AIR POLLUTION CAUSED BY INDUSTRIES

Jiming HAO and Guowen LI
Department of Evironmental Sciences and Engineering, Tsinghua University, Beijing 100084, P.R.China

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Summary

Our activities affect the environment and. the environment affects our health. As the number of humans on earth increases, our agricultural and industrial activities have a greater impact on the environment, particularly on the atmosphere. As our most precious resource, the atmosphere has been polluted, so it is imperative to take measures to control air pollution. It becomes necessary to know what the sources have been and how they operate. In this chapter, we first introduce five main air pollutants: carbon monoxide (CO), hydrocarbons, particulate, oxides of sulfur (SOx), and oxides of nitrogen (NOx). We then present the industrial emissions inventory. Finally, we analyze the character of air emissions from five main industrial sectors that are combustion sources: the petroleum industry, chemical industry, metallurgical industry, construction material industry, and paper and pulp manufacturing. The emission factors are based on the present processes. With the innovation of processes and the implementation of clean production, the factors will decrease gradually.

1. Introduction

Before we examine air pollution from industries, we need to understand the natural conditions and constituents of the atmosphere. The atmosphere, or air, is normally composed of about 79 percent nitrogen, 20 percent oxygen, and 1 percent mixture of carbon dioxide, water vapor, and small quantities of several gases. A list of these contents is given in Table 1 along with their average concentrations and approximate residence time. Based primarily on temperature, the atmosphere is divided into four layers: (I) *Troposphere* is the layer between the ground and a height of approximately 15km at the equator and 10 km at the poles. In the troposphere, the temperature typically decreases at the rate of 6.5°C/km, the air is relatively well mixed, and thermally driven convection is relatively strong. The troposphere is the layer that contains most of our air pollutants (II) *Stratosphere* is the layer between the troposphere and approximately 50km. There is little bulk mixing in this layer. The temperature is relatively constant except in the upper stratosphere, where the absorption of UV radiation by ozone causes the temperature to rise to approximately 0 °C. (III) *Mesosphere* is the layer between 50 and 85 km within which the temperature decreases almost linearly to approximately 175K. (IV) *Thermosphere* is the uppermost layer of the atmosphere. The temperature increases to approximately 1500K, but it cannot be measured with a thermometer because the molecular concentrations are very small--about 10^{13} molecules/cm^3 by comparison to the molecular concentration of 2.5×10^{19} molecules/cm^3 at the earth's surface (Table 1).

Pollution, as we discussed in the former chapter, is something produced by human beings that interferes with our well being. There are several natural sources that degrade the quality of the air, such as gases and particles from volcanoes, dust from natural sources or odors from decomposition of dead plants and animals. However, human beings do not control these phenomena, and they do not fit our definition of pollution. We will focus on the air pollutants from automobile emissions, chemical odors and factory smoke and their controls.

2. Main air Pollutants and Industrial Emissions Inventory

2.1 Major Air Pollutants

Air pollutants can be divided into two main groups—particulate and gaseous. The former group includes solid airborne particulates such as dust, fly ash, smoke, fog, soot, and fumes. Gaseous pollutants include carbon monoxide, hydrocarbon, oxides of sulfur, and oxides of nitrogen. These pollutants are known as primary air pollutants (see Table 2). These materials may interact with one another in the presence of an energy source to form new secondary air pollutants such as ozone and other very reactive materials. Secondary air pollutants also form from reactions with natural chemicals in the atmosphere.

Species	Average concentration /ppm	Approximate residence time	Species	Average concentration /ppm	Approximate residence time
Major species		10^6yr	Trace species		
N_2	780840	10yr	CO_2	350	15yr
O_2	209460		CH_4	1.72	10yr
H_2O	Variable		H_2	0.58	10yr
Inter gases			N_2O	0.33	150yr
Ar	9340		CO	0.05-0.2	65days
Ne	18		NH_3	0.01	20days
He	5.2		NO/NO_2	0.00004-0.001	1 day
Kr	1.1		O_3	0.02-0.05	
Xe	0.09		H_2O_2	0.001	
Sulfur			HNO_3	0.001-0.0001	

compounds			HC	0.001-050	
SO_2		40 days	CFC11	0.003	65yr
CS_2	0.0002	>1.8 × 105h			
H_2S	0.00001-0.0002	53h			
Free radicals					
OH.	$1\text{-}10\times10^6$ mol./cm^3				
HO_2.	1×10^9 mol./cm^3				

Source: Seinfeld (1986)

Table1: Composition of Atmosphere

Pollutants	Sources
Carbon monoxide(CO)	Incomplete burning of fossil fuels Tobacco smoke
Hydrogen Carbon	Incomplete burning of fossil fuels Tobacco smoke, Chemical processes
Particulate	Burning fossil fuels, Construction operations Industrial waste
Oxide of sulfur (SOx)	Burning fossil fuels, Chemical processes Smelting ores
Oxide of nitrogen(NOx)	Burning fossil fuels, Oxide of N_2 in atmosphere

Table 2: Sources of primary air pollutants

The quality of sulfur dioxide emission from both natural sources and man-made sources shows in Table 3.

