the presence of any unburned fuel or components such as C, H_2, CO, or OH, then the combustion is incomplete. Incomplete combustion can occur due to a lack

of oxygen, but it can also happen in the presence of excess oxygen. This can be caused by insufficient mixing between the fuel and the oxygen.

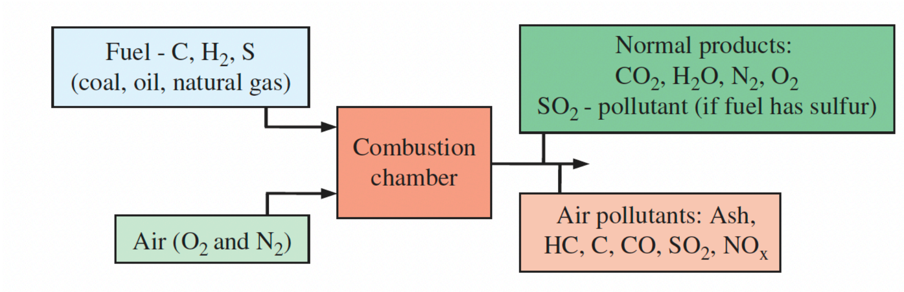


Figure 2.1. Combustion reactants and products when a hydrocarbon is burned with air.

Oxygen has a much greater tendency to combine with hydrogen to form H_2O than with carbon to form CO_2. So, even in the case of insufficient oxygen, usually all the hydrogen turns to H_2O, leaving carbon to end up as CO, or even as carbon particles (soot).

Other pollutants include NO_x, which is generated due to high-temperature reactions between nitrogen and oxygen. Particulate matter is also produced, mostly when coal or oil is burned. The particulate matter is usually called ash.

The figure below shows air pollutant emissions in Canada between 190 and 2022:

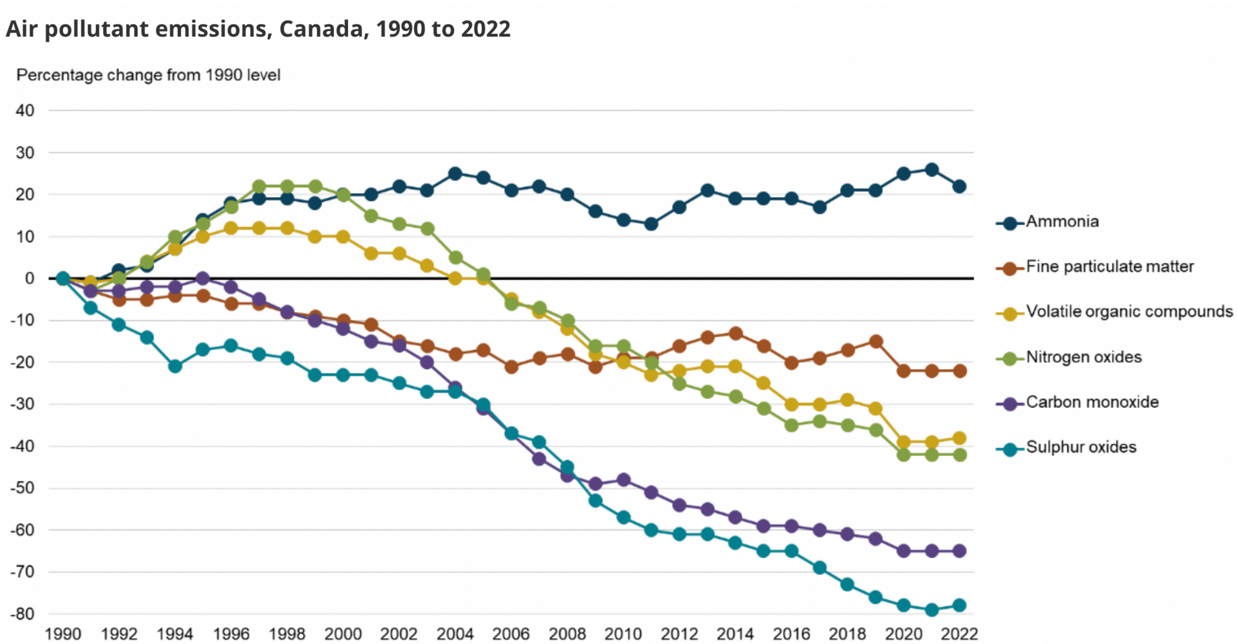


Figure 2.2. Air pollutant emissions in Canada between 190 and 2022. Values represent the percentage change from 1990 level.

