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Chlorine - Let's Not Ban It

"*God created 91 chemical elements, man more than a thousand and the devil created one: chlorine*."- Greenpeace Magazine, Belgium, August 1992

Greenpeace, a worldwide environmental activist group, has lobbied for a total ban on chlorine and chlorinated chemicals. Greenpeace charges that the use of chlorine in manufacturing processes and drinking water purification is causing higher rates of cancer than would otherwise occur. The organization also claims that the exposure of pregnant mothers to even tiny traces of chlorinated chemicals has negative effects on the development of their unborn children.[1]

Patrick Moore, one of the founders of Greenpeace, has this to say about the organizations campaign to ban chlorine. "At the time Greenpeace was adopting this policy I pointed out to them that adding chlorine to drinking water was the biggest advance in the history of public health. I also reminded them that the majority of our pharmaceuticals are based on chlorine chemistry. And for good measure I suggested that the best way to deliver the slightly chlorinated drinking water to the general public was in a PVC (polyvinyl chloride) pipe. They behaved as if these were minor exceptions to the general rule that chlorine should be banned worldwide, so I had to leave."[2] According to Moore, the Greenpeace anti-chlorine campaign of the late 1980s-early 1990s is an example of irrational positions (zero-tolerance positions that he believes are based more on sensation and fund-raising around scare tactics), "I was an international director, one of five. My fellow international directors had no science education,[...] and they decided we should start a campaign to ban chlorine worldwide. I said: "Chlorine is one of the elements in the periodic table. I don't think that's in our jurisdiction." And they said: "No, this is a good campaign. Chlorine is the devil's element, and it works really well for fund-raising and media and everything."

So chlorine has been a long-standing target of Greenpeace and other groups opposed to any use of man-made chemicals. "There are no known uses for chlorine which we regard as safe," said Greenpeace's Joe Thornton in a 1993 issue of *Science* magazine.[3]

These days Greenpeace claims it doesn't want to ban chlorine completely - at least not yet. Instead, they are urging water treatment facilities to switch from chlorine gas - the most affordable form of chlorination - to other disinfectants, unilaterally deemed by Greenpeace to be "inherently safer." Yet the alternative is still a chlorine product - only in liquid form.[4]

Chlorine is one of more than 100 elements that make up our universe and is one of the 20 or so elements that make up all living things. Chlorine occurs in nature in several forms, such as inorganic chloride salts (*i.e.*, sodium chloride, common table salt) and the numerous chlorinated organic (*i.e.*, containing carbon) compounds found in plants, the soil, the atmosphere and ocean life.[1]

Less well known - even to many scientists - is that nature produces an abundance of similar, and in some cases identical, halogenated compounds, some of which predate the beginning of life on Earth.[5]

Human-made compounds called organohalogens get loads of attention, as they are best known for their potentially harmful effect on the environment - substances like the CFCs (the ozone-damaging chemicals), dioxin (found in the herbicide Agent Orange), PCBs (industrial fluids) and several pesticides. However, here's the real kicker. Their naturally occurring cousins don't get the recognition they deserve, according to Dartmouth Chemistry Professor Gordon Gribble. Gribble has taken it upon himself to help scientists and the public understand that there are more than 4,000 naturally-occurring organohalogens, and many are similar or even identical to their synthetic counterparts.[6]

Gribble reports, "These include a relatively small number of abiogenic (from lifeless matter) organohalogens from volcanoes, forest fires, geothermal processes and meteorites, and a very large number of biogenic (from living matter) organohalogens produced by myriad living organisms as part of their chemical makeup that serve as hormones, pheromones, repellents and natural pesticides. From the chemically simple methyl chloride, methyl bromide and chloroform to the structurally complex vancomycin, pyrroindomycin and bastadins, the diversity of these organohalogens is unsurpassed among natural products. Most natural organohalogens contain chlorine (2,300) or bromine (2,100), but a significant number contain iodine (120) or fluorine (30). Several hundred marine natural products contain both chlorine and bromine."[7]

The roster of living organisms known to produce natural chlorinated organic compounds is a long one: humans, seaweeds, algae, assorted plants, some vegetables and fruits, fungi and mushrooms, lichen, microorganisms, marine creatures, frogs, insects and even some mammals.[1]

Hydrogen chloride is produced in massive amounts in volcanoes, and many chloride salts are present in the earth's crust. Combustion is also a major source of organochlorines. Natural combustion sources include lightning-induced forest and brush fires as well as volcanoes. Whenever organic material is burned in the presence of chloride, organochlorines are produced. These include dioxins, choromethane and other chlorine-containing compounds.[1]

Chlorine is used to purify drinking water and to disinfect swimming pools, both of which might otherwise be contaminated with fecal microorganisms that would cause diseases such as cholera, typhoid fever and dysentery. Some 98% of our public water systems are purified by chlorine or chlorine-based products.

