

## Chlorine in the World: Good or Bad?

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In recent times, chlorine and its compounds have come under public scrutiny. Greenpeace asserted, "There is no use of chlorine which we can regard as safe." (Malkin & Fumento, 1997.) Others have stated, "Dioxins are the most toxic chemicals made by mankind ..." (Chlorophiles, 1996, A). As with many useful raw materials from nature, chlorine is not without controversy. Doctors of chiropractic are advising their patients on health issues related to environmental contaminants; chlorine is one such ubiquitous contaminant. This presentation briefly explores some of the chemical characteristics, sources, commercial uses, workplace safety measures, and human health, environmental, social, and economic issues related to chlorine and its compounds.

Chlorine is a highly reactive, naturally occurring element (Chiras, 1994; Manahan, 1993; Patnaik, 1992). It makes up .045-.19% of the earth's crust and 2.9% of the world's oceans (Chlorophiles, 1996, B; Euro Chlor, 1997, A). "Only 15 elements make up 99.5% of the human body; elemental chlorine is the 10th most abundant. Only 16 elements make up 99.5% of the earth's crust, including air and water, and chlorine ranks 11th" (Euro Chlor, 1997, B). Chlorine is everywhere in nature and widely used by modern society in the manufacture of more than 10,000 products (Chlorophiles, 1996, C).

### Sources

Chlorine is manufactured in abundance for modern uses; over 23 billion pounds were produced in 1992 (EPA, 1994). In the U.S., it's produced in more than 40 chemical manufacturing facilities; in Europe, more than 79 plants (EPA, 1994; Euro Chlor, 1997, B). Man-made production levels are expected to peak sometime in the 1990s, then decline due to public concern over organochlorine compounds and their potentially adverse effects on people and the environment (EPA, 1994).

Nature is also a vigorous supplier of chlorine. In addition to its substantial presence in the earth's crust, oceans, and atmosphere, volcanic eruptions, forest fires, plants, animals, and virtually all decaying organic matter produce chlorine or chlorinated compounds (Euro Chlor, 1997, C). Over 1,500 organochlorine compounds have been identified in nature (Chlorophiles, 1996, B). Chlorine is ubiquitous and cannot be eliminated from nature or mankind; "The complete removal from the environment would be unattainable" (Malkin & Fumento, 1997). " and " Characteristics

Chlorine in its purest form is a highly reactive gas (EPA, 1994). It is a strong oxidizer of many elements (Manahan, 1993). Its solid or liquid form is the chloride ion, negatively charged, easily ionizable, and readily available in the world's oceans, our table salt, and even in our bodies. It may be found in combination with other elements to form compounds such as inorganic salts, acids, chloramines, or organochlorines (Chlorophiles, 1996, B; RPI, 1997, A). It is a greenish yellow gas with a suffocating odor (Patnaik, 1992).

Chlorine's highly reactive nature is described as "breakpoint chlorination." This means a chlorine reaction will start slowly but potentiate to faster reaction speeds, which may result in potentially explosive results with many other elements (RPI, 1997, B). It readily reacts with organic compounds to form alkyl halides, alkenyl halides, and aryl halides (Manahan, 1993), which have

become the focus of the environmentally concerned because of their toxic nature.

Dioxins, PCBs, and DDT are organochlorine compounds that represent a significant concern to many communities (Chiras, 1994; Greenpeace, 1997). Many organochlorine compounds are now called "endocrine disrupters" and have the capacity to mimic estrogen in the body (McLachlan & Arnold, 1996). Chlorine is also a key culprit in the formation of chlorofluorocarbons, which have been implicated in destruction of the ozone layer within the stratosphere (Chiras, 1994; Manahan, 1993; Towles, 1997). The chain reaction ability of chlorine enables one molecule to destroy 100,000 ozone molecules (Chiras, 1994).

### Commercial Use

Chlorine is used as a raw material for the creation of numerous products and compounds made of vinyl chloride plastics and polymer resins. It is used to manufacture such things as x-ray film, plumbing pipes, blood bags, IV tubes, packaging, rubber boots, imitation leather, wallpaper, computers, office equipment, garden furniture, and even kevlar vests (Envirolink, 1997; Euro Chlor, 1997, A; Howlett, 1995).