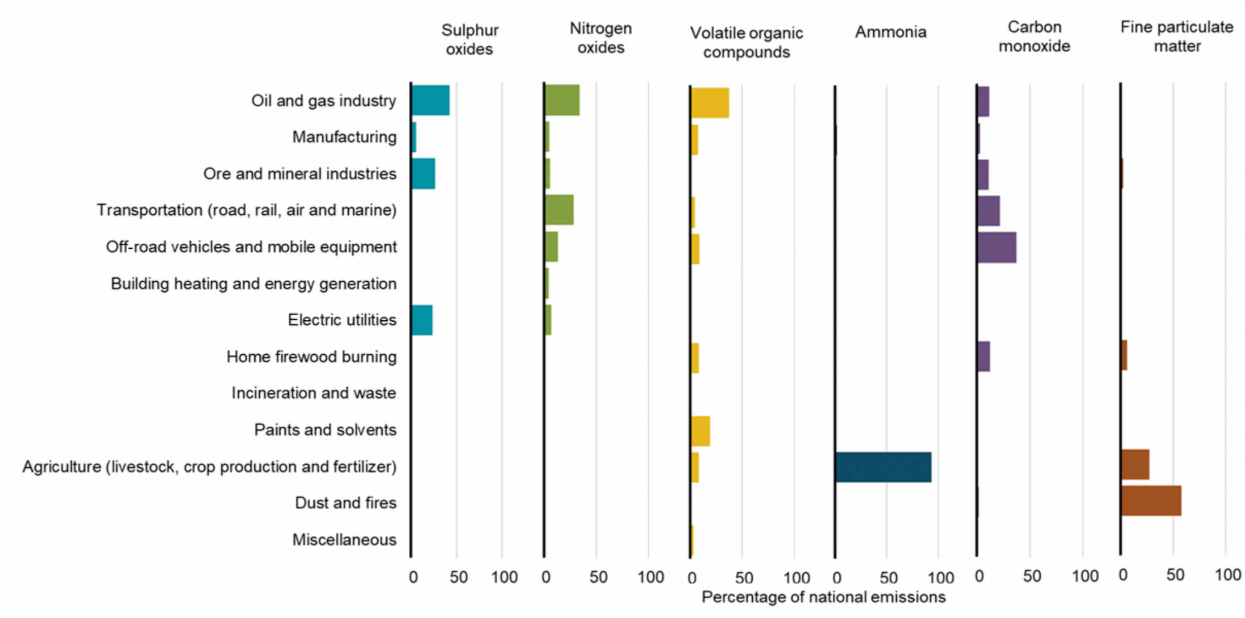
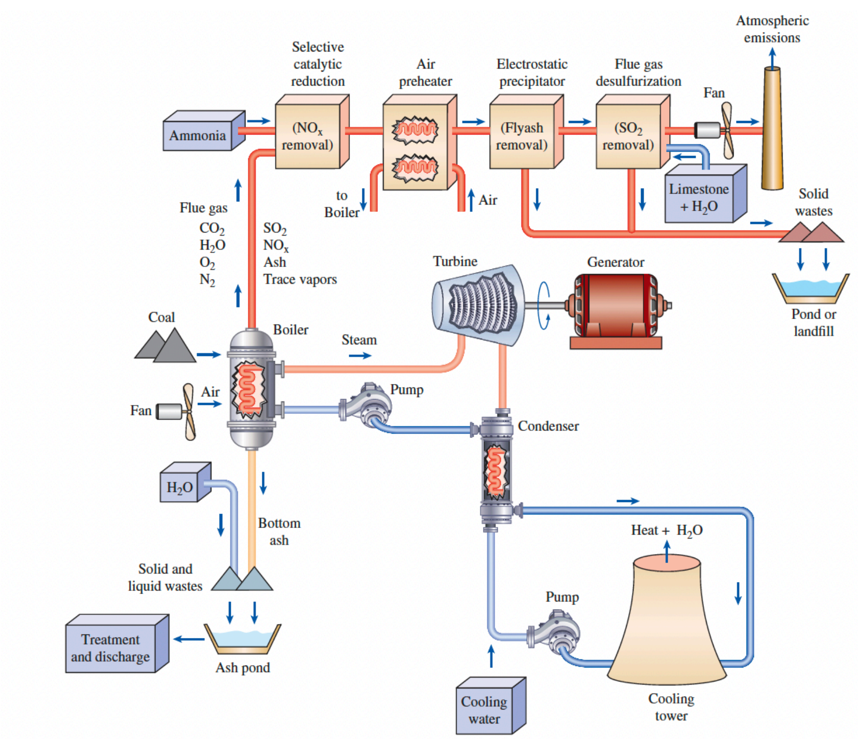


