An information search for properties, sources and environmental effects of exotic air pollutants.

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AN INFORMATION SEARCH FOR PROPERTIES, SOURCES AND ENVIRONMENTAL EFFECTS OF EXOTIC AIR POLLUTANTS

A Thesis
Submitted to the Faculty of Graduate Studies through the Department of Chemical Engineering in Partial Fulfilment of the Requirements for the Degree of Master of Applied Science at the University of Windsor

by

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Windsor, Ontario
1973
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ABSTRACT

A comprehensive summary of the properties, sources and environmental effects of fourteen exotic air pollutants has been prepared for the convenience of personnel concerned with the evaluation of potential dangers from specific materials and with the implementation of detection, monitoring and abatement procedures.
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PROPERTIES, SOURCES AND ENVIRONMENTAL EFFECTS OF EXOTIC AIR POLLUTANTS

Since the late 1960's, there has been a growing concern over the accumulation of heavy metals and chlorinated hydrocarbons in waterways, the atmosphere and in plant and animal life. The honest disagreements among reputable natural and social scientists and the questionable interpretations of facts by politicians and lobbyists have not helped to clarify the environmental picture. It is most unfortunate that medical research, proving that trace quantities of some heavy metals are vital to human health, should provide support for arguments denying the need for more stringent pollution control regulations.

Before intelligent decisions can be made with respect to the establishment of allowable emission limits for various gaseous and particulate pollutants, it is important to appreciate how critical such efforts must be. Some measure of the difficulties involved may be obtained from a consideration of just the popular literature and newspaper articles. For example, the July 1972 issue of Science Digest provides a very readable summary of the conflicting roles of some heavy metals.
Although trace amounts of cobalt are needed to make up 4% of the vitamin B<sub>12</sub> which prevents pernicious anemia in humans, and aids in the growth of animals, human intake of cobalt above the minimum requirements leads to serious complications. Heavy beer drinkers in Quebec, dying from damaged hearts, were apparently victims of cobalt sulfate used as a foam stabilizer.

Magnesium seems to be one metal that has yet to show bad effects on the human system. Some medical researchers believe that as much as 300 mg. of magnesium are required daily to minimize hardening of arteries and emotional difficulties and to promote rapid recovery of tired muscles.

On the other hand, cadmium seems to provide absolutely no benefits to human life. Accumulation of infinitesimal quantities of this metal has been blamed for damage to kidneys and testes, anemia and high blood pressure.

Zinc is another commonly used metal that has an important role in human development. A daily intake of less than 10 to 15 mg. can lead to stunted growth, underdeveloped testicles, rough skin, general lethargy and an inability to process sugar.

The effects of nickel have not been studied too extensively but it has been established that high nickel concentrations are always found after heart attacks in humans.

The benefits of iron in human systems are well documented. There is some concern that iron enrichment of common foods could create problems for some people.
Although selenium in trace amounts is necessary for animal life, it can become more toxic than arsenic or mercury.

So far, excesses of copper ingestion have not produced well recognized problems, but psychiatric studies show that some emotional illnesses are associated with high copper levels in the body.

There are growing suspicions that chromium is necessary for the process of sugar metabolism. Although vanadium has been shown to be involved in cholesterol metabolism in young chickens, there is no solid evidence to prove that it is required by humans. Low lithium concentrations in drinking water have been related to higher frequencies of hardening of the arteries, diabetes and high blood pressure. Recent data from Texas show that exceptionally high lithium concentrations in water supplies have apparently reduced admissions to mental institutions to 50% of the norm.

Fears of lead poisoning from auto exhausts have led to the development of leadless gasolines and spurred research on catalysts for carbon monoxide and nitrogen oxide removal. The Bell Telephone Laboratories apparent success in producing rare earth catalysts containing cobalt or manganese for conversion of carbon monoxide to harmless carbon dioxide now raises the question of whether emissions of cobalt, manganese or rare earths from the new converters can be more serious than the original carbon monoxide discharges.

The threat of cancer has done much to initiate serious interest in the effects of pollutants on the ecosystem. Two pathologists from New
York's Mount Sinai School of Medicine reported in July of 1972 that occupational exposure to asbestos by non-smokers is quite harmless. According to their studies, asbestos becomes dangerous only when associated with cigarette smoking. These conclusions may be hard to reconcile with those of researchers studying the high incidence of stomach cancer among the Japanese. The most recent medical opinions imply that the Japanese culinary technique of adding glucose and talc to make the rice more palatable is, in effect, adding asbestos into the daily diet by way of the talc.

The 1970 report of the California Department of Health and the State Air Resources Board suggests that photochemical smog creates no long-term carcinogenic trends but is responsible for increases in the death rate from heart disease. Respiratory diseases such as emphysema, bronchitis and asthma appear to be aggravated during smog episodes. High carbon monoxide concentrations in the atmosphere seem to contribute to myocardial infarctions.

Chlorinated hydrocarbons such as DDT, aldrin and dieldrin create controversies among environmentalists and agricultural experts. At the present time, it is still impossible to determine whether their benefits as insecticides outweigh their potential abilities of inducing cancer in humans. The world wide distribution of PCB focuses on the need for a better appreciation of sources of emissions and methods of abating emissions of pollutants whose overall effects on living systems are still unknown.
This report has been designed as a convenient source of information for government and industrial personnel concerned with the evaluation of potential dangers from specific air pollutants and implementation of detection, monitoring and abatement procedures. The format is based on discussions with Air Management Branch personnel and several participants at the Environmental Resources Conference on Cycling and Control of Metals which was held in Columbus, Ohio, 31 October - 2 November, 1972.
A. Ammonia

1. Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>Colourless alkaline gas</td>
</tr>
<tr>
<td>Formula</td>
<td>NH₃</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>17.03 g/mol</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>~33.35 °C</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>~77.7 °C</td>
</tr>
<tr>
<td>Critical Temperature</td>
<td>133.0 °C</td>
</tr>
<tr>
<td>Critical Pressure</td>
<td>1657 psi</td>
</tr>
</tbody>
</table>

Ammonia burns with a yellow flame in air or oxygen (ignition temperature 780°C) according to the process

\[ 4 \text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O} \]

An ammonia and air mixture will explode under certain conditions e.g. high temperature and pressure greater than atmospheric.

2. Potential Sources and Levels of Atmospheric Emissions

a. Natural Occurrence

The main emissions of atmospheric ammonia are the results of biological processes on land and sea areas. Frost and Sullivan [1] estimated that 3.7 x 10⁹ tons of ammonia are released into the atmosphere each year. Approximately 99.9% of this amount is produced by natural biological processes. The main biological source of ammonia is the decomposition of organic waste material. Ammonia is emitted into
the atmosphere from manure in piggeries [2] and other places where animals are kept. Significant amounts of ammonia from urea are lost by volatilization.

b. Waste Water Treatment in Sewage Plants

Ammonia is produced during treatment of waste water in sewage plants, [3] but no estimation has been made of these emissions.

c. Ammonia Plants

No information was found on the quantity of emissions from ammonia plants.

d. Coke Plants

Kapitulskii [4] studied the ammonia concentration in air sampled at the top of a coke oven. He found that during charging, the ammonia concentration was 6,300 to 8,000 µg/m³, and it was reduced to 3,500 to 4,400 µg/m³ by smokeless charging.

e. Internal Combustion Engines

It has been estimated that 2.0 lb. of ammonia are emitted per 1,000 gallons of fuel consumption in gasoline engines [5][6] and diesel engines [6]. It has been calculated that the total ammonia emitted into the atmosphere of Los Angeles from the consumption of gasoline alone in 1953 was about 5.0 tons a day [5].

f. Utility Industry

Ammonia is produced as a result of combustion of fossil
fueled. Sydney Miners [8] collection of ammonia emission rates from various reports [5,6,7] is presented in Table A.1.

<table>
<thead>
<tr>
<th>Combustion Source</th>
<th>Amount of Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>2 lb/ton</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>1 lb/1,000 gal</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>0.3-0.56 lb/10^6 ft^3</td>
</tr>
<tr>
<td>Bottled Gas (Butane)</td>
<td>1.7 lb/10^6 ft^3</td>
</tr>
<tr>
<td>Propane</td>
<td>1.3 lb/10^6 ft^3</td>
</tr>
<tr>
<td>Wood</td>
<td>2.4 lb/ton</td>
</tr>
<tr>
<td>Forest Fires</td>
<td>0.3 lb/ton</td>
</tr>
</tbody>
</table>

Table A.1: Ammonia Emissions From Combustion [8]

g. Oil Refineries

The predominant emissions of ammonia in oil refineries are from the catalyst regenerators in the catalytic cracking units. Table A.2 shows the ammonia levels from regenerator stacks of catalytic cracking units in the Los Angeles area [9].

<table>
<thead>
<tr>
<th>Unit Type</th>
<th>µg/m^3</th>
<th>Tons/Day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid Bed</td>
<td>47,000-470,000</td>
<td>4.2</td>
</tr>
<tr>
<td>Thermofor</td>
<td>20,000-72,000</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table A.2: Ammonia Emissions From Catalytic Cracking Unit Regenerator Stacks [9]

h. Foundries

Ammonia has been found in the exhaust emissions from some metallurgical plants, however, detailed studies have not been
carried out.

1. Incinerators

Incineration of waste materials generates ammonia that can be discharged into the atmosphere. Table A.3 shows the rate of ammonia emissions from incineration as compiled by Sydney Miner [8] from several reports.

<table>
<thead>
<tr>
<th>Combustion Source</th>
<th>µg/m^3</th>
<th>lb/ton of Material Burned</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-fired Domestic Incinerators</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shredded paper and domestic wastes</td>
<td>&lt;4,000</td>
<td></td>
</tr>
<tr>
<td>Municipal incinerators</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spray-chamber (Alhambra, Calif.)</td>
<td>20,000</td>
<td>0.3</td>
</tr>
<tr>
<td>Multiple chamber</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Other Incinerators</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single incinerator</td>
<td>400</td>
<td>0.3 - 0.5</td>
</tr>
<tr>
<td>Wood waste</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>Backyard paper and trimmings</td>
<td>45,000</td>
<td>1.8</td>
</tr>
<tr>
<td>Backyard 6 ft^3 paper</td>
<td>3,000</td>
<td>0.1</td>
</tr>
<tr>
<td>Backyard 6 ft^3 trimmings</td>
<td>100,000</td>
<td>4.4</td>
</tr>
<tr>
<td>Open dump burning</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Large gas-fired industrial units</td>
<td>400</td>
<td>2.3</td>
</tr>
<tr>
<td>Flue-fed apartment incinerators</td>
<td></td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table A.3: Ammonia Emissions From Incineration [8]

1. Fertilizer Plants

Minakami [10] who analyzed air pollutants in the exhaust of a fertilizer plant, showed that ammonia was emitted at a high concentration of about 660 ppm. It also has been reported that 2,600 tons of ammonia were released from a fertilizer plant in South Point, Ohio [24] each year.
3. Effects of Ammonia

a. On Humans

Jacobs [11] states that ammonia gas mainly affects the upper respiratory tract, with a small percentage reaching the lung at the inhaled concentrations. It is well known that gaseous ammonia intensely irritates moist tissue. High concentrations of ammonia cause cessation of respiration. At concentrations of 280,000 \( \mu g/m^3 \) to 490,000 \( \mu g/m^3 \) the gas can produce eye, nose and throat irritation and hypoesthesia.

Hemeon [12] suggested that zinc ammonium sulfate aerosols were in part responsible for the irritant effects of the air during the Donora Smog Episode in 1948.

b. On Animals

Weedon [13] found that guinea pigs and rabbits exposed to 1,740,000 \( \mu g/m^3 \) of ammonia developed acute and chronic lung lesions. Weatherby [14] found mild changes in kidneys, spleen, adrenals and liver of guinea pigs when exposed to 118,000 \( \mu g/m^3 \) of ammonia for 18 weeks.

c. On Vegetation

Thornton [15] found that ammonia at 700,000 \( \mu g/m^3 \) caused changes in the pH of tomato plant leaf and stem tissue but did not cause damage at lower concentrations. He also observed injury related to pH change and acute injury to the tissue of the plants, but without
damage to the chlorophyll. The effect of ammonia on plants depends on the concentration of ammonia and exposure time. The time required to produce 50 percent injury to exposed plant surfaces at 700,000 μg/m³ is 3 minutes for tomato leaves and 8 minutes for tobacco leaves. Stems are more durable, tomato stems need 60 minutes while tobacco needs up to 240 minutes exposure for 50% injury.

Benedict and Breen [16] state that ammonia produced spots of cell collapse and death, primarily along the margins of the leaves.

d. On Materials

Holbrow [17] studied the effects of ammonia on paint. He found that ammonia, associated with sulfur dioxide and moisture, formed crystals on the surface of paint which damaged the paint. Ammonia can also discolour some fabric dyes.

4. Environmental Air Standards

The American Conference of Governmental Industrial Hygienists recommended an occupational threshold limit for ammonia in the air of 35,000 μg/m³.

The ambient air standards for Czechoslovakia, the U.S.S.R. and Ontario, are shown below in Table A.4.
Table A.4: Ambient Air Quality Standards For Ammonia [18]

<table>
<thead>
<tr>
<th>Location</th>
<th>Basic Standard a ( \mu g/m^3 )</th>
<th>Average Time</th>
<th>Permissible b ( \mu g/m^3 )</th>
<th>Average Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Czechoslovakia</td>
<td>100</td>
<td>24 hr.</td>
<td>300</td>
<td>30 min.</td>
</tr>
<tr>
<td>U.S.S.R.</td>
<td>200</td>
<td>24 hr.</td>
<td>200</td>
<td>20 min.</td>
</tr>
<tr>
<td>Ontario, Canada</td>
<td>3,500</td>
<td>30 min.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a = Basic standard for long-term exposure
b = Permissible standard not to be exceeded more than once in any 4 hours

5. Detection and Measurement of Ammonia

In determining ammonia levels in air, the alkaline properties can be used. Methods for determining ammonia include the following:

i. Alkalimetric determination of \( NH_3 \) in amounts of the order of the MAK-value = 50 ppm. This method is used for air of fertilizer silos and other storage or working spaces by Österreichische Stickstoffwerke, (Linz [19]) for the determination of the ammonia level.

ii. Determination of low ammonia concentrations according to Buck and Stratmann [20].

iii. Determination of low ammonia concentrations via the indophenol reaction by Leithe and Petschle [21].

iv. Determination by direct UV spectrophotometry. Gunther, Barkley, Kolbezen, Blinn and Staggs [22] carried out the determination of ammonia in air by direct UV spectrophotometry at 204.3 \( \mu m \) in 10 cm quartz cells. The molar extinction coefficient at this wavelength is 2790. The concentration limit is 7 ppm.
v. The Nessler colourimetric method for analyzing ammonia in air [23].

6. Abatement Methods

Methods used to control other pollutants will also reduce the quantity of ammonia emitted into the atmosphere.

a. Smokeless Charging

Smokeless charging of coke ovens reduces emissions of ammonia from 6,300 and 8,000 μg/m³ to 3,500 and 4,400 μg/m³ [4] in the U.S.S.R.

b. Wet Scrubbers

Minakami, Oote, Matsuura and Ogawa [10] studied the control of emission of ammonia in fertilizer plants in Japan. They reduced the emission of ammonia from 660 ppm to 6.60 ppm by lowering the pH of the scrubber liquid, but emission of other oxidative gases was slightly increased.

c. Impregnated Activated Charcoal

Impregnated activated charcoal has been used to remove ammonia from the air in places where animals are kept. [25].

d. Bag Filters and Electrostatic Precipitators

These methods are used to remove ammonia in the solid state, in the form of ammonium compounds.
REFERENCES


2. Deadly Gases in Piggeries, German Research Service, 5 No. 5 P.9 (1966)


B. Arsenic and Its Compounds

1. Properties

Arsenic: Molecular Weight 74.92

Boiling Point 613°C (Subl.)

Metallic Arsenic is non-toxic.

White Arsenic: Formula \( \text{As}_2\text{O}_3 \)

Boiling Point 465°C
Melting Point 313°C
Sublimes at 193°C

Most compounds of arsenic, when heated in air, are converted to this tasteless, toxic, white powder.

Arsine: Formula \( \text{AsH}_3 \)

Boiling Point -55°C
Melting Point -155°C

Arsine is extremely toxic. It is formed wherever hydrogen is produced in the presence of arsenic.

Organic arsenates such as cacodylic acid \((\text{CH}_3)_2\text{HAsO}_2\) are toxic to plants, but relatively less toxic to animals. Calcium and lead arsenates, often used as pesticides, are toxic to animals, but less toxic to plants.
2. Potential Sources and Levels of Atmospheric Emissions

a. Smelters and Mills of Arsenical Ore

Arsenic is a by-product in the smelting of lead, copper, gold, nickel and cobalt. Its production, (as As$_2$O$_3$, white arsenic) is so great that the supply exceeds the demand [1]. In June 1962, a gold mine and smelter [2] reopened in one of the western states. After several months of operation, the emission control equipment was not working properly. Air samples taken at the plant showed 60 to 13,000 μg/m$^3$ of white arsenic. The results of analyses are shown on Table B.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>Arsenic Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue dust</td>
<td>Base of stack</td>
<td>44%</td>
</tr>
<tr>
<td>Roof dust</td>
<td>Shed near office</td>
<td>4.4%</td>
</tr>
<tr>
<td>Dust</td>
<td>Area near drying mill</td>
<td>2.7%</td>
</tr>
<tr>
<td>Dust</td>
<td>Roaster area</td>
<td>3.1%</td>
</tr>
<tr>
<td>Dust</td>
<td>Sulfide-ore feed</td>
<td>1.23%</td>
</tr>
<tr>
<td>June grass</td>
<td>Area near school</td>
<td>925 μg/g</td>
</tr>
<tr>
<td>Water</td>
<td>Tap water</td>
<td>30 μg/l</td>
</tr>
</tbody>
</table>

Table B.1: Arsenic Contamination In A Western Mining Community [2]

A clinical examination showed that thirty-two out of forty children who attended two schools had dermatosis associated with cutaneous exposure to arsenic, but no cases of dermatosis occurred among the older children who were bussed to a high school in a distant town. No new cases of dermatosis occurred after controls at the plant were working properly.

In 1903 to 1905, arsenical air pollution occurred in Montana [3,4]. A large amount of arsenic was emitted from a copper
Smelter. Many animals died from eating plants contaminated with arsenic trioxide carried as far as 15 miles from the smelter. It was found that the grass and moss in that area contained 405 ppm of arsenic trioxide. It was estimated that approximately 450 g/m³ of arsenic trioxide had been emitted from the stack.

Another arsenical air pollution episode occurred at a copper mine in northern Chile [5]. A survey of 124 workers showed arsenical melanosis in 7.25%, arsenical dermatitis in 5.65%, and perforation of the nasal septum in 1.6% of those tested.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Arsenic Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral (ore)</td>
<td>0.054%</td>
</tr>
<tr>
<td>Concentrated Ore</td>
<td>1.64%</td>
</tr>
<tr>
<td>Calcined Ore</td>
<td>0.30%</td>
</tr>
<tr>
<td>Dust from Electrostatic Precipitator</td>
<td>10.36%</td>
</tr>
<tr>
<td>Dust from Stack</td>
<td>16.64%</td>
</tr>
<tr>
<td>Soil in Plant</td>
<td>1,000 µg/g</td>
</tr>
<tr>
<td>Soil on Road to Plant</td>
<td>650 µg/g</td>
</tr>
<tr>
<td>Soil near Hospital</td>
<td>20 µg/g</td>
</tr>
<tr>
<td>Soil near Worker's Club</td>
<td>90 µg/g</td>
</tr>
<tr>
<td>Air at Roasting Plant</td>
<td>400 - 81,000 µg/m³</td>
</tr>
<tr>
<td>Air at Smelting Plant</td>
<td>400 - 54,000 µg/m³</td>
</tr>
</tbody>
</table>

Table B.2: The Concentration of Arsenic Near a Copper Mine in Northern Chile [5]

Rockstroh [6] found that 45 out of 111 workers employed at Aue, Saxony in a smelter processing nickel cobalt arsenide ores from Schneeeberg developed lung cancer.
b. Power Plants Which Burned Coal of High Arsenic Content

Coal contains 0.08 to 16 µg of arsenic per gram of coal [7]. As a result the air of most cities contains a small amount of arsenic. Analyses of the dust in Hamburg, Germany [7] and Leeds, England [7] have shown that dusts contained 30 to 230 µg of arsenic per gram. It was estimated that [8] 327 to 6,440 tons of arsenic were emitted into the atmosphere each year in the United States just from coal consumption. Data from measurements of the national air sampling network of the United States in 1964 showed [28] the results in Table B.3.

<table>
<thead>
<tr>
<th>City</th>
<th>Average Arsenic Concentration µg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Los Angeles</td>
<td>0.01</td>
</tr>
<tr>
<td>Detroit</td>
<td>0.03</td>
</tr>
<tr>
<td>Philadelphia</td>
<td>0.06</td>
</tr>
<tr>
<td>Chicago</td>
<td>0.03</td>
</tr>
<tr>
<td>New York</td>
<td>0.03</td>
</tr>
<tr>
<td>Cincinnati</td>
<td>0.03</td>
</tr>
<tr>
<td>Non-urban</td>
<td>0.00</td>
</tr>
<tr>
<td>Montgomery County</td>
<td></td>
</tr>
<tr>
<td>Humboldt County</td>
<td>0.00</td>
</tr>
<tr>
<td>Florida Keys</td>
<td>0.00</td>
</tr>
<tr>
<td>Parke County</td>
<td>0.01</td>
</tr>
<tr>
<td>Delaware County</td>
<td>0.00</td>
</tr>
<tr>
<td>Cape Vincent</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table B.3: Average Arsenic Concentration of Selected Urban and Non-Urban Areas of the United States [28].

Beneke, Dobisova and Macaj [9] examined the arsenic content in the hair of one control and 7 exposed groups of 10 year old boys from communities located approximately 1 km from the Novaky Power Plant in Czechoslovakia. This plant, burning a local coal of high arsenic content, emitted approximately 1 ton of arsenic per day in the form of white arsenic, despite the use of electrostatic eliminators. They
found over 3.5 times more arsenic in the hair of these children than in the control group.

c. **Cotton Gins and Cotton Trash Burning**

Arsenic compounds are used for weed control and as desiccants for cotton plants prior to machine picking. [9,10] Naturally, the dust emitted from cotton gins contains arsenic. The concentration of dust and arsenic observed near a cotton gin in Texas is shown in Table B.4.

<table>
<thead>
<tr>
<th>Distance from Gin (ft)</th>
<th>Range of Suspended Particulate Concentrations (µg/m³)</th>
<th>Range of Arsenic Concentrations (µg/m³)</th>
<th>Arsenic ppb/µg Particulates Ratio X 10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-300 down wind from gin</td>
<td>5,000–76,000</td>
<td>0.6–141</td>
<td>1.2–18.5</td>
</tr>
<tr>
<td>1,200–1,400 down wind from gin</td>
<td>385–187</td>
<td>0.07–0.08</td>
<td>3.7–2.1</td>
</tr>
<tr>
<td>2,200–8,000 down wind from gin</td>
<td>217–42</td>
<td>0.10–0.1</td>
<td>4.6–2.4</td>
</tr>
<tr>
<td>Up wind from gin</td>
<td>67–783</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table B.4: Suspended Particulate and Arsenic Concentrations in the Air Near Cotton Gins in West Texas, 1964 [12]

This table shows that the arsenic content is approximately 0.03 percent of the particulate matter.

Another particulate emissions study from Stoneville Cotton Gin [12] shows that the particulate emission concentration range is between 11,000 and 1,258,000 µg/m³.
<table>
<thead>
<tr>
<th>Sampling Point</th>
<th>Settling Chamber</th>
<th>Sampling Filter</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unloading Fan</td>
<td>183,000</td>
<td>820,000</td>
<td>820,000</td>
</tr>
<tr>
<td>Six-Cylinder Cleaner</td>
<td>1,190,000</td>
<td>30,000</td>
<td>1,258,000</td>
</tr>
<tr>
<td>Stick and Burr Machine</td>
<td>68,000</td>
<td>11,000</td>
<td>79,000</td>
</tr>
<tr>
<td>Seven-Cylinder Cleaner a</td>
<td>23,000</td>
<td>11,000</td>
<td>34,000</td>
</tr>
<tr>
<td>Seven-Cylinder Cleaner b</td>
<td>46,000</td>
<td></td>
<td>46,000</td>
</tr>
<tr>
<td>Condenser</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ a = \text{standard cyclone, 84-inch diameter} \]
\[ b = \text{high-efficiency, 34-inch diameter} \]

Table B.5: Particulate Emissions From Stoneville Cotton Gin

The burning of trash from a cotton gin is also a source of arsenic pollution [13], since approximately 37 percent of the gins incinerate the trash [12]. No estimation was made of the arsenic emissions from incinerators, but arsenic has been observed in the smoke from burning cotton burr trash [13].

d. Pesticides

Arsenical pesticides were used in agriculture prior to the invention of DDT. DDT or other organic insecticides have almost replaced arsenical insecticides nowadays. Excesses of lung cancers have been reported in German vineyardists who sprayed lead arsenate before 1942 [15].

e. Arsenic-Sprayed Tobacco Used in Cigarettes [16]

It is found that the arsenic content of cigarettes ranged up to 50 parts per million, 15 times the allowable limit for foods. [17]
f. Natural Occurrence

Virgin soils usually contain a few ppm of arsenic. It is so widely distributed that traces of it can be found almost everywhere. Arsenic is present in sea water at levels of 10 to 100 ppb. [29]

3. Effects of Arsenic and Its Compounds

a. On Humans

Metallic arsenic is non-toxic, but arsine $\text{AsH}_3$ is extremely dangerous. It has been reported that the fatal dose of arsenic trioxide by ingestion for man is 70,000 to 180,000 µg. [18]

i. Carcinogenesis

Buchanan [19] examined the cases of skin cancer following a prolonged period of medicinal administration (averaging 18 years) of inorganic trivalent arsenic. He states that cancer frequently (80 percent of published cases) follows the nonmalignant manifestation of keratosis, commonly on the palms of the hands or soles of the feet. The statement that arsenic is a skin and respiratory carcinogen [20] has received some support from the industrial hazards of above average mortality from lung cancer in South Rhodesian miners of gold-arsenical ores [21] and the frequent occurrence of lung cancer in German vineyard workers exposed to lead arsenate pesticides [15]. Frost [22] argued that arsenic might not be the carcinogen when other materials were present, such as nickel which occurs together with arsenic in industrial dust. Also, its failure to induce cancer in experimental animals
suggested that its carcinogenic properties may not be very significant.

ii. Dermatosis

Dermatosis occurred among children attending two schools during the year 1962, when emission controls failed at the gold mine and smelter in one of the western states [2].

iii. Irritation

Irritation of nasal mucosae and mild bronchitis are common symptoms of arsenic poisoning.

iv. Palmar Keratosis

Palmar keratosis of the hands and feet.

b. On Animals

In the western state gold mine episode [2], the pet population was reduced from over 24 to 1. The Montana [3,4] episode saw 625 sheep die out of a flock of 3500 while grazing 15 miles from the smelter. Frost [22] has reviewed the literature on the carcinogenic effects of arsenic. He reports that in more than 35 experiments, in which mice, rats, pigs and dogs were tested with arsenic compounds, negative results were obtained.

c. On Plants

Organic arsenates such as cacodylic acid ($\text{CH}_3\text{HAsO}_2$) are toxic to plants. Various varieties of organic arsenates have been
synthesized for use as desiccants for cotton plants prior to machine picking, to kill potato vines prior to machine picking, and to control aquatic weeds.

Sodium arsenite is used as a soil sterilant to control vegetations.

d. On Material

No information has been found on the effects of arsenic on material.

4. Environmental Air Standards

The American Conference of Governmental Hygienists [29] and the American Industrial Hygiene Association [18] recommended that threshold limit values for industrial workers of 8 hours per day be 500 µg/m³ for arsenic and its compounds and 200 µg/m³ for arsine.

U.S.S.R. [23] and Czechoslovakia set a basic 24 hour standard of 3 µg/m³ for arsenic and its compounds.

Stern [24] summarized the emission standards as reported in Table B.6.
<table>
<thead>
<tr>
<th>Location</th>
<th>Source of Emission</th>
<th>Standard Units</th>
<th>µg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Czechoslovakia</td>
<td>&lt; 5,000 cfm</td>
<td>0.03 kg/hr</td>
<td>115,000</td>
</tr>
<tr>
<td>Great Britain</td>
<td>0.05 grains/ft³</td>
<td>0.02 grains/ft³</td>
<td>46,000</td>
</tr>
<tr>
<td>Great Britain</td>
<td>&gt; 5,000</td>
<td>0.01 grains/ft³</td>
<td>23,000</td>
</tr>
<tr>
<td>New South Wales</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Queensland</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table B.6: Emission Standards for Arsenic in Effluent Air or Gases [24]

5. Detection and Measurement of Arsenic and Its Compounds

Impingers, electrostatic precipitators, and filters are commonly used for collection of dust and fumes of arsenic compounds.

Chemical methods are generally based on the principle that arsenic is expelled as AsH₃ from acid solution with zinc. The arsine is introduced into silver diethylthiocarbamate (AgDDTC) [18,19] or reacts with copper foil (Reinsch's method) or with silver nitrate or mercuric chloride (Gützeit's Test). Then the coloured complex formed is determined by

1. Neutron activation
2. Atomic absorption
3. Spectrophotometry

6. Abatement Methods

Any particulate material control equipment can reduce arsenic emissions, provided that it operates at a low temperature. Because arsenic trioxide sublimes at 192°C, temperatures of about 100°C will
condense the arsenic fumes.

iii. Electrostatic precipitators have been reported to reduce arsenic from 5-17 ppb to 0-4 ppb [26]

ii. Cooling flue bag houses

iii. Fabric filters

iv. Wet vacuum pumps were used at a chemical plant in the U.S.S.R. It was reported that 100% effectiveness was achieved [27].
REFERENCES


15. Braun, W., Cancer of the Skin and Inner Organs Caused By Arsenic; Contribution To Late Occupational Sequela Caused By Arsenic, German Medical Monthly, 3 p.321 (1958)


C. Asbestos

1. Properties

Asbestos is a general name given to a variety of useful fibrous minerals, usually 3 to 5 μ in diameter and 20 to 100 μ in length. The mineral is divided into two groups.

a. Pyroxenes – chrysotile

b. Amphiboles – crocidolite,amosite, tremolite, actinolite, and anthophyllite.

