UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL EFFECTS OF CHLORINE

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Chlorine

Chlorine (Cl_2), a greenish-yellow gas with a sharp odor is 2.5 times as heavy as air and 20 times as toxic as hydrogen chloride gas. During World War I, chlorine became notorious as a poisonous gas. When chlorine reaches the lung tissue, it combines with the hydrogen of water to form the highly corrosive hydrochloric acid (HCl). During this process, traces of ozone, another strong irritant, and free oxygen also are liberated according to the formulas:

$$Cl_2 + H_2) \longrightarrow HCl + HOCl$$
$$8\ HOCl \longrightarrow 6\ HCl + 2\ HClO_2 + O_2$$

(In sunlight or bright light, HOCl decomposes mainly as:

$$2\ HOCl \longrightarrow 2\ HCl + O_2.)$$

Uses of Chlorine

The largest consumer of chlorine is the chemical industry. The gas is used for preparation of organic and inorganic agents such as vinyl chloride plastics, pesticides and herbicides (e.g., DDT). The pulp and paper industry uses chlorine in bleaching operations[1]. Approximately 4% of all chlorine is used for water and sewage treatment (Tables 1 and 2). In addition, a variety of inorganic chemicals is prepared with chlorine, namely the chlorine salts, metals and other compounds; paint coatings; silicates (glass making); and phosphates.

Hydrochloric acid is emitted mainly from combustion of coal and oil (Table II). Between 0.01% and 0.5% of domestic coal is chlorine by weight, and 95% of that reaches the atmosphere as hydrochloric acid.[2] It has been estimated that the average chlorine content of coal is 0.2% and that 95% of this is converted to hydrochloric acid.[3]

Lapalucci and coworkers (4) estimated on a similar basis (i.e., 0.2% chlorine coal) that the stack of an 800-mw power plant will emit 11,300 cubic feet of hydrogen chloride each hour or 4560 tons each year. Near incineration dumps where poly-vinylchloride (vinyl plastics) is burned, hydrochloric acid is a major contaminant.

Chlorine usually is shipped in liquified form. During the liquification process it can become an important source of atmospheric contamination. When in contact with moisture, chlorine reacts to form hypochlorite, the active ingredient in liquid household bleaches, and hydrochloric acid, a strong corrosive irriting to the eyes and to the whole respiratory tract. In the United States, the industrial threshold limit value (TLV) for chlorine is 3 mg/meter^3 (1 ppm) for an 8-hour day, whereas Russia has adopted a more stringent limit of 1 mg/meter^3.

Chlorine Effects on Vegetation

The deleterious effects of chlorine compounds on plant life have been known and documented for well over a hundred years. In a 1951 report, Moyers (5) recounted a classic case in 19th centry England:

> In the early days of the Leblanc soda process, most of the hydrogen chloride from the treatment of salt with sulfuric acid was washed into the atmosphere causing extensive damage to plants near the factory. Between 1836 and 1863 scrubbers were installed at the various alkali works in England to remove at least 95 percent of the hydrogen chloride in the stack gases and in 1874 the concentration in these gases was limited to 0.45 mg per cubic meter, which eliminated crop damage. Hydrogen chloride is less toxic to plants than sulfur dioxide. The lesions are found principally on the margins or tips of the leaves, but sometimes between the veins as well.

Whereas SO_2 and flouride pose region-wide pollution problems, chlorine is found only where it is being used or where it is a byproduct of a manufacturing process. In recent years the localized damage from chlorine has been noted near swimming pools and sewage disposal plants. In one case, leaking cylinders used in water chlorination caused the damage. In another case at an industrial plant in Cincinnati, Ohio, (6) an accidental release caused severe damage in the immediate neighborhood. On the day after the release, leaves began to fall from tomato plants and trees in nearby yards. Silver maple trees had markings similar to those caused by SO_2. Extensive privet hedges in the area were almost bare. Plants reportedly have been defoliated with high level short-term field fumigations. The concentration of chlorine caused plant damage is greater than that reported for hydrogen fluoride and less than that reported for sulfur dioxide (7). Choride also can cause the type of marginal and tip necrosis induced by fluoride.

