American Chemistry Council

Chlorine Chemistry

# Natural Chlorine? You Bet!

## Chlorine's Natural Abundance

Most people know that table salt, a natural mineral essential for the proper functioning of our nervous and muscular systems, is sodium chloride. But many would be surprised to know that hundreds, probably thousands, of organic chlorine chemicals are produced by an array of biological and natural chemical processes in our environment. Many of these chemicals are identical to highly publicized manmade organochlorines: chlorophenols, chlorinated hydrocarbons, PCBs, CFCs and dioxins. But many others are entirely new molecular entities, many of which possess extraordinary and important biological properties similar to those of penicillin, morphine and the new anti-cancer drug taxol.

As a fundamental chemical element, chlorine is not only abundant in the Earth's crust (ranking 18th in the list of elements) but it is also ubiquitous in our soil, rivers, lakes, trees, plants and, of course, oceans. Like other common elements carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorous that are present in all living things, it would appear that chlorine and the other halogens (bromine, iodine and, to a lesser extent, fluorine) are present as well. Although only 30 natural organochlorines had been discovered by 1968, this number has grown to over 1,000. And more are being discovered every month.

Organochlorine and the related organobromine compounds are produced naturally by marine creatures (sponges, corals, sea slugs, tunicates, sea fans and jelly fish) and seaweed, plants, seeds, trees, fungi, lichen, algae, bacteria, microbes and insects. The ocean is the single greatest source of different organochlorines. Nearly 100 different organochlorine, organobromine and organoiodine compounds are present in "limu kohu," the favorite edible seaweed of most Hawaiians. Other seaweeds produce bromoform, chloroform, carbon tetrachloride, methyl bromide and numerous polyhalomethanes. It had been reported that ozone destruction in the lower Arctic atmosphere is linked to the bromoform that is produced in large quantities by sea ice algae. As a matter of fact, the "smell of the oceans" is probably due to these volatile organochlorines and other organohalogens. A species of marine worm from the Gulf of Mexico secretes 20 different halogenated compounds, mainly phenols.

# Chlorine Compounds Are Crucial for Survival

Extensive research has shown that these organochlorine compounds are not derived from pollutants but, rather, are produced by individual organisms for very specific purposes. They play an essential role in the organisms' survival, and their ability to synthesize these compounds has evolved over time under the stress of natural selection.

Many of these natural organochlorine compounds are used in chemical defense—as feeding deterrents, irritants, or pesticides or to facilitate food gathering. One marine algae compound, called telfairine, which is chemically similar to many chlorinated pesticides, is 100 percent lethal to mosquito larvae at ten parts per million (ppm), and a related natural chlorinated chemical is three times more effective than the commercial chlorinated pesticide Lindane against mosquito larvae.

Other organochlorines serve as hormones. Plants such as lentil and sweet pea use 4-chloroindoleacetic acid as a growth hormone, and a Chinese folk medicine plant contains five natural chlorinated compounds. The German cockroach manufactures two chlorinated steroids as trail pheremones used in food gathering; the Lone Star tick produces 2,6-dichlorophenol as a sex pheremone; and locusts employ chlorinated proteins to strengthen the cuticle. A Penicillium species produces 2,4-dichlorophenol, the same chemical that man uses to synthesize the herbicide 2,4-D. Recently, a tiny Ecuadoran frog was found to secrete a chlorinated alkaloid which is 500 times more powerful than morphine as a pain-killer and which is believed to thwart predators such as birds.

It is only a matter of time before many natural organochlorine compounds are found in humans. Indeed, organoiodines (thyroid hormones) and one organobromine compound are well humans. Indeed, organoiodines (thyroid hormones) and one organobromine compound are well known to be present in humans.

An astonishing research development is the discovery that our immune system actually uses chlorine, bromine and iodine to halogenate and kill invading microorganisms. For example, cellular enzymes in mammalian white blood cells oxidize natural blood chloride (bromide and iodide) into active chlorine. This causes the death of pathogens (bacteria, yeast, fungi and even tumor cells) by chlorination. chlorination is apparently as natural a biological process as blood clotting or salivation.

# Part of Nature's Recycling Process

Nature is an incredible recycling center. Insects, microorganisms and fungi all break down dead matter to simpler chemicals for reuse. One such organism, the white-rot fungus, decomposes dead trees and other forest plant material. A major natural byproduct of this biological decay is methyl chloride (chloromethane) the simplest organochlorine. Five million tons of this chemical are produced naturally every year. This amount dwarfs the 26 thousand tons produced annually by man. Some scientists believe that this natural methyl chloride is an innate regulator of stratospheric ozone.

Another breakdown process involves the biodegradation of humic and fulvic acids into phenols and chlorophenols. Several studies have shown that this natural production of chlorinated phenols outweighs man-made sources. For example, the total pool of chlorinated compounds in peat bogs in Sweden is several hundred thousand tons in areas where these chemicals can only be of natural origin. By comparison, the largest industrial source of these chemicals in Sweden is from the paper pulp industry, which produces 10,000 tons per year. Although "environmentalists" try to link the presence of organochlorine compounds in water samples to man-made causes, naturally produced chemicals have been found in groundwater samples dating back 5200 years.

Because organic matter contains natural chloride (up to 10,000 ppm) and this reacts to form organochlorines at high temperatures, methyl chloride, methyl bromide and many other haloalkanes are produced when organic matter burns.

This natural chemical process occurs in forest fires and volcanoes. In fact, it has been estimated that the largest [natural] source of dioxins in the environment is from forest fires, of which 200,000 occur annually (most of which are caused by lightening; e.g., the Yellowstone fires in 1988). Indeed, dioxins have been identified in 100-year-old preserved soil samples.

Both Mount St. Helens and Hawaii's Kilauea, the latter of which has been erupting since 1983, produce methyl chloride. The Kamchatka volcanoes in Siberia and Guatemala's Santiaguito volcano emit CFCs in quantities well above background levels. Many organochiorines now known to be produced by volcanoes including tetrachloroethylene, chloroform, carbon tetrachloride, methylene chloride and several of the CFCs, were formerly thought only to result from the actions of man! From one Kamchatka volcanic vent, $CF_2Cl_2$ was detected in levels of 160 ppb, 400 times that of the background atmosphere. Such natural chlorine and fluorine compounds are produced by the combustion of organic material, such as vegetation, sediments or fossil soils in the presence of chloride and fluoride minerals. The extent to which these natural organochlorines and CFCs contribute to the global picture vis-à-vis ozone depletion remains to be seen. A study of Mount St. Helens ash revealed the presence of three previously unknown isomers of polychlorobiphenyls (PCBs) presumably formed from the combustion of carbon- and chloride-rich plant material during the 1980 eruption.

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