Over 90% of the world's asbestos production is chrysotile.

2. Potential Sources and Levels of Atmospheric Emissions

a. Asbestos Mines and Asbestos Textile Mills

Sluis-Cremer [2] reported dust counts in asbestos mines and mills of South Africa as listed below.

<table>
<thead>
<tr>
<th>Location</th>
<th>Dust Count mppcf</th>
<th>(mppm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mines</td>
<td>Mill</td>
</tr>
<tr>
<td>Northwest-Cape Province</td>
<td>2.8-24 (100-840)</td>
<td>10-55 (360-1920)</td>
</tr>
<tr>
<td>Transvaal</td>
<td>2.3-6.5 (80-228)</td>
<td>4.6-20 (162-720)</td>
</tr>
</tbody>
</table>

Table C.1: Typical Emissions of Asbestos

He pointed out that the main sources of airborne asbestos were dumps and roads made from mine tailings. Laamanen, Noro and Raunio [3] investigated asbestos dust levels at a distance of 50 km from the mines in Finland. They found dust fall rates ranging from 1.52 g/100m²/month at 4 km to 34.6 g/100m²/month at 0.5 km. distances from

* mppcf = million particles per cubic foot
* mppm³ = million particles per cubic meter
* μC/g = micro-micro curies per gram
<table>
<thead>
<tr>
<th>Approximate Formula</th>
<th>Chrysotile ( \text{MgO-2SiO}_2 \cdot 2\text{H}_2\text{O} )</th>
<th>Crocidolite ( \text{Na}_2\text{O-3FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{8SiO}_2 \cdot \text{H}_2\text{O} )</th>
<th>Amosite ( \text{1.5MgO-5.5FeO} \cdot \text{8SiO}_2 \cdot \text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Percentage of Major Components</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica ( \text{SiO}_2 )</td>
<td>40.3</td>
<td>51.4</td>
<td>49.3</td>
</tr>
<tr>
<td>Alumina ( \text{Al}_2\text{O}_3 )</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrous oxide ( \text{FeO} )</td>
<td>1.0</td>
<td>20.3</td>
<td>40.9</td>
</tr>
<tr>
<td>Ferric oxide ( \text{Fe}_2\text{O}_3 )</td>
<td>1.5</td>
<td>17.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Manganese oxide ( \text{MnO} )</td>
<td></td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Calcium oxide ( \text{CaO} )</td>
<td>0.2</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Magnesium oxide ( \text{MgO} )</td>
<td>42.4</td>
<td>1.4</td>
<td>5.7</td>
</tr>
<tr>
<td>Sodium oxide ( \text{Na}_2\text{O} )</td>
<td></td>
<td>6.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Potassium oxide ( \text{K}_2\text{O} )</td>
<td></td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>Carbon dioxide ( \text{CO}_2 )</td>
<td>0.2</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Water of Crystallization ( \text{H}_2\text{O} )</td>
<td>13.7</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td><strong>Trace Organic Impurities</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil-wax (mg/100g fiber)</td>
<td>4-7.6</td>
<td>4-200</td>
<td>4-20</td>
</tr>
<tr>
<td>Benzo(a)pyrene (mg/g fiber)</td>
<td>non-detected</td>
<td>0.2-24</td>
<td>0.2-2.4</td>
</tr>
<tr>
<td><strong>Trace Inorganic Impurities</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(µg/g fiber)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>2</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Ga</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>2</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>V</td>
<td>50</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Bo</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Cu</td>
<td>35</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Ti</td>
<td>50</td>
<td>50</td>
<td>300</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Ni</td>
<td>5,000 (1,000-14,000)</td>
<td>&lt;10</td>
<td>1,000</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt;200</td>
<td>&lt;100</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Co</td>
<td>700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;5 (&lt;100)</td>
<td>&lt;5 (&lt;100)</td>
<td>&lt;5 (&lt;100)</td>
</tr>
<tr>
<td>Cr</td>
<td>130 (400-500)</td>
<td>180 (200)</td>
<td>7,000 (7,900)</td>
</tr>
<tr>
<td><strong>Radioactive Contaminants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>(µc/g fiber)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(^{40})</td>
<td>0.14</td>
<td>0.02</td>
<td>0.55</td>
</tr>
<tr>
<td>Th(^{238})</td>
<td></td>
<td>&lt;0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>Ra(^{226})</td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table C.2: Composition of Asbestos Minerals [1]
the sites.

b. **Construction and Demolition of Building Sites**

Sampling was conducted by Nicholson, Rohl and Ferrand [19] in lower Manhattan about construction sites where extensive spraying of asbestos-containing fireproofing was taking place. The results obtained are shown in Table C.3.

<table>
<thead>
<tr>
<th>Site</th>
<th>Asbestos Level in $10^{-9} \text{g/m}^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Down wind from source</td>
<td>45 - 180</td>
</tr>
<tr>
<td>2. 45° from source</td>
<td>15 - 30</td>
</tr>
<tr>
<td>3. Upwind from source</td>
<td>20</td>
</tr>
</tbody>
</table>

Table C.3: Asbestos Levels in Vicinity of Construction Sites (Spray Fireproofing) [19]

c. Industries manufacturing asbestos cement and building products [4].

d. Manufacturers of insulating materials, siding shingles, roofing shingles, tiles, flat and corrugated sheets, wallboard, clapboard and automobile undercoating [4].

e. Factories producing threads, yarns, wicks, cords, tapes, cloths, sheets and blankets. [4]

f. Production of friction materials, brake linings, clutch facing, gaskets, lagging cloths and asphalt tiles [4]. Ayer [5] and Lynch [6] have examined the emissions from brakes on automobiles and
found that the fiber is destroyed by the heat of friction to produce particulate matter of the original composition.

g. Manufacturers of electrical appliance, wire and heating equipment [4].

h. Filtering material manufacturers [4].

i. Production of asbestos sound insulation and homes or offices with asbestos acoustical tile [4].

j. Naturally occurring sources, such as wind and water erosion from exposed serpentine rock surfaces which contain minute quantities of asbestos fibers, and rock slides.

3. Effects of Asbestos

a. On Humans

i. Asbestosis

Pulmonary asbestosis usually develops after long exposure to high concentrations of asbestos dust [7].

ii. Pleural Calcification and Plaques [8]

Raunio [9] found 1516 adult cases of pleural calcification from 633,201 X-rays taken in 13 Finnish towns and 106 rural communes. In Tunsniemi commune, where an asbestos quarry is located, pleural calcification was found in 9 percent of the population.
iii. Cancer of the Lung

Cancer of the lung produced by asbestos has not yet been confirmed. Further study is needed. Langer and Selikoff [10] stated that chrysotile asbestos is commonly found in the lungs of people during autopsy work in New York city nowadays.

iv. Cancer of the Stomach

Cancer of the stomach. (Japan: rice with talc containing asbestos).

b. On Animals

Studies with experimental animals have shown that asbestos can induce asbestosis, cancer of the lung and mesothelioma and can form "asbestos bodies" [11,12,13,14].

c. On Vegetation

No information has been found in the literature on the effects of asbestos air pollution on plants.

d. On Materials

No information has been found in the literature on the effects of asbestos air pollution on materials.

4. Environmental Standards

The American Conference of Industrial Hygienists and the
American Industrial Hygiene Association [15] recommended an industrial threshold limit value for asbestos dust of 5,000,000 particles per cubic foot (5 mppcf) based on total dust count and on an 8 hour day, 40 hour week.

British Occupational Hygiene Society Standards [16] are maximum doses of

0.056 mppcf - years ($2 \times 10^6$ particle-years/m$^3$) for 50 years
0.112 mppcf - years ($4 \times 10^6$ particle-years/m$^3$) for 25 years
0.28 mppcf - years ($10 \times 10^6$ particle-years/m$^3$) for 10 years.

5. Detection and Measurement of Asbestos

The methods used [17] to count dust particles by microscopic analysis in the asbestos industry are not suitable for atmospheric asbestos air pollution. A method developed recently for measuring ambient concentrations of airborne asbestos, including the extremely small fibrils, by temperature ashing and ultrasonic breakdown has been reported by Thompson and Morgan [18]. Preliminary data obtained by this method showed that asbestos levels are about 2 $\mu$g/m$^3$ at a point source, 0.5 to 15 mg/m$^3$ at urban sites, and 0.1 mg/m$^3$ at a non-urban site.

Analytical methods and instrumentation used in the asbestos industry are listed below:

i. Microscopic particle counting of samples on membrane filters [17, 20, 21, 23]

ii. Thermal precipitators [17, 20, 23]
iii. Impingers [17,20,21,23]
iv. Royco particle counter [17,20,23]
v. Mass concentration methods [20,23]
vi. Microsieving [22]
vii. Digestion [22]
viii. Column chromatography of organics adsorbed on the surface [22].

ix. X-ray diffraction [22]
x. Low temperature ashing [22]
xi. Atomic absorption spectrophotometry [22]
 xii. Electron microprobe [22]
xiii. Neutron activation [22]
xiv. Owen jet counter [17, 20]
xv. Konimeter [17, 20]

6. Abatement Methods

i. Bag filter with ventilation system - cyclone may be used in asbestos industries [24]

ii. Wet processes to eliminate dust

iii. Enclosing the asbestos material in plastic-coated bags during transportation [24].

iv. Wetting asbestos material to eliminate dust emission cannot be done for many asbestos products.

v. Enclosing the area when asbestos material is applied required in New York.

vi. It is impossible to control emissions of asbestos fiber
from construction sites, but common sense and good care in handling can reduce the emissions [24].
REFERENCES


5. Ayer, H., and Lainhart, W.S., Personal Communication (October 1968)

6. Lych, J.R., Brake Lining Demonstration Products, Presented at the Engineers Round Table. 30th Annual Meeting, American Conference of Governmental Industrial Hygienists, St. Louis, Mo., (May 12, 1968)


D. Barium and Its Compounds

1. Properties

Barium is the least volatile of the alkaline-earth metals

- Atomic Weight: 137
- Melting Point: 710°C
- Boiling Point: 1500°C

The soluble salts of barium (barium chloride and barium carbonate) are known to be highly toxic when ingested. The insoluble compounds, such as barium sulfate, are non-toxic.

2. Potential Sources and Levels of Atmospheric Emissions

a. Diesel Fuel Additive

Barium-base organometallic compounds have been found effective in reducing black smoke emissions from diesel engines [1]. Miller [2] analyzed exhaust gases from commercial diesel engines using the barium-base additive fuel and an untreated fuel. He noted little change in the average size of the particles, but the total number of particles was reduced by the barium addition. The size of particles ranged from 1.5 to 74 microns in diameter. Solids scraped from the vehicle muffler showed the presence of carbon and barium sulfate.

Golothan's [1] analyses of the solids emitted from some operating diesel vehicles and a number of test diesel engines
are shown in Tables D.1, D.2, D.3 and D.4.

<table>
<thead>
<tr>
<th>Table</th>
<th>Engine Speed (rpm)</th>
<th>Engine Load (psi bmeP)</th>
<th>Fuel Type</th>
<th>Exhaust Sampling Position (ft. from Engine)</th>
<th>Fuel Consumption (lb/hr)</th>
<th>Soluble Barium in Exhaust Solids (% wt. of total Ba)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.1</td>
<td>1,500</td>
<td>90</td>
<td>A</td>
<td>10</td>
<td>7.2</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>90</td>
<td>B</td>
<td>10</td>
<td>7.5</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>90</td>
<td>C</td>
<td>10</td>
<td>7.3</td>
<td>5.5</td>
</tr>
<tr>
<td>D.2</td>
<td>1,000</td>
<td>100</td>
<td>A</td>
<td>10</td>
<td>19.3</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>100</td>
<td>B</td>
<td>10</td>
<td>17.5</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>100</td>
<td>C</td>
<td>10</td>
<td>18.0</td>
<td>7.5</td>
</tr>
<tr>
<td>D.3</td>
<td>2,000</td>
<td>83.0</td>
<td>A</td>
<td>10</td>
<td>36.0</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>2,000</td>
<td>80.5</td>
<td>B</td>
<td>10</td>
<td>35.4</td>
<td>25.5</td>
</tr>
</tbody>
</table>

Table D.1: Analysis of Solids Emitted From 1.5 Litre Automotive Diesel Engine With 4-Cylinder, High-Speed, Four-Stroke Unit Pre-chamber Engine, With Ricardo MKV Combustion Chambers [1]

Table D.2: Analysis of Solids Emitted From 5.8 Litre, Truck-Type Diesel Engine With 6-Cylinder, Direct-Injection, Four-Stroke Unit [1]

Table D.3: Analysis of Solids Emitted From Two-Stroke Automotive Diesel Engine With 3-Cylinder, Opposed-Piston, Automotive Two-Stroke Unit [1]

Fuels*:  
- A = Automotive gas oil (0.3% wt. sulfur) + antismoke additive to 0.15% wt. barium in fuel
- B = 0.15% wt. sulfur fuel + antismoke additive to 0.15% barium in fuel
- C = Automotive gas-oil (0.3% wt. sulfur) + antismoke additive to 0.075% wt. barium in fuel.
<table>
<thead>
<tr>
<th>VEHICLE</th>
<th>ENGINE</th>
<th>TYPE OF TEST</th>
<th>CONCENTRATION OF ANTISMOKE ADDITIVE IN FUEL*(ZWT Ba)</th>
<th>OPERATING CONDITION</th>
<th>SAMPLE COLLECTION TECHNIQUE</th>
<th>SOLUBLE Ba IN EXHAUST (% WT OF TOTAL Ba)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tanker</td>
<td>8.4 litre direct-injection</td>
<td>Driving on test track</td>
<td>0.075</td>
<td>Normal driving for 126 miles</td>
<td>Dismantlable silencer</td>
<td>1.4</td>
</tr>
<tr>
<td>7-Ton Truck</td>
<td>5.4 litre direct-injection</td>
<td>Driving on test track</td>
<td>0.15</td>
<td>30 mph in third gear</td>
<td>Filtration end of exhaust pipe</td>
<td>5.5</td>
</tr>
<tr>
<td>Mini-bus</td>
<td>1.6 litre pre-chamber</td>
<td>Driving on motorway</td>
<td>0.15</td>
<td>53 mph in top gear</td>
<td>Filtration end of exhaust pipe</td>
<td>10.0</td>
</tr>
<tr>
<td>Sedan</td>
<td>1.5 litre pre-chamber</td>
<td>Chassis dynamometer operation</td>
<td>0.075</td>
<td>60 mph in top gear</td>
<td>Filtration end of exhaust pipe</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table D.4: Analysis of Solids Emitted From Diesel Vehicles [1]

Fuel*: Automotive Gas-Oil, containing 0.3% wt. sulfur.

Golothan [1] concluded that the maximum amount of soluble barium compounds emitted in exhaust gases at full load would be 12,000 µg/m³ based on 0.075 percent by weight of added barium with 25 percent of the total barium in the exhaust solids being soluble.

b. Refineries, Mines and Mills Producing Barite

No information was found on the atmospheric emission of barium and barium compounds from the barite-using and barite-producing plants.
c. **Manufacturers of Lithopone and Other Barium Compounds**

Lithopone is a white powder, consisting of approximately 70 percent barium sulfate and 30 percent zinc sulfide, used in the manufacture of white pigment. No information on the levels of atmospheric emission was found.

d. **Power Plants and Utilities Using Coal as Fuel**

Trace quantities of barium are found in coal [3]. The percentage of barium in coal ash depends on the origin as shown in Table D.5.

<table>
<thead>
<tr>
<th>SOURCE OF COAL</th>
<th>PERCENTAGE OF BARIUM IN ASH</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Virginia</td>
<td>0.05 to 0.44</td>
</tr>
<tr>
<td>North Dakota</td>
<td>0.15</td>
</tr>
<tr>
<td>Alaska (Nenana Field)</td>
<td>0.4 to 0.8</td>
</tr>
<tr>
<td>England</td>
<td>0.0' to 4.3</td>
</tr>
<tr>
<td>Nova Scotia</td>
<td>0.0018 to 0.22</td>
</tr>
<tr>
<td>Germany (Newrode)</td>
<td>0.22</td>
</tr>
<tr>
<td>Germany, Brown Coal</td>
<td>0.0001</td>
</tr>
<tr>
<td>Portugal, Anthracite</td>
<td>0.01 to 0.1</td>
</tr>
<tr>
<td>Norway, (Spitsbergen)</td>
<td>0.1 to 0.2</td>
</tr>
</tbody>
</table>

Table D.5: Barium Content in Coal Ash [3]

No information was found on the atmospheric emission levels of barium from these sources.

e. **Plants Using Barium Carbonate as a Raw Material**

Barium carbonate is used in the ceramic industry, in clay wares, in glassware, in steel hardening, in photographic paper, and as a rat poison. [4,5]
f. **Plant Using Barium Chloride**

Barium chloride is used in producing blanc fine in manufacturing barium colours, as a water softener, steel hardening ingredient, and for medicinal purposes [4,5].

3. **Effects of Barium and Its Compounds**

a. **On Humans**

i. **Effects on Gastrointestinal Tract**

One case is reported [6] in which 7 grams of barium chloride had been taken, causing severe abdominal pain leading to near death.

ii. **Effects on Muscle**

Ingested soluble barium compounds cause a strong stimulating effect on all muscles of the body, including the heart muscle [6,7].

iii. **Effects on the Central Nervous System**

Some cases have been reported where paralysis following the ingestion of soluble barium compounds occurred [6,7].

iv. **Irritation of Eyes, Nose, Throat and Skin**

Symptoms have been reported [8], which were caused by exposure to dusts and fumes of barium sulfide, barium oxide and
barium carbonate.

v. Baritosis

Inhalation of barium compounds causes a pneumoconiosis called baritosis, which occurred in workers exposed to powders of barium sulfate in Italy, in barite miners in the U.S., Germany and Czechoslovakia, in workers producing lithopone, and among workers exposed to barium oxide [8].

b. On Animals

Miller [2] exposed white rats to ten times the concentration of exhaust that would be emitted from a bus burning barium-base additive fuel. After ten exposures with alternate fresh air cycles, no unusual changes were found.

Browning [6] reported that when guinea pigs inhaled barite dust in the test, nodular granulation of the lungs, characteristic of baritosis, was found.

Bronchogenic carcinoma developed in rats injected with radioactive barium sulfate [7].

c. On Vegetation

No information was found on the effect of environmental barium on vegetation.
d. **On Material**

No information was found on the effect of environmental barium on material.

4. **Environmental Standard**

The American Conference of Governmental Industrial Hygienists in 1967 recommended an 8 hour threshold limit of 500 \( \mu g/m^3 \) for occupational exposure to the soluble compounds of barium in working areas.

5. **Detection and Measurement of Barium and Its Compounds**

a. **Emission Spectrographic** [3]

Barium compound samples, which are soluble in hydrochloric acid, can be analyzed by this method.

b. **Atomic Absorption Spectrometry** [9]

The minimum detectable limit is 0.02 \( \mu g/m^3 \) for barium when analyzed by atomic absorption based on an air sample of 2,000 \( m^3 \) [9].

6. **Abatement Methods**

The emission of barium and barium compounds into the atmosphere is in the form of solid particulates. Standard emission control equipment can be used in mills, mines and plants producing barium or using barium as a raw material. Typical control equipment could be

1. Filtration Houses
ii. Electrostatic Precipitators

iii. Wet Scrubbers.

iv. Cyclones

No information was found on the control of emissions of barium compounds in the exhaust from diesel engines burning barium-base additives used as smoke suppressants. From the experiments of Golethan, it is apparent that by using a minimum amount of barium-base additive and higher % wt. sulfur fuel, lower soluble barium levels in the exhaust lead to reduced barium emissions to the atmosphere.
REFERENCES


E. Beryllium and Its Compounds

1. Properties

Beryllium is a hard, silver-white metal.

- Density: 1.8
- Atomic Weight: 9.013
- Melting Point: 1281° C
- Boiling Point: 2970° C

Beryllium does not react with water, even when red hot, but reacts with caustic alkali solutions. Beryllium oxide is only feebly basic. Beryllium chloride is volatile and fumes in air. Beryl (3 BeO· Al₂O₃ · 6SiO₂) is the only mineral of beryllium of commercial importance. Laboratory studies have revealed that the toxicity of beryllium oxide produced at 1,600° C is considerably less than that of oxides produced at relatively low temperatures (500° C), as confirmed by tests on animals.

2. Potential Sources and Levels of Atmospheric Emissions

a. Mining, Extracting and Refining Beryllium From Beryl Ore

Dust is created by cutting, grinding and crushing operations. Fumes consist primarily of the oxide created from condensation of vapours formed during melting, pouring or welding processes [1].

Mining of beryl ore is not considered a potential source of beryllium air pollution, since no known cases of berylliosis have been caused by inhalation of beryl dust [2].

Eisenbud and co-workers [3] estimated that one extraction
plant discharged 5 kg. of beryllium per day.

b. Atmospheric Emissions of Beryllium From Coal Consumption

Beryllium is a trace element in coals. The amount of beryllium in coal depends on the origin as shown in Table E.1

<table>
<thead>
<tr>
<th>Area</th>
<th>Average</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northern Great Plains</td>
<td>1.5 ppm</td>
<td>&lt; 0.1 - 9.1</td>
</tr>
<tr>
<td>Eastern Interior</td>
<td>2.5 ppm</td>
<td>0.5 - 12.0</td>
</tr>
<tr>
<td>Appalachian Regions</td>
<td>2.5 ppm</td>
<td>0.1 - 31.0</td>
</tr>
</tbody>
</table>

Table E.1: Beryllium Content In The U.S. Coals [4]

Although the concentration of beryllium in coal is low, it is important to realize that over 500 million tons of coal are burned yearly in the U.S. alone. The amount of beryllium discharged into the atmosphere may be quite significant. The percentage of ash from the coals was 1.9 to 3.7 and these ashes contained 0.0005 - 0.020 percent beryllium [16].

c. Beryllium - Copper Alloys

A large amount of commercial beryllium is used as a hardening agent in alloys, especially for beryllium-copper alloy. The major emissions of dusts and fumes of beryllium oxide are from the alloying processes and in the reduction processes to refine scrap alloy.

Sterner and Eisenbud [10] investigated the amount of beryllium disease cases occurring with greater frequency in the neighbour-
hood of a plant than within the plant itself. Of the people living
within 1/4 mile of the plant, and exposed to 1 μg/m³ of beryllium,
approximately 1% contracted beryllium disease. Only 0.5% of the
plant employees showed any ill effects even though they were exposed
to concentrations at least 1,000 times higher.

Kettering Laboratory, University of Cincinnati, Ohio [5]
investigated the concentrations of beryllium in the air at various
locations in a beryllium-copper plant in the year 1960 and found the
results as shown in Table E.2

<table>
<thead>
<tr>
<th>Location</th>
<th>Hours</th>
<th>Concentrations μg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide Area</td>
<td>92</td>
<td>72.5 149.4 0.4 - 1,050.00</td>
</tr>
<tr>
<td>Arc Furnace Area</td>
<td>92</td>
<td>50.0 87.6 22.1 - 502.00</td>
</tr>
<tr>
<td>Mixing Area</td>
<td>92</td>
<td>14.4 21.6 0.03 - 452.90</td>
</tr>
<tr>
<td>Cropping Area</td>
<td>92</td>
<td>33.6 52.8 14.0 - 399.00</td>
</tr>
<tr>
<td>Casting Area</td>
<td>86</td>
<td>14.6 39.8 0.2 - 535.00</td>
</tr>
<tr>
<td>Fisher Furnace Area</td>
<td>91</td>
<td>28.8 40.8 0.2 - 340.00</td>
</tr>
<tr>
<td>Oliver Saw Area</td>
<td>90</td>
<td>21.1 25.6 &lt;2.5 - 92.00</td>
</tr>
<tr>
<td>All Areas</td>
<td>635</td>
<td>28.4 60.3 0.3 - 1,050.00</td>
</tr>
</tbody>
</table>

Table E.2 Beryllium Concentrations In A Beryllium-Copper Plant
(Two Hour Averages) [5]

d. Rocket Fuel Additive [5]

Finely powdered metallic beryllium is used as an additive
in rocket fuels for increasing performance. One analysis of rocket
exhausts found that 50 percent of the total beryllium was beryllium
oxide, 40 percent beryllium fluoride and the rest was mostly beryllium
chloride [6]. Another analysis conducted by Kettering Laboratory [5]
revealed that 70% of the total metallic beryllium used as fuel additive
was recovered in the residue, with the remaining 30% assumed to be emi-
ted into the atmosphere.

e. **Fluorescent Tubes**

Prior to 1949, beryllium oxide, used in the manufacture of fluorescent light tubes, caused many cases of beryllium disease which helped to initiate the control of beryllium usage and emissions.

f. **Machine Shops and Foundries**

Hazardous concentrations may be expected whenever certain beryllium compounds are heated even to moderate temperatures [7]. For small machine shops and foundries, which do not have adequate emission control equipment, the possibility of beryllium emission to the neighborhood is quite high. Worker's clothes, contaminated with beryllium dust, could result in inhalation during home laundering, of 17μg of beryllium per day as reported by Eisenbud [3].

g. **Beryllia Ceramics Industry**

The use of beryllium oxide for the beryllia ceramics industry require 5% of the beryl production. It is estimated to increase at least 10-15% in the near future.

3. **Effects of Beryllium and Its Compounds**

The major hazard from beryllium arises from inhalation of beryllium or its compounds.
a. On Humans

i. Acute Beryllium Disease of the Respiratory System

Acute chemical pneumonitis may occur after inhalation of virtually any beryllium compound, especially the metal oxide, sulfate, fluoride, hydroxide, and chloride. The upper regions of the respiratory tract may be affected, with acute inflammation of the mucosa and submucosal tissues [8]. The degree of response depends upon the concentration, duration and type of exposure [2]. Deaths have resulted from exposure to high concentrations of soluble salts in industrial beryllium processing plants [2] [3]. Hall and co-workers [11] found that all cases had occurred after exposure to concentrations in excess of 100 µg/m³, and when concentrations of the soluble beryllium compounds exceeded 1,000 µg/m³, acute disease occurred in most of the victims. No damage resulted from exposure to concentration of 4 µg/m³ in experimental animals [9].

ii. Acute Beryllium Disease of Skin, Eye, and Other Systems

Skin may be damaged by soluble salts of beryllium. Dermatitis occurs frequently on the exposed portions of the body [12]. The soluble salts of beryllium also affect mucous membranes of the conjunctiva, nose, nasopharynx, trachea, and bronchf [13].

Hazard [14] reported that moderate inflammation of the liver was noted and there was some evidence of severe central necrosis, focal hemorrhage of the spleen, and mild edema of the brain.

iii. Chronic Beryllium Disease of the Respiratory System

Chronic pulmonary beryllium disease (berylliosis)
follow, more prolonged exposure to lower concentrations. It has a latent period which may range from a few months to 23 years [15]. De Nardi et al [8] reported, in 1953, that 47 survivors of acute beryllium disease were observed for as long as 12 years with no evidence of the chronic disease in any person, but further studies showed that a number of them suffered from chronic disease-[17], with high mortality. In 1966, 498 chronic cases had been recorded in the Beryllium Registry with about 400 being industrial cases, and about 60 nonindustrial [18].

Beryllium causes granulomatous reactions in the lung which may produce severe and permanent respiratory damage or death [13]. The National Academy of Sciences – National Research Council [18], states that the pathogenesis of chronic beryllium disease is still unknown. Because only a small percentage of the persons exposed to high concentrations developed the disease, some investigators assumed that there is an immunological abnormality associated with the disease—or that the susceptibility is in some way related to an inborn error of metabolism. The council states further, that one of the factors that complicated the interpretation of the epidemiological studies may be the extremely small amounts of beryllium—containing materials alleged to have produced the disease.

Hall and partners [19], who in 1959 analyzed 382 cases from the Beryllium Case Registry, reported the symptoms of chronic disease as dyspnea (69%), loss of weight (61%), cough (78%), increased fatigue (34%), pains in the chest (31%), loss of appetite (26%), and general weakness (17%).

iv. Chronic Beryllium Disease Effects on Other Systems

It is believed that most systems of the body can be affected by beryllium except organs in the pelvic area. There is evidence
that beryllium affects enzyme systems. Chronic beryllium disease is also induced on the skin and the subcutaneous tissues by soluble salts of beryllium which cause contact dermatitis as well as conjunctivitis.

v. Carcinogenicity

According to the National Academy of Science - National Research Council reports of 1966 [18], there is no evidence of community or industrial exposure to beryllium compounds being associated with an increase in the incidence of cancer in humans.

Hardy [20] pointed out that there were only five cases of lung cancer and one bone tumor, out of 725 individuals listed in the Beryllium Case Registry in 1964. Since beryllium has a long residence time in the body, it still may have a cancer-producing effect. It has been shown on experimental animals that beryllium does induce primary pulmonary cancer in rats and monkeys [23].

b. On Animals

Increasing cases of beryllium disease in and around industrial plants lead to extensive programs of animal experiments studying the nature of the toxic effects of beryllium and its compounds. As early as 1935 Marradi-Fabroni [37] observed acute and subacute bronchiolitis and pneumonitis in guinea pigs exposed to atmospheres of beryllium. In 1947 Sprague and partners [21] reported on experiments with various animals exposed to beryllium sulfate dusts and beryllium metal fumes in atmospheric concentrations of 800,000 μg/m³. Mice died within 11 days while with dogs, rabbits and guinea pigs, acute damage was observed in the lungs, liver and kidneys. Concentrations as high as 24,000,000 μg·min/m³ would produce pulmonary hemorrhage and death. Hall et al. [22] reported that beryllium fluoride was more toxic than beryllium sulfate. Exposure to 1 mg/m³ of beryllium fluoride resulted in lung damage, in cats, dogs, rabbits, and rats, roughly comparable in extent and degree to that produced by 10 mg/m³ of beryllium sulfate. It was observed that beryllium tended to accumulate in the lungs, pulmonary lymph nodes, liver, skeleton, and bone marrow of dogs.
The rate of deposition in the lungs and lymph nodes increased with the duration of exposure. In 1950 Hall et al. [11] exposed six different species of animals to aerosols of different grades of beryllium oxide dust at mean concentrations of 85,000 μg/m³, six hours daily, five days per week for 10 to 17 days. All oxides were reported to produce acute pneumonitis.