In 1955, Zimmerman (7) of Boyce Thompson Institute exposed 19 species of plants to chlorine at concentrations between 0.46 and 4.67 ppm, and 16 species experienced leaf spotting. Brennan, et al., (8) exposed tomato plants to three different Cl_2 levels for two and three hour periods, periodically spraying half of the plants with water and leaving the other half unsprayed. Wet and dry plants responded similarly: Whereas a concentration of 0.31 ppm caused no damage, 0.61 ppm caused slight injury and 1.38 ppm caused severe damage.

Chlorine in water exists partly in true solution and partly as HCl and the relatively unstable HOCl. Stanford Research Institute has reported injury to alfalfa and radishes after exposure to 0.10 ppm Cl_2 for two hours (7).

As with sulfur dioxide, the middle-aged leaves are most susceptible to chlorine injury, followed by the oldest and then the youngest leaves.

The injury by the Cl_2 resembles that induced by flouride, but frequently the effects more nearly resemble those of sulfur dioxide gas.

Hydrochloric Acid Mist and Chlorine Effects Observations

On August 14, 1969, vegetation injury from chlorine and acid mist was observed in Washington, West Virginia at a farm 3/4 mile northeast of the Amax specialty metals plant, producer of metals such as zirconium and hafnium. Such production involves complex metallurgical and chemical processes that can result in injurious emissions. For example, chlorine emission reportedly reached as much as 45 pounds per hour.

The farm's apple trees, grape vines, red buds, corn, and hibiscus all evidenced severe injury. The leaf tissue of broad leaf plants was discolored brownish-orange, and necrotic spots had formed on leaf surfaces. Injured apple and maple trees showed defoliation. Typical of chlorine damage, middle-aged and old leaves were most readily injured.

In October 1966, Hindawi (6) visited an eastern community to examine vegetation because residents had complained of acid mist smell and damage to trees, shrubs, and ornamental plants. Severe air pollution damage was evident on specimens of maple, cherry, red bud, rose bush, and begonia, accompanied by early leaf abscission. This damage resembles injury by hydrogen fluoride and sulfur dioxide.

Local emissions of hydrochloric acid mist and chlorine came from a glass manufacturing company, where the basic process reduces $SiCl_4$ in high-temperature ovens to produce fused silica glass. The company exhausted the waste gases through four stacks, two 125 feet high and two 105 feet high. Although HCl and Cl_2 were the main pollutants in the effluent, some silicon dioxide and silica gel also carried over, giving the effluent a bluish cast as it left the stack.

Table 3 shows HCl and Cl_2 emissions from three samples taken in each stack taken when, according to the company, the plant was operating at approximately 50% of its capacity. Total loading of HCl and Cl_2 at these conditions was 220 pounds per hour.

During night and early morning hours when winds are light and temperatures are cool, meteorological estimates of ground-level HCl concentrations indicate that about 0.5 ppm should be experienced about a mile downwind of the plant. Similar concentrations should occur on cloudy or mostly cloudy days with gentle winds. On bright sunny days with low wind speeds, concentrations should be much greater and the maximum concentrations should occur within a mile of the plant. However, because of terrain variations in the vicinity of the manufacturing plant, large variations from these estimates may be expected.

Hydrogen chloride gas has a high affinity for water, and once absorbed into water it becomes hydrochloric acid. In this instance, the plant damage, orange-brown in color and mainly marginal or in the necrotic area, could have been caused by chlorine diffusing through the margin of the leaves as droplets of acid.

However, chemical analyses of the tissue of injured silver maples showed a chloride content of 4700 ppm, compared to 3800 ppm for uninjured silver maple trees.