Figure 2.3. Distribution of air pollutant emissions by source in Canada in 2022.

Two general methods are commonly used to reduce emissions. The first one is to design and optimize the combustion process. The second one involves different sorts of after-treatment of the exhaust gases leaving the combustion chamber. The figure below shows some environmental controls for major pollutants in a coal-fired power plant.



Coal Composition

Ultimate analysis	As received, wt%
Carbon	63.75
Hydrogen	4.50
Nitrogen	1.25
Sulfur	2.51
Chlorine	0.29
Ash	9.70
Moisture	11.12
Oxygen	6.88

Figure 2.4. Environmental controls for major pollutants in a coal-fired power plan.

2.2. Particulate Matter (PM)

Particulate matter refers to small solid and liquid particles suspended in air. The most common PM produced are ash and soot from the combustion of coal and oil. PM can be classified based on their size.

PM10	particulate matter that are less than 10 micrometres. They are also called coarse particulate matter.
PM2.5	particulate matter that are less than 2.5 micrometers. They are also called fine particulate matter.

PM 2.5 are more dangerous to health than PM 10. This is because their very small size allows them to go deeply into the respiratory system. They are associated with significant health effects, including asthma, bronchitis, cardiovascular and lung disease, and cancer.
PM and ash due to the combustion of coal must be removed using environmental controls. Despite the significant progress with such controls, some ash and other PM still remain in the combustion gases and are emitted to the atmosphere. It is estimated that about 1 gram of PM is released to the environment for each kWh of electricity produced by a coal-fired power plant.
The collected ash from the power plant that was successfully removed from the combustion gases is, however, transported using water, leading to the pollution of lakes and rivers.
One common way to collect and remove flying ash particles (fly ash) from the combustion gases is the use of an electrostatic precipitator (ESP), where ash particles are bombarded with negative ions while they are passing between two plates, and the particles are then moved towards a positively charged plate to be collected.

Example 2.1

The Genesee 3 coal-fired power plant located in Alberta uses coal with the following composition on a mass basis: 67% carbon (C), 5% hydrogen (H_2), 9% oxygen (O_2), 2% nitrogen (N_2), 1.5% sulfur (S), 8.5% ash, and 7% moisture. The heating value of the coal is 28,400 kJ/kg.
The plant consumes coal at a rate of 2,000 kg/day and operates 65% of the time annually to meet local energy demands.
(a) Calculate the total amount of ash entering the plant per year.
(b) Determine the amount of ash entering the plant per megajoule (MJ) of heat input to the plant.
(c) If only 2% of the ash entering the plant is emitted into the atmosphere with combustion gases, calculate the mass of ash emitted per kilowatt-hour (kWh) of electricity produced. Assume the plant converts 40% of the heat input into electricity due to its efficiency.

2.3. Sulfur Dioxide (SO2)

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

$$S + O_2 \rightarrow SO_2$$

Coal contains the most sulfur among fossil fuels (range 0.4 to 4.0% by mass). Oil contains between 0.3 and 2.3%. While natural gas contains varying amounts of sulfur, it is removed in gas treatment plants.
During the combustion of coal, 95% of S is oxidized to SO_2, about 2%-5% does not get burned and ends up in the solid ash particles. Less than 1% of the SO_2 formed during the combustion further reacts with O_2 to form SO_3. The SO_3 can react with water vapor in the combustion gases to form H_2SO_4 (sulfuric acid). SO_2 released into the atmosphere can also form sulfates, which are components of acid rain.
Regulations limit the maximum sulfur level; for example, for motor vehicles, there are different techniques that can be used to reduce SO_2 emissions by up to 99%. This is critical since SO_2 is a very toxic pollutant and can have a significant health impact.