Source	Discharging quantity	Source	Discharging quantity
Man-made	103.8	Natural source	147
Coal burning	62	Marine	94
Petroleum burning	25.5	Land	48
Petroleum refinery	3.7	Volcano	5
Metallurgy	10.7	Total	250.8
Other industry	1.9		

Table 3: Sulfur dioxide discharge 106t/a

Oxides of Sulfur (SOx): Oxides of sulfur (SOx) are compounds of sulfur and oxygen that are mostly produced when sulfur-containing fossil fuels are burned. Coal and oil were produced from organisms that had sulfur in their living structure. When the coal or oil was formed, some of the sulfur was incorporated into the fossil fuel. The sulfur is released as sulfur oxide when the fuel is burned. Simultaneously, a large quantity of sulfur oxides is released along with the exhaust gas in metallurgy and vitriol producing process. The reactions involved are as follows:

Burning of elemental sulfur: $S+O_2=SO_2$, $SO_2+0.5O_2=SO_3$

Burning of iron sulfur ore: $4FeS_2+11O_2=2Fe_2O_3+8SO_2$, $SO_2+0.5O_2=SO_3$
Burning of organic sulfur compounds:
$CH_3CH_2CH_2CH_2SH \rightarrow H_2S+2H_2+2C+C_2H_4$
$2H_2S+3O_2 \rightarrow 2SO_2+2H_2O$

Oxides of nitrogen (NOx): As a category of primary air pollutants, oxides of nitrogen (NOx) emitted from industries are a mixture of nitrogen oxide (NO) and nitrogen dioxide (NO_2). About half of NOx, or up to 5.21×10^6 t/a, is produced by human activities such as fossil free burning, production of nitric acid and nitrogenous fertilizer, and other industrial processes. Table 4 shows the quantity of NO_X discharged estimated by Stedman (1983) and Logan (1983).

Source	Discharging quantity	
	Stedman(1983)	Logan(1983)
Natural source	65	96-126
Lighting	10	26
Stratosphere input	3	2
Oxide of NH_3	3	3-33
Burning of biomass	16	39
Discharge of soil	33	26
Man-made sources	66	108

Table 4: NOX discharge 106t/a

There are two kinds of NOx from fuel combustion: one is thermal NOx, from N_2 and O_2 reaction when burned at high temperature, and the other is fuel NOx, which is the decomposed and oxidized compounds of nitrogenous compounds in fuel such as pyridine (C_5H_5N), piperidine ($C_5H_{11}N$) and carbazole ($C_{12}H_9N$) at high temperature. Most of fuel NOx is NO, less than 10% NO is oxidized to NO_2 in flue gas.

Carbon Monoxide (CO): Carbon monoxide is produced when organic materials, such as gasoline, coal, wood, and trash, are incompletely burned. The reactions are following:

$C+0.5O_2 \rightarrow CO \quad C+CO_2 \rightarrow 2CO$

Due to the lack of oxygen, the oxidation rate from CO to CO_2 is very slow. Improvements in combustion equipment and technology cause the discharge of CO from stationary sources to decrease gradually. Table 5 shows the contribution of CO from different sources.

Source	Discharge	Source	Discharge
Industry	300-500	Oxidization of methane	400-1000
Burning of biomass	300-700	Oxidization of other	
Activity of creature	60-160	Hydrocarbon	200-600
Discharge of sea	20-200	Total	1800-2700

Table 5: CO discharge 106t/a

*Hydrocarbon (HC)***:** Hydrocarbons are a large family of compounds, which include most organic compounds with less than about 12 carbon atoms. They are either evaporated from fuel or are remnants of fuel that did not burn completely. Table 6 shows the contribution of hydrocarbon from different sources.

Source	Discharge	Source	Discharge
Coal	2.9	Dissolvent	10
Thermal power	0.2	Burning of rubbish	25
Industrial	0.7	Burning of lumber	0.7
Resident and commerce	2.0	Forest fire	1.2
Petroleum	48.4	Total	88.2
Petroleum refinery	6.3		
Gasoline	34		
Diesel oil	0.1		
Heavy oil	0.2		
Evaporation of oil	7.8		

Table 6: Hydrocarbon discharge 106t/a

Particulates: Particulates, small pieces of solid materials dispersed into the atmosphere, constitute the third largest category of air pollutants. Smoke particles from fires, bits of asbestos from brake linings and insulation, dust particles, and ash from industrial plants contribute to the particulate load.