Vorwald [23] found that pulmonary cancer was induced in monkeys by an atmospheric concentration of 35 μg/m³ of beryllium sulfate aerosol. It was reported that primary pulmonary cancer occurred in nearly 100 percent of a group of rats exposed daily for 13 months to beryllium sulfate aerosol in concentrations of 21 to 42 μg/m³ [24]. Primary pulmonary cancer appeared as early as nine months after inhalation.

c. On Vegetation

Romney, Childress, and Alexander [25] concluded after experiments on bush-bean growth in nutrient solution containing various concentrations of beryllium that it was toxic in excess of 1 ppm in soil solutions. Decreased growth rates were observed at increased beryllium concentrations. No information has been found on harmful effects to vegetation subjected to ambient air concentrations.

d. On Materials

No information has been found in the literature on the effects of beryllium air pollution on materials.

4. Environmental Air Standards

Environmental Standards for atmospheric concentrations of beryllium were first proposed in the U.S. by a Beryllium Advisory Committee of
the U.S. Atomic Energy Commission in 1948. During the past years the AEC and the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists had adopted the recommended standards of 2 $\mu$g/m$^3$ as the average concentration to which persons may safely be exposed throughout an eight hour day.

In 1966, the Advisory Centre on Toxicology of the National Academy of Science - National Research Council recommended the tentative air quality criteria [26] to be the following:

1. for continuous exposure, a level of 0.01 $\mu$g/m$^3$, average over a 30-day period, applies.

ii. for intermittent exposure to beryllium compounds arising from rocket motor firings, the following limits apply:

(a). soluble beryllium compounds; 75 $\mu$g-min/m$^3$ within the limits of 10-60 minutes, accumulated during any two consecutive weeks.

(b). beryllium oxide comparable to a product calcined at temperatures around $400^\circ$C: 75 $\mu$g-min/m$^3$ within the limits of 10-60 minutes accumulated during any two consecutive weeks.

(c). beryllium oxide comparable to a product calcined at temperatures in excess of $1,600^\circ$C; 1,500 $\mu$g-min/m$^3$ within the limit of 10-60 minutes accumulated during any two consecutive weeks.

In the Soviet Union the maximum concentration of beryllium in production facilities was set at 1$\mu$g/m$^3$ [27]. Mil'nikov [28] recommends a value of

1 to 2 $\mu$g/m$^3$ for beryllium acetate

10 to 20 $\mu$g/m$^3$ for finely divided beryllium oxide in a factory for a six hour day.
Typical data from measurements made in 1964 by the National Air Sampling Network of the U.S. on beryllium levels in American cities are shown in Table E.3.

<table>
<thead>
<tr>
<th>City</th>
<th>Maximum Concentration μg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detroit</td>
<td>0.001</td>
</tr>
<tr>
<td>Philadelphia</td>
<td>0.000</td>
</tr>
<tr>
<td>Chicago</td>
<td>0.001</td>
</tr>
<tr>
<td>New York</td>
<td>0.000</td>
</tr>
<tr>
<td>Cincinnati</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table E.3 Maximum Concentration of Beryllium in Selected U.S. Cities in 1964 [29]

5. Detection and Measurement of Beryllium Compounds

The most common method of determining beryllium concentrations in air is by means of a high volume sampler.

Atmospheric beryllium may be analyzed by the following methods:

2. Photoneutronic [31]
3. Morin Fluorescent Method [32]
4. Mass Spectrometric [33]
5. Gas Chromatographic [34]
6. Spectrochemical [35]
7. Colorimetric [36]

6. Abatement Methods

Most particulate control equipment can reduce beryllium emissions from beryllium processing plants. Typical wet chemical processes can be carried out in

1. Scrubbers
ii. Packed Towers
iii. Wet Cyclones
iv. Organic Wet Collectors

For dry processes it is possible to consider

1. Filter Bag Houses
2. Electronic Precipitators
3. Cyclones
4. Reverse-jet Bag Collectors
REFERENCES


17. Handy, H. L., Personal Communication to National Air Pollution Control Administration, dated (July 15, 1969)


28. Mil'nikov, V.V., Material on Toxicology of Beryllium Acetate, Pharmacol., Toxicol., 3, (1959)


F. Boron and Its Compounds

1. Properties

Boron occurs naturally only in combined forms, usually as an alkaline earth borate or as boric acid. Crystalline boron, in large samples, is relatively nonreactive; however, powdered boron reacts readily and violently with oxidizing agents— in some cases igniting or exploding.

- Atomic Weight: 10.82
- Isotopes of Mass Number: 10 and 11
- Density: 2.24–2.34
- Melting Point: 2200°

2. Potential Sources and Levels of Atmospheric Emissions

There are many compounds of boron, but only a few are significant as air pollutants. Boron dusts, boric acid, borax, boric acid esters, boron halides and boron hydrides are typical boron compounds of environmental importance. Of these compounds the boron hydrides, diborane B₂H₆ (gas), tetraborane B₄H₁₀ (liquid B.P. 186°C), pentaborane B₅H₉ (liquid), and deca-borane B₁₀H₁₄ (solid) are considered to be the most serious health hazards to humans and animals.

a. High-energy Fuels and Propellants

Diborane has been used as a high-energy fuel and propellant. Because of its disadvantages in handling, (diborane is self-igniting in air, is a colorless poisonous gas, will readily explode, reacts violently with moisture), several higher-molecular-weight compounds are now available for this purpose. According to Crocknell [1] pentaborane is probably the most promising synthetic fuel for ramjets and as an afterburner fuel for turbojets. Pentaborane is a colourless liquid with strong toxic properties. It is not spontaneously inflammable in cool air, but may explode in a hot
environment. The exhaust gas samples consist of boron or boron compounds. Exhaust gas samples showed no appreciable health hazards to human or animals [2]. Decaborane is also used as a fuel for rockets.

b. **Iron Industry**

Boron dusts are emitted to the atmosphere by the iron industry. Two samples from a baghouse charged by air from a gray iron furnace in the Los Angeles area, contained 500 and 540 \( \mu g/g \) of boron in the total samples [3].

c. **Manufacturers of Boric Acid or Users of Boric Acid as a Raw Material**

Boric acid has a variety of applications in industrial processes. It is very commonly used in households for washing eyes, because of its nonirritating mildly antiseptic qualities. It is used in glazing in the ceramics industry, as a hardening agent in steel, and as a raw material for other boron compounds. It is also used in cosmetics, latex paints, dye stabilizers, electroplating, flameproofing and in photography.

d. **Power Plants and Utilities Using Coal as Fuel**

Boron is a trace constituent of coals with the amount of boron depending on the origin of the coal, as shown in Table 1.

<table>
<thead>
<tr>
<th>Area</th>
<th>Concentration in Coal (ppm)</th>
<th>Concentration in Coal Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northern Interior</td>
<td>116</td>
<td>0.005 - 0.65</td>
</tr>
<tr>
<td>Eastern Interior</td>
<td>96</td>
<td>--</td>
</tr>
<tr>
<td>Appalachian Regions</td>
<td>25</td>
<td>--</td>
</tr>
<tr>
<td>West Virginia</td>
<td>--</td>
<td>0.008 - 0.095</td>
</tr>
<tr>
<td>North Dakota</td>
<td>--</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table F.1. Boron Content in U.S. Coals and Coal Ash

No information has been found in the literature concerning the levels of emissions to the atmosphere from these sources.
e. Glass and Ceramic Industries

Borax \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \) is an important component in the manufacture of glasses and ceramics.

f. Gasoline, Diesel, Aircraft Turbine Fuels and Other Petroleum Product Fuels

Borax and boric acid esters are used in petroleum fuels and solvents as additives to prevent the growth of micro-organisms.

g. Fertilizer Plants

Boron is an essential trace element for the health of many crops. Borax is used in artificial fertilizers as an important component. Large amounts of borax act as a herbicide.

3. Effects of Boron and Its Compounds

a. On Humans

Sax [5] considered boron and its compounds as moderately to highly toxic to man through ingestion and inhalation.

i. Central Nervous System

Sax [5] states that boron hydrides can produce severe central nervous system irritation when inhaled.

ii. Other Symptoms

Diborane and Pentaborane produce chest tightness, cough, headaches, nausea, chills, drowsiness, dizziness, convulsions and signs of liver damage.

b. On Animals

No ill effects were noted when cows were fed with 16 ppm boron alternately with one percent borax for 42 days. Adams (6) reported
that internal administration of pentaborane has produced death, preceded by listlessness, incoordination, tremors, convulsions and coma. Inhalation of highly concentrated diborane for 25 minutes killed experimental rats. Severe eye irritation had been produced in rabbits when 0.2 ml of borane fuel were administered to the eyes.

Acidic solutions of 5 percent boric acid were non-irritating to eyes and skin, but alkaline solutions produced a slight irritation. Boron oxide administered to the skin of a rabbit reddened the area, but no other symptoms developed. No ill effects were noted in experimental animals, (rats and guinea pigs) when exposed to 40,000 µg/m³ boron oxide for six hours per day over a period of six weeks [6]. In another experiment all ten rats and ten mice died when exposed continuously for seven hours to 20 ppm of boron trichloride in air [6].

c. **On Vegetation**

Plant life needs small quantities of boron, but large amounts are extremely toxic to vegetation.

d. **On Material**

No information has been found in the literature on the effects of boron on materials.

4. **Environmental Air Standards**

The American Conference of Governmental Industrial Hygienists in 1967 recommended the following **Threshold Limit Values for boranes**:

- Diborane: 0.100 ppm (100 µg/m³)
- Pentaborane: 0.005 ppm (10 µg/m³)
- Decaborane: 0.050 ppm (300 µg/m³)
- Boron Oxide: 15,000 µg/m³

Hyatt and Milligan [7] suggest that the concentration for boric acid dust be kept below 2,000 µg/m³.
5. Detection and Measurement of Boron Compounds

Several techniques for determining the presence of boron are available.

i. Coulometric Titration Method [8]

ii. Spectrophotometric Method [9]

iii. Fluorimetric Method

iv. Radioactive Method

6. Abatement Methods

Most particulate control equipment can reduce boron emissions from boron processing plants. Very little has been done to reduce air pollution by boron. In areas using high-energy boron fuels, careful handling of these fuels has been enforced to prevent accidental spilling.
REFERENCES


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G. Cadmium and Its Compounds

1. Properties

Cadmium is a white metal. It is ductile at ordinary temperatures. It is very slowly oxidized in moist air, but will burn when heated, forming brown fumes of the oxide.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>8.65 (20°C)</td>
</tr>
<tr>
<td></td>
<td>8.01 (330°C)</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>112.41</td>
</tr>
<tr>
<td>Melting Point</td>
<td>321°C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>767°C</td>
</tr>
</tbody>
</table>

Cadmium does not occur in the free state. It is commonly found accompanying zinc blende, copper, and lead ore and zinc in calamine.

2. Potential Sources and Levels of Atmospheric Emissions

a. Refineries of Zinc, Copper, Lead and Cadmium Extraction Plants

Cadmium is produced as a by-product in the refining of other metals, mostly from zinc smelting. Cadmium dust and fumes are produced in the extraction, refining and processing of metallic cadmium. These production facilities are considered to be the most prominent sources of cadmium emission into the atmosphere. The evaluation of cadmium concentrations in zinc refinery dusts and in exhaust gases of copper smelters in Russia are shown in Tables G-1 and G-2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>By Chemical Analysis</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td></td>
<td>0.42%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>By Ratio Analysis</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium Sulfate</td>
<td></td>
<td>0.54%</td>
</tr>
<tr>
<td>Cadmium Oxide</td>
<td></td>
<td>0.04%</td>
</tr>
<tr>
<td>Cadmium Oxide - Iron Oxide</td>
<td></td>
<td>0.16%</td>
</tr>
<tr>
<td>Cadmium Sulfide</td>
<td></td>
<td>0.03%</td>
</tr>
</tbody>
</table>

Table G.1 Cadmium Concentrations in Zinc Refinery Dusts [1]
<table>
<thead>
<tr>
<th>Activity</th>
<th>Cadmium Content of Gas (g/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverberatory Smelting</td>
<td>1,500</td>
</tr>
<tr>
<td>Blast Furnace Smelting</td>
<td>2,000</td>
</tr>
<tr>
<td>Bessemer Process</td>
<td>3,200</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>6,700</strong></td>
</tr>
</tbody>
</table>

Table G.2 Cadmium Content in Exhaust Gas of Copper Smelting Works [1]
*Grams of Cadmium in Exhaust Gas Per Metric Ton of Copper Produced

A study of Robertson [2], of the Hudson Bay Mining and Smelting Company Ltd., reported that prior to the improvement of the method of recovering cadmium, the amount of cadmium in the dust flows from the smelter stack ranged from 0.3 to 0.4 tons/day. Little and Martin [44] while analyzing the levels of cadmium in elm leaves found that levels ranged from 50 ppm dry matter to less than 0.25 ppm at distances of 250 meters to 15 kilometers from a smelter.

b. Electroplating Industries

The largest single use of cadmium is in the electroplating industry. It was calculated that about 60% of the cadmium in the U.S.S.R. was used in electroplating in 1956 [3].

c. Welding or Cutting of Cadmium - Plated Metal Parts

Zavon and Meadows [3] reported a case of two employees of a local utility cutting cadmium - coated bolts with an oxygen - propane torch. One man died and the other required medical treatment. After the incident the cutting was repeated and air samples collected from the cutting surface showed the concentration of cadmium to be 38.6 mg/m³ and a zinc concentration of 5.17 mg/m³.

d. Cadmium Alloys and Solder Industries

The percentage of cadmium in alloys and solders is high.
For example -

cadmium-silver-copper alloy is 97.65% cadmium
white cadmium-nickel alloy is 93.65% cadmium
in silver-cadmium solder the cadmium content is 95.00%.

In the process of casting these alloys and some lower concentration cadmium alloys, it is apparent that cadmium may be emitted into the atmosphere, if it is not properly controlled. There is evidence showing that workers in industries casting cadmium alloys suffer from emphysema and proteinuria disease [4].

e. Production of Alkaline Batteries [5]

Increasing use of cadmium in cadmium-nickel batteries may lead to another source of air pollution. Cadmium may be released not only from the production facilities of the batteries, but also after the dumping of used batteries in scrap yards.

f. Cadmium Pigment Industries

The analysis of Pribil and Vesely [6] showed typical cadmium contents of paints to be of the order shown in Table G.3.

<table>
<thead>
<tr>
<th>Material</th>
<th>Percent of Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium red</td>
<td>69.92</td>
</tr>
<tr>
<td>Lithopone 30%</td>
<td>0.05</td>
</tr>
<tr>
<td>Lithopone 60%</td>
<td>0.05</td>
</tr>
<tr>
<td>Stachtolith</td>
<td>0.05</td>
</tr>
<tr>
<td>Cadmium red + Lithopone 60%</td>
<td>56.09</td>
</tr>
<tr>
<td>Cadmium red + Lithopone 30%</td>
<td>7.01</td>
</tr>
<tr>
<td>Stachtolith + Lithopone 60%</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table G.3. Cadmium Content of Paints

8. Manufacture of Fertilizers

Common superphosphate fertilizers containing 50 to 170 ppm of cadmium may be considered as a source of hazardous pollutants introduced into the environment.
h. **Pesticides [7]**

Cadmium is also used in many pesticides, often as cadmium chloride, cadmium chlorate and cadmium succinate.

i. **Cigarette**

Nandi and partners [8] who subjected six different brands of cigarette filters (after smoking) to analysis of cadmium content in whole cigarettes, cigarette ash and filters (after smoking) showed that the whole cigarettes content is 22.7 μg Cd/20 cigarettes. After smoking, 16% and 15% of the cadmium in the whole cigarette were found in the ash and filters respectively. The rest, about 70%, was assumed to pass into the atmosphere with the smoke.

Table G.4 shows some typical data from this study:

<table>
<thead>
<tr>
<th>Brand</th>
<th>Pack</th>
<th>Whole Cigarettes</th>
<th>Ash</th>
<th>Filters</th>
<th>Total Cadmium in Smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>24.0</td>
<td>3.2</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>24.5</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>24.5</td>
<td>4.0</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>28.0</td>
<td>4.2</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>20.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>27.0</td>
<td>3.0</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>19.0</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>23.0</td>
<td>4.2</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>23.0</td>
<td></td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>20.0</td>
<td>2.6</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>21.0</td>
<td></td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>23.0</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>18.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>22.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>22.7 (100%)</td>
<td>3.6 (16%)</td>
<td>3.3 (15%)</td>
<td>16.0 (69%)</td>
</tr>
</tbody>
</table>

Table G.4 Cadmium Content of Cigarettes (μg/20 Cigarettes) [8]
3. Effects of Cadmium and Its Compounds

Tucker [9] states that the rate of absorption of cadmium from food and water by human beings is very slow. About 98% of the cadmium we eat or drink is, in fact, excreted in the normal way within 48 hours. Most mammals, including humans, absorb between 10% and 15% of inhaled cadmium when particles are small as in air pollution areas.

a. On Humans

1. Pulmonary Emphysema

Pulmonary emphysema is the most typical symptom of chronic cadmium poisoning due to inhalation of cadmium fumes, cadmium oxide dust, or cadmium salts. Many cases [3] [10] [11] have been reported in which persons poisoned by cadmium fumes showed severe pulmonary emphysema, and some suffered death.

2. Hypertension and Atherosclerosis

Cadmium has been linked to high blood pressure by the studies of Perry and Schroeder [12]. Their work showed a correlation between the cadmium content of kidneys and hypertension in both humans and rats. Carroll [13] showed that the death rate from hypertension and arteriosclerotic heart disease in 28 U.S. cities has a significant correlation (r = 0.76) with the cadmium concentration in the air. According to Nilsson [14] the analyses of humans who die from hypertensive effects (such as brain haemorrhage) show that cadmium accumulations in the kidneys are significantly higher than those of non-hypertensive subjects.

3. Kidney Damage

Kidneys and other tissues of infants do not contain cadmium in detectable quantities but cadmium accumulates slowly in the kidneys and livers with age [19]. There is no doubt that cadmium damage to
the kidney causes proteinuria. Many cases of this effect have been confirmed by Friberg [15], Potts [16], Suzuki [17] and Piscator [18]. They reported that high incidence of proteinuria was found in workers in the alkaline battery industry and the cadmium industry. Kidney damage is now considered to be a classical syndrome of chronic cadmium poisoning, which has been shown to result from exposure to the soluble salts of cadmium sulfide and cadmium stannate [20].

iv. **Nephrolithiasis** [21]

Nephrolithiasis was also reported in about 25% of the workers in the Swedish alkaline battery industry.

v. **Itai-Itai (Ouchi-Ouchl) Disease**

Itai-Itai disease was first described at the 17th meeting of the Japanese Association of Orthopaedic Surgeons. This disease was caused by chronic cadmium poisoning. Cadmium accumulation leads to bone porosity and to the total inhibition of the bone repair mechanisms so that, stage by stage, as the disease progresses, the load-bearing bones of the skeleton suffer deformation, fracture and collapse. The disease was limited to women over 40 years of age in an area which is cadmium rich both from mining and zinc smelting [23]. The other areas of occurrence of this disease were where the consumption of cadmium was more than 600 µg/day. Normal man consumes 60 µg/day in Japan. The main contributor of the cadmium is normal foodstuff, of which a half is rice and soya [22], (cadmium content in the range of 0.37 to 3.36 ppm dry [9] from agricultural land that becomes seriously contaminated by cadmium.)

vi. **Carcinogenesis**

It is also believed that cadmium may induce cancer in humans. Potts [16] reported that from a total of 70 cadmium workers five
deaths were due to cancer. Carcinogenic effects have been induced in experimental animals [30] [31] [32].

b. On Animals

Many experiments have been conducted to study the toxicity of cadmium by injection into the animals, by concoction in their diets and through inhalation. Schroeder and coworkers [24] showed that the life span of rats and mice fed with cadmium was shorter than that of control groups.

i. Hypertension

Schroeder [25] showed cadmium as a cause of hypertension in both humans and rats. Third [26] [27] studied the hypertension effects in rabbits and dogs, and found that all hypertensive tissues had significantly higher cadmium concentrations than the corresponding normal tissues, and the hypertensive kidney had the highest cadmium content.

ii. Anemia

Dalhamm and Friberg [28], and Carlson and Friberg [29] studied the effects of cadmium by injecting cadmium sulfate [28] and radioactive cadmium-115 [29] in rabbits in doses of 650 µg per kg of body weight. They found a reduction of 40% to 50% in haemoglobin, and a 30% to 50% reduction in erythrocytes within 10 weeks which caused anemia in the rabbits. They concluded that it is possible that cadmium is transported to the bone marrow, where it inhibits the synthesis of haemoglobin and induces anemia.

iii. Proteinuria

Dalhamm and Friberg [28] found that 16 out of 18 rabbits suffered proteinuria after 1 to 2 month's exposure to a dose of cadmium of 650 µg per kg body weight. Upon microscopic examination, the rabbits showed pronounced damage to the renal tabuli.
iv. Carcinogenic Effects

Many investigators have studied the carcinogenic effects of cadmium on animals. Gunn et al. [30] reported induced sarcomas in rats injected with cadmium chloride at the injection area, Heath and co-workers [31] with cadmium metal powder, and Kazantzis et al., [32] with cadmium sulphide and cadmium oxide.

v. Reproductive and Other Systems

Cadmium may be toxic to most systems. There was evidence of disorders of the nervous system in rats fed with cadmium acetate (5 ppm). Ten rats out of 84 died with nervous disturbances [24]. Yoshikawa and partners [33] showed histological changes in the stomach, intestines and orchis of rats fed with cadmium stearate. All experimental animals showed retardative growth. Many investigations focused on the damaging effect of cadmium on the reproductive system. Parizek [34] studied the destructive effect of cadmium ion on testicular tissue. Roe and partners [35] reported that cadmium causes atrophy of the testis which is followed by hyperplasia of the interstitial-cell element and, in some cases, the development of interstitial-cell tumors. In Japan, Maskawa et al., [36], studied the behavior of the testis and intratesticular ovarian grafts in male rats following injection with cadmium.

c. On Vegetation

Schroeder et al., [37] investigated the damage to roots of vegetables by cadmium from 20% superphosphate fertilizer in soil.

d. On Materials

No information has been found in the literature on the effects of cadmium and its compounds on materials.
4. **Environmental Air Standards**

The American Conference of Governmental Industrial Hygienists [38], recommended the following cadmium Threshold Limit Values for industrial workers in 1967:

- Cadmium oxide fumes 100 µg/m³
- Cadmium metal dusts and soluble salts 200 µg/m³

The U.S.S.R. recommended the Threshold Limited Value of 100 µg/m³ per eight hours for cadmium oxide for industrial workers.

The British Commonwealth countries set the emission standards of cadmium in effluents to be in

<table>
<thead>
<tr>
<th>Great Britain</th>
<th>39,000 µg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>New South Wales</td>
<td>23,000 µg/m³</td>
</tr>
<tr>
<td>Queensland</td>
<td>23,000 µg/m³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cities</th>
<th>Max. Concentration µg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chicago</td>
<td>0.049</td>
</tr>
<tr>
<td>Detroit</td>
<td>0.000</td>
</tr>
<tr>
<td>New York</td>
<td>0.040</td>
</tr>
<tr>
<td>Philadelphia</td>
<td>0.110</td>
</tr>
<tr>
<td>Newark</td>
<td>0.350</td>
</tr>
<tr>
<td>Cincinnati</td>
<td>0.110</td>
</tr>
<tr>
<td>St. Louis</td>
<td>0.290</td>
</tr>
</tbody>
</table>

Table G.5 Concentrations of Cadmium in the Air of Selected U.S. Cities in 1964

5. **Detection and Measurement of Cadmium Compounds**

Samples of cadmium dusts and fumes may be collected by impingers, electrostatic precipitators, filters and high volume filtration samplers.

Atmospheric cadmium may be analysed by the following methods:

1. Emission Spectroscopic [40]
2. Atomic Absorption [39]
3. Polarographic [41]
4. Colorimetric [42]
5. Low Solubility of Products of Reactions of Cadmium Complex Anions with Tetrazole Derivatives [43]
6. Abatement Methods

General particulate control equipment can prevent air pollution by cadmium dusts, fumes and mists from zinc, copper, lead refineries and the cadmium industry. The following methods can be utilized.

i. Filter Bag Houses
ii. Electrostatic Precipitators
iii. Cyclones
iv. Scrubbers
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44. Little, P. and M.H. Martin, A Survey of Zinc, Lead and Cadmium in Soil and Natural Vegetation Around A Smelting Complex, Environmental Pollution, 3, No. 3, pp. 241-253, (July 1972)
H. Chlorine

1. Properties

Chlorine is a gas at normal temperatures. It does not occur in the free state in nature because of its high reactivity with many substances. Among the naturally occurring chlorine compounds are common salt (sodium chloride - NaCl, which is found in the sea and in the form of rock salt), potassium chloride (sylvine) and potassium magnésium chloride (carnallite).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Weight</td>
<td>35.45</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>-34.5°C</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>-100.95°C</td>
</tr>
<tr>
<td>Density gas</td>
<td>3.214 g/l at 0°C, 1 atm</td>
</tr>
<tr>
<td>Density liquid</td>
<td>1468 g/l at 0°C</td>
</tr>
</tbody>
</table>

2. Potential Sources and Levels of Atmospheric Emissions

a. Power Plants and Utilities Using Chlorine Containing Coals as Fuel

It has been calculated [1] that from an 800 - MW power plant, burning coal with 0.2 percent chlorine, 11,000 standard cubic feet per hour of hydrogen chloride are discharged from the stack. This emission represents 4,560 tons per year.

Selvig and Gibson [2] determined that the chlorine content of U.S. coals may range from 0.01 to 0.46 percent. According to Crossley [3], the chlorine content of English coals range from 0.01 to 1.0 percent and depended upon the area from which it is mined.

b. Manufacturers of Chlorine

There are three major processes for the production of chlorine [4].

i. Electrolytic diaphragm cells account for over two-thirds of the chlorine production.

ii. Electrolytic mercury cells account for about one-fourth of the total chlorine production.

iii. Fusion electrolysis of chloride salts produces less than five percent of the total chlorine production.

The possible sources for atmospheric chlorine emission from these plants are liquefaction processes, filling of containers, the cleaning of used tank cars containing residual chlorine, and the blow down
system treating the sniff gas or blow gas, which consists of air and about 20 to 50 percent chlorine.

c. **Chemical Industries**

Chemical industries which use chlorine for the manufacture or preparation of chemical compounds must be considered as potential chlorine polluters. The following are some typical industries:

i. Pesticide and herbicide producers (DDT, dichloro-diphenyl-trichloro-ethane, benzene hexachloride, and toxaphene).

ii. Chlorinated hydrocarbon producers

iii. Plastic and fiber industries producing PVC, vinyl chloride and vinylidene chloride.

iv. Bleaching compound and detergent industries

v. Suppliers of solvents such as carbon tetrachloride, methylene chloride and trichloroethylene.

vi. Refrigerant producers of freons and genetrons.

vii. Glycerine and glycol manufacturers

viii. Rubber reclaiming operations.

ix. Food processing industries

d. **Pulp and Paper Manufacturers**

This industry consumes about 16 percent of the total chlorine production according to the report of the U.S. Department of Commerce of 1967. It is possible that chlorine may be emitted into the atmosphere during usage.

e. **Water and Sewage Treatment Plants**

About four percent of the total chlorine production is used
in these treatment plants during the process of chlorination.

f. **Transportation and Accidental Leakage**

There have been many cases [5] [6] [7] [8] [9] in the past where chlorine leaked from cylinders or accidentally spilled during transportation causing damage to humans, animals and vegetation.

3. **Effects of Chlorine**

a. **On Humans**

The sensitivity of humans to chlorine gas varies greatly among individuals [10]. There is some evidence suggesting that humans can develop some tolerance to low concentrations of chlorine.

i. **On the Respiratory System**

Because of chlorine's strong oxidizing and bleaching properties, its main effect is the irritating and corrosive action on the mucosa of the eyes, nose, throat, and respiratory tract at low concentrations. There have been many investigations of the effects of varying chlorine concentrations on human beings. Table H.1 shows the results of several investigators.