The World Health Organization estimates that worldwide, 25,000 children die every day from waterborne diseases resulting form a lack of water disinfection. A decision by officials in Peru, based on studies from the United States EPA that stated chlorine may create a slight cancer risk, led them to stop chlorinating much of the country's drinking water. This has been blamed for a devastating cholera epidemic in which 700,000 illnesses were recorded, as well as 6,000 deaths in Peru and other countries in Central and South America in the early 1990s.[8]

Dioxin

One way that Greenpeace has gained attention to its campaign against chlorine is by linking it to dioxin, a widely feared chlorine-containing chemical. Upon closer inspection, both the link and the basis for the fear are typical of scare tactics used by this organization.[1]

Gribble adds, "The name 'dioxin' technically refers to a family of about 75 chemicals, but in public discourse it generally refers to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), thought to be the most toxic of the group. Dioxins are produced during any combustion process - waste incineration, running motor vehicle engines, steel making and smelting, residential wood burning and even forest fires. They are also produced when chlorine is used to bleach paper pulp, a fact often cited by Greenpeace as one reason to ban or restrict the use of chlorine. Yet the amount of dioxin produced by the paper pulp industry in the U.S. is extraordinarily small - less than one pound annually from the whole industry. Even this small amount is being steadily reduced as paper manufacturers switch from chlorine to chlorine dioxide, a less reactive form of chlorine that produces fewer toxic emissions."[1]

Greenpeace claims that incineration of chlorine-containing products also produces dioxin. Once again, Greenpeace tells only the truth they want you to hear. Since combustion of virtually any compound produces dioxins, singling out chlorinated compounds is disingenuous, notes Gribble. And indeed, the amount of dioxin produced by incinerating chlorine-containing products is vanishingly small. A properly operating incinerator will have dioxin emissions below detection levels. The dioxin emitted by the 22 million wood burning fireplaces in homes in the U.S. dwarfs the amount released by the incineration of chlorine-containing products. And the dioxin produced "naturally" by forest fires exceeds by thousands of times the amount produced by water incinerators each year.[1]

Life-threatening health effects in humans have not been linked definitively to dioxin, despite our fears to the contrary. Over 40,000 scientific papers have provided enormous information about this greatly misunderstood chemical, and the scientific and medical communities will continue to monitor the health of those people who have been exposed to large amounts of dioxins. The evidence now in hand does not support claims that dioxin is a major health threat.[1]

Humans

Humans naturally produce the iodinated hormone thryoxine, which regulates basal metabolism and was thought for a hundred years to be the only organohalogen made by the human body. However, recent studies demonstrate that our bodies produce bleach (hypochlorous acid) and chlorine gas! White blood cells use chloride and the enzyme myeloperoxidase to kill microbial pathogens and perhaps tumor cells. Byproducts of these reactions include chlorinated proteins and nucleic acids. This chlorination process is an essential component of the immune system. Humans deficient in myeloperoxidase are highly susceptible to bacterial infections, particularly pneumonias. Of the few organo-bromines synthesized by the human body, the first to be found, a bromoester in cerebrospinal fluid, induces REM (rapid eye movement) sleep.[5]

Industry

Industry takes a lot of hits regarding organohalogens. However, as in with dioxins, some data are either held back or simply ignored. One example is the burning of biomass. Gordon Gribble notes, "Significant amounts of nonbiogenic organohalogens come from burning biomass. People set most fires; only 10% are caused by lightning or other natural sources. Together, these sources of biomass combustion release large quantities of methyl chloride (900,000 tons per year) and lesser amounts of methyl bromide (10,000 to 50,000 tons per year). The global input per year of atmospheric methyl chloride is estimated at four million tons. These figures dwarf the 10,000 tons per year coming from industry."[5]

Natural compounds

In recent times, researchers have developed a technique for determining whether an organohalogen compound is natural or anthropogenic (man-made). The method relies on the fact that natural compounds have more carbon-14 than anthropogenic compounds, the latter of which are derived from petroleum for which the carbon-14 content has been depleted over the eons.[9] This work has provided evidence that some HOCs (halogenated organic compounds) found in animal tissues, air, humans,and food are not industrial but rather natural products. For example, two methoxylated polybrominoted diphenyl ethers (MeO-PBDEs) isolated from a True's beaked whale were shown to be natural by virtue of their radiocarbon content.[10] A similar analysis of an isolated mixed halogenated 2,2'-dimethyl bipyrrole (DMBP-Br_6Cl_2) revealed that it too was natural.[11]