2.2 Industrial Emissions Inventory

Due to the wide variety of industrial processes, reliable determinations of industrial emissions have been found to depend on individual types of treatment. This is expensive and time-consuming, as it involves detailed study and testing of specific plants and processes. In some cases, data on industrial emissions could be obtained by means of questionnaires sent to the individual plants requesting information on processes, types and quantities of process exhaust, air cleaning equipment and fuel consumption. Frequently, the industries themselves do not have on-line data of this sort. Consequently, insufficient or incomplete results can be expected. Information on air emissions can also be obtained by using engineering estimates which are based on the raw materials or fuel consumed in a given process and reported figures on types and rate of pollutants emitted per unit weight of raw material or fuel used in a particular process. Unfortunately, there does not exist a sufficient body of readily available and reliable information on process emissions derived from actual tests, so it is difficult to obtain satisfactory results. The detailed procedure for making an industrial survey involves the use of a computer card identifying each establishment and its location. A detailed questionnaire sent to each establishment to collect information, which includes data on plant size, operating schedule, fuel usage, processes, and solvent usage. This procedure may provide more reliable results.

Emission factors, which have been applied to source data to yield emission data for SOx, NOx, HC, CO, particulates and so on, exist for a wide variety of industrial processes such as fuel burning, chemical production, manufacturing processes, and solvent usage.

Classification of air pollution sources and emissions are showed in Table 7.

Source type	Category	Examples	Pollutants
Dust production Process	Crushing, grinding screening, demolition milling	Road mix plants Urban renewal Grain elevators	Mineral and organic particulates
Combustion	Fuel burning	Home heating unit Power plants	SOx, NOx, CO, smoke, fly-ash organic vapors,
	Motor vehicles	Autos, buses and trucks Community and apartment	metal oxide particles and odors
	Refuse burning	house incinerator, open burning dums	
Manufacturing processes	Metallurgical plants	Smelters, steel mills, aluminum refineries	Metal fume, fluorides SOx
	Chemical plants	Petroleum refineries, pulp mills, super phosphate fertilizer plants, cement plants	H_2S, Sox, F, organic vapor, particle, odors
	Waste recovery	Metal scarp yards, auto body burning, rendering plants	Smoke, soot, organic vapor, odors
Solvent	Spray painting	Furniture and appliance finishing	Organic phosphates, chlorinated
	Inks	Photogravure and printing	hydrocarbons, As, Pb
	Solvent cleaning	Dry cleaning, degreasing	

Table 7: Classification of air pollution sources and emissions

3. Combustion Sources and their Emission Characterization

Combustion refers to the rapid oxidation of substances (usually referred to as fuels) with the evolution of heat. Most fuels are a mixture of chemical compounds referred to as hydrocarbons, such as coal, fuel oil and natural gas, which, when burned, are converted into final products of carbon dioxide and water. The reaction products of the combustion process are collectively called combustion products, and include CO_2, H_2O, CO, HC, SO_2, SO_3 and NOx. In the case of fuels containing halides (usually chlorine and fluorine), the combustion products may contain hydrochloric or hydrofluoric acids (HCl, HF) and trace quantities of organohalides such as dioxins and furans.

In general, the combustion process can be represented by the following equation.

Fuel + Oxidant + Diluent → Combustion Products + heat
$CxHy+aO_2+bN_2 \rightarrow xCO_2+yH_2O+zNOx+mSO_2+nN_2+ash$

Most combustion systems operate with an overall excess of air to ensure complete combustion. The excess air would then function as an additional diluent, contribute to the combustion products and result in the emission of gaseous or particulate pollutants.

Based on the physical states in which they are found in nature, fuels can be classified as solid, liquid, or gaseous, with coal, fuel oil, and natural gas being the three most common examples of each. The following sections describe these three fuels and their emission characteristics.