Chlorinated solvents are used by many industries. The production of pulp and paper uses chlorine dioxide or similar chlorinated compounds as bleaching agents in their production process (AET, 1994). Bleaching agents are especially important in the production of recycled paper (Chlorine Chemistry Council, 1997, A). Organic chlorinated solvents such as trichloroethylene are also widely used as degreasing agents and then disposed of as spent solvents. Their disposal requires proper treatment under RCRA, but residues may still find their way into the environment as water and soil contaminants despite efforts at proper hazardous waste management (Chiras, 1994; EPA, 1994; Manahan, 1994).

Chlorofluorocarbons, or freons, have been used for years in the refrigeration industries as blowing agents. Their release into the atmosphere poses a threat to the integrity of the ozone layer (Manahan, 1994; Towles, 1997).

It is estimated that 85% of all modern pharmaceuticals include chlorine as a primary constituent, or depend on it in the production of the actual end product (Malkin & Fumento, 1997; Howlett, 1995). Many of the newer generation antibiotics are made of chlorinated compounds, which have been highly effective in stopping mutated pathogens.

Chlorine is the cornerstone element of modern pesticide success (Chiras, 1994; Klaassen, 1996; Manahan, 1993). Chlorinated pesticides are credited with protecting as much as 96% of the world's modern crop production from insect pest destruction (Malkin & Fumento, 1997; Chiras, 1994; Howlett, 1995).

Chlorine's greatest use has been in the virtual elimination of waterborne disease from public water supplies. Chlorine is used to purify and disinfect 98% of all public drinking water used by the modern world (Malkin & Fumento, 1997; Chlorine Chemistry Council, 1997, B).

### Exposure Routes

The main exposure route of chlorine gas is through inhalation (Klaassen, 1996; Williams & Burson, 1985; Zenz & Cordasco, 1994). Gas exposures are usually occupational and require immediate removal from contaminated areas. Diffusion across the lung alveoli is rapid; however, the immediate threat may be suffocation followed by upper respiratory irritation (Zenz & Cordasco, 1994). Environmental releases may undergo rapid hydrolysis by other air molecules and form hydrochloric acid droplets causing acid clouds. This new compound poses new risk of respiratory

injury to humans, as well as property, crop, and livestock damage (Manahan, 1993).

The other chief exposure route of chlorinated compounds is oral ingestion (Chiras, 1994; EPA, 1994; Manahan, 1993). Chlorine is present in the atmosphere, our food, water, soil, and even within our own bodies. These compounds may be ingested by way of contamination to our food, soil, and water as in pesticide residues, industrial waste contaminants, disinfectants, medications, dioxins or PCBs from chemical degradation. Other chlorinated compounds from industrial or natural sources may be orally ingested (Chiras, 1994).

Drinking and bathing in chlorinated water exposes people to approximately 200 different organochlorine compounds. Bathing facilitates both dermal absorption and inhalation exposures to organochlorines. Some compounds like trihalomethanes (e.g., Chloroform) are volatile and readily pass through the alveolar membranes of the lung to the blood supply. That long, hot shower can mean a large exposure to organochlorines.

Chlorinated solvents such as dichloromethane, chloroform, and carbontetrachloride may also be rapidly absorbed through the skin. Many of these types of compounds are lipophilic and will pass through the body's phospholipid bilayer membrane to exert toxic effects (Klaassen, 1996).

### Chlorine in the Body

Chlorine is an essential element to human life. It is the body's 10th most concentrated element in the form of chloride ion. Under normal conditions, the kidney resorbs chloride ions in an effort to maintain an adequate supply for vital metabolic processes (Hardman, 1996). Chloride plays a major role as an extracellular ion due to its electrical charge. This is important in nerve conduction, muscle contraction, membrane potential, and cellular homeostasis. It is essential in the body's maintenance of an acceptable acid base balance range. Chloride can be exchanged for bicarbonate molecules and excreted when the body needs to prevent metabolic acidosis (Guyton, 1976).

### Toxicokinetics

The myriad of chlorinated compounds presents many different models for the absorption, distribution, biotransformation, and elimination of the specific compound itself. For example, animal models reveal that once chlorine is in the body, it is rapidly distributed in the blood compartment with peak levels measured within two hours. The highest concentrations are seen in the plasma, then the bone marrow, kidneys, testes, lungs, skin, GI, liver, and the carcass (EPA, 1994). Non-combined chlorine is rapidly cleared through the kidney into the urine. Animal studies revealed 81% excretion within 96 hours as chloride ions (EPA, 1994).

