# ENVIRONMENTAL EFFECTS OF TOXIC MATERIALS FROM OIL AND GAS COMBUSTION

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## Summary

Emissions from oil combustion are composed mainly of carbon dioxide and water. Other gaseous emissions from combustion include sulfur oxides, nitrogen oxides, organic compounds, carbon monoxide, particulate matter, mainly in the form of carbon particles (soot), and several metals. Some of these pollutants react in the atmosphere, giving rise to other pollutants like ozone, sulfates, and nitrates.Several non-health impacts from oil (petroleum) combustion emissions have been observed; these effects are represented mainly by acid deposition, effects on vegetation, alteration of atmospheric visibility, increased turbidity of the atmosphere, and damage to materials. All effects have a cost thus there is also an economic effect also, loss of historical buildings; there is also a concern over food chain as well as about the effects on animals and aquatic life.This chapter will describe combustion emissions, the main non-health effects caused by oil combustion emissions, and the importance of individual pollutants.

#### 1. Introduction

Fuels from oil are basically fuel oils used in industry and, on a smaller scale, in power

plants. Diesel oil is used in buses and trucks, gasoline for cars, kerosene is used in airplanes, and liquefied petroleum gas (LPG) is used mainly for domestic and commercial cooking.

These fuels may also contain other elements, specifically sulfur, which causes the formation of sulfur oxides  $(SO_x)$ . The most common of these latter is sulfur dioxide  $(SO_2)$ , which accounts for approximately 98% of all sulfur oxides, and a small amount of sulfur trioxide  $(SO_3)$ . The presence of nitrogen in the fuel and in the combustion air causes the formation of nitrogen oxides, NO and NO<sub>2</sub>. High temperatures in the combustion chamber, and especially close to the flame, favor the formation of NO. Downstream of the flame part of the NO is converted to NO<sub>2</sub> when it reacts with oxygen from air, resulting in less than 10% of NO<sub>2</sub> in the total NO<sub>x</sub> emissions. In the atmosphere, the normal tendency is the oxidation of NO to NO<sub>2</sub>, but in some circumstances, like smog conditions, NO<sub>2</sub> can be reconverted to NO, giving rise to the formation of ozone and other photochemical oxidants.

Traces of metals also are contained in fuels from oil, particularly in liquid fuels, like lead, arsenic, cadmium, barium, chrome, cobalt, copper, manganese, molybdenum, nickel, and vanadium. During combustion, these metals are emitted to the atmosphere. Gasoline may still contain tetraethyl lead, increasing the emission of lead and lead compounds to the atmosphere. This raises the participation of liquid fossil fuels and some of its compounds to the atmosphere, relative to gaseous fuels.

Incomplete combustion results in the emission of carbon monoxide, hydrocarbons, and other volatile organic compounds, and carbon particles (soot). The combustion process in stationary sources is easier to control than in mobile sources, usually resulting in fewer emissions. In mobile sources, especially motor vehicles, the combustion control process conditions are variable, resulting in greater emissions per volume of fuel burned. This is a problem in big cities. The use of modern electronically controlled systems has resulted in combustion improvement in these sources, and consequently, in reduced emissions of incomplete combustion products. Also, design modifications and the increasing use of pollution control systems, such as the catalyst converter in cars, have resulted in even more reduced emissions of pollutants such as carbon monoxide, hydrocarbons, other volatile organic compounds, and nitrogen oxides. In the United States in 1985, road vehicles were responsible for 70% of CO emissions, 45% of NO<sub>x</sub> emissions, and 34% of hydrocarbons. If airplanes, trains, and ships are included, transportation becomes responsible for almost 40% of total volatile organic compounds emitted to the atmosphere in the US. In Europe the major anthropogenic source of nitrogen oxides and volatile organic compounds is road transportation. In OECD (Organization for Economic Cooperation and Development) countries, motor vehicles represent 47% of total NOx emissions, 39% of HC emissions, and 66% of CO emissions. Approximately half of the oil production in the world is consumed by motor vehicles.

With the present growth of motor vehicle trade, it is predicted that the number of vehicles on our roads will reach roughly one billion by 2030. With all other emissions from oil combustion in stationary sources and with maritime and air transportation sources included, one can see that oil combustion is the major anthropogenic source of CO,  $NO_x$  and HC. In the developing world, mega-cities like Sao Paulo in Brazil and

Mexico City, transportation burning diesel oil or gasoline is also the major source of CO,  $NO_x$ , and HC.