Inhalation of massive doses of chlorine gas will damage lung tissues. Death may follow by suffocation. Symptoms observed in persons suffering heavy exposure to chlorine following the accidental gas escape in Brooklyn New York [9] and accidental spilling in a rural community of Barre, Louisiana [8] included choking, nausea, vomiting, retching, dyspnea, burning eyes, headache, dizziness, anxiety, and syncope. There are very few cases in which chlorine has entered into the blood system through inhalation, because it is very reactive with mucosa, and thus normally damage
is in localized areas. There is no doubt that acute chlorine exposure causes temporary illness, but without evidence of permanent damage. In order to study the chronic effects of chlorine, many investigators [15] [16] [17] had conducted follow-up studies of many cases. The common opinion is that complete recovery will generally occur rapidly if there is no further exposure provided that the illness is not too severe.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Exposure Time</th>
<th>Effects</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm</td>
<td>µg/m³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 or less</td>
<td>3,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>3,000 - 6,000</td>
<td>working conditions</td>
<td>Becomes disturbed &amp; noticeable symptoms</td>
</tr>
<tr>
<td>3-6</td>
<td>9,000 - 18,000</td>
<td></td>
<td>May work without interruption</td>
</tr>
<tr>
<td>4</td>
<td>12,000</td>
<td></td>
<td>Stinging or burning sensation to eyes, nose and throat</td>
</tr>
<tr>
<td>5-8</td>
<td>15,000 - 25,000</td>
<td>working conditions</td>
<td>Slight smarting of the eyes and irritation of the nose and throat</td>
</tr>
<tr>
<td>10</td>
<td>30,000</td>
<td>&lt; 1 min</td>
<td>Workers continually exposed to chlorine are able to tolerate for significantly long period</td>
</tr>
<tr>
<td>14-21</td>
<td>40,000 - 60,000</td>
<td>30-60 min</td>
<td>Sever coughing and eye irritation</td>
</tr>
<tr>
<td>40-60</td>
<td>120,000 - 180,000</td>
<td>30-60 min</td>
<td>Dangerous</td>
</tr>
<tr>
<td>100</td>
<td>290,000</td>
<td>&lt; 1 min</td>
<td>Amount dangerous in 30 minutes to one hour</td>
</tr>
</tbody>
</table>

Table H.1 Effects on Man Due to Inhalation of Chlorine Gas

11. Sensory Effects

Different investigators have proposed different odor
threshold values for chlorine. Stayzhkin [18] gives 750 μg/m³, Takhirov [19] suggests 880 μg/m³, and Stern [20] 940 μg/m³. Takhirov [19] who studied sensory thresholds for the eye, states that the threshold for chlorine effect on eye sensitivity to light was the same as for the odor threshold of 800 μg/m³.

b. On Animals

A large number of experiments studying the harmful effects of various chlorine concentrations on animals has been done in the past years. Heyroth [10] reported that there was no damage when experimental animals were repeatedly exposed to 20.7 ppm of chlorine. Experimental dogs were not killed when exposed to chlorine concentrations below 280 ppm for 30 minutes. However, in these dogs, acidosis increased rapidly when the concentration was raised to 800 ppm for about 2 1/2 hours. For guinea pigs low concentrations of chlorine can accelerate the course of experimental tuberculosis [21]. At concentrations of 300 ppm cats die after a period during which conjunctiva are inflamed and there is coughing and dyspnea [10]. Weedon and co-workers [22] reported, in 1940, that approximately 50% of mice died when exposed to 250 ppm of chlorine for 448 minutes; cats at 1,000 ppm with 28 minutes of exposure. Rats have almost the same tolerance towards chlorine as mice. Several domestic animals died as a result of an accidental spillage of chlorine in La Barre, Louisiana [8].

c. On Vegetation

Brennan and partners [23], who studied the effects of various concentrations (0.1 to 1.5 ppm) of chlorine gas in the atmosphere on 26 different species of plants, concluded that plants varied in sensitivity to the gas and in symptom expression following exposure to a toxic dose. The most common symptoms of chlorine poisoning were necrosis and bleaching of
the foliage after one or two days exposure. Plants did not accumulate chloride in the tissue following the exposure. Zimmerman [5] [6] reported similar responses in 16 species of plants exposed to chlorine concentrations ranging from 0.46 to 4.67 ppm. The most characteristic symptom was spotting of the leaves, with leaf fall occurring after moderate to severe injury. Stem tissue was bleached and had a cooked appearance when tomato, buckwheat, and tobacco plants were exposed to 1,000 ppm chlorine by Thornton and Setterstrom [24]. Barton [25] studied the chlorine effects on moist and dry seeds of radish and rye. He found that moist seeds were much more sensitive to chlorine than dry seeds. Delay in germination after exposure was the characteristic effect. Thornton and Setterstrom [24] found that tomato plants kept in sunlight gave greater changes in pH with chlorine exposure than those kept in darkness. This means that plants are injured by chlorine to a greater extent during clear than during cloudy weather. Many cases [5] [6] [7] [26] have been reported in which vegetation has been damaged by accidental chlorine leakage.

d. On Materials

It is possible that atmospheric chlorine gas may damage material, because of its high reactivity with almost all metals and nonmetals. This implies that chlorine in sufficiently high concentrations in the atmosphere may corrode metals, discolor painted materials and bleach textile fibers. Niskanen and Franklin [27], who studied the urban atmospheric corrosion of copper and some copper alloys, found that the corrosion products of copper consisted mainly of Cu2O, and also of undetermined copper chloride, and basic copper chloride.
4. **Environmental Air Standards**

West Germany [28] has recommended an eight-hour Threshold Limit Value for chlorine of 3,000 μg/m³ (1 ppm).

The American Conference of Governmental Industrial Hygienists in 1967 adopted an eight-hour Threshold Limit Value for chlorine of 3,000 μg/m³ (1 p.p.m.).

Russia (30) recognized 1,000 μg/m³ (0.33 ppm) as a maximum eight-hour occupational exposure for chlorine.

5. **Detection and Measurement of Chlorine**

Most of the methods used for the determination of atmospheric chlorine are based on common oxidation reactions which are not specific for chlorine but may detect other oxidants, such as ozone, bromine, nitrogen oxides and sulfur oxides.

The methods most frequently applied are

i. Colourmetric methods with 0-tolidine. Amounts as low as 0.2 μg chlorine can be detected with this reagent [31].

ii. Colourmetric methods with 3,3-dimethylnaphthidine. This reagent is about eight times more sensitive than 0-tolidine [31].

iii. Neutron activation and gamma-ray spectrometric [32].

iv. Gas chromatographic [33].

v. Platinum-silver galvanic half cell in a bromide containing electrolyte and a phosphate buffer [34].

vi. Photometric [35]

vii. X-ray method [36]
6. Abatement Methods

Many methods have been used for the control of chlorine emissions. The most common are wet scrubbers, the following being typical apparatus:

i. Water scrubbers

ii. Caustic gas-recovery scrubbers [37].

iii. Carbon tetrachloride scrubbers [38].
REFERENCES


9. Chasis, H. et al., Chlorine Accident in Brooklyn, Occupational Med. 4, p. 152, (1947)


14. Chemical Safety Data Sheet SD-80, Chlorine, Manufacturing Chemists


I. Chromium and Its Compounds

1. Properties

Metallic chromium does not occur in the free state in nature. It is found in combination with oxygen in chrome ochre, (chromium sesquioxide, Cr₂O₃) associated with more or less earthy matters. Chromite, FeO·Cr₂O₃, is the chief ore of chromium. Chromium also occurs as lead chromate in crocoite or crocoisite PbCrO₄.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Weight</td>
<td>52.01</td>
</tr>
<tr>
<td>Density</td>
<td>7</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1830°C</td>
</tr>
</tbody>
</table>

Chromium is a bluish-white metal, capable of taking a very high polish. It is extremely hard, being harder than iridium and steel. Under ordinary conditions it is stable in air, but it is superficially oxidized when heated in air or oxygen. It retains a brilliant finish when exposed to all normal atmospheric corroding agents, including rain, snow, sea-water, hydrogen sulhide, sulphur dioxide and sulphur compounds generally.

Chromium forms a series of compounds corresponding to the oxidation states +2, +3 and +6. The chromous compounds, in which the chromium exhibits the +2 oxidations state, are so readily oxidized in air, or in aqueous solution that they are seldom encountered. Chromic compounds are trivalent and amphoteric. The oxides, Cr₂O₃ or CrO₇²⁻ are referred to as chromites. The hexavalent chromates are acidif₂. They are usually water soluble and form the chromate ion (CrO₄²⁻) or dichromate ion (Cr₂O₇²⁻).

2. Potential Sources and Levels of Atmospheric Emissions

a. Mining and Smelting of Chromite Ore

During the process of grinding ore, finely divided particles
containing chromium are probably emitted into the atmosphere. In the roasting facilities chromium fumes will cause air pollution if proper controls are not provided.

b. **Metallurgical Industry**

About 57 percent of the total chromite ore, FeO·Cr₂O₃, is used in the metallurgical industry according to the reports in the Minerals Year Book. [1]. Most of the chromite ore is used for production of chromium metal or chrome alloys. These alloys form the basis for a great variety of useful steels, such as stainless steel, austenite steels, high-speed steels, high temperature steels, and nonferrous alloys. Air pollution by chromium compounds from these sources is likely to be as fumes and particulates generated during processing. Ruhling [4] reported that chromium concentrations in mosses called Hypnum Cupressiforme in the vicinity of a ferro-alloy plant were 12,000 ppm compared with 10 ppm in normal Swedish locations.

c. **Chromate Chemical Industry**

It was calculated in the Mineral Year Book that 13% of the chromite ore is used to produce chromate and dichromate compounds in the U.S. In 1953 Gafafer [2] reported that the average dust content inside the six studied chromate plants was 170 μg/m³ as hexavalent chromium. Air samples at the effluence of some of the exhaust systems showed up to 148,000 μg/m³ of chromate. It is clear that chromate-producing plants can be significant sources of chromium air pollution.

d. **Refractory Industry**

About 30% of the chromite ore is used in refractory materials. Because chromite has a high melting point and is chemically inert, it is used
to manufacture refractory bricks and linings for metallurgical furnaces. It is therefore possible that chromium dusts or fumes may be emitted into the atmosphere not only during the production of the bricks but also by erosion of furnace interiors.

e. **Chrome Plating Operations**

Desbaumes and Ramachioti [3] investigated the chromium content in plants and soil near a chrome plating installation. They reported that a high content of chromium was emitted from the chrome plating operation. The level of chromium in the plant tissue varied widely from less than 1 to 9.8 μg/g of tissue. The surface of a garden had a content of 8.4–30 μg/g of soil, while at a depth of 30 cm, the soil contained 30–71 μg/g. By comparison soil from a garden in Valais had a chromium content of 1.1–1.9 μg/g.

f. **Paint and Pigment Industries**

Chromium may be emitted into the atmosphere during the production of paint and pigments using chromates, chromic oxide, and dichromate as constituents. Spraying of chromate paint on steel or alloy surfaces can be considered as a source of chromium air pollution. There is evidence that chromate paint can cause chromate dermatitis [5].

g. **Power Plants and Utilities Using Chromium Containing Coals as Fuels**

The concentration of chromium in coal depends on the area from which it was mined. Table I.1 shows the concentration of chromium in coal and coal ash.
<table>
<thead>
<tr>
<th>Source of Coal</th>
<th>Chromium in Coal in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>7</td>
</tr>
<tr>
<td>Northern Great Plains</td>
<td>20</td>
</tr>
<tr>
<td>Eastern Interior</td>
<td>13</td>
</tr>
<tr>
<td>Appalachian Region</td>
<td>0.03 to 3.3</td>
</tr>
<tr>
<td>Japan</td>
<td>50</td>
</tr>
<tr>
<td>Germany</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>U.S. Northern Great Plains</th>
<th>Chromium in Coal Ash, Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Carolina, peat</td>
<td>&lt; 0.0001 to 0.03</td>
</tr>
<tr>
<td>Pennsylvania, anthracite</td>
<td>0.019 to 0.025</td>
</tr>
<tr>
<td>Pennsylvania, Cambria County</td>
<td>0.001 to 0.01</td>
</tr>
<tr>
<td>Pennsylvania, Washington County</td>
<td>0.027</td>
</tr>
<tr>
<td>Texas, Colorado, North and South Dakota</td>
<td>0.013</td>
</tr>
<tr>
<td>Nova Scotia</td>
<td>0.01 to 0.1</td>
</tr>
<tr>
<td>England: Vitrain</td>
<td>0.0018 to 0.0079</td>
</tr>
<tr>
<td>Newcastle</td>
<td>0.01 to 0.1</td>
</tr>
<tr>
<td>German: Neuwrode</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>0.014</td>
</tr>
</tbody>
</table>

Table I.1 Chromium in Coal and Coal Ash [6]

Cuffe and Gerstle [7], who studied metal emissions from coal fired power plants, found the chromium emission shown in Table I.2.

<table>
<thead>
<tr>
<th>Type of Boiler Firing</th>
<th>Coal Rate ton/hr</th>
<th>Ash in Coal (as fired) %</th>
<th>Fuel gas Volume Scfm x 10³</th>
<th>Chromium Emissions µg/m³</th>
<th>g/min</th>
<th>g/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>Vertical</td>
<td>65.6</td>
<td>20.2</td>
<td>397.4</td>
<td>409.9</td>
<td>220</td>
<td>18</td>
</tr>
<tr>
<td>Corner</td>
<td>56.1</td>
<td>14.9</td>
<td>362.9</td>
<td>351.0</td>
<td>1900</td>
<td>130</td>
</tr>
<tr>
<td>Front-wall</td>
<td>52.2</td>
<td>10.3</td>
<td>329.0</td>
<td>328.0</td>
<td>1100</td>
<td>160</td>
</tr>
<tr>
<td>Spreader-stoker</td>
<td>9.2</td>
<td>8.4</td>
<td>53.9</td>
<td>59.6</td>
<td>450</td>
<td>350</td>
</tr>
<tr>
<td>Cyclone</td>
<td>64.4</td>
<td>7.7</td>
<td>553.6</td>
<td>500.8</td>
<td>1900</td>
<td>500</td>
</tr>
<tr>
<td>Horizontally opposed</td>
<td>9.6</td>
<td>8.2</td>
<td>62.2</td>
<td>62.2</td>
<td>2200</td>
<td>410</td>
</tr>
</tbody>
</table>

Table I.2 Chromium Emissions from Coal-Fired Power Plants [7]

B: Before fly-ash collection
A: After fly-ash collection
h. **Cement Factories**

Keenan and Perone [8] reported that cement contains hexachromium ranging from 0.03 to 7.8 μg per gram of cement and 27.5 μg to 60 μg of total chromium per gram of cement depending on the origin of the cement manufactured.

i. **Asbestos**

Caze [9] has shown that the chromium concentration found in chrysotile, the most common asbestos mineral, was 1,000 μg per gram of fiber. It is the second highest trace inorganic impurity found in asbestos.

j. **Corrosion Inhibitor Manufacturers**

Soluble chromates are effective inhibitors against the corrosion of iron, steel, zinc, aluminium, copper, brass, lead and most alloys. These inhibitors are widely used in cooling-towers, air conditioning equipment, automobile radiators, cooling systems for diesel engines, (such as locomotive, marine and stationary diesel engines) boilers and coolers. There is evidence of chromate dermatitis in railroad employees working with diesel locomotives, [10]. The use of sodium chromate and complex chromate salts in wooden cooling towers as wood preservatives and corrosion inhibitors may lead to another source of chromium air pollution. This possibility arises from the large amount of water vapor that may carry chromium compounds into the atmosphere during evaporation.

k. **Welding or Cutting Operations**

Fregert and Ovrum [11] and Shelley [12] have reported chromate dermatitis caused by welding fumes which contain hexavalent chromium.

l. **Matches and Fireworks**

Matches contain a small amount of potassium dichromate.
Fireworks contain some chromium compounds to produce different colours upon firing. It is likely that chromium can be introduced into the atmosphere during match lighting and display of fireworks.

3. Effects of Chromium and Its Compounds

The toxicity of chromium on humans and animals depends on the chemical state of the chromium. Baetjer [13] reported that chromium metal and trivalent chromium are thought to be relatively far less toxic than hexavalent chromium which may produce a variety of effects. Hexavalent compounds are extremely irritative, corrosive, and toxic to body tissues and probably exhibit carcinogenic effects [2] [3]. However Fregert [14] and Cohen [15] reported that trivalent chromium can produce such harmful effects as dermal sensitivity and can cause dermatitis. It is believed that chromium is an essential element for the normal function of carbohydrate metabolism [22].

a. On Humans

i. Respiratory System

The main characteristic symptom of chromium hazard to workers in the chromium industry is the perforation of the nasal septum [13] [16] due to inhalation of chromate dust or chromic acid mist. Edmundsen [17], who studied 285 cases of male workers in the production areas of a large chromate producing plant, shows that 61.4 percent of them showed nasal perforation. These were incidents of congestion of the larynx, hyperemia, chronic inflammation of the lungs, emphysema, tracheitis, chronic bronchitis and pneumonia among chromate workers [13]. It takes longer than five years to develop chronic bronchitis, and more than nine years to produce pneumoconiosis in workers when exposed to 4,500 to 9,200 μg/m³ of chromium [18].
II. Carcinogenesis

There are many cases [19] [20] [21] showing that chromate workers suffer cancer in the respiratory tract. Gafafer [2] reported in 1953 in the U.S.A. that the death rate due to cancer of the respiratory tract for chromate workers was 28 times greater than for other males of the same age group. There is no evidence to show that chromium causes cancer in organs other than those of the respiratory tract. The time of exposure and concentration of chromium in the inhaled air conducive to cancer are not known. It was presumed by Gafafer [2] and Baetjer [13] that cancer is induced by acid soluble, water-insoluble chromium compounds [2], hexavalent compounds, dichromates, or chromic acid [13].

iii. Skin

It is generally accepted that chromium compounds produce hypersensitivity. Contact with these compounds results in inflammation of intact skin. There have been many cases reported of chromate dermatitis among workers in the cement industries [23], assemblers in an automobile factory [24], workers in wet sanding of primer paint on car bodies [5], and railroad employees working with diesel locomotives [10]. Besides chromate dermatitis, chromium compounds also induce ulcers called chrome holes [2] [13], generally on areas where chromate dust can accumulate.

b. On Animals

Hueper and Payne [26] stated that chromium compounds induce cancer in experimental rats, especially high solubility compounds such as calcium chromate. Gross and co-workers [25] produced hypersensitivity in guinea pigs with potassium dichromate and chromic chloride. Baetjer and
partners [13] [27] exposed mice to atmosphere containing 1,500 µg/m³ Cr as CrO₃. Inhalation for four hours daily, five days per week, for as long as a year produces no harmful effects. When the concentration was raised to 7,000 µg/m³ as CrO₃ for 37 hours over ten days, fatalities resulted. Pathological changes occurred in lungs of rabbits and cats inhaling air with chromate levels of 1,000 – 50,000 µg/m³ for 14 hours per day over 1 to 8 month periods. Cats developed bronchitis and pneumonia from inhaling dichromate at levels of 11,000–23,000 µg/m³ for two to three hours over 5 days. No effect was induced in rabbits subjected to the same concentrations and exposure times. Schroeder [28] showed that chromium is an essential element in the diet of rats. Deficiency of chromium will produce a syndrome similar to diabetes.

c. **On Vegetation**

No information has been found in the literature on the effects of atmospheric chromium compounds on vegetation. Chromium in soil can stimulate plant growth. Its toxicity to plants depends upon concentration, pH of the soil and the tolerance of each type of plant to the metal.

d. **On Materials**

It has been observed that chromic acid mists from plating factories damage paints and construction materials [13]. It is probable that chromic acid mists can cause corrosion of metals and construction materials, discolor paint and damage paper and textiles; because of the strong acid and strong oxidizing properties.

4. **Environmental Air Standards**

In 1967 the American Conference of Governmental Industrial Hygienists and the American Industrial Hygiene Association recommended an eight
hour Threshold Limit Value of 100 μg/m³ for chromic acid and chromate.

The U.S.S.R. set a value of 1.5 μg/m³ for chromates as the maximum permissible single dose and the maximum permissible average daily concentration. For trivalent chromium and its compounds, the maximum allowable concentration has been set at 250 μg/m³ for a single exposure and 80 μg/m³ for an average 24-hour exposure.

Table 1.3 shows the levels of chromium in the air over typical American cities.

<table>
<thead>
<tr>
<th>Cities</th>
<th>Maximum Concentration μg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chicago</td>
<td>.052</td>
</tr>
<tr>
<td>Detroit</td>
<td>.049</td>
</tr>
<tr>
<td>Los Angeles</td>
<td>.033 (1963)</td>
</tr>
<tr>
<td>New York</td>
<td>.019</td>
</tr>
<tr>
<td>Philadelphia</td>
<td>.028</td>
</tr>
<tr>
<td>Newark</td>
<td>.063</td>
</tr>
<tr>
<td>Baltimore</td>
<td>.350</td>
</tr>
<tr>
<td>Cincinnati</td>
<td>.240</td>
</tr>
</tbody>
</table>

Table 1.3 Concentration of Chromium in the Air of Selected U.S. Cities in 1964 [29]

5. Detection and Measurement of Chromium Compounds

Samples of chromium dusts and fumes may be collected by impingers, electrostatic precipitators, filters and high volume filtration samplers.

Atmospheric chromium may be analysed by the following methods:

i. Atomic Absorption Spectroscopic [30]

ii. Neutron Activation [31]

iii. Emission Spectroscopic [32]

iv. Ring Oven Technique [33]

v. Colorimetric Reagent [34]
6. **Abatement Methods**

General particulate control equipment can prevent air pollution by chromium particulate emission from chromium industries. The following methods can be used:

1. **Filter Bags**
2. **Electrostatic Precipitators**
3. **Scrubbers**
4. **Cyclones**

In controlling chromic acid mists in chrome plating industries, it is recommended that slot hoods be used to capture the chromic acid mists discharged from the plating solutions. It is believed that coatings of synthetic materials which float on the electrolyte may suppress chromic acid mists by preventing the mists from leaving the solutions.
REFERENCES


J. Copper and Its Compounds

1. Properties

Copper is the first element of subgroup IB of the Periodic Table. The natural material is a mixture of the two isotopes Cu$^{63}$ with 29 protons and 34 neutrons, and Cu$^{65}$ with 29 protons and 36 neutrons. The metal does not burn in air, but gradually forms cuprous (Cu$_2$O) and cupric oxide (CuO) on its surface when heated to redness. Although unaffected by dry air at ordinary temperatures, exposure to moist air causes the formation of a beautiful green coating or patina.

Copper is widely distributed in many parts of the world. It is found in a variety of mineral ores, that are classified into three groups: sulfide, oxidized, and native copper.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Weight</td>
<td>63.54</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1083°C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>2595°C</td>
</tr>
<tr>
<td>Density</td>
<td>8.94 at 20°C</td>
</tr>
</tbody>
</table>

2. Potential Sources and Levels of Atmospheric Emissions

Emissions of copper to the atmosphere from various sources in the U.S. during 1969 were 13,680 tons according to the estimates of Davis [1].

a. Metallurgical Processing of Primary Copper

Davis [1] estimated that about 64 percent of the total copper emissions to the atmosphere came from this source. Heaney [2] investigated the distribution of trace elements in the vicinity of an integrated primary copper production facility. He concluded that constituents of the settleable and suspended particulate (such as copper) show seasonal variations. The dustfall values tend to decrease during the windy months of the year and increase
with onset of calm weather and inversion conditions. The suspended particulate shows the reverse of this situation with higher values occurring during the windy months. The units that discharge fumes, dusts, slags, and residues containing copper are dryers, roasters, furnaces, converters and other equipment. In most cases emitted materials are collected, retreated and recycled. However, results from 6 metallurgical operations, involving the processing of copper-bearing ores and the production of copper, showed that emissions of copper to the atmosphere can be more than 40 pounds of copper per ton of primary copper produced with averages of about ten pounds per ton [1]. Table J.1 shows the seasonal variation of copper levels measured in suspended and settleable particulates [2].

<table>
<thead>
<tr>
<th>Month</th>
<th>Settleable Particulates lb/ Mft/30 days</th>
<th>Suspended Particulates µg Cu/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>450</td>
<td>0.8</td>
</tr>
<tr>
<td>February</td>
<td>270</td>
<td>0.6</td>
</tr>
<tr>
<td>March</td>
<td>90</td>
<td>0.4</td>
</tr>
<tr>
<td>April</td>
<td>250</td>
<td>0.4</td>
</tr>
<tr>
<td>May</td>
<td>110</td>
<td>0.3</td>
</tr>
<tr>
<td>June</td>
<td>110</td>
<td>0.3</td>
</tr>
<tr>
<td>July</td>
<td>100</td>
<td>0.3</td>
</tr>
<tr>
<td>August</td>
<td>370</td>
<td>0.3</td>
</tr>
<tr>
<td>September</td>
<td>310</td>
<td>0.3</td>
</tr>
<tr>
<td>October</td>
<td>280</td>
<td>0.4</td>
</tr>
<tr>
<td>November</td>
<td>230</td>
<td>0.7</td>
</tr>
<tr>
<td>December</td>
<td>260</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table J.1 Copper in Suspended and Settleable Particulate (Average of All Stations) [2]

b. **Mining and Milling**

There are no records available for copper emission to the atmosphere from mining and milling operations. It is generally agreed by mine operators that there are slight emissions due to handling, crushing, and as a wind loss from tailings. Davis [1] estimated about 190 tons of copper emissions
to the atmosphere from this source.

c. **Iron and Steel Industry**

Steel mills are considered to be important sources of copper emissions to the atmosphere. Trace quantities of copper enter the process in the raw materials. The copper is emitted as a constituent of the particulate matter in the effluent gas streams. Davis [1] estimated that copper emissions to the atmosphere from blast furnaces totaled 1,070 tons, while open-hearth and basic oxygen units contributed 1,550 and 70 tons respectively in the U.S. in 1969. The copper content of the particulate discharge from an open-hearth furnace was found to be approximately 0.5% [3].

d. **Brass and Bronze Smelting and Refining Industry**

The principal source of atmospheric emissions in the brass and bronze ingot industry is the refining furnace. Some particulate emissions result from the preparation of raw materials and the pouring of ingots. Particulate emissions from refining furnaces in the brass and bronze ingot industry average 60 to 80 pounds per ton of ingots produced [4]. The range of copper content is from 0.05 to 1.0 percent [5].

e. **Power Plants and Utilities Using Coal as Fuel**

During the combustion of coal, copper is discharged to the atmosphere with the ash, partly in bottom ash and partly in the fly ash. The fly ash averages about 65 percent of the total ash. Davis [1] estimated that the total copper emissions from coal burning sources in 1969 in the U.S. were 2,910 tons. Table J.2 shows the copper content in coals from various sources. Table J.3 shows the copper levels in coal ash.
### Copper Content in Coal [6]

<table>
<thead>
<tr>
<th>Source of Coal</th>
<th>Copper in Coal, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northern Great Plains</td>
<td>15</td>
</tr>
<tr>
<td>Eastern Interior</td>
<td>11</td>
</tr>
<tr>
<td>Appalachian Region</td>
<td>15</td>
</tr>
<tr>
<td>English Coal</td>
<td>1 to 170</td>
</tr>
<tr>
<td>Romanian Coal</td>
<td>1.87 to 14.68 (gram/ton)</td>
</tr>
</tbody>
</table>

**Table J.2 Copper Content in Coal [6]**

<table>
<thead>
<tr>
<th>Source of Coal</th>
<th>Cu in Ash, Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td></td>
</tr>
<tr>
<td>Northern Great Plains</td>
<td></td>
</tr>
<tr>
<td>North Dakota</td>
<td></td>
</tr>
<tr>
<td>Pennsylvania, Anthracite, Do</td>
<td></td>
</tr>
<tr>
<td>Texas, Colorado, North &amp; South Dakota</td>
<td></td>
</tr>
<tr>
<td>West Virginia</td>
<td></td>
</tr>
<tr>
<td>England, Newcastle</td>
<td></td>
</tr>
<tr>
<td>Germany, Westphalia</td>
<td></td>
</tr>
<tr>
<td>Germany, brown coal</td>
<td></td>
</tr>
<tr>
<td>Portugal, anthracite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.002 to 0.07</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>0.001 to 0.01</td>
</tr>
<tr>
<td></td>
<td>0.03 to 0.07</td>
</tr>
<tr>
<td></td>
<td>0.01 to 0.1</td>
</tr>
<tr>
<td></td>
<td>0.022 to 0.10</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>0.016 to 0.054</td>
</tr>
<tr>
<td></td>
<td>up to 0.001</td>
</tr>
<tr>
<td></td>
<td>0.001 to 0.01</td>
</tr>
</tbody>
</table>

**Table J.3 Copper in Coal Ash [6]**

f. **Incineration**

Cross and co-workers [7] reported that when burning a combination of refuse and sewage sludge, in which the ratio of refuse to sludge was approximately 3.5 to 1, the copper emissions were $5.7 \times 10^{-2}$ pounds per ton of charge. Another source shows that copper emissions are $4.2 \times 10^{-2}$ pounds per ton of charge when burning refuse alone. Davis [1] estimated U.S. copper emissions from incineration of refuse and sewage sludge in municipal incinerators to be nearly 460 tons in 1969.

3. **Effects of Copper and Its Compounds**

a. **On Humans**

Copper is a highly dangerous metal. It may be detrimental to a great number of enzymes, yet it is an essential constituent of living systems.
and must be built into certain proteins [8]. Among copper compounds, copper sulfate, CuSO$_4$, is the only toxic one.

1. **Copper Fever**

Inhalation of very fine particles may cause metal fume fever. According to Friberg and Tberysin typical initial symptoms of copper inhalation are sweetish taste in the mouth, dryness of the pharynx, and burning of the eyes. A few hours subsequent to inhalation, fever, severe headache, leukocytosis, general lassitude, and catarrhal symptoms appear [9].

11. **Copper Sulfate**

The toxicity of copper sulfate is chiefly due to its corrosive action. It usually causes immediate vomiting. The general symptom of copper sulfate ingestion is bluish-green corrosion of mucous membranes and repeated vomiting of blue-green masses, followed at an early stage by the passage of profuse watery stools containing blood. Almost 100 percent of the copper which has been absorbed is stored in the liver [9].

b. **On Animals**

Recently many investigations have been conducted on the harmful effects of copper and its compounds on protozoan, fish and phytoplanktons in polluted water. Very few reports can be found concerning the effects of copper air pollution, because metallic copper in particulate matter is relatively insoluble and need not be considered too dangerous.

Bischoff [10] examined animals which died from poisoning or had to be slaughtered after fly dust, which contained about 2.5% of Cu and 23 mg. AS$_2$O$_3$/kg, was discharged by a Cu smelting plant. An increased Cu content was found in almost all livers. Clinical symptoms such as miscarriage, sterility
and lack of milk led to the assumption that the As found in the fly ash contributed to the poisoning. Perhaps Cu and As undergo some chemical reaction in the fly dust to increase the overall toxicity.

Hatsura [11] investigated the penetration of copper oxide from the lungs into the blood and internal organs of albino rats, exposed to 50 - 80 mg/m^3 of copper oxide dust for 15, 20, 35, 60 and 180 minutes. Edema and swelling of the ultrastructures of the lung cells were observed.

Baker [12] studied the effects of various levels of copper on the morphology of winter flounder. He found that high and medium levels resulted in fatty metamorphosis in the liver, necrosis in the kidney, destruction of the hemopoietic tissue and gross changes in gill architecture. McKin et al [13] followed the changes in the blood of brook trout after copper exposure while Hubbschman [14] studied the effects of copper on crayfish. Mandelli [15] and Button et al [16] studied the inhibitory effects of copper on marine phytoplankton and microorganisms.

c. **On Vegetation**

No information has been found on the effects of atmospheric copper and its compounds on vegetation. Some experiments had been done to study the concentrations of copper reducing the rates of photosynthesis of algae [25].

d. **On Materials**

No information has been found on the effects of atmospheric copper and its compounds on materials.
4. **Environmental Air Standards and Atmospheric Concentrations**

No information has been found on atmospheric standards for copper.