Note that sulfur can also combine with hydrogen at high temperatures to form H_2S (hydrogen sulfide).

$$S + H_2 \rightarrow H_2S$$

Which is a poisonous, corrosive, flammable, and explosive gas. Long-term exposure to H_2S is associated with nervous and respiratory system effects, as well as eye effects.

2.4. Nitrogen Oxides (NOx)

Nitrogen oxide (NO_x) and nitrogen dioxide (NO_2) are generated during the combustion of fossil fuels such as coal, oil, or natural gas. Most of the NO_x emissions from the combustion system to the atmosphere are NO, but it gradually turns into NO_2 by reacting with oxygen in the air.
During very high temperatures, like in internal combustion engines, a dissociation reaction can occur that can break down the bonds between different components, for example:

$$N_2 \rightarrow 2N$$

$$O_2 \rightarrow 2O$$

$$H_2O \rightarrow OH + \tfrac{1}{2}H_2$$

This leads to different scenarios for the formation of nitrogen oxides:

$$N_2 + O \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

$$N + OH \rightarrow NO + H$$

$$NO + O_2 \rightarrow NO_2 + O$$

$$NO + H_2O \rightarrow NO_2 + H_2$$

NO_x can also be formed by the reaction of monoatomic nitrogen and oxygen particles in fuel. For example, coal can contain about 10% oxygen and 1% nitrogen by mass.
Nitrogen oxide emissions are greatly reduced in gasoline-burning automobiles by the catalytic converter. In Diesel engines, an exhaust gas recycling (EGR) system is used instead. The EGR recycles up to 30% of the exhaust gases to the combustion chamber. These gases do not react with air but absorb heat in the chamber to reduce the temperature (lowering the risks of dissociation reactions). In large combustion engines, such as those used in electricity production or in ships, tiny water droplets are injected into the combustion chamber. Water absorbs heat and evaporates, reducing the temperature.
Other approaches include optimizing the design and operation of the combustion chamber and burners, or installing a selective catalytic reduction (SCR) unit right after the boiler. This unit uses catalytic material to promote the conversion of NO_x into N_2. Finally, ammonia (NH_3) can be injected into the combustion gas stream.

$$NO + NH_3 + \tfrac{1}{4}O_2 \rightarrow N_2 + \tfrac{3}{2}H_2O$$

$$NO_2 + 2NH_3 + \tfrac{1}{2}O_2 \rightarrow \tfrac{3}{2}N_2 + 3H_2O$$

Since such reactions require a temperature above 400°C, this is why such units are installed just after the boiler.

Nitrogen oxides react in the atmosphere to form ground-level ozone. They also contribute to smog and the acidification of water and soils. The primary health effects of NO_2 are related to respiratory illnesses such as asthma and bronchitis.

2.5. Hydrocarbons (HC)

Fossil fuels are primarily made of hydrocarbons (HC). During the combustion process, some of the fuel cannot find enough oxygen to react with. As a result, some HC or carbon might exist in the products.
A lack of air certainly can contribute to unburned HC. But, even in the presence of stoichiometric or excess air, unburned HC can still remain. This will be primarily due to low mixing between the air and the fuel.
Note that the term volatile organic compounds (VOC) is also used to refer to the HC found in the exhaust.

$$C_mH_n + w\,(O_2 + 3.76N_2) \rightarrow a\,CO_2 + b\,H_2O + c\,CO + d\,N_2 + e\,C\,(\text{solid})$$

The unburned carbon soot particles can sometimes be seen as black smoke. These are small particles with diameters between 10 and 80 nm.
In some engines (Diesel engines), particulate traps are used to collect soot particles. The traps are cleaned or regenerated periodically by burning the collected particles. Note that Diesel engines usually generate less HC at the exhaust because they use a much higher air-fuel ratio (18-70) compared to gasoline engines (12-18).
HC components and carbon soot particles in the air act as irritants and odorants. Some might be considered carcinogenic.