Health Effects

Chlorine concentrations of 3 to 6 ppm (9 to 18 mg/meter^3) cause stinging and burning in the eyes (10). Exposures to concentrations of 14 to 21 ppm for 30 to 60 minutes cause pulmonary edema, emphysema, and bronchitis, usually accompanied by marked muscular soreness and headache (11). Long term (up to 9 months) exposure of rabbits to chlorine concentrations of 0.7 to 1.7 ppm resulted in weight loss and a high incidence

Acute epidemics have repeatedly resulted in accidents while handling or emptying liquid chlorine containers. On January 31, 1961 (13) for instance, 6000 gallons of liquid chlorine spilled from a tank car torn open in a train wreck in the rural community of LaBarre, Louisiana. The gas cloud covered approximately six square miles and 1000 people had to be evacuated. Seven hours later the chlorine gas concentrations were still 400 ppm at a distance of 75 yards (about 70 meters) from the site of the accident and 10 ppm at the fringe of the cloud. As a result of this accident, about 100 people were treated for varying degrees of respiratory illness, and some developed congestive heart failure. An 11-month old infant died, as well as 500 animals including dogs, cats, horses, mules, chickens, hogs, cows, and ducks.

Only two months later in March (14), another accident occurred in Maryland. Supposedly empty liquid chlorine cylinders were being unloaded from a freighter in the Baltimore harbor. The main valve of a cylinder snapped off, immediately afflicting 156 persons with hemorrhages from the lungs or asthma-like wheezing and pneumonia-like lung infiltration. Some injuries persisted for 19 to 35 months and resulted in long-term pulmonary impairment.

More recently (15), 27 persons were treated in St. Luke's Hospital in Cleveland after a leak occurred in a liquid chlorine storage tank on May 9, 1969. Eighteen of them subsequently underwent a series of pulmonary function studies up to 14 months after the exposure. Although obstruction and hypoxemia (low oxygen levels in blood) cleared within three months, five persons still had persistently reduced air inflow after 14 months.

These experiences have prompted health authorities to enact strict precautionary rules for handling liquid chlorine cylinders, rules including plans for evacuating populations near threatened areas.

Chronic Effects

The numerous reports of acute poisoning by chlorine gas contrast with the great paucity of information on the chronic effect of minute amounts. Most observations have been made in factories producing the chemical. As early as 1909, Ronzani (16) observed that men working with chlorine aged prematurely, suffered from bronchial trouble, and were predisposed to tuberculosis. Corrosion of teeth was widespread because of the hydrochloric acid formed when chlorine combined with moisture of the mouth.

Veterans of World War I, hospitalized after gassing with chlorine, developed permanent lung damage and emphysema. Dr. Walbott (17) observed several individuals with advanced emphysema initiated by exposure to chlorine gas in World War I. In some he was able to pinpoint a specific area of the lungs showing a localized process, suggestive of a primary corrosion of bronchial and pulmonary tissue at the site of impact. This so-called asthma resists treatment that usually benefits allergic asthma.

When chlorine is combined with hydrochloric acid, a higher concentration is required for detection of the odor than for each gas individually (17).

Effect of Hydrochloric Acid and Chlorine Gas on Materials

In the literature reviewed, no information was found describing corrosion or damage to material from exposure to environmental concentrations of the hydrochloric acid and chlorine. However, it is well-known that hydrochloric acid and solutions are extremely corrosive to most metals and alloys (18, 19). Mellor (20) has summarized 24 studies on hydrochloric acid corrosion of various hard and mild steels and cast iron. He noted that corrosion of cast iron and steel increases regularly as the concentration of acid increases. This suggests that chlorine in sufficiently high concentrations would corrode metals, discolor and damage painted material, and damage textile and fibers.

Summary and Conclusion

- Chlorine, an odorous gas, is 2.5 times as heavy as air and more toxic than hydrogen chloride gas.

- Chlorine is used in bleaching operations, purification of water and preparation of organic and inorganic agents.

- Chlorine pollution is not a widespread problem like sulfur dioxide. Chlorine gas damage on vegetation has been noticed near swimming pools, sewage disposal plants, and other localized sources of chlorine.