Copper was found in the air of all cities and nonurban areas by the national air sampling network in 1966 [17]. The annual averages for atmospheric copper in cities ranged from 0.01 - 0.57 μg/m³ and 0.01 - 0.25 μg/m³ for nonurban areas. Copper concentrations in the lower atmosphere between California and Hawaii were found to vary from 0.0044 μg/m³ to 0.051 μg/m³ [18]. Table J.4 shows annual ranges of copper concentrations for 1968 in New York city.

<table>
<thead>
<tr>
<th>Area</th>
<th>Copper Concentrations μg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bronx</td>
<td>0.03 - 0.27</td>
</tr>
<tr>
<td>Lower Manhattan</td>
<td>0.09 - 0.30</td>
</tr>
<tr>
<td>Tuxedo New York</td>
<td>0.012 - 0.086</td>
</tr>
<tr>
<td>NASN Manhattan</td>
<td>0.03 - 0.25</td>
</tr>
</tbody>
</table>

Table J.4 Annual Ranges of Copper Concentrations for 1968 in New York [19]

5. **Detection and Measurement of Copper and Its Compounds**

Many techniques have been used to analyze for copper in the air. Typical methods include the following:

i. Anodic Stripping Voltammetric [20]

ii. Atomic Absorption Spectroscopic [21] [19]

iii. Colorimetric-Nephelometric [22]

iv. Dithiooxamide Crayon and the Ring-Oven Technique [23]

v. Thermal Neutron Activation [18]

vi. Neutron Activation and Gamma-Ray Spectrometric [24]
General particulate control equipment can minimize air pollution by copper particulate emissions from copper emission sources. The following are typical control devices:

i. Electrostatic Precipitators
ii. Cyclones
iii. Filter Bags
iv. Scrubbers
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K. **Fluorine and Its Compounds**

1. **Properties**

Fluorine is a light canary-yellow gas which condenses to a clear yellow liquid.

- **Boiling Point:** -187°C
- **Melting Point:** -223°C
- **Atomic Weight:** 18.996

Fluorine does not occur freely in nature, but occasionally has been found in crystals of fluorspar, and in the mineral cryolite. Fluorine is probably the most active element known. It combines with hydrogen explosively even in the dark, and at temperatures as low as -210°C. Fluorine is a very powerful oxidizing agent.

Hydrogen fluoride, HF, is a limpid liquid which fumes strongly in air. It is very poisonous and dangerous to handle.

- **Boiling Point:** 19.4°C
- **Crystal Melting Point:** -83°C
- **Freezing Point:** -102.5°C

Hydrogen fluoride is very soluble in water, forming the corrosive liquid, hydrofluoric acid.

2. **Potential Sources and Levels of Atmospheric Emissions**

Airborne fluoride can be of two types, gaseous or particulate, depending upon the sources, each of which can contain components differing in solubility.

a. **Steel Smelting**

Steel smelting operations in which fluorspar is used as flux
can be sources of fluorine emission. It was estimated that, in 1961, the equivalent of 10,000 tons of fluorine were emitted in England and Wales during the manufacture of steel [1]. Schrenk and partners [2] reported that levels of 4,600 µg/m³ of fluoride were measured in waste gases from a blast furnace in a steel plant and a maximum value of 17,650 µg/m³ had been found in the open-hearth stack.

It was estimated that 39 pounds of fluoride were emitted from this U.S. plant each day. A monthly average of 4.5 gram of soluble fluoride per 100 m² had been found near the centre of Rotherham at a distance of approximately one and one-half miles from a steel-works using fluorspar in open-hearth furnaces. This situation differs significantly from a rural area in Essex, England exhibiting 0.69 gram per 100 m² per month [1].

b. Power Plants and Utilities Using Coal as Fuel

It was estimated that 5000 tons of fluorine were emitted into the atmosphere yearly in England and Wales from the industrial and domestic use of coal in 1961 [1]. Fluorine, as a trace constituent of coals, may range from 0 to 175 parts per million, but generally less than 80 ppm [3].

Table K.1 shows some fluorine levels in typical coals

<table>
<thead>
<tr>
<th>Area</th>
<th>Concentration in Coal, ppm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Southern Illinois</td>
<td>167</td>
<td>[4]</td>
</tr>
<tr>
<td>Western Pennsylvania</td>
<td>85</td>
<td>[4]</td>
</tr>
<tr>
<td>Western Coals</td>
<td>40 - 132</td>
<td>[5]</td>
</tr>
<tr>
<td>Japanese Coals</td>
<td>100 - 480</td>
<td>[6]</td>
</tr>
</tbody>
</table>

Table K.1 Fluorine Content in Coals
c. **Superphosphate and Other Phosphate Fertilizer Plants Using Fluorine Containing Rock Phosphate as Raw Material**

Atmospheric fluoride emissions from these sources are likely to consist of both gaseous and particulate materials. In 1960, it was estimated that fluoride emissions from a triple-superphosphate factory could range from 200 to 3,500 pounds per day [7]. Lindberg [8] found air concentrations of fluoride from 0.098 to 0.485 mg/m$^3$ at a distance of 3000 meters from a superphosphate plant. Derryberry and co-workers [9] reported fluoride concentrations in a phosphate fertilizer atmosphere ranging from 1.78 to 7.73 mg/m$^3$.

There are many instances showing that men working in phosphate fertilizer plants suffer from abnormalities in radiographic bone density, unusually high concentrations of urinary fluoride, higher incidence of albuminuria and x-ray demonstrable pulmonary changes [10].

d. **Cryolite Industries**

The mining and processing of cryolite (AlF$_3$·3NaF) is a major source of atmospheric fluorides. In 1973, Roholm [11] reported that the air of some rooms in the cryolite factory often contained 30-40 mg F/m$^3$. In two enclosed areas, concentrations of fluoride were more than 9,000 greater.

e. **Aluminium Reduction Plants**

Cryolite (AlF$_3$·3NaF) is used in the manufacture of aluminium as a molten flux with alumina (aluminium oxide). Fluoride compounds are lost partly by sublimation and partly by reaction with the hydrogen content of raw materials. Agate and co-workers [12], who investigated fluorosis near Fort William, Scotland in 1949, found that fluoride concentrations in the furnace room ranged from 0.14 to 3.13 mg/m$^3$. The atmospheric fluoride concentrations downwind from the plant were 0.22 mg/m$^3$ at a distance of 200 yards and 0.04 mg/m$^3$ in the centre of Fort William, a mile away.
Elevated fluoride concentrations were found in the soil several miles from the plant. Vegetation contained enough fluoride to affect cattle seven miles downwind. Sadilova [13] reported 0.01 to 0.13 mg/m³ of fluoride in the vicinity of aluminium plants. The total amount of fluoride emitted to the atmosphere by this industry depends upon the process and control equipment. Moser [14] reported a gaseous emission of 0.56 kg F and a dust emission of 4.5 kg F per ton of aluminium processed, while Ender [15] reported approximately 20 kg F per ton of aluminium. Robak [16] found that fluorides induced injuries to coniferous forests over distances of 32 km from the aluminium emitting sources. However, destruction of some species may occur at distances of only 10 to 13 km.

f. Cement Processing Industries

It was estimated that in 1961 500 tons, expressed as fluorine, were emitted from the cement industry yearly in England and Wales [1]. It is believed that the fluoride emitted from these sources comes from the fluoride containing rocks used during processing.

g. Heavy Clay, Pottery, Tile, Brick and Ceramics Industries

A wide range of fluorine concentrations from 20 to 7400 ppm are distributed among soils. Sandy soils are among the lowest, while clay soils are high in fluorine content. Mollisols may contain from 300 to 7400 ppm of fluorine. It was reported in 1961 that 500 tons of fluorine were emitted annually in England and Wales from the heavy clay industry and 50 tons from the pottery industry [1].

h. FLOX, Fluorine as Propellants and Freon

The use of FLOX (fluorine-oxygen mixtures) and fluorine as the
oxidizer in rocket engines may introduce another source of fluorine emission to the atmosphere. Exhaust products from the launch vehicle mainly in the form of hydrogen fluoride, and losses during handling of FLOX can become serious problems [18]. The Freons, used as aerosol propellants, although non-toxic in themselves, can be hazardous when heated to decomposition temperatures to produce HF, HCl, and phosgene [17].

1. Insecticides

There are several types of fluorine compounds used as insecticides. Fluoroacetamide is a typical example.

3. Natural Occurrence

The compounds of fluorine are widely distributed in minerals as cryolite, fluor spar and small quantities are found in some of the micas. This element is also said to occur in all rocks, thermal waters, and vapors coming from beneath the earth's crust. Fluoride gases and fluoride-bearing ash are released by active volcanoes [19]. There were many incidents of injuries caused by naturally occurring fluorides. In 1845 the eruption of Hekla crippled and killed many animals in Iceland. Roholm clarified the cause of this epidemic by identifying the symptoms as typical of chronic fluoride poisoning. Gaud et al. [20] reported, in 1934, that the crippling diseases of cattle, horses, and sheep in Algeria, Tunisia and Morocco were due to fluoride dusts blown from the phosphate deposits out-cropping in those areas. Similar problems also occurred in Tennessee where soils near outcroppings of phosphate rock contained as much as 7000 ppm F. Fluorosis induced by grazing on dusty vegetation was responsible for animal deterioration.
3. Effects of Fluorine and Fluorides

a. On Humans

Almost all fluorine compounds, particularly the gaseous ones, can produce harmful effects on humans and animals. Elemental fluorine gas is approximately 10 times more toxic than HF on inhalation and oxygen fluoride OF\textsubscript{2} is roughly 20 times more toxic than F\textsubscript{2}. Rye [22] suggests that upon inhalation gaseous fluorides are absorbed more rapidly than are the less soluble fluoride containing dusts. However Collings et al. [23] believed all forms of fluoride are equally well absorbed by the lungs. Trace amounts of fluorides are beneficial particularly in the prevention of dental cavities, but large amounts create harmful effects.

i. Osteosclerosis

When fluorides are absorbed by the body either through inhalation or ingestion, a portion is stored in the bone while some appears in the urine. Deposition of fluorine in skeletal tissues seems related to the apatite structure of bone. The mineral phase of bone structure is hydroxyapatite [Ca\textsubscript{10} (PO\textsubscript{4})\textsubscript{6} (OH)\textsubscript{2}] which is analogous to crystalline fluorapatite [Ca\textsubscript{10} (PO\textsubscript{4})\textsubscript{6} F\textsubscript{2}]. The interchangeability of the fluoride ions for hydroxyl groups seem to favor its deposition in bone [24]. With continuing absorption and storage, the concentration of fluoride in bones continues to increase, but more slowly and eventually a steady state is achieved for a given relatively constant intake. At this stage the skeletal deposition consists chiefly of replacing fluoride lost during the metabolic turnover of bone. The increased storage may lead eventually to osteosclerosis [27]. These are many cases involving the aluminium industries [25] [12] [26], the cryolite industry [11] and phosphate fertilizers [9] [22]. Derryberry et al., [9] and Rye [22] suggested
that workmen whose average urinary fluoride concentration was not more than 4 mg/l in samples randomly collected would never develop osteosclerosis, while Irwin recommended 5 mg/l as the limit.

ii. **Dental Fluorosis (Mottling)**

The degree of dental fluorosis has often been used as an index of fluoride exposure in humans, but it is important to note that dental mottling only occurs if the fluoride is ingested during the period of tooth formation, i.e., pre-eruption [28]. Statistics compiled by Leone [29] from studies in the U.S. indicated that under American conditions, the prolonged ingestion of fluorides, in concentrations up to 8 ppm in drinking water, does not produce harmful physiological effects in humans except for dental mottling. The degree of mottling is observed only when fluorides are consumed during early years from 0 - 12 and at levels in excess of 2.0 ppm. Lindberg [8] found evidence of dental fluorosis and a low incidence of dental caries in school children in the area near a superphosphate plant. Sadilova [13] reported increased mottled dental enamel and lowered dental caries in the vicinity of aluminium plants.

iii. **Other Systems**

Hydrogen fluoride and fluorine are both highly reactive gases. There is no doubt that if they come in contact with skin or eyes, irritation and burns will result if concentrations are high enough. Other symptoms associated with fluoride intoxication include anemia, blood derangements, gastro-intestinal and neurological problems [28].

b. **On Animals**

The toxicity of fluorides to animals depends on the type of
fluoride ingested and degree of absorption into the bloodstream. The main intake of fluorides by animals is from grazing on pastures in the vicinity of fluoride emitting plants or those subject to dust from natural sources of fluoride.

1. **Animal Fluorosis**

The amount of fluoride stored in the bone increases within limits over a period of time apparently without changes in structure and function. At a more advanced stage high levels of fluoride will cause structure changes [30], that are usually first noticed as lameness or stiffness which can develop in one leg after another [28]. Characteristic pathologic bone changes have been observed radiographically in animals that have consumed high levels of fluorine for long periods of time. Porosis, sclerosis, hyperostosis and osteomalacia or any combination of these bilateral bone changes may occur [30]. In adult animals not unduly exposed to fluoride, the fluoride concentrations in whole bone rarely exceed 1,000 ppm (dry, fat-free basis). No abnormalities are detected in bones containing up to 2,500 ppm fluoride, but microscopic alterations are seen with higher levels approaching 5,000 ppm [32]. Most tissues and kidneys were found to contain only 5 ppm and 20 ppm respectively. There are many examples [1] [30] [31] [11] [20] of animal fluorosis in industrial fluorine emitting and natural occurrence regions, and also as a result of injection of fluorine into experimental animals.

2. **Other Systems**

Dental lesions, which are induced during tooth development and indicate the level of fluoride ingestion during the formation of enamel and dentine, are the most sensitive clinical sign. The degree of dental fluorosis can be correlated with the amount of fluorine in the bones, degree
of osteofluorosis, duration of exposure, age of animal during fluoride ingestion, amount of fluoride ingested during tooth formation, and other reactive processes of the body [30]. Other symptoms such as dryness and stiffness of hide, poor condition of the hair, elongated hooves, diarrhoea, impaired appetite, decreased weight gain, lowered milk yield, emaciation, cachexia, anaemia and various metabolic changes have been reported in the literature [33].

c. On Vegetation

Gaseous fluorides, such as hydrogen fluoride (HF) and silicon tetra-fluoride (SiF₄), are among the most toxic of all pollutants detrimental to vegetation [34]. Fluoride tolerance varies greatly among species and depends on the type of fluorine pollutant, environmental factors and susceptibility of the plant to fluorine which varies with the stage of development [35]. There are two types of fluorine injuries observed in plants (chlorosis and necrosis). Chlorosis appears at lower exposure-dosage values of fluorides. It is believed that plant leaves remove gaseous fluorides from the air and accumulate substantial quantities in leaf tissue. The accumulation is greatest in leaf tips or along the margin of older leaves. The result is a bleaching effect of chlorophyll in the area. General symptoms of chlorosis from low dosages of HF show small, irregularly shaped chlorotic spots at the tips and margins of the leaves, while the occurrence of necrosis is usually along the margins and tips of young leaves. It was also found that fluorides interfere with fertilization by inhibiting pollen germination or pollen tube growth [36] and by inhibiting a number of enzymes that are active in plant metabolism [28]. Brewer and co-workers estimated that the yield from orange trees was reduced by 15 and 22 percent when 75 and 150 ppm of fluoride had accumulated in the foliage [37].
d. **On Materials**

Because hydrogen fluoride and fluorine are both highly reactive gases, there is no doubt that atmospheric fluoride may cause damage to some materials. Hydrogen fluoride will etch glass if samples are exposed over prolonged periods to certain concentrations, especially if the glass surface is frequently covered with a film of water.

4. **Environmental Air Standards**

The Threshold Limit Value adopted by the Conference of Governmental Industrial Hygienists in 1953 for fluorine gas was 0.1 ppm. The generally accepted safe level for hydrogen fluoride in the air is 3 ppm.

The Emergency Exposure Limits (EEL) recommended by the NAS-NRC Committee on Toxicology are [10].

<table>
<thead>
<tr>
<th></th>
<th>10 min</th>
<th>30 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine (F₂), ppm</td>
<td>15</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Hydrogen fluoride (HF), ppm</td>
<td>20</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

The Maximum Allowable Concentrations (MAC) recommended by the U.K. Atomic Energy Authority Health and Safety Branch are [17].

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>0.2</td>
<td>mg/m³</td>
</tr>
<tr>
<td>Hydrogen Fluoride</td>
<td>2.0</td>
<td>mg/m³</td>
</tr>
<tr>
<td>Fluoride</td>
<td>2.5</td>
<td>mg/m³</td>
</tr>
</tbody>
</table>

For Ontario an index of 0.24 µg/m³ is recommended [28]. The total fluoride content of the normal London, England air would be of the order of 0.1 - 0.15 µg/m³. It was reported that during a 30-day sampling period in the industrial area of Hamilton, Ontario the airborne fluoride level was greater than 1.8 µg/m³ [28].
5. Detection and Measurement of Fluorine and Fluorides

Several techniques for determining the presence of fluorine and fluoride are available including:

i. Chemisorption method according to Buck and Stratmann [38]

ii. Titration of fluorine with thorium nitrate and alizarin sulfonylic acid [38]

iii. Volumetric determination [39]

iv. Fluorometric determination method [40]

v. Automatic hydrogen fluoride recording [41]

vi. Use of Ion Specific Electrodes [42]

6. Abatement Methods

General particulate control equipment can prevent air pollution by fluoride particulate emission from fluoride emitting industries. The following are typical industrial devices:

i. Electrostatic Precipitators

ii. Cyclones

iii. Filter Bags

iv. Scrubbers

For control of gaseous fluoride wet scrubbers are generally used.
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L. Hydrocarbons and Their Derivatives

Definitions

Hydrocarbons are compounds whose molecules consist of atoms of hydrogen and carbon only. Their derivatives are compounds having additional elements such as oxygen, nitrogen, sulfur, or chlorine. They may be gaseous, liquid or solid. They are found in nature or synthesized. The molecular weights of known hydrocarbons vary from 16.04 for methane to 9,000 for synthetic high molecular weight paraffins. The most prolific sources of hydrocarbons are petroleum and coal for the non-aromatic and aromatic series. Some of them are toxic, some are explosive. The volatility of hydrocarbons decreases with increasing carbon number. Those with a carbon number greater than about 12 are generally not found in appreciable concentrations in the gas phase in the atmosphere. Higher molecular weight hydrocarbons may exist as particles or in association with particulate matter. Hydrocarbons having a carbon number of 1 to 6 are gaseous at ordinary temperatures and pressures. Compounds with carbon number greater than 5 are liquids or solids in the pure state.

Hydrocarbons and their derivatives in the atmosphere can be classified into two categories. Primary compounds are those directly emitted into the atmosphere by technological or natural sources. Secondary compounds are those derived from atmospheric reactions of unstable hydrocarbon molecules or derivatives with substances in the atmosphere. Gaseous hydrocarbons are considered to be essential for the formation of photochemical air pollution. It is significant that those hydrocarbons are serious threats entirely due to their role as precursors of other compounds formed in the atmospheric photochemical system and not because of the direct effects of the hydrocarbons.
themselves. The rate of photochemical air pollution relates directly to the rate of concentration decrease of hydrocarbons. The commonly recognized products of photochemical reactions are: ozone, nitrogen dioxide, aldehyde, peroxycetyl nitrates (PAN), and some other minor products. Polynuclear aromatic hydrocarbons (PAH) occur in the atmosphere primarily as adsorbed compounds on soot particles. The estimate of total hydrocarbon emissions from major stationary sources is about 26 million tons per year [7], while the estimation for the transportation sources is about 17 million tons per year in 1968 in the U.S. [8]. Methane is the most abundant and stable hydrocarbon found in the air. The average methane level in Los Angeles air is 3.22 ppm.

Hydrocarbons and their derivatives discussed in this report are those considered to be potential pollutants in the atmosphere, which effect human health, animals and plant life, if certain concentrations are reached.
1. **Properties**

Aldehydes are members of an important class of organic compounds characterized by the presence of a carbonyl group (\(-\text{C}=\text{O}\)) and have at least one of the bonds from the carbon atom of the carbonyl group joined to a hydrogen atom. The lowest members of the series are irritating and unpleasant, but a pleasant odor develops with increasing molecular weight. The first member of the series of aldehydes, formaldehyde, is a gas at room temperature and pressure. The boiling points of succeeding members increase with the molecular weight. The first two members, formaldehyde and acetaldehyde are miscible with water in all proportions. In general solubility in water decreases with increasing molecular weight except where the presence of other groups within the molecule may exert significant influence. Formaldehyde and acrolein are the major aldehydes of interest to air pollution studies, due to their effects on humans and because their concentrations are generally higher than those of other aldehydes present in the atmosphere.

2. **Potential Sources and Levels of Atmospheric Emissions**

The potential sources of aldehydes that pollute the atmosphere result from two main processes: incomplete combustion of organic compounds and atmospheric photochemical reactions.

a. **Mobile Combustion**

This source includes automobiles, diesel vehicles and aircraft. Automobile exhaust must be a major source of aldehyde air pollution. The important factors affecting the concentration of aldehydes emitted are type of gasoline, type of engine, different engine modes and condition of the engine [1].
Formaldehyde is the major aldehyde from automobile and diesel vehicles. Analysis by various investigators showed that formaldehyde accounted for 50 to 70% of the total aldehydes, while acrolein was responsible for 3 to 10 percent (on a mole basis) [2] [3] [4]. Four engine, jet, aircraft discharge 0.2 to 2 pounds of aldehydes per hour into the atmosphere [1] [5] [6] with formaldehyde content generally being greater than sixty percent of the total aldehydes measured [6].

The following tables summarize some of the reports on aldehyde emissions from automobile engines, diesel engines and commercial aircraft.

<table>
<thead>
<tr>
<th>Source</th>
<th>Aldehydes As Formaldehyde $\mu g/m^3$</th>
<th>Formaldehyde $\mu g/m^3$</th>
<th>Acrolein $\mu g/m^3$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel: House Brand</strong> (Mid-Continent Area Regular Grade)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>58,800</td>
<td>24,000</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td>40 mph cruise</td>
<td>184,800</td>
<td>99,600</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td>50 mph cruise</td>
<td>114,000</td>
<td>48,000</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td>60 mph cruise</td>
<td>112,800</td>
<td>46,800</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td>40 mph 2/3 max torque</td>
<td>115,200</td>
<td>39,600</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td>Acceleration (15-60 mph in 25 sec)</td>
<td>72,000-142,000</td>
<td>36,000-46,800</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td>Deceleration (50-15 mph in 25 sec)</td>
<td>289,000-967,200</td>
<td>106,800-282,000</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td><strong>West Coast regular brand (WOGA No. 3)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>60,000</td>
<td>34,800</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td>40 mph cruise</td>
<td>140,400</td>
<td>80,400</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td>60 mph cruise</td>
<td>114,000</td>
<td>49,200</td>
<td></td>
<td>3,9</td>
</tr>
<tr>
<td>40 mph 2/3 max torque</td>
<td>61,200</td>
<td>36,000</td>
<td></td>
<td>3,9</td>
</tr>
</tbody>
</table>

Table L(1) - Aldehyde Emissions From Automobile Engines
<table>
<thead>
<tr>
<th>Source</th>
<th>Aldehydes As Formaldehyde ( \mu g/m^3 )</th>
<th>Formaldehyde ( \mu g/m^3 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Coast aromatic (WOCA No. 2A)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>88,800</td>
<td>19,200</td>
<td>3, 9</td>
</tr>
<tr>
<td>40 mph cruise</td>
<td>180,000</td>
<td>54,000</td>
<td>3, 9</td>
</tr>
<tr>
<td>60 mph cruise</td>
<td>106,800</td>
<td>39,600</td>
<td>3, 9</td>
</tr>
<tr>
<td>40 mph 2/3 max torque</td>
<td>129,600</td>
<td>21,600</td>
<td>3, 9</td>
</tr>
<tr>
<td>West Coast paraffinic (WOCA NO. 2P)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>62,400</td>
<td>32,400</td>
<td>3, 9</td>
</tr>
<tr>
<td>40 mph cruise</td>
<td>163,200</td>
<td>97,200</td>
<td>3, 9</td>
</tr>
<tr>
<td>60 mph cruise</td>
<td>128,400</td>
<td>51,600</td>
<td>3, 9</td>
</tr>
<tr>
<td>40 mph 2/3 max torque</td>
<td>98,400</td>
<td>57,600</td>
<td>3, 9</td>
</tr>
<tr>
<td>Gasoline, 707 in (^3) (44 - passenger coach)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>36,000; 0.048 SCFH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Acceleration</td>
<td>19,200; 0.157 SCFH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cruise 30 mph</td>
<td>8,400; 0.048 SCFH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Deceleration</td>
<td>343,200; 0.756 SCFH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Chicago Transit Driving Pattern</td>
<td>0.17 SCFH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Propane, 477 in (^3) (50 passenger coach)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>36,000; 0.025 SCFH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Acceleration</td>
<td>21,600; 0.157 SCFH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cruise, 30 mph</td>
<td>27,600; 0.123 SCFH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Deceleration</td>
<td>206,400; 0.247 SCFH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Chicago Transit Driving Pattern</td>
<td>0.11 SCFH</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Table L (1) - 1 Aldehyde Emissions From Automobile Engines
<table>
<thead>
<tr>
<th>Source</th>
<th>Aldehydes (µg/m³) (As Formaldehyde)</th>
<th>Formaldehyde (µg/m³)</th>
<th>Acrolein (µg/m³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel, 2 cycle, 426 in³ (45-passenger coach)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>10,800; 0.073 SCFH</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Acceleration</td>
<td>20,400; 0.509 SCFH</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cruise, 30 mph</td>
<td>13,200; 0.203 SCFH</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Deceleration</td>
<td>34,800; 0.541 SCFH</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Chicago Transit Driving Pattern</td>
<td>0.24 SCFH</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Diesel, 4 cycle, No. 2 fuel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>8,160</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>No load</td>
<td>2,160</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>1/2 load</td>
<td>8,160</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Full load</td>
<td>5,160</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Diesel, 2 cycle, No. 2 fuel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idle</td>
<td>13,200</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>No load</td>
<td>8,760</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1/2 load</td>
<td>9,720</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Full load</td>
<td>15,600</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1,200 rpm, no load</td>
<td>49,200</td>
<td>39,600</td>
<td>12,500</td>
<td>4</td>
</tr>
<tr>
<td>1/4 load</td>
<td>21,600</td>
<td>14,400; 0.06 lb/gal fuel</td>
<td>4,500</td>
<td>4</td>
</tr>
<tr>
<td>1/2 load</td>
<td>28,800</td>
<td>21,600</td>
<td>3,500</td>
<td>4</td>
</tr>
<tr>
<td>3/4 load</td>
<td>26,400</td>
<td>21,600</td>
<td>4,500</td>
<td>4</td>
</tr>
<tr>
<td>Full load</td>
<td>38,400</td>
<td>31,200; 0.05 lb/gal fuel</td>
<td>2,000</td>
<td>4</td>
</tr>
<tr>
<td>1,500 rpm, no load</td>
<td>50,400</td>
<td>33,600</td>
<td>13,750</td>
<td>4</td>
</tr>
<tr>
<td>1/4 load</td>
<td>34,800</td>
<td>21,600</td>
<td>3,500</td>
<td>4</td>
</tr>
</tbody>
</table>

Table L(1) - 2' Aldehyde Emissions From Diesel Engines
<table>
<thead>
<tr>
<th>Source</th>
<th>Aldehydes (µg/m³) (As Formaldehyde)</th>
<th>Formaldehyde (µg/m³)</th>
<th>Acrolein (µg/m³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 load</td>
<td>32,400</td>
<td>20,400</td>
<td>4,250</td>
<td>4</td>
</tr>
<tr>
<td>3/4 load</td>
<td>31,200</td>
<td>22,800</td>
<td>4,750</td>
<td>4</td>
</tr>
<tr>
<td>Full load</td>
<td>55,200</td>
<td>37,200</td>
<td>7,500</td>
<td>4</td>
</tr>
<tr>
<td>1,800 rpm, no load</td>
<td>48,000</td>
<td>39,600</td>
<td>12,500</td>
<td>4</td>
</tr>
<tr>
<td>1/4 load</td>
<td>34,800</td>
<td>24,000</td>
<td>8,000</td>
<td>4</td>
</tr>
<tr>
<td>1/2 load</td>
<td>28,800</td>
<td>18,000</td>
<td>6,500</td>
<td>4</td>
</tr>
<tr>
<td>3/4 load</td>
<td>44,400</td>
<td>36,000</td>
<td>5,750</td>
<td>4</td>
</tr>
<tr>
<td>Full load</td>
<td>67,200</td>
<td>48,000</td>
<td>8,250</td>
<td>4</td>
</tr>
</tbody>
</table>

Table L (1) - 2 Aldehyde Emissions From Diesel Engines

<table>
<thead>
<tr>
<th>Source, turboprop, T-56</th>
<th>Aldehydes (As Formaldehyde)</th>
<th>Formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Departure*</td>
<td>0.14 lb</td>
<td></td>
</tr>
<tr>
<td>Arrival*</td>
<td>0.13 lb</td>
<td></td>
</tr>
<tr>
<td>100% power (take off)</td>
<td>0.5 lb/hr</td>
<td>0.2 lb/hr.</td>
</tr>
<tr>
<td>75% power (cruise &amp; approach)</td>
<td>0.2 lb/hr.</td>
<td>0.2 lb/hr.</td>
</tr>
<tr>
<td>65% power (idle)</td>
<td>0.3 lb/hr</td>
<td>0.2 lb/hr.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source, conventional jet, J-57</th>
<th>Aldehydes (As Formaldehyde)</th>
<th>Formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Departure*</td>
<td>0.19 lb</td>
<td></td>
</tr>
<tr>
<td>Arrival*</td>
<td>0.25 lb</td>
<td></td>
</tr>
<tr>
<td>100% power (take off)</td>
<td>0.5 lb/hr</td>
<td>0.4 lb/hr.</td>
</tr>
<tr>
<td>75% power (cruise &amp; approach)</td>
<td>0.4 lb/hr</td>
<td>0.3 lb/hr.</td>
</tr>
<tr>
<td>65% power (idle)</td>
<td>0.4 lb/hr</td>
<td>0.4 lb/hr.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source, fan-jet, TF-33</th>
<th>Aldehydes (As Formaldehyde)</th>
<th>Formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Departure*</td>
<td>1.00 lb</td>
<td></td>
</tr>
<tr>
<td>Arrival*</td>
<td>1.20 lb</td>
<td></td>
</tr>
</tbody>
</table>

Table L(1) - 3' Aldehyde Emissions From Commercial Aircraft [6]
<table>
<thead>
<tr>
<th>Source</th>
<th>Aldehydes (As Formaldehyde)</th>
<th>Formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% power (take off)</td>
<td>0.4 lb/hr.</td>
<td></td>
</tr>
<tr>
<td>75% power (cruise &amp;</td>
<td>0.3 lb/hr.</td>
<td></td>
</tr>
<tr>
<td>approach)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65% power (idle)</td>
<td>0.4 lb/hr.</td>
<td></td>
</tr>
</tbody>
</table>

*Based on 4 Engines, Taxiing Time, plus Take Off and Climb-Out or Approach and Landing

Table L (1) - 3 Aldehyde Emissions From Commercial Aircraft [6]

b. **Stationary Combustion Sources**

These sources consist of power plants and utilities using coals, fuel oil or natural gas as fuel. Such sources may become potential polluters, if the equipment is not operating correctly or the control methods are inadequate.