Besides the direct emission of pollutants by combustion sources, the transformation of some of these pollutants in the atmosphere also occurs. Pollutant transformation in the atmosphere occurs in what are called "secondary pollutants," such as those belonging to the group of photochemical oxidants, being ozone the most important photochemical oxidant and also the formation of sulfate and nitrate particles. Photochemical pollutants are formed by reaction of nitrogen oxides, hydrocarbons, and other volatile organic compounds, in the presence of solar radiation. Particles of sulfate and nitrate are formed due to the oxidation of sulfur oxides and nitrogen oxides compounds, especially in smog conditions. Sulfate particles are of great interest in relation to the visibility of the atmosphere. Several other chemical reactions can occur in the atmosphere depending on the substances and chemical radicals present, and in the meteorological conditions, such as calm wind conditions and the presence of thermal inversions resulting in the formation of other gases and particles. The atmosphere sometimes can be compared to a big reaction chamber during a photochemical smog. This situation is frequent in big metropolitan regions all over the world. Emissions from oil and gas combustion play an important role in these reactions.

Pollutant	Fuel oil (kg/10 <sup>6</sup> kcal)	1% sulfur fuel oil (kg/10 <sup>6</sup> kcal)	Natural gas (kg/10 <sup>6</sup> kcal)	Ratio 1% fuel oil emission/ Natural gas emission <sup>b</sup>
Sulfur dioxide	1.88S <sup>c</sup>	1.88	.0011	1,709
Nitrogen oxides	0.65	0.65	0.418	1.56
Carbon monoxide	0.06	0.06	0.149	0.4
Particulate	0.11S + 0.04	0.15	0.0034	44.1
Methane	$0.008(A)^{d}$	0.008	0.0041	1.95
Non-methane total organic compounds (NMTOC)	0.006(A) <sup>d</sup>	0.006	0.0154	0.39
Carbon dioxide	$296.4(B)^{e}$	296.4	213.33	1.39

<sup>a</sup> Based on U.S. Environmental Protection Agency (1996). *Compilation of air pollutant emission factors*. NC: USEPA, Research Triangle Park. And fuel oil with heating content of 10 000 kcal/L and natural gas with heating content of 9000 kcal/Nm<sup>3</sup> <sup>b</sup> Assuming same combustion efficiency between fuel oil and natural gas

 $^{c}$ S = sulfur content (% in weight)

<sup>d</sup> A = average between power plant and industrial combustion

 $^{e}$ B = average between low sulfur and high sulfur grade 6 fuel oil

Table 1. Emission estimate for fuel oil and natural gas combustion<sup>a</sup>

Metal	Emission from fuel oil grade 6 combustion (g/10 <sup>6</sup> kcal)	Emission from natural gas combustion (g/10 <sup>6</sup> kcal)	Ratio between fuel oil emission and natural gas emission for same heating input
Arsenic	0.0158	0.00036	43.90
Barium	0.0308	0.00078	48.70
Cadmium	0.0048	0.00196	2.45
Chromium	0.0101	0.00249	4.06
Cobalt	0.0722	0.00015	481.30
Copper	0.0211	0.00151	13.97
Lead	0.0181	0.00048	37.57
Manganese	0.0360	0.00068	52.94
Molybdenum	0.0094	0.00196	4.78
Nickel	1.0140	0.00373	271.85
Vanadium	0.3816	0.00409	93.30

<sup>a</sup> Based on U.S. Environmental Protection Agency (1996). *Compilation of air pollutant emission factors*. NC: USEPA, Research Triangle Park. And fuel oil with heating content of 10 000 kcal/L and natural gas with heating content of 9000 kcal/Nm<sup>3</sup>.

Table 2. Comparison between emissions of selected metals from fuel oil and natural gas combustion<sup>a</sup>

Natural gas is cleaner than liquid fuels derived from oil. Nevertheless, environmentally speaking, it is not a completely clean fuel.. In stationary sources, emissions from natural gas combustion are smaller in relation to sulfur dioxide, nitrogen oxides, particulate, methane carbon dioxide, and metals. In relation to CO and non-methane total organic compounds, natural gas combustion emits more than fuel oil combustion in stationary sources, as shown in Tables 1 and 2.

The participation of fuel oil from petroleum and natural gas in power plants was relatively small in the late 1940s, when most energy was generated from coal. The use of fuel oil in the world energy matrix since then has increased, reaching approximately 40% by the end of the 1980s. During the same period, the use of coal as an energy source has decreased by around 25%. The use of natural gas as substantially increased since the 1970s, reaching 20% participation by 1990, and with the likelihood that it will continue to increase throughout the next century.

A world view of energy scenarios shows that in 2010 the participation of oil will decrease to about 33% and the participation of natural gas will increase to about 25%, and a decrease in the participation of coal will occur, which is estimated to be about 23% at that time.