3.1 Coal Combustion

Coal is the most readily available energy source throughout the world. While coal is important to the development of industry, it results in air pollution when burned. During combustion, the coal is subject to either or both oxidizing and reducing conditions because of the presence of oxygen, carbon, and carbon monoxide in the bed. The air pollutants from the combustion of coal include particulates, SOx, NOx, HC, and CO. Amounts of each are highly dependent on the type of coal, combustion process, and operation of the process. The particulates consist mostly of ash particles. They also include unburned coal blown out during the turbulent combustion. Typical pulverized coal-fired boiler flue gas contains 2-10ppm CO, 3.9-5.1% O_2, and 14.3-15.3% CO_2. Gaseous emissions of sulfur oxides in the process of coal combustion are largely SO_2 and to a much smaller extent, SO_3 and gaseous sulfates. These compounds form as the organic and pyritic sulfur in the coal is oxidized during the combustion process. On average, 98% of the sulfur present in bituminous coal will be emitted as gaseous sulfur oxides, whereas somewhat less will be emitted when sub-bituminous coal is fired. Generally, boiler size, firing configuration, and boiler operations have little effect on the percent conversion of fuel sulfur to oxides of sulfur. Nitrogen oxides are produced in the combustion process by at least two different mechanisms: one source is from the molecular nitrogen in the combustion air (thermal NOx), the other is from the nitrogen in the fuel being burnt (fuel NOx). Generally, the amount of nitrogen in the fuel is relatively small compared with that in the combustion air, therefore, fuel NOx is only a small part of total NOx. The relative contributions of these two formation pathways depend on the combustion conditions, the type of boiler, and the type of fuel being burnt. Large coal-fired boilers emit more NOx than any other combustion source. The combustion paradox is that the size increase of boilers will increase nitric oxide but decrease CO and HC. The reverse is true. Volatile organic compounds (VOCs) and carbon monoxide (CO) are unburned gaseous combustibles that are also emitted from coal-fired boilers, but generally in quite small amounts. However, during start-up, temporary upsets, or other conditions preventing complete combustion, unburned combustible emissions may increase dramatically. The VOC and CO emissions per unit of fuel that is burned are normally lower from pulverized-coal or cyclone furnaces than from smaller stokers and hand-fired units where operating conditions are not as well controlled.

Table 8 lists the uncontrolled emission factors from the different types of furnaces discussed for particulate, SOx, NOx, CO, and HC.

Furnace			Uncontrolled Emission, g/kg coal				
Boiler category	Heat input 10^6kcal/hr	type	Particulatematter[a]	SOx[b]	CO	HC[c]	NOx[d]
Utility or large		Pulverized	8A	19S	0.5	0.15	9

industrial	> 25	Cyclone	1A	19S	0.5	0.15	27.5
Commercial or		Underfeed &					
industrial	2.5-25	crossfeed	2.5A	19S	1	0.5	7.5
		Overfeed	6.5A	19S	1	0.5	7.5
Small commercial		Overfeed	1A	19S	5	5	3.0
or domestic	< 2.5	Hand fired	20	19S	45	45	1.5

[a] A = Weight percent ash in coal.
[b] S = Weight percent sulfur in coal, pollutant weight is reported as SO_2.
[c] Pollutant weight is reported as CH_4.
[d] Pollutant weight is reported as NO_2.

Table 8: Typical Uncontrolled Emission from Coal Combustion

3.2 Oil Combustion

The most common liquid fuel used in utility processes is fuel oil derived from crude petroleum. Fuel oils are broadly classified into distillate kerosene and residual fuel oils. The former is mostly used for domestic and small commercial applications; the latter is used in utility and industrial boilers. Emissions from fuel oil combustion depend on the grade and composition of the oil, the type and size of the boiler, the firing practices used, and the level of equipment maintenance. Properly designed and operated oil-fired boilers produce less uncontrolled air pollution emission than coal-fired boilers but more than gas-fired boilers.

Boiler	Fuel oil	Uncontrolled Emissions, g/l of Fuel				
		particulate	SOx[a]	CO	HC[b]	NOx[c]
Utility or large						
Industrial	Residual	1	19.2S	0.4	0.25	0.12
Commercial or	Residual	2.75	19.2S	0.5	0.35	0.12
industrial	Distillate	1.8	17.2S	0.5	0.35	0.25
Small commercial						
or domestic	Distillate	1.2	17.2S	0.6	0.35	0.25

[a] S = weight percent sulfur in oil; pollutant weight is reported as SO_2.
[b] Pollutants weight is reported as CH_4
[c] Pollutants weight is reported as NO_2; use one-half this value for tangentially fired boilers.

Table 9: Typical uncontrolled emission from oil combustion

Horizontal firing and tangential firing are the two basic arrangements used in oil combustion systems. The oil is directed toward the center of the furnace in a horizontally fired system resulting in a hotter flame and the formation of about twice the NOx as is formed by tangentially fired oil furnaces. Large boilers burn hotter and produce more NOx than small one. About 0.65% of sulfur dioxide converts to sulfur trioxide in an oil-fired boiler. Table 9 lists typical uncontrolled emissions for horizontally fired oil furnaces.

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Biographical Sketches

Mr. Jiming Hao is a professor and dean in the Institute of Environmental Sciences and Engineering, Tsinghua University, Beijing, P. R. China. He was born on August 25, 1946 in Shandong Province of China, received his Ph. D degree from the University of Cincinnati in 1984.

Mr. Guowen Li is a post-doctor in the department of Environmental Sciences and Engineering, Tsinghua University, Beijing, P. R. China. He was born on April 4, 1968 in Shannxi Province of China, received his Ph. D degree from the University of Xi'an Architecture & Science in 1999.