Aldehydes and formaldehyde have been found in small amounts from sources that burn coal. Data from the U.S. Department of Health, Education and Welfare in 1966 [11] showed that the discharge of aldehydes as formaldehyde was 0.005 lb/ton of coal burned. Haney, Risman and Cumnar [12] estimated that average emission from distillate oil was 2.07 pounds of aldehydes per 1,000 gallons of oil, while emission from residual oil was 1.3 pounds. Weisburd [13] reported that aldehyde emissions from power plants were about $1$ lb/10$^6$ ft$^3$ (0.02 lb/1000 lb of gas) and for industrial operations about $2$ lb/10$^6$ft$^3$ (0.1 lb/1,000 lb of gas).

The following tables summarize typical reports on aldehyde emissions from stationary combustion sources:
<table>
<thead>
<tr>
<th>Type of Boiler Firing</th>
<th>Formaldehyde lb/10^6 Btu</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Suspension-Fired Units</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vertical</td>
<td>2.5 x 10^{-4}</td>
<td>14</td>
</tr>
<tr>
<td>Corner</td>
<td>1.7 x 10^{-4}</td>
<td>14</td>
</tr>
<tr>
<td>Front-wall</td>
<td>1.4 x 10^{-4}</td>
<td>14</td>
</tr>
<tr>
<td>Spreader-stoker</td>
<td>0.6 x 10^{-4}</td>
<td>14</td>
</tr>
<tr>
<td>Cyclone</td>
<td>1.7 x 10^{-4}</td>
<td>14</td>
</tr>
<tr>
<td>Horizontal opposed</td>
<td>1.0 x 10^{-4}</td>
<td>14</td>
</tr>
<tr>
<td><strong>Grate-Fired Units</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chain grate</td>
<td>1.4 x 10^{-4}</td>
<td>15</td>
</tr>
<tr>
<td>Spreader stoker</td>
<td>2.2 x 10^{-4}</td>
<td>15</td>
</tr>
<tr>
<td>Underfeed stoker</td>
<td>2.1 x 10^{-4}</td>
<td>15</td>
</tr>
<tr>
<td>Underfeed stoker</td>
<td>3.8 x 10^{-4}</td>
<td>15</td>
</tr>
<tr>
<td><strong>Source</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power Plants</td>
<td>0.005 lb/ton of coal</td>
<td>11</td>
</tr>
<tr>
<td>Industrial Stokers</td>
<td>0.005 lb/ton of coal</td>
<td>11</td>
</tr>
<tr>
<td>Domestic Units</td>
<td>0.005 lb/ton of coal</td>
<td>11</td>
</tr>
</tbody>
</table>

Table L (1) - Aldehyde Emissions From Coal Combustion

<table>
<thead>
<tr>
<th>Source</th>
<th>µg/m³</th>
<th>ppm</th>
<th>lb/hr</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel oil No. 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scotch marine boiler 150 hp</td>
<td>6,000</td>
<td>5</td>
<td>0.04</td>
<td>16</td>
</tr>
<tr>
<td>Ceramic kiln</td>
<td>4,200</td>
<td>3.5</td>
<td>0.0037</td>
<td>16</td>
</tr>
<tr>
<td>Ceramic kiln</td>
<td>4,080</td>
<td>3.4</td>
<td>0.020</td>
<td>16</td>
</tr>
<tr>
<td><strong>Fuel oil, heavy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fire tube boiler, 120 hp</td>
<td>8,400</td>
<td>7</td>
<td>0.05</td>
<td>16</td>
</tr>
<tr>
<td>Scotch marine boiler 125 hp</td>
<td>10,800</td>
<td>9</td>
<td>0.08</td>
<td>16</td>
</tr>
<tr>
<td>Water tube boiler 245 hp</td>
<td>9,600</td>
<td>8</td>
<td>0.2</td>
<td>16</td>
</tr>
<tr>
<td>Water tube boiler 425 hp</td>
<td>4,800</td>
<td>4</td>
<td>0.2</td>
<td>16</td>
</tr>
<tr>
<td>Water tube boiler 460 hp</td>
<td>8,400</td>
<td>7</td>
<td>0.2</td>
<td>16</td>
</tr>
<tr>
<td>Water tube boiler 500 hp</td>
<td>20,400</td>
<td>17</td>
<td>1.0</td>
<td>16</td>
</tr>
</tbody>
</table>

Table L(1) - Aldehyde Emission From Combustion of Fuel Oil
<table>
<thead>
<tr>
<th>Source</th>
<th>mg/m$^3$</th>
<th>ppm</th>
<th>lb/hr</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water tube boiler, 580 hp</td>
<td>10,200</td>
<td>8.5</td>
<td>0.12</td>
<td>16</td>
</tr>
<tr>
<td>Water tube boiler, 870 hp</td>
<td>57,600</td>
<td>48</td>
<td>1.8</td>
<td>16</td>
</tr>
<tr>
<td>Fuel oil, No. 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fire tube boiler, 60 hp</td>
<td>10,800</td>
<td>9</td>
<td>0.017</td>
<td>16</td>
</tr>
<tr>
<td>Fire tube boiler, 300 hp</td>
<td>7,200</td>
<td>6</td>
<td>0.08</td>
<td>16</td>
</tr>
<tr>
<td>Scotch marine boiler, 200 hp</td>
<td>62,400</td>
<td>52</td>
<td>0.50</td>
<td>16</td>
</tr>
<tr>
<td>Scotch marine boiler, 350 hp</td>
<td>3,600</td>
<td>3</td>
<td>0.06</td>
<td>16</td>
</tr>
<tr>
<td>Water tube boiler, 100 hp</td>
<td>6,000</td>
<td>5</td>
<td>0.013</td>
<td>16</td>
</tr>
<tr>
<td>Water tube boiler, 200 hp</td>
<td>9,600</td>
<td>8</td>
<td>0.04</td>
<td>16</td>
</tr>
<tr>
<td>Water tube boiler, 245 hp</td>
<td>8,400</td>
<td>7</td>
<td>0.04</td>
<td>16</td>
</tr>
<tr>
<td>Oil heater</td>
<td>13,200</td>
<td>11</td>
<td>0.015</td>
<td>16</td>
</tr>
</tbody>
</table>

| Kerosene burners                           |          |     |       |           |
| Fan-assisted pot (20,000 k cal/hr output)  |          |     |       |           |
| Good condition                             | 4,800    | 4   |       | 1         |
| Bad condition                              | 16,800   | 14  |       | 1         |
| Wallflame (10,000 k cal/hr output)         |          |     |       |           |
| Good condition                             | 3,600    | 3   |       | 1         |
| Bad condition                              | 30,000   | 25  |       | 1         |
| Pressure atomizing (10,500 kcal/hr output) |          |     |       |           |
| Good condition                             | 3,600    | 3   |       | 1         |
| Bad condition                              | 12,000   | 10  |       | 1         |

Table L (1) - 5 Aldehyde Emission From Combustion of Fuel Oil
<table>
<thead>
<tr>
<th>Source</th>
<th>Aldehyde $\text{kg/m}^3$ (lb/10^6 $\text{Btu}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas-fired appliances and industrial and commercial equipment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bunsen burner</td>
<td>2,400</td>
<td>1</td>
</tr>
<tr>
<td>Oven range</td>
<td>13,200 (0.02)</td>
<td>1</td>
</tr>
<tr>
<td>Water heater, 100 gal</td>
<td>9,600 (0.01)</td>
<td>1</td>
</tr>
<tr>
<td>Floor furnace</td>
<td>3,600 (0.005)</td>
<td>1</td>
</tr>
<tr>
<td>Steam boiler (10^7 Btu/hr)(low fire)</td>
<td>6,000 (0.01)</td>
<td>1</td>
</tr>
<tr>
<td>Industrial burners</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boilers and process heaters</td>
<td>58,800</td>
<td>1</td>
</tr>
<tr>
<td>Scotch marine boilers</td>
<td>(0.0028)</td>
<td></td>
</tr>
<tr>
<td>Fire tube boilers</td>
<td>2,400 - 8,400</td>
<td>1</td>
</tr>
<tr>
<td>Water tube boilers</td>
<td>4,800</td>
<td>1</td>
</tr>
<tr>
<td>75 gal water heater</td>
<td>3,600 - 13,200</td>
<td>1</td>
</tr>
<tr>
<td>Space heater</td>
<td>2,400</td>
<td>1</td>
</tr>
<tr>
<td>Bake oven</td>
<td>7,200</td>
<td>1</td>
</tr>
<tr>
<td>Industrial oven, indirect</td>
<td>3,600 - 7,200</td>
<td>1</td>
</tr>
<tr>
<td>Ceramic kilns, indirect</td>
<td>2,400 - 8,400</td>
<td>1</td>
</tr>
<tr>
<td>Power plants</td>
<td>0.02 lb/1,000 lb gas</td>
<td>13</td>
</tr>
<tr>
<td>Industrial</td>
<td>0.1 lb/1,000 lb gas</td>
<td>13</td>
</tr>
<tr>
<td>Domestic and commercial</td>
<td>0.25 lb/1,000 lb gas</td>
<td>13</td>
</tr>
</tbody>
</table>

Table L (1) - 6 Aldehyde Emissions From Natural Gas Combustion
c. **Incinerators**

Inefficient incinerators cause hydrocarbon emissions as a result of incomplete combustion. Jacobs [17] reported that formaldehyde and acrolein are probably the principal aldehydes discharged from such incinerators. It has been estimated that open burning of refuse is responsible for 3.0 to 4.0 pounds of aldehydes per ton of refuse [12].

Table L (1) - 7 shows typical emissions from incinerators.

<table>
<thead>
<tr>
<th>Source</th>
<th>Aldehydes (As Formaldehyde)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Domestic Incinerators</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AGA prototype, shredded paper</td>
<td>9,600 - 25,200 µg/m³; 0.9-2.3 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>AGA prototype, USASI domestic wastes</td>
<td>9,600 µg/m³; 0.8 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>AGA prototype, other refuse mixtures</td>
<td>20,400-26,400 µg/m³; 1.2-3.1 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>New manufacturers' units, shredded paper</td>
<td>4,800-80,400 µg/m³; 0.17-15.9 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>New manufacturers' units, USASI domestic wastes</td>
<td>30,000-48,000 µg/m³</td>
<td>1</td>
</tr>
<tr>
<td>Older units, shredded paper</td>
<td>28,800 - 57,600 µg/m³</td>
<td>1</td>
</tr>
<tr>
<td>Older units, USASI domestic wastes</td>
<td>6,000-36,000 µg/m³; 5 - 6 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>Domestic, single chamber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without auxiliary gas burning</td>
<td>6 lb/ton refuse</td>
<td>18</td>
</tr>
<tr>
<td>With auxiliary gas burning</td>
<td>2 lb/ton refuse</td>
<td>18</td>
</tr>
<tr>
<td><strong>Municipal Incinerators</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glendale, California with scrubber</td>
<td>1,200 - 12,000 µg/m³</td>
<td>1</td>
</tr>
<tr>
<td>Glendale, California without scrubber</td>
<td>1,200-26,400 µg/m³</td>
<td>1</td>
</tr>
<tr>
<td>Alhambra, California with spray scrubber</td>
<td>58,000 µg/m³; 1.1 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>Three units in California with scrubber</td>
<td>10,800-32,400 µg/m³</td>
<td>1</td>
</tr>
</tbody>
</table>

Table L(1) - 7' Aldehyde Emissions From Incinerators
<table>
<thead>
<tr>
<th>Sources</th>
<th>Aldehydes (As Formaldehyde)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three units in California without scrubbers</td>
<td>1,200-56,400 µg/m³</td>
<td></td>
</tr>
<tr>
<td>Incinerator, multi-chamber</td>
<td>1.1 lb/ton refuse</td>
<td>19</td>
</tr>
<tr>
<td><strong>Other Incinerators</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single chamber</td>
<td>0.03 - 2.7 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>Wood waste</td>
<td>40,800 µg/m³; 1.8 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>Backyard (Battelle), paper and trimmings</td>
<td>912,000 µg/m³; 29 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>Backyard, 6 ft³, paper</td>
<td>58,000 µg/m³; 2.1 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>Backyard, 6 ft³, trimmings</td>
<td>122,400 µg/m³; 5.7 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td>Backyard, 3 ft³, mixed rubbish</td>
<td>5.1 lb/ton</td>
<td>1</td>
</tr>
<tr>
<td><strong>Commercial and Domestic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small and/or single stage</td>
<td>3 lb/ton refuse (0.1-4.5 lb/ton)</td>
<td>12</td>
</tr>
<tr>
<td><strong>Industrial and Commercial</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single chamber</td>
<td>5 - 64 lb/ton</td>
<td>18</td>
</tr>
<tr>
<td>Multiple chamber</td>
<td>0.3 lb/ton refuse (0.14-0.85 lb/ton)</td>
<td>18</td>
</tr>
<tr>
<td>Apartment, flue-fed</td>
<td>5 lb/ton refuse</td>
<td>19</td>
</tr>
<tr>
<td><strong>Incinerator, Automobile</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Afterburner on</td>
<td>3,600 µg/m³</td>
<td>20</td>
</tr>
<tr>
<td>Afterburner off</td>
<td>19,200 µg/m³</td>
<td>20</td>
</tr>
</tbody>
</table>

Table L (1) - 7 Aldehyde Emissions From Incinerators

d. Petroleum Refineries

Petroleum refineries can be local sources of aldehyde emission into the atmosphere. The major contributors are catalytic cracking units, with smaller amounts being emitted from the refinery boilers, process heaters, and compressor engines [21]. Table L (1) - 8 shows aldehyde emissions from oil refineries in the Los Angeles area.
<table>
<thead>
<tr>
<th>Unit Source</th>
<th>Aldehyde (µg/m³)</th>
<th>(As Formaldehyde) ppm</th>
<th>Emission Rates in lb/1000 bl tons/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic Cracking</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unit Fluid</td>
<td>3,600-48,00</td>
<td>3-130</td>
<td>19</td>
</tr>
<tr>
<td>Thermoform</td>
<td>10,800-232,400</td>
<td>9-177</td>
<td></td>
</tr>
<tr>
<td>Boiler and Process</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater</td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>Fuel gas</td>
<td></td>
<td>3.1 lb/1000 ft³ gas</td>
<td></td>
</tr>
<tr>
<td>Fuel oil</td>
<td></td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Compressor Internal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combustion Engines</td>
<td></td>
<td>0.11 lb/1000 ft³ gas</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>2.4</td>
</tr>
</tbody>
</table>

Table L(l)-8 Aldehyde Emissions From Los Angeles Oil Refineries [21]

e. Glycerine, Oil and Fat Industries

Aldehydes from these sources are acrolein resulting from the thermal decomposition of glycerine [22].

f. Formaldehyde Manufacturers and Applications of Formaldehyde

Most of the formaldehyde is manufactured by the oxidation of methanol. A small amount is produced by the partial oxidation of gaseous hydrocarbons. Levaggi and Feldstein [23], analyzing for aldehydes in the effluent from a formaldehyde plant, found that approximately 3,000,000 µg/m³ of acetaldehyde were present. Formaldehyde use in numerous chemical industries for synthetic resin consumes over half of the production. It is also used in the synthesis of organics, resins, rubber, tanning, paper, cosmetics, food, dyes, medicinals, disinfectants and fumigants, textiles, insecticides, metal and explosive production.
Drying and Baking Operations

These sources contribute significantly to the aldehyde air pollution problem. Major amounts come from the drying of coatings. Coating compounds, dissolved in an organic solvent, are dried or baked in an oven to remove the solvent. Typical examples of such operations are automobile painting, coating of paper with resins or adhesives, and application of protective coatings to metals. Table L (1)–9 shows aldehyde emission levels in typical industrial oven effluents.

<table>
<thead>
<tr>
<th>Process</th>
<th>Predominant Solvent Type</th>
<th>Aldehydes (as Formaldehyde) (μg/m³)</th>
<th>Formaldehyde (μg/m³)</th>
<th>Acrolein (μg/m³)</th>
<th>Persp. Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesive coating</td>
<td>Low boiling alkanes</td>
<td>88,800(5)</td>
<td>73,200–106,800</td>
<td>800(2)</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,000(6)</td>
<td>1,200–6,000</td>
<td></td>
<td>12.5</td>
</tr>
<tr>
<td>Tube coating</td>
<td>Alcohols</td>
<td>5,100(4)</td>
<td>0–12,000</td>
<td>2,700(4)</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19,800(6)</td>
<td>1,200–51,600</td>
<td></td>
<td>12.5</td>
</tr>
<tr>
<td>Auto body painting</td>
<td>Mixed ketones</td>
<td>15,000(4)</td>
<td>4,600–32,400</td>
<td>9,800(4)</td>
<td>3,325(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27,960(4)</td>
<td>14,800–56,400</td>
<td>19,200(3)</td>
<td>1,975(2)</td>
</tr>
<tr>
<td>Container coating</td>
<td>High boiling alkanes</td>
<td>52,800(4)</td>
<td>33,600–102,000</td>
<td>19,200(4)</td>
<td>9,300(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27,000(4)</td>
<td>12,000–34,800</td>
<td>9,600(4)</td>
<td>9,300(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>79,200(4)</td>
<td>34,800–134,400</td>
<td>37,200(4)</td>
<td>10,000–15,500</td>
</tr>
<tr>
<td>Container coating</td>
<td>Aromatics</td>
<td>22,800(4)</td>
<td>8,400–21,400</td>
<td>3,840(4)</td>
<td>1,875(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33,960(4)</td>
<td>20,400–45,600</td>
<td>6,000(4)</td>
<td>1,775(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60,600(4)</td>
<td>39,600–87,600</td>
<td>15,000(4)</td>
<td>7,000(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>79,200(4)</td>
<td>58,900–132,000</td>
<td>8,400(4)</td>
<td>5,280(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>490,800(4)</td>
<td>277,200–820,800</td>
<td>7,800(4)</td>
<td>21,750(2)</td>
</tr>
<tr>
<td>Container coating</td>
<td>Aromatics</td>
<td>82,800(4)</td>
<td>45,600–105,000</td>
<td>35,600(4)</td>
<td>21,750(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60,000(4)</td>
<td>26,400–91,200</td>
<td>25,200(4)</td>
<td>11,500(2)</td>
</tr>
</tbody>
</table>

Number in parentheses represents number of determinations made.
G: From vent near oven entrance; B: From oven; C: Near front of oven at inlet to exhaust system; D: From stack after passing through direct-flame, gas-fired afterburner; E: From stack after passing through catalytic afterburner.

May be in error due to interfering compound.

Table L(1)–9 Aldehyde Emissions From Industrial Oven Effluents [24]
h. **Photochemical Formation**

Significant amounts of atmospheric aldehydes, especially formaldehyde, appear as major products of the photooxidation of unsaturated and aromatic hydrocarbon pollutants. Acrolein is derived mainly from the photooxidation of diolefins, such as 1,3-butadiene. The photochemical reactions in the atmosphere depend on the light acceptor, (that is nitrogen dioxide), the variable intensity of the light and the concentrations of the unsaturated hydrocarbons. Many experimental studies have been done on photooxidation of hydrocarbons with oxides of nitrogen and ozone in the irradiation chamber [25] [26] [27] [28] [29] [30] [31] [32] [33] [34] [35]. The Altshuller and Bufalini [36] summary of the yields of formaldehyde, acrolein and total aldehydes from photooxidation of hydrocarbons by oxides of nitrogen in relation to initial concentrations is shown in Table I (1-10). Altshuller [37] showed that for air samples taken in Los Angeles, California, between 7 and 8 a.m., the content of formaldehyde was approximately 120 µg/m³ (0.1 ppm). Upon irradiating the samples in sunlight for several hours, the formaldehyde increased to 420 µg/m³ (0.35 ppm). The final concentration of aldehydes (as formaldehyde) was approximately 600 µg/m³ (0.5 ppm). Thus formaldehyde accounted for about 60 percent of the total aldehydes in the irradiated mixture.
<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Formaldehyde</th>
<th>Acetaldehyde</th>
<th>Acrolein</th>
<th>Acetone</th>
<th>Total or other aldehydes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0.35&lt;sup&gt;a&lt;/sup&gt;, 0.45&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&lt;0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>0.22&lt;sup&gt;c&lt;/sup&gt;, 0.45&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Butene</td>
<td>0.40&lt;sup&gt;a&lt;/sup&gt;, 0.45&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.4&lt;sup&gt;a&lt;/sup&gt;, 0.15-0.2&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
<td>0.03-0.05&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Isobutene</td>
<td>0.45&lt;sup&gt;a&lt;/sup&gt;, 0.4&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.6&lt;sup&gt;e&lt;/sup&gt;, 0.5-0.7&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>0.9&lt;sup&gt;a&lt;/sup&gt;, 0.5&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>0.35&lt;sup&gt;g&lt;/sup&gt;, 0.33&lt;sup&gt;h&lt;/sup&gt;</td>
<td>0.4&lt;sup&gt;i&lt;/sup&gt;, 0.15&lt;sup&gt;j&lt;/sup&gt;, 0.6&lt;sup&gt;g&lt;/sup&gt;, 0.25-0.4&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-2-butene</td>
<td></td>
<td>1.40&lt;sup&gt;a&lt;/sup&gt;, 1.5&lt;sup&gt;f&lt;/sup&gt;, 0.9-1.2&lt;sup&gt;h&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>0.6&lt;sup&gt;a&lt;/sup&gt;, 0.6&lt;sup&gt;e&lt;/sup&gt;, 0.5&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.9&lt;sup&gt;a&lt;/sup&gt;, 0.8-1.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.55&lt;sup&gt;a&lt;/sup&gt;, 0.25&lt;sup&gt;j&lt;/sup&gt;</td>
<td>~0.02&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;b&lt;/sup&gt;, 0.98&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>0.55&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td>0.2&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>2-Methyl-1-butene</td>
<td>0.5&lt;sup&gt;a&lt;/sup&gt;, 0.3&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.75&lt;sup&gt;a&lt;/sup&gt;, 0.4-0.5&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
<td>0.45&lt;sup&gt;a&lt;/sup&gt;, 0.3-0.4&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>1,3-Pentadiene</td>
<td>0.65&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methyl-1,3-Pentadiene</td>
<td>0.55&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>0.35&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-3-hexene</td>
<td></td>
<td></td>
<td></td>
<td>0.4&lt;sup&gt;i&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>2,3-Dimethyl-2-butene</td>
<td>0.25&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>0.4&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3-Dimethyl-1,3-butadiene</td>
<td>0.65&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Heptene</td>
<td>0.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Xylene</td>
<td>0.15&lt;sup&gt;k&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.15&lt;sup&gt;k&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>0.15&lt;sup&gt;k&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,4,5-Tetramethylbenzene</td>
<td>0.15&lt;sup&gt;k&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Schuck and Doyle. [25]  
<sup>b</sup> Stephens and Scott. [26]  
<sup>c</sup> Albright and Cohen. [27]  
<sup>d</sup> Stephens. [28]  
<sup>e</sup>Schuck. [29]  
<sup>f</sup>Sigsby. [30]  
<sup>g</sup> Stephens. [31]  
<sup>h</sup>Tuesday. [32]  
<sup>i</sup> Albright and Bufalini. [33]  
<sup>j</sup> Leighton. [34]  
<sup>k</sup> Vrbaski and Cvitanovic. [35]

Table L (1)–10 Yields of Carbonyl Compounds in Experimental Photooxidation of Hydrocarbons with Oxides of Nitrogen [36]

3. Effects of Aldehydes

a. On Humans

Unsaturated and halogenated aldehydes generally cause more significant ill effects to humans than do the saturated aldehydes. Aromatic and heterocyclic aldehydes are least offensive. The toxicity of aldehydes generally decreases as the chain length increases [38].
Irritation

The principal effect of lower, water-soluble aldehydes, especially formaldehyde vapors, is on the mucous membranes of the eyes, nose, and the upper respiratory tract, where irritation becomes significant. The higher, less soluble aldehydes, tend to penetrate more deeply into the respiratory tract and may affect the lungs [40]. Repeated exposures may result in chronic irritation of those organs [40]. Formaldehyde vapors may also cause skin irritation. Renzetti and Schuck [39], who studied the photooxidation of hydrocarbons, found that formaldehyde and acrolein were the major cause of the eye irritation produced by photochemical products. Symptoms that have been observed from nonfatal exposures to formaldehyde include lacrimation, sneezing, coughing, dyspnea, a feeling of suffocation, rapid pulse, headache, weakness and fluctuation in body temperature. There are many reports which indicate that irritation of the eyes and upper respiratory tract can first be detected at formaldehyde levels of 12 to 1230 µg/m³ (0.01 to 1.0 ppm) [38] [41] [42] [43] [44] [45]. Fassett [38] noted that discomfort occurs when the concentration reaches 2,460 to 3,690 µg/m³ (2 to 3 ppm) and the discomfort increases rapidly and mild lacrimation may appear in some cases when the concentration reaches 4,920 to 6,150 µg/m³ (4 to 5 ppm). At concentrations of 12,300 to 24,600 µg/m³ (10 to 20 ppm), breathing becomes difficult, coughing occurs, burning of the nose and throat becomes more severe, and the irritation extends to the trachea [38]. It has been estimated that exposure to 61,500 to 123,000 µg/m³ (50 to 100 ppm) for 5 to 10 minutes might cause serious injury [38].

Acrolein vapors are highly toxic to humans. They are extremely irritating to the eyes and respiratory tract [38] [40] [46] [49]. Repeated
contact with the skin may produce chronic irritation and dermatitis. Symptons reported after inhalation of acrolein include lacration, swelling of the eyelids, shortness of breath, pharyngitis, laryngitis, bronchitis, oppression in the chest, somnolence, and asthma [38] [47] [48] [49]. Concentrations of acrolein as low as 675 μg/m³ (0.25 ppm) can cause moderate irritation of the eyes and nose in five minutes [47] [49]. Sim and Pattle [50] have reported that lacration occurred within 20 seconds at 1,880 μg/m³ (0.67 ppm) and only within five seconds at 2,800 μg/m³ (1.04 ppm). Smith [49] reported that a five second exposure at 14,800 μg/m³ (5.5 ppm) caused moderate eye and nasal irritation, while a 20 second exposure is painful. It is intolerable to humans when the concentration is over 58,640 μg/m³ (21.8 ppm). Repeated contact with the skin may produce chronic irritation and dermatitis.

b. **On Animals**

Many investigations have been conducted to study the damage to experimental animals. No cases of serious injury or death have been recorded for animals subjected to normal environmental aldehyde exposure. The principal effect observed in the experimental animals is primary irritation to the mucous membranes of the eyes, nose and the upper respiratory tract. High concentrations of aldehyde and longer exposure periods may cause injury to the lungs and other organs as well. Dalhamn [51], who studied mucous flow and ciliary activity in the trachea of rats exposed to formaldehyde, found that when the rats were exposed to 3,690 μg/m³ (3 ppm) for 50 seconds or 615 μg/m³ (0.5 ppm) for 150 seconds, there was cessation of the ciliary beat in the anesthetized respiratory tract. Murphy [52] et al found that the alkaline phosphate activity in the liver was increased in a group of eight rats
inhaling 4,200 µg/m³ (3.5 ppm) formaldehyde for 18 hours. Salem and Cullumbine [53] exposed groups of 50 mice, 20 guinea pigs and 5 rabbits simultaneously to formaldehyde at 23,400 µg/m³ (19 ppm) and other aldehydes for at least 10 hours. Autopsy on the animals killed showed hemorrhages and edema in the lungs and evidence of hyperemia and perivascular edema in the liver.

Acrolein is much more irritating and toxic than the aliphatic aldehydes. The lethal concentration (LD₅₀) of acrolein for rats is approximately one-third that for formaldehyde. Gusev et al. [54], exposing groups of rats to various concentrations of acrolein in air for several weeks, found that at a concentration of 1,520 µg/m³ for 24 days the animals showed a loss of weight, a decrease in cholinesterase activity of whole blood, changes in conditioned reflex activity, a fall of coproporphyrin excretion in the urine, and an increase in the number of luminescent leukocytes in the blood. Pattle and Cullumbine [55] found that 50 percent of mice and guinea pigs died after exposure to 28,245 µg/m³ (10.5 ppm) for six hours. Lung damage was also noted in rats six months after exposure to 538,000 µg/m³ (200 ppm) acrolein for ten minutes each week for 10 weeks [56]. An increase in alkaline phosphatase activity in the livers of rats exposed to acrolein was also reported [52].