Carbon tetrachloride is also rapidly absorbed into the system, but it is metabolized in the liver. This lipophilic compound is concentrated in the liver and then biotransformed by cytochrome p-450 enzyme to CCL3 and then to CCL300. This is an example of bioactivation of CCL4 metabolites to produce free radical peroxidation and can cause permanent liver damage (Klaassen, 1996).

Pesticides like DDT were banned because of their lipophilicity and tendency to be concentrated and stored in the body fat. In the 1960s, worldwide levels of DDT in humans were estimated to be 5-15 ppm in all tissues with fat storage levels of 2 ppm. The bioavailable compound is the only portion that is detoxified by glutathione conjugation in the liver and excreted into the bile and then the feces (Klaassen, 1996). Unfortunately, stored reservoirs of DDT are not readily cleared and remain for long periods of time with a prolonged half-life of up to 50 years (McLachlan & Arnold, 1996). DDT has been shown to accumulate in aquatic, mammalian, and avian life (Envirolink, 1997).

### Toxicodynamics

Chlorine has a high acute toxicity level to aquatic organisms, many as low as 1 mg/L concentration. For example, .29 mg/L will kill trout, and .71-.82 ppm will kill a sun fish, while much higher levels, 137-293 ppm, are needed to kill a rat (EPA, 1994). The high aquatic toxicity is what makes chlorine good for disinfecting water. Chlorine seems to be well tolerated by humans; experiments have tested levels of 2.5 mg/day for 90 days which produced no adverse effects; however, levels above 25 ppm in drinking water make it unpalatable and 93 ppm will irritate the throat (EPA, 1994). Chlorine is a primary irritant to humans, causing adverse reactions to mucus membranes of the upper respiratory system.

The major concern is about organochlorinated compounds like PCBs, dioxins, and DDT. PCBs are notorious chlorinated compounds that may be orally ingested from contaminated water, soil, food, and bioaccumulated in living organisms. Arctic diets high in fish have been shown to be high in PCBs bioaccumulated by marine life (Klaassen, 1996). PCBs have been tagged "xenoestrogens" and "endocrine disrupters" because of their ability to mimic estrogen receptor activity and induce cancers (Chlorine Chemistry Council, 1997, C; Klaassen, 1996; McLachlan & Arnold, 1996). Most organochlorinated compounds are lipophilic and stored in fat. They are also biotransformed in the liver and excreted into the bile and mammary milk (Klaassen, 1996).

Organochlorinated compounds have toxicity profiles that can vitally damage every system of the body. The major emphasis and concern is over those that induce mutagenesis, genotoxicity, and carcinogenicity (Chiras, 1994; Envirolink, 1997; Greenpeace, 1997; Manahan, 1993).

#### Workplace Safety Measures

Great efforts are being taken to protect employees from chemical exposures in the workplace; protection from chlorine is no exception. The Occupational Safety and Health Administration (OSHA) has set the permissible exposure limit (PEL) at 1 ppm over an 8-hour time weighted average (TWA), while the National Institute for Occupational Safety and Health (NIOSH) has recommended a lower limit of .5 ppm (NIOSH, 1994; OSHA, 1994). Levels of 10 ppm chlorine gas exposure are considered an immediate danger to life and health (IDLH). Workers who use chlorine must use appropriate respiratory protection, limit atmospheric exposure to 5 ppm, and be trained in "hazard communication" per the 29 CFR 1910.1200 OSHA regulations (OSHA, 1994). Other chlorine compounds have their own PELs and threshold limit values (TLVs) set and recommended by either OSHA, NIOSH, or ACGIH. For example, chlordane, a common pesticide, has a PEL of .5 mg/m<sup>3</sup>, while chlorine dioxide PEL is set at .1 ppm (NIOSH, 1994). Approximately 2,200 chemicals have TLVs and fewer have PELs, many are chlorinated compounds. Much work is needed to be done to accurately set TLVs and PELs for the many more chemicals in use and the new chemicals being created annually for use in industry.

#### Environmental Impact

The real environmental impact of chlorine is still being measured. No one really knows all the potential ramifications of chlorine, its multitude of compounds and their impact on human health and the environment. Catastrophes like Times Beach, Missouri and Love Canal, New York have demonstrated the magnitude of social and economic response precipitated by concerns for potential adverse health effects to human kind. The Superfund law set aside \$16.3 billion to clean up communities decimated by chemical contamination (Chiras, 1994).