2.6. Carbon Monoxide (CO)

Carbon monoxide is a colorless, odorless, poisonous gas. It is mostly produced when there is a fuel-rich mixture (not enough air or oxygen in the air-fuel mixture).

$$C + \tfrac{1}{2}O_2 \rightarrow CO$$

CO can also react again with O_2, if available, to create CO_2

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

If O_2 is not enough available, then CO will be present in the products. CO emissions can be limited by using more air, better mixing of the air and the fuel, and increasing the combustion time.
In gasoline engines, most CO is produced at engine startup and acceleration, during which the engine runs with a fuel-rich mixture. The percentage of CO in the exhaust gases can vary between 0.1% to 5%. Diesel engines have the tendency to generate less CO since they have excess air in the air-fuel mixture.
The main risk with CO is that it can deprive the body's organs of getting enough oxygen by binding with the red blood cells that would otherwise carry oxygen. At low levels, CO decreases the amount of oxygen to the brain and other vital organs. At high levels, CO can be fatal.

2.7. Ozone, Smog, and Acid Rain

In Montreal, we are used to experiencing episodes of smog (smoke + fog = smog). This dark yellow or brown haze builds up in large, stagnant air. Smog, or photochemical smog, is mostly made up of ground-level ozone (O_3), but it also contains other chemicals like CO, PM (soot, dust, and volatile organic compounds).
Note that ozone in the upper atmosphere protects from harmful UV rays, but ozone at ground level is a pollutant and harmful to lungs, biological tissues, and trees.
Possible reactions that can lead to smog are:

$$NO_2 + \text{energy from sunlight} \rightarrow NO + O + \text{smog}$$

$$O + O_2 \rightarrow O_3$$

NO_2 from vehicles or power plants.
Ozone can irritate the eyes and can damage the lungs. It can also lead to shortness of breath, fatigue, and headaches. Every exposure to ozone causes a little damage to the lungs, just like cigarette smoke, eventually reducing lung capacity. The recommendation is to stay indoors and minimize physical activity. Smog can also harm vegetation by damaging leaf tissues.
The most effective way to reduce ground-level ozone is to reduce NO_x emissions and HC emissions.
Sulfur oxides and nitrogen oxides react with water vapor and other chemicals in the upper atmosphere in the presence of sunlight to form sulfuric and nitric acids. The acids formed usually dissolve in the suspended water droplets in clouds as fog and precipitate as acid rain. Acid rain can be as acidic as lemon juice.
An example of a reaction is:

$$H_2O + SO_2 + ½O_2 \rightarrow H_2SO_4$$

or simply

$$H_2O + SO_2 \rightarrow H_2SO_3$$

Sulfuric acid droplets can penetrate deeply into the lungs during respiration and damage them. When falling on the ground, the soil is capable of neutralizing a certain amount of acid, but the emissions produced by power plants and motor vehicles have exceeded this capacity. As a consequence, many lakes and rivers near industrial areas have become too acidic for fish to grow. Forests are also experiencing a slow death from absorbing the acids through their leafs.

Example 2.2

A transport truck equipped with a diesel engine operates with an average air-fuel ratio of 18 kg of air per kg of fuel. The engine uses light diesel fuel containing 750 ppm sulfur by mass. During operation, all the sulfur in the fuel is assumed to convert to SO2 in the engine's combustion chamber, and subsequently, all the SO_2 is converted to sulfurous acid (H_2SO_3) in the atmosphere.
If the truck engine consumes air at a rate of 336 kg/h, calculate the mass flow rate of H_2SO_3 released into the environment due to this process

2.8. The Greenhouse Effect

The surface of the Earth warms up during the day as a result of the absorption of solar energy and cools down at night by radiating part of its energy into deep space as infrared radiation. Carbon dioxide (CO_2), water vapor, and other gases like methane (CH_4) and nitrous oxide (N_2O) act like a blanket and keep the Earth warm at night by blocking part of the heat radiated from the Earth. Such gases are called greenhouse gases (except for water, which precipitates as rain or snow). However, excessive amounts of these gases disturb this delicate balance by trapping too much energy. This causes the average temperature of the Earth to rise and leads to global warming or global climate change.
Controlling and limiting CO_2 emissions from automotive vehicles and power plants can significantly contribute to reducing global warming. To give an example, 1 kWh of electricity from a fossil power plant generates between 0.6 to 1.0 kg of CO_2, and 1 L of gasoline can produce up to 25 kg of CO_2.