Several investigators have reported that significant increases in death rates due to pulmonary edema were found for both formaldehyde and acrolein in the presence of other aerosols [69].

c. On Vegetation

The potential damage to plants by aldehydes alone is not very significant. However, results from many reports suggest that the product mixtures obtained from the irradiation of aldehyde hydrocarbons, or hydrocarbons including
aldehyde-nitrogen oxide mixtures may cause injury to plants.

Hindarvi and Altshuller [57] reported that irradiated propionaldehyde and nitrogen oxide mixtures in air do cause damage to tobacco wrapper, pinto bean leaves and petunias, but no injury was reported when formaldehyde was used instead. Haagen-Smit [58] also found no evidence of injury to alfalfa exposed to 2,400 µg/m³ (2 ppm) formaldehyde after two hours, but when the concentration increased to 8,400 µg/m³ (7 ppm) a typical alfalfa damage occurred after five hours exposure. Aerolein was shown to be more phytotoxic than formaldehyde. Haagen-Smith [58] reported that oxidant-type damage to alfalfa grown in a greenhouse was observed after exposure to 250 µg/m³ (0.1 ppm) of acrolein for nine hours. Darley and co-workers [59] found oxidant-type damage when 14-day old pinto bean plants were exposed to approximately 5,000 µg/m³ (2 ppm) of acrolein for four successive 35-minute periods.

d. On Materials

No information has been found in the literature on the effect of atmospheric aldehydes on materials.

4. Environmental Air Standards

The American Conference of Governmental Industrial Hygienists has adopted the 8-hour Threshold Limit Values for occupational exposure to aldehydes as shown in Table L (1)-11.

The American Industrial Hygiene Association recommended that ambient air quality values for formaldehyde and acrolein be as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Limit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>0.1 ppm</td>
<td>120 µg/m³</td>
</tr>
<tr>
<td>Acrolein</td>
<td>0.01 ppm</td>
<td>25 µg/m³</td>
</tr>
<tr>
<td>Total aldehydes</td>
<td>0.2 ppm</td>
<td>240 µg/m³</td>
</tr>
</tbody>
</table>

(as formaldehyde)
<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>ppm</th>
<th>µg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>200</td>
<td>360,000</td>
</tr>
<tr>
<td>Acrolein</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Chloroacetaldhey</td>
<td>1</td>
<td>3,000</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>2</td>
<td>6,000</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>5</td>
<td>6,000</td>
</tr>
<tr>
<td>Furfural</td>
<td>5</td>
<td>20,000</td>
</tr>
</tbody>
</table>

Table L(1)–11 Eight-Hour Day Threshold Limit Values [60]

West Germany, Russia and Czechoslovakia adopted the air quality standards for formaldehyde and acrolein summarized in Table L (1)–12.

<table>
<thead>
<tr>
<th>Country</th>
<th>Aldehydes</th>
<th>Basic Standard Concentration</th>
<th>Time Concentration</th>
<th>Permissible Levels (&lt;4hr)</th>
<th>Time</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>µg/m³</td>
<td>ppm</td>
<td>Period, hr.</td>
<td>µg/m³</td>
<td>ppm</td>
</tr>
<tr>
<td>West Germany</td>
<td>Formaldehyde</td>
<td>36</td>
<td>0.03</td>
<td>0.5</td>
<td>84</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Acrolein</td>
<td>10</td>
<td>0.003</td>
<td>0.5</td>
<td>25</td>
<td>0.009</td>
</tr>
<tr>
<td>Russia</td>
<td>Formaldehyde</td>
<td>14.4</td>
<td>0.01</td>
<td>24</td>
<td>42</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Acrolein</td>
<td>100</td>
<td>0.03</td>
<td>24</td>
<td>300</td>
<td>0.11</td>
</tr>
<tr>
<td>Czechoslovakia</td>
<td>Formaldehyde</td>
<td>18</td>
<td>0.01</td>
<td>24</td>
<td>60</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table L (1)–12 Air Quality Standards for Formaldehyde and Acrolein [60]

Table L (1)–13 shows typical aldehyde levels in selected U.S. cities in 1967.
<table>
<thead>
<tr>
<th>Cities</th>
<th>Max. Concentration μg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>New York</td>
<td>22</td>
</tr>
<tr>
<td>Cincinnati</td>
<td>35</td>
</tr>
<tr>
<td>Cleveland</td>
<td>15</td>
</tr>
<tr>
<td>Oklahoma</td>
<td>161</td>
</tr>
<tr>
<td>Chicago</td>
<td>25</td>
</tr>
<tr>
<td>Boston</td>
<td>78</td>
</tr>
<tr>
<td>Detroit</td>
<td>129</td>
</tr>
<tr>
<td>St. Louis</td>
<td>92</td>
</tr>
</tbody>
</table>

Table L (1)-13 Concentrations of Aldehydes in the Air of Selected U.S. Cities in 1967

5. Detection and Measurement of Aldehydes

The methods used for measuring carbonyl hydrocarbons (aldehydes and ketones) are based mostly on condensation reactions [61]. The following are typical methods for analysis of aldehydes in the atmosphere:

i. Bisulfite method [62]

ii. Colorimetric method with 3-methyl 2-benzothiazole-hydrazone (MBTH) [63]

iii. Colorimetric determination of formaldehyde with chromotropic acid [64]

iv. Infrared spectroscopic [65]

v. Polarographic method [67]

vi. Gas chromatographic method [67]

vii. Spectrophotometric method [68]

6. Abatement Methods

Since aldehydes in the atmosphere result from two main sources (incomplete combustion of organic compounds and/or products of photochemical reactions involving hydrocarbons and nitrogen oxides) effective complete combustion can
reduce substantially such emissions into the atmosphere. Reduction of hydrocarbons in the atmosphere also reduces photochemical reactions, and consequently decreases the amount of aldehydes. The following methods can be used to control hydrocarbon emissions:

i. Incineration

ii. Activated - carbon adsorption

iii. Absorption

Incineration by direct flame or catalytic afterburning can decrease hydrocarbon emission but may create greater amounts of aldehydes and other oxygenated hydrocarbons.
REFERENCES


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37. Altshuller, A.P., Director; Division of Chemistry and Physics, National Air Pollution Control Administration, Cincinnati, Ohio, Personal Communication, (May, 1969)


44. Roth, H.P., and E.A. Swenson, Physiological Studies of Irritant Aspects of Atmospheric Pollution, Report to the Los Angeles County Air Pollution Control District, Los Angeles, California, (1957)


52. Murphy, S.D., H.V. Davis, and V.L. Zaratzian, Biochemical Effects in Rats from Irritating Air Contaminants, Toxicol. Appl. Pharmacol., 5, no. 5, pp. 520-528, (Sept. 1964)


60. Threshold Limit Values for 1967, Adopted at the 29th Annual Meeting of the American Conference of Governmental Industrial Hygienists, Chicago, Illinois, (May 1-2, 1967)


L (2) Ethylene

1. Properties

Ethylene is a colourless, sweetly odorous, hydrocarbon gas of the olefin series.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>H₂C = CH₂</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>28.05</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>-103.9°C (760 mm)</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-169.4°C</td>
</tr>
<tr>
<td>Solidifies at</td>
<td>-181°C</td>
</tr>
</tbody>
</table>

This hydrocarbon is found in natural gas, and is produced, to some extent, by the destructive distillation of coal or wood. It is also formed by cracking of petroleum. Ethylene undergoes a number of reactions that depend upon addition to the double bond. For example, it can be polymerized to form the plastic material polyethylene.

2. Potential Sources and Levels of Atmospheric Emissions

Ethylene is one of the major growth petrochemicals in the world. Most of the ethylene is manufactured by the cracking of petroleum fractions or natural gas by means of pyrolytic processes. It may also form as a by-product during incomplete combustion of hydrocarbons and other organic substances.

a. Automobile and Diesel Engines

Ethylene has been found as a component of automobile and diesel combustion exhausts. It has been estimated that, in general, automobiles produce approximately 78 pounds of ethylene per ton of gasoline consumed [1]. Many investigations have been done to determine the ethylene concentration in automobile exhaust in relation to the engine mode [2] [3], to fuel type [4]
and the effect of hot and cold starts in winter and summer [5]. The data in these reports suggest that the ethylene concentrations vary considerably with the operating mode, with the acceleration mode producing the most. High olefin content in the fuel will produce more ethylene in the exhaust. The effect of hot and cold starts in winter and summer is not significant on the concentration of ethylene in the exhaust.

Table L (2).1 shows ethylene concentrations in automobile exhaust.

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Concentration of Ethylene (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Idle</td>
<td>Acceleration</td>
</tr>
<tr>
<td>Automobile Engine</td>
<td>200</td>
<td>270</td>
</tr>
<tr>
<td>Automobile Engine</td>
<td>188</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>15-30 mph</td>
<td>30 mph</td>
</tr>
<tr>
<td>Automobile Engine*</td>
<td>81</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>15-30 mph</td>
<td>30 mph</td>
</tr>
<tr>
<td>1962 V-8</td>
<td>390</td>
<td>168-233</td>
</tr>
<tr>
<td></td>
<td>15-60 mph</td>
<td>50 mph</td>
</tr>
<tr>
<td></td>
<td>25 sec.</td>
<td>555 (40 mph)</td>
</tr>
</tbody>
</table>

Table L(2).1 Ethylene Concentrations in Automobile Exhaust

The same engine but modified by adding air injection, leaner carburetor, and 10° spark retard.

Table L(2).2 shows the concentration of ethylene in diesel engine exhaust.

Altshuller and Bellar [29] reported that ethylene concentrations in the ambient air of Los Angeles reached maximum daily values ranging between 80 to 130 µg/m³. These high values were during the heavy traffic hours and persisted for at least one hour.
<table>
<thead>
<tr>
<th>RPM</th>
<th>Load</th>
<th>4-cycle, 6-cylinder, 300 HP Turbocharged Engine</th>
<th>2-cycle, 6-cylinder, 200 HP Engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>600</td>
<td>0</td>
<td></td>
<td>6.85, 10.1</td>
</tr>
<tr>
<td>740</td>
<td>0</td>
<td></td>
<td>12.2, 14.2</td>
</tr>
<tr>
<td>800</td>
<td>**</td>
<td>16</td>
<td>4.20, 7.2</td>
</tr>
<tr>
<td>1,000</td>
<td>1/4</td>
<td>12.2, 14.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Full</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>1,050</td>
<td>0</td>
<td>8.93, 9.52</td>
<td></td>
</tr>
<tr>
<td>1,200</td>
<td>1/4</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3/4</td>
<td>11</td>
<td>10.7, 21.0</td>
</tr>
<tr>
<td></td>
<td>Full</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>1,300</td>
<td>**</td>
<td>13.7, 19.4</td>
<td></td>
</tr>
<tr>
<td>1,500</td>
<td>0</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/4</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Full</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>1,520</td>
<td>**</td>
<td>18.5, 14.2</td>
<td></td>
</tr>
<tr>
<td>1,600</td>
<td>3/4</td>
<td>23.9, 31.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Full</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>1,780</td>
<td>**</td>
<td>27.3, 29.6</td>
<td></td>
</tr>
<tr>
<td>1,800</td>
<td>0</td>
<td>13</td>
<td>30.2, 35.1</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>13</td>
<td>82.8</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/4</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Full</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>2,200</td>
<td>Full</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>600-2,200</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table L (2).2 Ethylene in Diesel Exhaust [6][7]

* *Load provided by a club propeller; load a function of rpm.

The ethylene emission from automobile exhaust in Los Angeles has been estimated at 60 tons per day.

b. **Incinerators**

Incomplete combustion of solid organic waste may be a major source of ethylene emission into the atmosphere. It is very important to have adequately designed incinerators to minimize ethylene emissions. Table L(2).3, shows the concentrations of ethylene in the effluents from some typical incinerators.
<table>
<thead>
<tr>
<th>Incinerators</th>
<th>Concentrations of Ethylene $\mu$g/m$^3$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-chamber</td>
<td>23,000 to 31,000</td>
<td>8</td>
</tr>
<tr>
<td>Multiple-chamber</td>
<td>less than 11,500</td>
<td></td>
</tr>
<tr>
<td>Pyrolysis of solid municipal waste</td>
<td>460,000 to 39,330,000</td>
<td>9</td>
</tr>
</tbody>
</table>

Table L(2).3 Ethylene in Incinerator Effluents

c. **Manufacture of Ethylene and Plants Using Ethylene as a Raw Material**

This source of ethylene emission may be a local pollution problem. According to Hall and co-workers [10], air samples, taken from locations near a polyethylene factory in Texas, showed that the atmospheric ethylene concentration ranged from 560 to 3450 $\mu$g/m$^3$. Symptoms of damage to cotton and other crops were found as far as four miles downwind from the factory. Ethylene is used extensively as a raw material in the manufacture of organic chemicals and plastics, especially polyethylene. Typical chemicals produced from ethylene are ethyl alcohol, ethylene oxide, ethylene glycol, ethyl chloride, ethylene dichloride and styrene.

d. **Burning of Agricultural Wastes**

The burning of agricultural wastes can be considered as another source of ethylene pollution. The levels of ethylene emissions resulting from the burning of agricultural wastes depend on the type of waste and moisture content. Emission rates range from 0.3 to 3.5 lb/ton of waste material [1] [11].

e. **Natural Occurrence**

Research has shown that ethylene is produced naturally by
flowers, fruits, leaves and within tissues of some plants. It serves as a hormone in regulating growth, development, and other processes such as the ripening of fruit [12] [13] [14]. Biale et al [14] reported that some fruits such as cherimoya produce as much as 186 μl/kg-hr ethylene, apples and pears produce 112 and 122 μl/kg-hr ethylene respectively.

3. Effects of Ethylene

   a. On Humans

   Ethylene is not toxic, but it does participate in the creation of photochemical reaction products which may have harmful effects on humans. At high concentrations it acts as an asphyxiant, may cause narcosis and unconsciousness. Concentrations of 75 to 90 percent ethylene in oxygen have been used as anesthetics in hospitals.

   b. On Animals

   Concentrations of 75 to 90 percent ethylene in oxygen act as an anesthetic and produce no notable side effects except nausea in experimental animals [15]. Hirschfelder and Ceder [16] studied the effect of ethylene inhalation on the growth rate of rats in 1930. They concluded that experimental concentrations of ethylene, as high as 11,500,000 μg/m³ for 17 days, do not appreciably affect the growth rate of rats.

   c. On Plants

   Research with several unsaturated and saturated hydrocarbons proved that only ethylene is a significant phytotoxicant at known ambient concentrations. Ethylene interferes with the normal action of plant hormones and growth regulators rather than being a highly lethal gas that can readily
kill tissue [17]. The significant effects of ethylene on plants are:

i. growth inhibition [18]
ii. epinasty of leaves in sensitive plants [19]
iii. abscission of leaves [20]
iv. colour changes in leaves and flowers, and death of flower parts [21]
v. retardation of elongation and radial swelling or thickening of the stem [17] [19].

In 1908, Crocker and Knight [22] studied the abnormal growth of flowers in greenhouses. They found that ethylene in illuminating gas was responsible. A three day exposure to 115 µg/m³ (0.1 ppm) ethylene prevented the flowers from opening, while a 12 hour exposure to 575 µg/m³ (0.5 ppm) caused the flower to close.

Table L(2).4 summarizes the works of several investigators who studied the effect of ethylene on plants.

<table>
<thead>
<tr>
<th>Plants</th>
<th>Response</th>
<th>Dosage Concentration</th>
<th>Dosage Time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pepper and tomato</td>
<td>abscission</td>
<td>115 µg/m³ 0.1 ppm</td>
<td>&lt; 8 hr</td>
<td>26</td>
</tr>
<tr>
<td>flower flower buds</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Snapdragon petals</td>
<td>abscission</td>
<td>575 µg/m³ 0.5 ppm</td>
<td>1 hr</td>
<td>26</td>
</tr>
<tr>
<td>Cotton leaves</td>
<td>abscission</td>
<td>685 µg/m³ 0.6 ppm</td>
<td>1 month</td>
<td>23</td>
</tr>
<tr>
<td>Orchids dry sepal</td>
<td>dry sepal (slight)</td>
<td>5.75 µg/m³ 0.005 ppm</td>
<td>24 hr</td>
<td>26</td>
</tr>
<tr>
<td>Orchids dry sepal</td>
<td>dry sepal (slight)</td>
<td>345 µg/m³ 0.3 ppm</td>
<td>1 hr</td>
<td>26</td>
</tr>
<tr>
<td>Orchids dry sepal</td>
<td>dry sepal (slight)</td>
<td>57.5 µg/m³ 0.05 ppm</td>
<td>6 hr</td>
<td>26</td>
</tr>
<tr>
<td>Orchids dry sepal</td>
<td>dry sepal (slight)</td>
<td>11.5 µg/m³ 0.01 ppm</td>
<td>24 hr</td>
<td>26</td>
</tr>
<tr>
<td>Carnation flower closes</td>
<td>flower closes</td>
<td>115 µg/m³ 0.1 ppm</td>
<td>6 hr</td>
<td>26</td>
</tr>
<tr>
<td>Carnation flower closes</td>
<td>flower closes</td>
<td>575 µg/m³ 0.5 ppm</td>
<td>24 hr</td>
<td>22</td>
</tr>
<tr>
<td>Carnation flower doesn't open</td>
<td></td>
<td>115 µg/m³ 0.1 ppm</td>
<td>3 days</td>
<td>22</td>
</tr>
</tbody>
</table>

Table L(2).4 Relationships Between Response and Dosage of Some Plants to Ethylene
Table L(2).4 Relationships Between Response and Dosage of Some Plants to Ethylene

4. Environmental Air Standards

The ambient air quality standards recommended in 1968 by the American Industrial Hygienist Association for ethylene are listed in Table L(2).5.

<table>
<thead>
<tr>
<th>Location</th>
<th>1-hour Maximum</th>
<th>ppm</th>
<th>8-hour Maximum</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural</td>
<td>287.5</td>
<td>0.25</td>
<td>57.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Residential</td>
<td>575</td>
<td>0.50</td>
<td>115</td>
<td>0.10</td>
</tr>
<tr>
<td>Commercial</td>
<td>862.5</td>
<td>0.75</td>
<td>172.5</td>
<td>0.15</td>
</tr>
<tr>
<td>Industrial</td>
<td>1,150</td>
<td>1.00</td>
<td>230</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table L(2).5 U.S. Ambient Air Quality Standards for Ethylene [27]
Russia has recommended 3,000 μg/m³ (2.3 ppm) ethylene for a 24 hour average as the ambient air quality standard [28].

5. Detection and Measurement of Ethylene

Ethylene samples can be collected into an evacuated container by the grab sampling method [1] [6].

Atmospheric ethylene may be analysed by the following methods:

i. Gas Chromatographic [1] [29] [30]
ii. Infrared Spectroscopic [6] [31] [32]
iii. Mass Spectrometric [21] [33]
iv. Manometric [34]

6. Abatement Methods

Improvement of techniques leading to complete combustion in engines, oil fired boilers and incinerators can reduce ethylene emissions into the atmosphere substantially. Ethylene emission from petroleum refineries, organic plants and polyethylene plants can be controlled by the methods generally used for hydrocarbons namely by:

i. Absorption method
ii. Vapor recovery methods
iii. Waste heat boilers
iv. Incinerators
REFERENCES


28. Katz, M. Recent Developments in Ambient Air Quality Guides in Relation to Control of Atmospheric Effluents. Pulp Paper Mag. Can. 69, No. 4, p. 60,


Polynuclear Aromatic Hydrocarbons (PAH)

1. Introduction

Polynuclear Aromatic Hydrocarbons are compounds that contain multiple benzene rings. All carbonaceous matter, of whatever origin (coal, oil, wood, gas or pure organics) will, if incompletely burned at high temperature, give rise to polycyclic aromatic hydrocarbons and certain of their oxidation products. It is well known that many of these substances are in the air of all large cities of the world as man-made pollutants. Moreover some of these pollutants have been linked with carcinogenic effects on animals and many are believed to be carcinogenic to humans. Although no suspected organic carcinogens has been experimentally proven to cause lung cancer in humans, there is evidence linking the higher mortality rates from lung cancer to air pollution among urban residents [1] [3] [4] [5] [6] [7] [8] [9] [10] [11], and among persons indulging in prolonged and excessive cigarette smoking [1] [12] [13] [14]. Probably the first fundamental study to show the direct relation between cancer incidence and polycyclic aromatic hydrocarbons in the air was initiated by Stocks [2] in 1957 in the North Wales and Liverpool Hospital Region.

Polynuclear aromatic hydrocarbons in the atmosphere are considered to be solids, most likely as adsorbed compounds on soot particles, with the quantity in the gas phase being significantly small [15]. Benzo (a) pyrene (3, 4 - benzopyrene or BaP) is the most extensively studied polycyclic aromatic hydrocarbon. It is considered to be the most active carcinogen to experimental animals and has been found in the air of all the 103 urban areas surveyed by the U.S. Public Health Service in the late 1950's. Concentrations of BaP ranged from 0.11 to 61 micrograms per 1000 cubic meters of air, with a geometric mean concentration of 6.6 in urban areas. Nonurban concentrations were much
lower ranging from 0.01 to 1.9 µg/1000m³ with a geometric mean concentration of 0.4 [16] [17]. Sawicki [18] showed that the atmospheric concentrations of 3,4 - benzpyrene in the highly industrialized European cities are definitely higher than the concentrations found in the large American cities. This difference is probably due to the extensive use of coal for space heating. Sawicki [18] also pointed out that the amounts of polynuclear aromatic hydrocarbons are roughly proportional to the amount of 3,4 - benzpyrene - that is, with larger concentrations of BaP, larger concentrations of the other polynuclear aromatic hydrocarbons were found. The atmospheric concentrations of BaP in urban areas vary with the season. Investigation showed that in all cases summer levels are much lower than winter levels.

Not all of the PAH are carcinogenic. Some are inactive. Some are considered to be weakly, moderately or strongly active. Some PAH are believed to be anticarcinogenic. Fractions of tar showed that highly fluorescent portions were the active ingredients of the tumor-producing constituents. Further work indicated that certain PAH, such as BaP contained in the tar, are responsible in part for the tar's carcinogenic effect [48]. There is also evidence that other organic compounds may be carcinogenic. Cook et al. [38] showed that a fraction of mineral oil free of benzo (a) pyrene was carcinogenic to man. Four other types of carcinogens, besides PAH, have been found in the urban atmosphere. These include polynuclear aza heterocyclic compounds, polynuclear imino heterocyclic compounds (in air polluted by coal-tar-pitch fumes), polynuclear ring carbonyl compounds and alkylating agents. The carcinogenicity of the last two needs more confirmation [18]. Falk and co-workers [45] state that the experimental carcinogenicity of certain pure polycyclic aromatic hydrocarbons is a matter of universal agreement.

Table L(3).1 shows carcinogenicity and anticarcinogenicity of some
PAH compounds present in polluted air.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Abbreviation</th>
<th>Carcinogenicity Ref 19</th>
<th>Carcinogenicity Ref 20</th>
<th>Anticarcinogenicity Ref 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo (a) pyrene</td>
<td>BaP</td>
<td></td>
<td>++</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Benzo (e) pyrene</td>
<td>BeP</td>
<td></td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Benzo (b) fluoranthene</td>
<td>BbFl</td>
<td></td>
<td>++</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>Benzo (j) fluoranthene</td>
<td>BjFl</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo (k) fluoranthene</td>
<td>BkFl</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Benzo (g, h, i) perylene</td>
<td>C22H12</td>
<td>B(g,h,i)P</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Benzantracene</td>
<td>Benz</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Anthanthrene</td>
<td>Anth</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>A</td>
<td></td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>Fluor</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>Phen</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>P'</td>
<td></td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Perylene</td>
<td>Per</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table L(3.1) Carcinogenicity and Anticarcinogenicity of Some PAH Compounds
<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Abbreviation</th>
<th>Carcinogenicity Ref 19</th>
<th>Carcinogenicity Ref 20</th>
<th>Anticarcinogenicity Ref 20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coronene</td>
<td><img src="image1" alt="Formula" /></td>
<td>Cor</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fluorene</td>
<td><img src="image2" alt="Formula" /></td>
<td>F</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Benzo (a) Fluorene</td>
<td><img src="image3" alt="Formula" /></td>
<td>BaF</td>
<td>-</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Chrysene</td>
<td><img src="image4" alt="Formula" /></td>
<td>Chry</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>

Table L(3).1 Carcinogenicity and Anticarcinogenicity of Some PAH Compounds

+++: strongly active, ++: moderately active, +: weakly active, -: Inactive

2. Potential Sources and Levels of Atmospheric Emissions

The major source of atmospheric PAH is the incomplete combustion of organic matter. A secondary source is probably the photochemical decomposition of other organic compounds into PAH. Sawicki [17] suggests that high ratios of BaP/B(g, h, i)P and BaP/Cor indicate possible air pollution from coal burning while very low ratios suggest pollution from auto exhaust or that the pollutants do not come from high coal burning sources. He further suggests that the high ratio of P/BaP might indicate that the pollutants have been emitted just recently into the atmosphere. On the other hand a low ratio would probably suggest that the particulates have been in contact with air and sunlight for an extended period of time, since pyrene is less stable at warm temperature and in sunlight in the atmosphere. Hangebrauck and co-workers [25], who compared PAH emissions with other products of incomplete combustion, suggest that PAH emission rates are generally high when carbon monoxide and total gaseous hydrocarbons are high. Kuratsune [37] reported that coal soot has a higher concentration of benzpyrene than auto exhaust soot.
a. **Power Plants and Utilities Using Coals as Fuel**

The most important source of PAH is the inefficient combustion of coal, typically from residential and small industrial coal-fired furnaces [21]. The highest emission rates of BaP, ranging from 3800 to 3,300,000 g per million Btu gross heat input, come from tests on hand-fired and underfeed stoker-fired domestic units without combustion control. Tables L(3).2 and L(3).3 show the emission rates of PAH from coal-fired residential furnaces and coal-fired power plants respectively.

Tabbins [22] and co-workers reported an extensive investigation of the products of combustion showing that a wide variety of PAH compounds are produced during the combustion process. Their presence in the effluent gases does not necessarily mean they were originally present in the fuel. On the other hand, Tye and co-workers [23] showed that BaP and benz(a) anthracene and other PAH are actually present in bituminous coal. They reported concentrations of BaP in the extracts ranging from 0.03 to 0.10% with greater percentages in high volatility coals than in the Pocahontas types. Studies [31] [32] in England show a lower incidence of lung cancer among coal miners than in the general population. This probably implies that the PAH present in raw coal have no apparent biological effect in that form [23].
<table>
<thead>
<tr>
<th>Firing Method</th>
<th>1000 micrograms per million Btu heat input</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BaP</td>
</tr>
<tr>
<td>Underfeed</td>
<td></td>
</tr>
<tr>
<td>Stokers</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
</tr>
<tr>
<td>Handstoked</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>1,700</td>
</tr>
<tr>
<td>Stoked</td>
<td>3,300</td>
</tr>
</tbody>
</table>

Table L(3).2 Emission of PAH from Coal-Fired Residential Furnaces [21]
<table>
<thead>
<tr>
<th>Type of Unit</th>
<th>Fuel rate (ton/hr)</th>
<th>Test Condition</th>
<th>Sampling Point</th>
<th>BaP</th>
<th>P</th>
<th>BeP</th>
<th>Per</th>
<th>B(ghi)P</th>
<th>Anth</th>
<th>Cor</th>
<th>A</th>
<th>Phen</th>
<th>Fluor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulverized coal (vertically-fired, dry-bottom furnace)</td>
<td>64.5</td>
<td>100% load</td>
<td>B</td>
<td>49</td>
<td>150</td>
<td>45</td>
<td>16</td>
<td>370</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>65.2</td>
<td>100% load</td>
<td>A</td>
<td>22</td>
<td>130</td>
<td>19</td>
<td>190</td>
<td>210</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>67.0</td>
<td>100% load</td>
<td>A</td>
<td>19</td>
<td>120</td>
<td>19</td>
<td>120</td>
<td>410</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>48.0</td>
<td>75% load</td>
<td>B</td>
<td>55</td>
<td>180</td>
<td>55</td>
<td>33</td>
<td>190</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>46.2</td>
<td>75% load</td>
<td>A</td>
<td>440</td>
<td>840</td>
<td>250</td>
<td>66</td>
<td>160</td>
<td>35</td>
<td>4.7</td>
<td>110</td>
<td>820</td>
<td>1700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A</td>
<td>130</td>
<td>74</td>
<td>79</td>
<td>33</td>
<td>83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulverized coal (front-wall fired dry-bottom furnace)</td>
<td>52.0</td>
<td>100% load</td>
<td>A</td>
<td>17</td>
<td>200</td>
<td>14</td>
<td>14</td>
<td>200</td>
<td></td>
<td>160</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.5</td>
<td>100% load</td>
<td>B</td>
<td>21</td>
<td>160</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulverized coal (tangentially-fired, dry-bottom furnace)</td>
<td>56.6</td>
<td>100% load</td>
<td>A</td>
<td>140</td>
<td>140</td>
<td>4.9</td>
<td>7.1</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>390</td>
</tr>
<tr>
<td>Pulverized coal (opposed-downward inclined burners, wet-bottom furnace)</td>
<td>8.8</td>
<td>100% load*</td>
<td>A</td>
<td>140</td>
<td>130</td>
<td>22</td>
<td>120</td>
<td>1100</td>
<td>93</td>
<td>19</td>
<td>65</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.8</td>
<td>100% load**</td>
<td>A</td>
<td>140</td>
<td>130</td>
<td>22</td>
<td>120</td>
<td>1100</td>
<td>93</td>
<td>19</td>
<td>65</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.1</td>
<td>100% load*</td>
<td>A</td>
<td>140</td>
<td>130</td>
<td>22</td>
<td>120</td>
<td>1100</td>
<td>93</td>
<td>19</td>
<td>65</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Crushed coal (cyclone-fired) wet-bottom furnace</td>
<td>59.0</td>
<td>100% load</td>
<td>A</td>
<td>370</td>
<td>1800</td>
<td>34</td>
<td>360</td>
<td>110</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>66.8</td>
<td>100% load</td>
<td>A</td>
<td>76</td>
<td>250</td>
<td>36</td>
<td></td>
<td>110</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crushed coal Spreader stoker (travelling grate)</td>
<td>9.0</td>
<td>75% load</td>
<td>A</td>
<td>24</td>
<td>59</td>
<td>9.3</td>
<td>59</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.2</td>
<td>75% load</td>
<td>A</td>
<td>&lt;15</td>
<td>52</td>
<td>9.3</td>
<td>59</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.3</td>
<td>75% load</td>
<td>A</td>
<td>&lt;15</td>
<td>21</td>
<td>9.3</td>
<td>59</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulverized coal Water-tube boiler (dry-bottom furnace)</td>
<td>9420</td>
<td>1b/hr</td>
<td>A</td>
<td>32</td>
<td>240</td>
<td>92</td>
<td>370</td>
<td>550</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table L(3). 3 PAH Emission From Coal-Fired Power Plants [21]

* with fly-ash reinjection  ** without fly-ash reinjection
A: sampling point after fly-ash collector  B: before fly-ash collector
<table>
<thead>
<tr>
<th>Type of Unit</th>
<th>Fuel rate (ton/hr)</th>
<th>Test Condition</th>
<th>Sampling Point</th>
<th>BaP</th>
<th>P</th>
<th>BeP</th>
<th>Per</th>
<th>P(shi)P</th>
<th>Anth</th>
<th>Cor</th>
<th>A</th>
<th>Phen</th>
<th>Fluor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-tube boiler (chain-grate stoker)</td>
<td>12,400 1b/hr.</td>
<td></td>
<td></td>
<td>37</td>
<td>390</td>
<td>130</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>680</td>
<td></td>
</tr>
<tr>
<td>Water-tube boiler (with reinjection)</td>
<td>4,290 1b/hr</td>
<td></td>
<td></td>
<td>26</td>
<td>590</td>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>Spreader stoker</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Underfeed Stokers</td>
<td>317 1b/hr</td>
<td></td>
<td></td>
<td>10,000</td>
<td>16,000</td>
<td>7,900</td>
<td>1,600</td>
<td>4,500</td>
<td>290</td>
<td>330</td>
<td>850</td>
<td>10,000</td>
<td>38,000</td>
</tr>
<tr>
<td>Stokers</td>
<td>214 1b/hr</td>
<td></td>
<td></td>
<td>120</td>
<td>1,700</td>
<td>230</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1,000</td>
<td>3,200</td>
</tr>
</tbody>
</table>

Table L(3).3 PAH Emission From Coal-Fired Power Plants [21]

A: Sampling point after fly-ash collector
B: Before fly-ash collector
Hangebrauck and co-workers [21] have estimated annual Benzo(a)pyrene emission for the United States from coal-fired heat generation. Their results are shown in Table L(3).4.