Organochlorines and their recent link to hormone-induced cancers have drawn great attention to dioxins, PCBs, pesticides, solvents, and other chlorinated hydrocarbons. Their long-term effects are yet to be clearly understood. Whether synthetic or naturally occurring, the public is concerned about contamination by chlorine and its compounds to their food, water, and the environment.

Chlorinated chemicals have been shown to adversely impact marine, avian, and terrestrial life causing concern for human kind and preservation of our future (Chiras, 1994).

Chlorofluorocarbons make up only .000225 % of the major "greenhouse gasses" but are expected to persist in the atmosphere for the next 100 years (Chiras, 1994). Even though the U.S. has phased out CFCs, many countries have not. Mounting concerns persist to avoid potential "global warming," and reduction of chlorinated compounds remains a part of the major control strategies (Chiras, 1994). Much more has to be learned about chlorine and its compounds.

#### Risk vs. Benefit

Modern science defines risk as "possibility x consequences" (Chlorophiles, 1997). Responsible risk assessment methods call for hazard identification, dose-response assessment, exposure assessment, and risk characterization (NRC, 1993). In order to accurately evaluate each of the many thousands of chlorinated compounds, this process should be applied exhaustively for each of the specific compounds. The reality is that 50,000 to 70,000 people die each year from toxic exposure and related chronic disease (Landrigan, 1992). Williams & Burson (1985) estimated that some 100,000 new chemicals are created every year and some 60,000 are used continuously in industry, while only 20% have been tested for carcinogenicity, and even fewer have been tested for other types of toxicity (Landrigan, 1992).

Clearly, chlorine has demonstrated great benefits to mankind through its many applications to our health, life, convenience, and technology (Chlorophiles, 1997; Chlorine Chemistry Council, 1997, D; Howlett, 1995). The risks associated with technology, synthetics, discovery, and the modern world have been equally earth shaking. We have seen the devastation possible from chlorinated compounds like PCBs can that virtually destroy communities, as it did to Times Beach, Missouri in 1983 (Chiras, 1994). The jury is still out on the final sentencing for chlorine. It is certain that chlorine cannot be eliminated entirely, but its production, use, and disposal can be responsibly managed; that challenge belongs to industry and consumers.

#### Social Issues and Economic Impact

As long as people demand the luxury and standards of modern society, the chemical engineers, inventors, and scientists will continue creating new chemicals and using those presently known to meet those needs and wishes.

Efforts are being made to find alternatives to certain chlorinated compounds (AET, 1994) as well as the complete elimination of other chemicals. DDT has been outlawed for several years in the U.S. Chlorofluorocarbons were scheduled to be phased out of use by 1997. Dioxins and PCBs are not produced intentionally, but are unwanted byproducts of other chemical processes (Chlorophiles, 1996, D).

Policy makers have responded to the wishes of the people by legislating over 70 environmental laws since the 1940s and promulgating over 200,000 regulations, many of which pertain to our health and the environment (Ray, 1993). The Rio and Montreal Earth Summits are testament to the global concerns for the environment and its impact to us all.

The economic impact that chlorine has on our nation's fiscal health is significant. Chlorine provides 1.3 million jobs to American workers with wages totaling \$31 billion in 1990 (Heartland Inst., 1997). Over 370,000 people are directly employed in the manufacture of chlorine used by multiple industries worldwide. Chlorine-based pharmaceuticals is a \$50 billion per year industry (Chlorine Chemistry Council, 1997, B). The estimated monetary savings of using chlorine rather than more

costly alternatives is over \$90 billion to U.S. consumers each year (Chlorine Chemistry Council, 1997, B)

## Conclusions

Significant gains have been made in environmental, health, and safety management of chlorinated compounds and other hazardous wastes and compounds. The surface of our understanding and knowledge is but scratched; much is known about chlorinated chemicals, but much more is not. Scientists continue to work feverishly to find new and better ways to achieve the clean environment desired by all. Commitment to a sustainable earth is no longer a dream, but a reality to be practiced. Doctors of chiropractic can participate by advising their patients to filter chlorine from their drinking and bathing water. Reasonable avoidance of contact with chlorine and organochlorines is prudent.

Alternative water purification methods devoid of chlorine should be carefully evaluated and pursued if safe, reasonable, and cost efficient. It is certain that complete avoidance of chlorine is not possible or desirable, but with a little effort, we can each play an important role in reducing potentially hazardous chemical exposure to our patients.

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