- An accidental release of chlorine causes severe vegetation damage in the immediate neighborhood.

- The concentration of chlorine required for plant damage is greater than that reported for hydrogen flouride and less than that reported for sulfur dioxide.

- Chlorine irritates mucosal membranes such as the eyes and respiratory tract because Cl_2 combines with moisture to form HCl.

- Acute epidemics have repeatedly resulted from accidents associated with the handling or emptying of liquid chlorine cylinders.

- Chlorine and hydrochloric acid mist and solutions are extremely corrosive to most metals and alloys.

- Hydrochloric acid is produced when water absorbs the hydrogen chloride gas. Hydrogen chloride is produced by the acid salt process, by direct synthesis, and from chlorination of organic compounds.

The burning of coal and/or chlorinated plastics and paper is another source of hydrochloric acid pollution.

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Table I. Uses of chlorine and hydrochloric acid in 1969 in the United States[2]

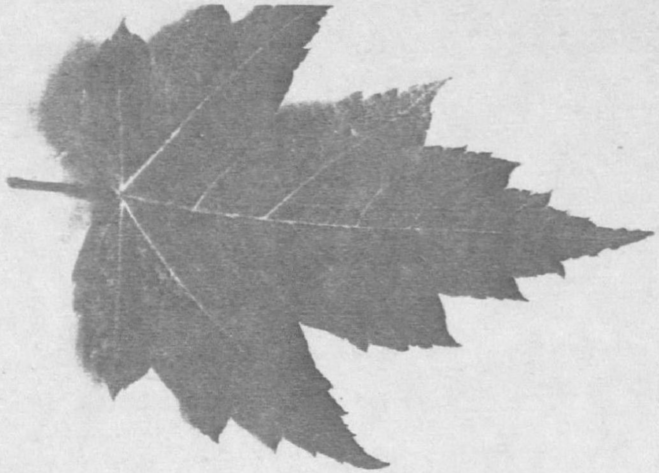
Chlorine	Percent	Hydrochloric Acid	Percent
Organic chlorinations	78.5	Organic chlorinations	50.0
Pulp, paper bleaching	15.0	Treatment of oil wells	17.0
Water, sewage treatment	3.5	Metallurgical processes	17.0
Manufacturing bleaches	2.0	Metal pickling	7.0
Metallurgical processes	1.0	Food processing	4.0
		Miscellaneous inorganic chemicals	5.0

Table II. Estimated United States emissions of chlorine and hydrochloric acid in 1969 (tons/year)[2]

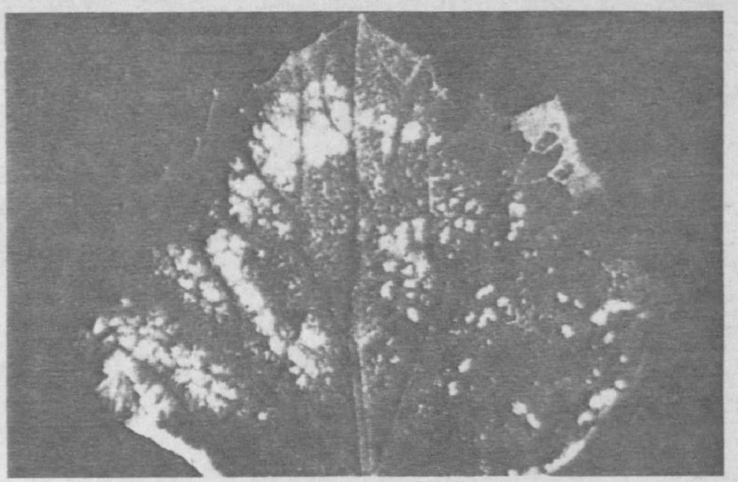
Source	Estimated Emissions	
	Chlorine	Hydrochloric acid
Chlorine manufacture	47,000	0
Hydrochloric Acid manufacture	800	5,700
Chemical and industrial processes	30,400	27,400
Combustion	0	874,500
Total	78,200	907,600