<table>
<thead>
<tr>
<th>Source</th>
<th>Estimated BaP Emission Rate</th>
<th>Estimated Annual Consumption of Production</th>
<th>Estimated Annual BaP Emission (tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat generation:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal-residential</td>
<td>microg/10^6 Btu</td>
<td>(10^{15} Btu)</td>
<td></td>
</tr>
<tr>
<td>i. hand-stoked</td>
<td>1,400,000</td>
<td>0.26</td>
<td>400</td>
</tr>
<tr>
<td>ii. underfeed</td>
<td>44,000</td>
<td>0.20</td>
<td>9.7</td>
</tr>
<tr>
<td>Commercial</td>
<td>5,000</td>
<td>0.51</td>
<td>2.8</td>
</tr>
<tr>
<td>Industrial</td>
<td>2,700</td>
<td>1.95</td>
<td>5.8</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>418.3</td>
</tr>
</tbody>
</table>

Table L(3).4 Estimation of Annual BaP Emission in the U.S. [21]

b. Power Plants and Utilities Using Oil and Gas as Fuels

Howe [24] reported that the BaP emissions from liquid-petroleum-fired units were low. The emissions from gas burning units were also low with about the same levels as oil-fired units when compared with equivalent sized coal-fired units. Hangebrauck and co-workers [21] state that BaP concentrations were found in some of the oil-burning units tested, while pyrene was present in all sources. They estimated annual BaP emission from oil and gas-fired units to be only 3.3 tons for the United States. Smith [26] reported BaP emissions into the atmosphere from oil burners to be 0.04 to 0.10 pounds per million pounds of oil. Table L(3).5 shows PAH emissions from oil and gas fired units.
<table>
<thead>
<tr>
<th>Firing Method</th>
<th>Type of Unit</th>
<th>Use</th>
<th>Fuel Rate lb/hr</th>
<th>Micrograms per million Btu heat input</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BaP</td>
</tr>
<tr>
<td>Oil</td>
<td></td>
<td></td>
<td></td>
<td>BaP</td>
</tr>
<tr>
<td>Steam-atomized</td>
<td>Water-tube</td>
<td>Process Heating</td>
<td>1,100</td>
<td>&lt; 20</td>
</tr>
<tr>
<td></td>
<td>boiler</td>
<td>Hospital Heating</td>
<td>35</td>
<td>900</td>
</tr>
<tr>
<td>Low-pressure</td>
<td>Scotch-marine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>air-atomized</td>
<td>boiler</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>Cast-iron</td>
<td>Home Heating</td>
<td>8.8</td>
<td>&lt; 40</td>
</tr>
<tr>
<td>atomized</td>
<td>sectional</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>boiler, Hot-</td>
<td>Hot-air furnace</td>
<td>4.4</td>
<td>&lt; 60</td>
</tr>
<tr>
<td>Vaporized</td>
<td>Hot-air</td>
<td>Home Heating</td>
<td>1.2</td>
<td>&lt; 100</td>
</tr>
<tr>
<td></td>
<td>furnace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Premix</td>
<td>Fire-tube</td>
<td>Process Heating</td>
<td>402</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>burners</td>
<td>boiler</td>
<td>Hospital Heating</td>
<td>42</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Scotch-marine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>Double-shell</td>
<td>Home Heating</td>
<td>7.9</td>
<td>&lt; 20</td>
</tr>
<tr>
<td></td>
<td>boiler</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Premix</td>
<td>Hot-air</td>
<td></td>
<td>7.4</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>burners</td>
<td>furnace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wall-space</td>
<td></td>
<td>0.51</td>
<td>270</td>
</tr>
</tbody>
</table>

Table L(3).5 PAH Emissions From Oil and Gas-Fired Units [25]
Incineration and Open Burning Sources

The emission rates of PAH from refuse burning depend on the efficiency of combustion. Inefficient combustion in small incinerators and open burning gives rise to considerable emissions of BaP and PAH into the atmosphere. Table L(3).6 shows PAH emissions from incineration and open burning sources. Hangebrauck and partners [21] estimated 20.2 tons of total BaP emissions from incineration and open burning sources in the United States.
<table>
<thead>
<tr>
<th>Type of Unit</th>
<th>Sampling Point</th>
<th>Micrograms per Pound of Refuse Charged</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BaP</td>
</tr>
<tr>
<td>Municipal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 ton/day Multiple Chamber</td>
<td>Breaching (before Settling Chamber)</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>Breaching (before scrubber)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stack (after scrubber)</td>
<td>0.089</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 ton/day Multiple Chamber</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stack</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Stack</td>
<td>260</td>
</tr>
<tr>
<td>Commercial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.3 ton/day Single Chamber</td>
<td>Stack</td>
<td></td>
</tr>
<tr>
<td>3 ton/day Multiple Chamber</td>
<td>Stack</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stack</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>Stack</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td>Stack</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Stack</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stack</td>
<td></td>
</tr>
</tbody>
</table>

Table L(3).6 PAH Emission from Incinerators and Open Burning [25]
d. **Motor Vehicles**

Colucci and Begeman [27] reported that automotive BaP contributes 5 to 42 percent of the total emissions based on ratios of lead to BaP in exhaust and in the atmosphere. Results from experimental investigations indicate that older, higher-mileage vehicles and those with poorly adjusted engines yield the highest emission rates [21]. Usually gasoline or diesel-powered trucks give higher BaP emission rates than do automobiles. The emissions are also dependent upon the type of fuel used. Long-chain paraffins, widely found in fuels and plants, serve as special precursors of PAH.

Annual BaP emissions from automobiles, trucks and diesel engines were estimated to be 8.6 tons, > 10 tons, and 2.0 tons respectively in the U.S. [21]. Table L(3).7 shows the PAH emission rates from automobiles and trucks of two known manufacturers. Colucci and Begeman [28] studied BaP and BaA (benzo (a)anthracene) air pollutants in relation to automotive traffic in New York. They reported that BaP concentrations ranged from 0.1–9.4 µg/1000 m³. Levels were higher during the day than at night, and highest in autumn and winter. They found that BaP and BaA concentrations were highest at sites with highest concentrations of both automotive-derived pollutants (CO and lead) and non-automotive-derived pollutants (vanadium and sulfate), and lowest values were reported at sites with lowest concentrations of automotive and nonautomotive pollutants. This study implies that atmospheric PAH carcinogens are derived from both automotive and nonautomotive sources.
<table>
<thead>
<tr>
<th>Year</th>
<th>Vehicle Mileage</th>
<th>Micrograms per Vehicle Mile</th>
<th>P</th>
<th>P</th>
<th>P</th>
<th>Bap</th>
<th>Bap</th>
<th>Bap</th>
<th>1,591</th>
<th>1,197</th>
<th>1,537</th>
<th>1,397</th>
<th>1,537</th>
</tr>
</thead>
<tbody>
<tr>
<td>1962</td>
<td>19,000</td>
<td>5.6</td>
<td>81</td>
<td>9.5</td>
<td>0.78</td>
<td>5.5</td>
<td>5.8</td>
<td>5.8</td>
<td>2.30</td>
<td>9.6</td>
<td>5.3</td>
<td>5.8</td>
<td>9.6</td>
</tr>
<tr>
<td>1963</td>
<td>26,000</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>0.34</td>
<td>10.7</td>
<td>3.6</td>
<td>4.6</td>
<td>6.7</td>
</tr>
<tr>
<td>1964</td>
<td>49,000</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>0.24</td>
<td>17.2</td>
<td>3.9</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>1965</td>
<td>56,000</td>
<td>21.5</td>
<td>21.5</td>
<td>21.5</td>
<td>21.5</td>
<td>21.5</td>
<td>21.5</td>
<td>21.5</td>
<td>0.39</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td>1966</td>
<td>11,000</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>1.56</td>
<td>15.0</td>
<td>2.4</td>
<td>10.3</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Make</th>
<th>AUTOMOBILES</th>
<th>TRUCKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4 car average:</td>
<td>4,900</td>
</tr>
<tr>
<td>B</td>
<td>2-truck average:</td>
<td>6,400</td>
</tr>
</tbody>
</table>

Table L(3): PAH Emission from Motor Vehicles [21]
Petroleum Refineries

The major emissions of PAH from petroleum refineries come from Houdriffow Catalytic Cracker (HCC), Thermofor Catalytic Cracker (TCC) and Fluid Catalytic Cracker (FCC) units. Concentrations of PAH in the waste gases of catalyst regenerators were higher from HCC and TCC air-lift units than FCC units. Estimates of annual U.S. BaP emissions from HCC and TCC air lifts without CO waste heat boilers were 5.6 and 13.0 tons respectively. Table L(3).8 shows PAH emissions from the three CO waste heat boilers, effecting complete combustion of the regenerator fuel gases, to be reduced to almost insignificant levels.
<table>
<thead>
<tr>
<th>Unit</th>
<th>Sampling Point</th>
<th>Process Rate</th>
<th>Thousand Micrograms Per Barrel Oil Charged (fresh-feed &amp; recycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>bpd</td>
<td>recycle</td>
</tr>
<tr>
<td>FCC</td>
<td>Regenerator Outlet</td>
<td>20,000</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>CO Boiler Outlet</td>
<td>23,000</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Regenerator Outlet</td>
<td>46,250</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>CO Boiler Outlet</td>
<td>46,600</td>
<td>44</td>
</tr>
<tr>
<td>HCC</td>
<td>Regenerator Outlet</td>
<td>37,200</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>CO Boiler Outlet</td>
<td>34,400</td>
<td>27</td>
</tr>
<tr>
<td>TCC</td>
<td>Regenerator Outlet</td>
<td>37,200</td>
<td>30</td>
</tr>
<tr>
<td>(Airlift)</td>
<td></td>
<td>19,600</td>
<td>15</td>
</tr>
<tr>
<td>TCC</td>
<td>Regenerator Outlet</td>
<td>22,800</td>
<td>42</td>
</tr>
<tr>
<td>(Airlift)</td>
<td></td>
<td>23,800</td>
<td>45</td>
</tr>
<tr>
<td>TCC</td>
<td>Regenerator Outlet</td>
<td>13,200</td>
<td>31</td>
</tr>
<tr>
<td>(Bucket lift)</td>
<td></td>
<td>10,000</td>
<td>33</td>
</tr>
</tbody>
</table>

Table L(3).8 PAH Emissions From Various Catalytic Cracking Units [21]
f. **Industrial Processing Plants**

The studies of Hangebrauck et al. [21] on asphalt air-blowing processes, an asphalt hot-road-mix plant, a carbon-black manufacturing operation, a chemical complex, and a steel and coke facility showed they were not major sources of BaP. Only pyrene emissions were high from the asphalt air-blowing processes. Tanimura [29] found the concentrations of BaP in an iron and steel works listed in Table L(3).9. He also reported that average concentrations of BaP at seven sites in the neighbouring industrial town were 7.70 μg/100 m³ in winter and 2.56 μg/100 m³ in summer for suspended particulates, and 7.26 μg/m²/5 hours in winter and 4.20 μg/m³/5 hours in summer for falling particulates [30].
<table>
<thead>
<tr>
<th>Site</th>
<th>Plant</th>
<th>Bap in Suspended Particulates µg/100m³</th>
<th>Bap in Falling Particulates µg/m²/5 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Winter 1963-64</td>
<td>Summer 1964</td>
</tr>
<tr>
<td>Furnace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke oven side</td>
<td>Coke making plant</td>
<td>150.6</td>
<td>314.1</td>
</tr>
<tr>
<td>Blast furnace side</td>
<td>Iron making plant</td>
<td>107.3</td>
<td>154.6</td>
</tr>
<tr>
<td>Open hearth side</td>
<td>Steel making plant</td>
<td>29.1</td>
<td>27.9</td>
</tr>
<tr>
<td>Converter side</td>
<td>Steel making plant</td>
<td>-20.9</td>
<td>29.8</td>
</tr>
<tr>
<td>Electric furnace side</td>
<td>Steel making plant</td>
<td>57.6</td>
<td>43.1</td>
</tr>
<tr>
<td>Normalizing furnace side</td>
<td>Rolling mill plant</td>
<td>22.7</td>
<td>29.9</td>
</tr>
<tr>
<td>Continuous furnace side</td>
<td>Rolling mill plant</td>
<td>7.1</td>
<td>13.4</td>
</tr>
<tr>
<td>Boiler side</td>
<td>Electric plant</td>
<td>29.8</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-furnace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mold yard (1)</td>
<td>Steel making plant</td>
<td>19.3</td>
<td>16.0</td>
</tr>
<tr>
<td>Mold yard (2)</td>
<td>Steel making plant</td>
<td>65.7</td>
<td>78.1</td>
</tr>
<tr>
<td>Roughing mill stand</td>
<td>Rolling mill plant</td>
<td>7.0</td>
<td>4.7</td>
</tr>
<tr>
<td>Three-high mill stand</td>
<td>Rolling mill plant</td>
<td>100.0</td>
<td>417.0</td>
</tr>
<tr>
<td>Discharge side</td>
<td>Sintering plant</td>
<td>28.0</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-producer</td>
<td>Rolling mill plant</td>
<td>29.7</td>
<td>50.1</td>
</tr>
<tr>
<td>Tilting table side</td>
<td>Coke making plant</td>
<td>48.5</td>
<td>55.1</td>
</tr>
<tr>
<td>Coke conveyor belt side</td>
<td>Sintering plant</td>
<td>21.3</td>
<td>40.8</td>
</tr>
<tr>
<td>Return hopper side</td>
<td>Sintering plant</td>
<td>12.4</td>
<td>35.3</td>
</tr>
<tr>
<td>Return feeder side</td>
<td>Steel making plant</td>
<td>4.0</td>
<td>4.6</td>
</tr>
<tr>
<td>Crane garter above</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>open-hearth</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>42.0</td>
<td>75.2</td>
</tr>
</tbody>
</table>

Table L(3).9 Concentrations of Benzo(a) pyrene [29]
g. **Cigarette Smoking**

Cigarette smoking probably is a very minor source of PAH emission into the atmosphere. Since the products of tobacco combustion are similar to the products of combustion of other fuels, they include CO, oxides of nitrogen and tars of a complex sort which contain BaP capable of causing cancer in experimental animals [1]. Table L(3).10 shows concentrations of BaP in cigarette smoke [71].

<table>
<thead>
<tr>
<th>Cigarette</th>
<th>Micrograms BaP per 100 cigarettes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GC</td>
</tr>
<tr>
<td>A-7</td>
<td>2.9, 3.4, 2.7, 2.9</td>
</tr>
<tr>
<td>A-7a</td>
<td>4.0, 4.1</td>
</tr>
<tr>
<td>AE-50</td>
<td>2.6, 2.7</td>
</tr>
<tr>
<td>K-1</td>
<td>1.9, 1.6*</td>
</tr>
<tr>
<td>G-1</td>
<td>1.8*, 1.8*</td>
</tr>
</tbody>
</table>

* Fractionation Method A; all others by Method B

Table L(3).10 Concentrations of BaP in Cigarette Smoke [71]

h. **Rubber Tire Dust**

No data have been found on the emission of BaP from rubber tire dust, but it is believed that rubber tire dust is a source of BaP emission into the atmosphere.

3. **Effects of Polynuclear Aromatic Hydrocarbons**

PAH are present in the atmosphere primarily as compounds adsorbed on soot particles [5]. The particle size on which the PAH are adsorbed is critically important with respect to the biological effect of the PAH. Particles in the size range 125Å to 2.5 μm are of great biological significance [34]. Falk and coworkers suggested that the size of the particulates on which the carcinogenic PAH are adsorbed also determines the rate of elusion of the PAH from the particles to our respiratory tract inside the body [35].
a. On Humans

In 1775 Sir Percival Pott reported a high incidence of scrotal cancer among chimney sweeps. This evidence indicated the presence of some carcinogenic factors in soot. The effect of soot or tar in producing skin cancer remained unproven until 1915, when Yamagiva, Ishikawa, and Tsutsui succeeded in inducing skin tumours by repeated applications of tar to the skin of rabbits and mice [36].

1. Cancers of the Skin

Polycyclic aromatic hydrocarbons have several characteristics which distinguish them from many of the other carcinogens. They act at the site of application. The effective dose is minute, of the order of micrograms, and they have been found to induce tumours in almost every tissue and animal species on which they have been tested [36]. Cancer of the skin among workers in the coal tar and pitch industry was first described by Butlin [39] in 1892. Henry reported in 1945 that 2,229 of 3,753 cases of industrial skin cancers were attributed to exposure to pitch and tar. The remaining were associated with exposure to mineral oils such as petroleums. The incidence of skin cancer has increased from an average of 170 to 190 yearly for many years in England to 220 cases per year in 1945 [40] and to 256 cases by 1953 [41]. Cancers of the skin have been reported after occupational exposure to tar and pitch with a latent period of from 15 to 25 years prior to their induction. Sladder [42] observed that incidence of skin cancer reached 66% after 10-15 years of exposure to pitch and 100% after 40 years. Cahman [43] compared the benzo(a)pyrene content of various industrial products. He reported a 0.3% - 0.8% content for coal tar, 0.03% for soot, and 0.003% - 0.004% for American shale oil.
Cottini and Mazzone [42] applied a 1% benzene solution of 
BaP daily to the skin of 26 human volunteers. The treatment was suspended 
after a maximum of 120 applications when infiltration occurred. They ob-
erved erythema, pigmentation, desquamation, verrucae formation and infil-
tration occurring in sequence. Rhoads [44] and partners reported similar 
changes in humans and mice following painting with benzo(a)pyrene. The 
conclusion, that benzo(a)pyrene painted on human skin in these experiments 
would have produced cancers if the treatment had been continued, appears 
justified.

11. Lung Cancer

No suspected carcinogenic PAH has been proven experimentally 
to cause lung cancer in humans. The increasing mortality rate from lung can-
cer has been related to exposure to polluted air by urban populations. In 
urban areas with relatively high smoke or air pollution levels the lung can-
cer death rates are considerably greater than in small town or rural areas 
where the air pollution levels are of much lower intensity [1]. It is gener-
ally agreed that a history of cigarette smoking is usually related to the risk 
of developing lung cancer. Hammond and Horn [13] reported that after correcting 
for the differences in smoking habits between urban and rural residents in the 
U.S., the rate of lung cancer was still 25 percent lower in rural areas. It 
seems to indicate that the joint effect of cigarette smoking and air pollution 
is additive rather than multiplicative, but the evidence is still inconclusive 
[11] [46] [47].

Stocks and Campbell [1] observed a higher incidence of lung 
cancer among persons living in an area in which BaP was known to be present 
in the atmosphere. Table I(3).11 shows lung cancer death rates and levels of 
BaP in the air in communities near Liverpool.
<table>
<thead>
<tr>
<th>Community</th>
<th>Type</th>
<th>Benzpyrene content in Micrograms per 100 M³ Air</th>
<th>Standardized Lung Cancer Death Rate 1950-54 Expected rate 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conway Valley</td>
<td>Village</td>
<td>0.1</td>
<td>59</td>
</tr>
<tr>
<td>Llangefni</td>
<td>Village</td>
<td>0.3</td>
<td>53</td>
</tr>
<tr>
<td>Ruthin</td>
<td>Small Town</td>
<td>0.5</td>
<td>15</td>
</tr>
<tr>
<td>Blaenau</td>
<td>Town</td>
<td>0.7</td>
<td>62</td>
</tr>
<tr>
<td>Flint</td>
<td>Industrial Town</td>
<td>1.85</td>
<td>74</td>
</tr>
<tr>
<td>Ormskirk</td>
<td>Industrial Town</td>
<td>2.2</td>
<td>95</td>
</tr>
<tr>
<td>Hoylake</td>
<td>Resort City</td>
<td>0.3</td>
<td>98</td>
</tr>
<tr>
<td>Wrexham</td>
<td>Industrial Town</td>
<td>1.95</td>
<td>78</td>
</tr>
<tr>
<td>Chester</td>
<td>Industrial Town</td>
<td>1.45</td>
<td>112</td>
</tr>
<tr>
<td>Bootle</td>
<td>Suburb-Liverpool</td>
<td>3.75</td>
<td>146</td>
</tr>
<tr>
<td>Warrington</td>
<td>Industrial Town</td>
<td>4.4</td>
<td>115</td>
</tr>
<tr>
<td>St. Helens</td>
<td>Industrial Town</td>
<td>4.75</td>
<td>111</td>
</tr>
<tr>
<td>Birkenhead</td>
<td>Harbor Town</td>
<td>3.3</td>
<td>132</td>
</tr>
<tr>
<td>Liverpool</td>
<td>Harbor and Industrial Town</td>
<td>2.95-6.75</td>
<td>158</td>
</tr>
</tbody>
</table>

Table L(3).11 Lung Cancer Death Rates and BaP Levels in the Air in Communities near Liverpool [1]

Shahab [10], Gorman [49] and Buck and Wicken [50] observed a relationship between the increased mortality from lung cancer and the concentration of carcinogenic PAH in urban areas. In England a high mortality among various groups of gas and tar workers was noted by Kennaway and Kennaway [31]. Doll [51] studied the causes of death among 2,071 male pensioners of a London gas company and found that the number of deaths from lung cancer was approximately double that expected by comparison with male inhabitants of London of the same ages (25 against 13.8 expected). Bonnet [52] reported from Switzerland that a workman, who was occupationally exposed to tar where he could have inhaled 320 µg of BaP per hour, developed a lung cancer. Konstantinova and Cherstova [19] studied the effect of dust and other airborne contaminants on lung cancer morbidity in the vicinity of two petroleum refineries of Ufa in Russia. They stated that the lung cancer mortality rates per 10,000 populations were 0.8 for the control area and 1.28 for the contaminated area.
Zeidberg et al. [53] reported on a study of 9,313 individuals in Nashville, Tennessee, in which they found no evidence of a relationship between air pollution and cancer morbidity rates. Sawicki [18] suggests that because airborne carcinogens are so numerous, further investigation into the composition of polluted atmospheres must be carried out. However, Falk et al. [45] concluded that the difficulty of induction of pulmonary cancer with PAH in experimental species may well reflect the low incidence of occupational lung cancer.

iii. Gastric Cancer

Gastric cancer has been linked with the presence of suspended particulate matter in the atmosphere. Winkelstein and Kantor [54] found that mortality rates from gastric cancer in a selected population were twice as high in areas of high suspended particulate as in areas of low pollution. The Nashville study [55] found that the soiling indices were correlated directly with mortality from stomach cancer and with the prevalence of bladder, esophagus, and prostate cancers.

b. On Animals

Extensive investigations of the effects on experimental animals by PAH compounds, such as BaP, that pollute the atmosphere have been carried out. Of the hydrocarbon carcinogens present in urban atmospheres, BaP is considered the most active carcinogen on animals. Much of the work has been done by skin painting with extracts of chimney soots [56], road dusts [57], and vehicular exhausts [58] [59], or by injection of these extracts [60] [61]. Not many investigations have involved inhalation studies. Probably Yamagiva, Ishikawa, and Tsutsui were the first workers who succeeded in
inducing skin tumors by repeated applications of tar to the skin of experimental animals [36]. Klär painted mice with a 0.25% benzene solution of BaP and produced skin cancers [62]. Kennaway produced tumors in mice with a synthetic compound 1,2, 5,6-dibenzanthracene [36]. Toth and Shubik [63] investigated carcinogenesis in AKR mice injected subcutaneously with BaP and dimethylnitrosoamine (DMN). Mice injected with BaP produced malignant lymphomas more rapidly, and developed lung adenomas. Bogacz and Koprowski [64] compared the carcinogenic properties of air pollutants, tobacco tar and BaP by means of correlated cytopathologic studies. It was found that mice treated intravaginally with air pollutants and tobacco tar developed cellular abnormalities and histologic lesions that were morphologically indistinguishable from those accompanying the development of BaP - induced carcinoma. Olsen et al., [65] compiled from various sources the carcinogenicity of atmospheric pollutants on mice as demonstrated with organic extracts. When pollutant extracts were administered to mice, whether by painting or by subcutaneous injection, local tumors, papillomas, carcinomas, or sarcomas, sometimes accompanied by multiple pulmonary adenomas generally resulted.

c. **On Vegetation**

No information on the effect of PAH on vegetation has been found.

d. **On Materials**

No information on the effect of PAH on materials has been found.
Environmental Air Standards

The American Conference of Governmental Industrial Hygienists in 1967 recommended Limits of 200 µg/m³ for an 8-hour workday for coal tar and pitch volatiles (benzene fractions containing anthracene, BaP, phenanthrene, acridine, chrysene, pyrene, etc.).

Table L(3).12 shows summer and winter concentrations of BaP for various urban atmospheres as compiled by Savicki [18].

<table>
<thead>
<tr>
<th>Location</th>
<th>Year</th>
<th>Summer (Low)</th>
<th>Winter (High)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgium</td>
<td>1960</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>Liege</td>
<td>1964</td>
<td>9</td>
<td>170</td>
</tr>
<tr>
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<td>1962</td>
<td>14</td>
<td>73</td>
</tr>
<tr>
<td>Prague</td>
<td>1964</td>
<td>6.4</td>
<td>15.4</td>
</tr>
<tr>
<td>Denmark</td>
<td>1961-1963</td>
<td>10</td>
<td>390</td>
</tr>
<tr>
<td>Copenhagen</td>
<td>1962</td>
<td>3</td>
<td>72</td>
</tr>
<tr>
<td>Germany</td>
<td>1966</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>Hamburg</td>
<td>1949</td>
<td>12</td>
<td>137</td>
</tr>
<tr>
<td>Great Britain</td>
<td>1949-1950</td>
<td>20</td>
<td>78</td>
</tr>
<tr>
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<td>1955</td>
<td>13</td>
<td>73</td>
</tr>
<tr>
<td>Stockholm</td>
<td>1955</td>
<td>13</td>
<td>73</td>
</tr>
<tr>
<td>Budapest</td>
<td>1955</td>
<td>13</td>
<td>73</td>
</tr>
<tr>
<td>Italy</td>
<td>1958</td>
<td>17.5</td>
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<tr>
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<td>0</td>
<td>212</td>
</tr>
<tr>
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<td>1961</td>
<td>0</td>
<td>29</td>
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<tr>
<td>Catanzaro</td>
<td>1961</td>
<td>0</td>
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<td>1961</td>
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<td>0</td>
<td>29</td>
</tr>
<tr>
<td>San Francisco</td>
<td>1960</td>
<td>0</td>
<td>29</td>
</tr>
<tr>
<td>South Charleston, W Va</td>
<td>1960</td>
<td>0</td>
<td>29</td>
</tr>
</tbody>
</table>

Table L(3).12 Concentrations of BaP in Summer and Winter [18]
5. **Detection and Measurement of PAH**

Because PAH are usually associated with particulates, samples are often collected as particulates with a high volume air sampler.

The PAH are generally removed from the particulates by solid-liquid extraction and separated into the different PAH type by column chromatography, thin-layer chromatography, or gas chromatography [67].

Several techniques for analysis of PAH are available including the:

i. Ultraviolet-visible absorption spectra method

ii. Fluorescence spectra method

iii. Piperonal test [68]

iv. Thermochromic test [69]

v. Photodynamic bioassay technique [70]

6. **Abatement Methods**

Improving the efficiency of combustion techniques of carbonaceous materials, including fuel oil and diesel combustion in motor vehicles, refuse burning, and domestic and industrial facilities that burn coal, oil, or gas, can reduce emissions of PAH substantially.

Emissions of PAH from catalytic regenerators of petroleum catalytic cracking units can be reduced to negligible amounts through the use of carbon monoxide waste heat boilers [21].
General control equipment for hydrocarbon emission from industrial processes can include the following:

1. Adsorption Methods

2. Vapor Recovery Systems

3. Cyclones for Particulates

4. Wet Scrubbers
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