The alteration of the world energy matrix, converting to a greater use of crude oil and natural gas instead of coal had environmental pressure as the main driving force. It is likely that that this driving force will continue, and probably increase during the twenty-first century, enabling the population to have cleaner energy sources, such as solar and wind energy, with little, or at least a smaller, environmental impact.

Coal combustion has the biggest air pollution potential when compared to fuel oil and natural gas combustion. Its use requires high investments in air pollution control systems usually in relation to particulate and sulfur dioxide control. In some cases, nitrogen oxides control systems are also required. Emissions from fuel oil combustion usually do not require control of particulate emissions as the particulate emission potential of fuel oil combustion is small but, as in the case of coal, air pollution abatement systems are required for sulfur dioxide control when the fuel has a high sulfur content. Sometimes regulations may require the abatement of nitrogen oxides. Natural gas does not require control for particulate and for sulfur dioxide, but it would be necessary to install nitrogen oxides abatement systems. Thus, when discussing the environmental effects of oil and natural gas combustion, it is necessary to consider that it is not possible to separate the effect of air pollution caused by coal combustion from the air pollution created from other fossil fuels. Nevertheless, it is also important to bear in mind that air pollution from coal combustion predominates due to its higher air pollution potential. For example, when one discusses acid rain, natural gas emissions have a smaller participation, because of its small sulfur content. Instead, the contribution in relation to nitrogen oxides is of greater importance. It is also necessary to take in consideration the use of sulfur dioxide treatment systems, an environmental requirement since the 1970s. The use of sulfur dioxide treatment systems has decreased emissions of sulfur dioxide substantially. Although on a smaller scale, nitrogen oxide treatment systems have also been adopted in countries with stringent environmental regulations. Sulfur dioxide treatment systems are important in power plants that use coal and fuel oil. On the other hand, nitrogen oxide treatment systems are important for power plants that use coal, fuel oil, or even natural gas.

In Europe, environmental regulations have pushed big sources of sulfur dioxide emissions to reduce their emissions, particularly in power plants. Reduction in emission of this pollutant, by adding air treatment systems is in the order of 70% to 80%. This reduction can be assumed to have occurred in OECD countries in the 1970s and in the 1980s, in sources using coal or high sulfur fuel oil. In the United States, the Clean Air Act Amendments of 1990 call for a reduction in sulfur emissions. The main aim of this reduction is to decrease acidic deposition. In Europe, a Sulfur Protocol was signed in 1994, with a schedule of agreed emission reductions to be achieved between the years 2000 and 2010. The biggest cut in sulfur emissions will be in Germany (87%). Austria, Denmark, Finland, Sweden, and United Kingdom will have to cut their emissions by 80% relative to 1980 figures. However, Portugal and Greece will have to cut their sulfur emissions by only 3% and 4% respectively. In Latin America, Brazil is an example of regulation calling for reduction in sulfur dioxide emissions from combustion processes. In the Sao Paulo Metropolitan Region a 66% reduction in sulfur dioxide emissions was necessary to meet the air quality standards set at the beginning of the 1980s when the major individual contributors were asked to reduce emissions by 80%. Besides the importance of oil and gas combustion emissions in relation to health, emissions can also cause several effects for the environment. For example, acid rain, with consequences to aquatic and terrestrial ecosystems, vegetation damage, visibility reduction and increased turbidity, directly or indirectly after chemical transformation in the atmosphere. Also, materials can suffer the effects of air pollution caused by oil and natural gas combustion, like metal corrosion, the alteration construction materials, and rubber cracking.

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#### **Biographical Sketch**

**Joao Vicente de Assuncao** was born in July 30, 1944. He is a Professor of Air Pollution Fundamentals and Control, he is also a member of the Graduate Adviser Group and the former Chief of the Environmental Health Department at the School of Public Health, University of Sao Paulo where he is also responsible for the laboratory on Air Quality and Ventilation. He received his doctorate at the University of Sao Paulo (Brazil) and his Master of Science degree at the University of Pittsburgh (USA). He also received a bachelor degree in Chemical Engineering by the Sao Paulo Catholic University and a Sanitary Engineer degree by the University of Sao Paulo.

He has conducted research in a variety of air pollution-related areas, including automobile emissions characterization, environmental planning, chlorofluorocarbons emissions in refrigerating and air conditioning systems, air emissions impact in the environment, dioxins and furans, and air pollution prevention and control.

He worked for the Sao Paulo State Environment Agency for 15 years. He served as short term consultant for the World Health Organization, for the United Nations Environment Program, and for the United Nations Development Program.

He is a member of several professional societies, including the Air and Waste Management Association (A&WMA). He is the former Chair of the Brazil Section of the A&WMA. He has participate in several training programs, seminaries and conferences on environmental issues in Brazil, Germany, Japan, Mexico, the United States of America, and Venezuela.