Table III. Stack Emissions from Glass Manufacturing Plant (ppm)[6]

Stack No.	HCl	CL_2
1	119	0.91
2	473	0.56
3	302	0.52
4	421	0.92



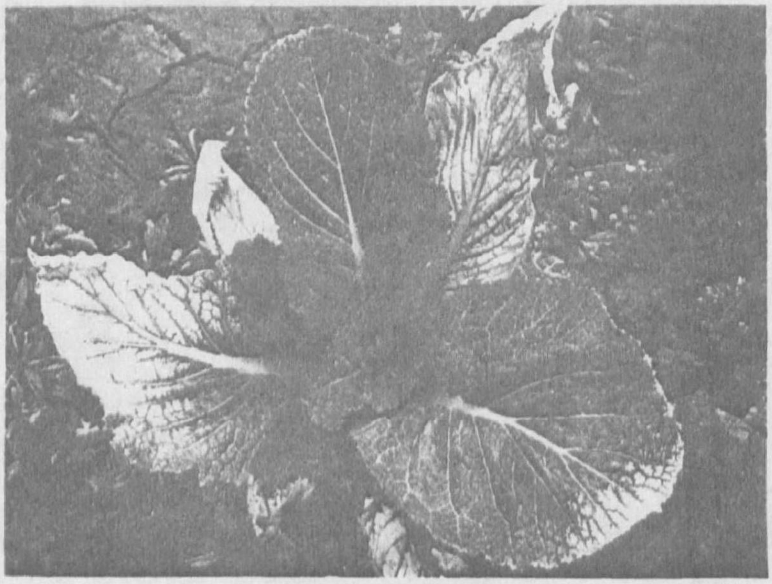
Chlorine injury to silver maple leaves is similar to sulfu, dioxide injury.



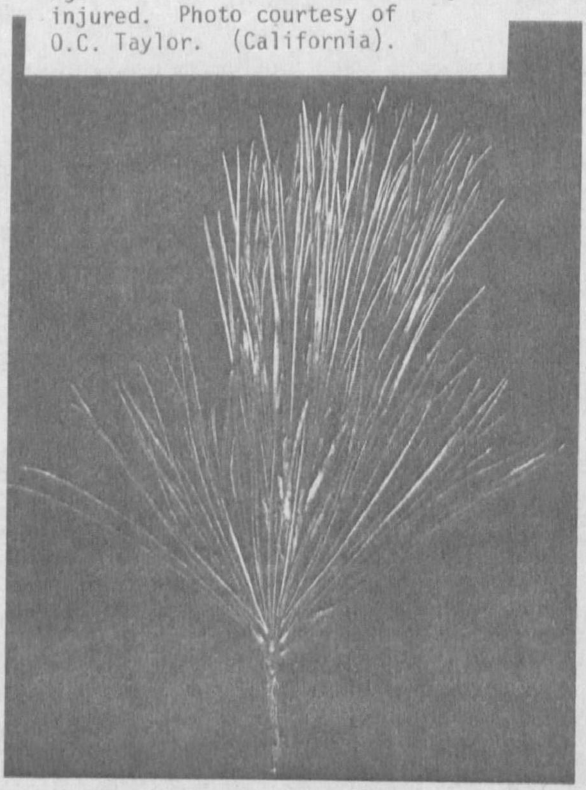
. *Cucumber leaf exposed to 0.75 ppm Cl_2 for 4 hours shows injury similar to sulfur dioxide injury.*

Figure 7. Injury on begonia leaves caused by chlorine and hydrochloric acid mist.

Figure 6. Injury on redbud leaves caused by chlorine and hydro chloric acid mist.



Chlorine injury to mustard leaves observed in the field. The middle aged and the old leaves severley injured. Photo courtesy of O.C. Taylor. (California).



Chlorine injury to white pine observed in the field. Photo courtesy of A.C. Hill. (Utah).