2.9. CO_2 Production

When an HC is burned, the carbon is first converted to CO:

$$C + ½O_2 \rightarrow CO$$

And then to CO_2

$$CO + ½O_2 \rightarrow CO_2.$$

When O_2 is lacking, a part of the exhaust gases contains CO, which is a dangerous emission. This is not the case for CO_2. CO_2 is not a pollutant, but it is still undesirable in high quantities because of its primary role as a greenhouse gas.
CO_2 emissions can be reduced by using more efficient engines or by switching to renewable, clean energy sources.

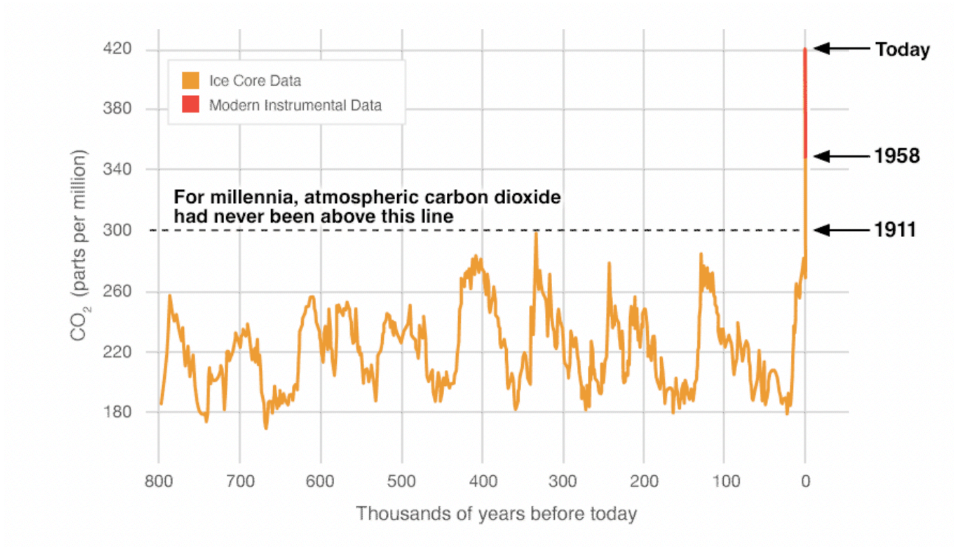


Figure 2.5. Variation if CO_2 level during earth's last three glacial cycles.

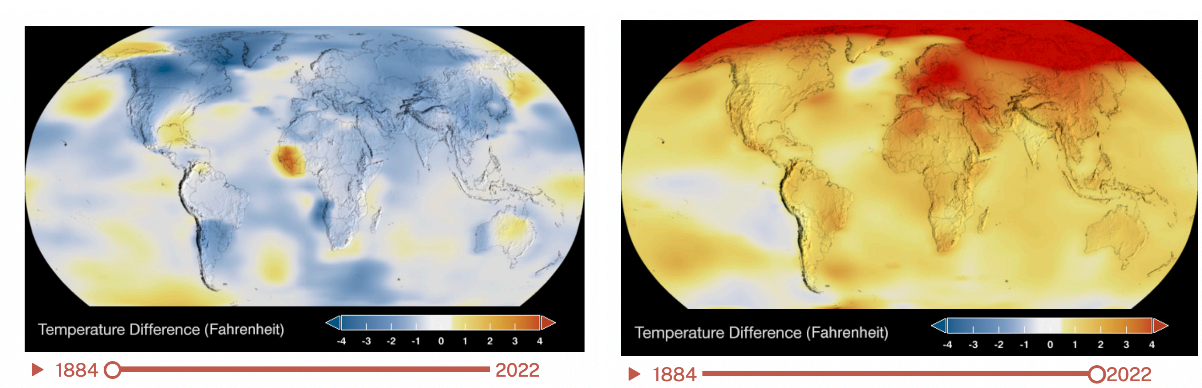


Figure 2.5. Change in global surface temperatures. (left) in 1884, (right) in 2022. Dark blue shows areas cooler than average. Dark red shows areas warmer than average. Short-term variations are smoothed out using a 5-year running average to make trends more visible in this map.

Example 2.3

A midsize car operates on gasoline with a fuel efficiency of 6.7 L/100 km. The density of the gasoline is 740 kg/m³.
(a) Calculate the amount of CO_2 emitted by the car in g/km, assuming complete combustion of the fuel.
(b) Determine the total CO_2 emissions released into the environment per year if the car is driven 20,000 km annually.