Scientists Emma Teuten and Christopher Reddy found their pre-industrial HOC samples in a most unlikely place - whale oil from the Charles W. Morgan, one of the last whaling ships operating during the 19th and 20th century. Built in 1841 in New Bedford, Massachusetts, the ship traveled the world looking for whales, often on voyages of three years or more. The ship is now preserved and on public display at Mystic Seaport in Mystic, Connecticut. The researchers found eleven HOCs in one sample of antique whale oil. These results provide further evidence that naturally-produced HOCs were accumulating in marine mammals long before human-produced varieties.[12] ***P&SF***

References

1. Gordon W. Gribble, *The Future of Chlorine*, *Heartland Perspectives* (May 1, 1996); http://www.heartland.org/policybot/results/9333/The_Future_of_Chlorine.html.

Continued on page 17.

• Immerse a clean steel panel in a sample of the cleaner at operating temperature, time and concentration. Rinse and observe for any water breaks on the panel. If there are water breaks, add perhaps 10 to 20% of the initial makeup to the sample. Repeat the cleaning step and water break test on a new panel. If there is no water break, dip the rinsed panel in dilute acid (*e.g.*, 5% hydrochloric or sulfuric), then rinse again. If a water break is observed, repeat the suggested add of cleaner, and repeat the sequence of rinse and acid dip, followed by a rinse. If these steps confirm no water breaks, the cleaner can be expected to continue production operation. The optional cleaner addition is made as per the results of the described test.

The analysis portion is meant to be an aid to help ensure satisfactory cleaning. In this regard, the operator may obtain additional useful data to determine dump cycles more accurately. The ability to extend the bath service life reduces costs in these practical ways: less down time (offset cutting production, reduce labor to change cleaner baths with maintenance), possibly consume less cleaner and ease demand on the waste treatment system (less cost for treatment additives). Better ongoing cleaning results in fewer rejects that would have to be scrapped or re-worked. In either case, the production time lost and labor involved with rejects will add an additional cost.

Calculate cost

Many of you may recall Larry Durney, who contributed much to practical metal finishing. To me, Larry was a great source of knowledge, who always challenged me to work things out in a practical, sensible manner. An example is a system of calculating cleaning costs. I would like to pass along one of Larry's many valuable tips. An approach to determining cleaning costs can be given by the following equation:

$$C = \frac{S}{P \times D} + \frac{M}{P \times D} + \frac{R}{P} + \frac{W}{P \times D}$$

KEY:

C = production standard (*e.g.*, the cost to clean 1,000 ft^2 of parts).
S = the cost of chemicals, including makeup and maintenance.
M = the cost of dumping a cleaner and replacing it with a new makeup.
R = the cost to rework rejects or scrap parts.
W = the cost for waste treatment of the dumped cleaner.
P = daily production of parts in units (ft^2, etc.)
D = number of working days the cleaner is used in production during its service life.

Fact or Fiction?

Continued from page 15.

2. Marni Soupcoff, "Patrick Moore on where Greenpeace has it Wrong: Chlorine, Forests, Genetic Modification and Nuclear Energy," nationalpost.com (May 12, 2008); http://network.nationalpost.com/np/blogs/fullcomment/archive/2008/05/12/patrick-moore-on-where-greenpeace-has-it-wrong-chlorine-forests-genetic-modification-and-nuclear-energy.aspx.
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4. Angela Logomasini, "Utopian Policymaking," nationalreview.com (May 5, 2003); http://www.nationalreview.com/comment/comment-logomasini050503.asp.
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7. Gordon W. Gribble, "Natural Organohalogens: A New Frontier for Medicinal Agents?," *Journal of Chemical Education*, **81** (10), 1441 (2004).
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10. E. L. Teuten, L. Xu & C.M. Reddy, "Two Abundant Bioaccumulated Halogenated Compounds are Natural Products," *Science*, **307** (5711), 917 (February 11, 2005).
11. C. M. Reddy et al., "Radiocarbon Evidence for a Naturally Produced Bioaccumulating Halogenated Organic Compound," *Environ. Sci. Technol.*, **38** (7), 1992 (2004).
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Corrections to the March 2009 issue

Although it was quickly corrected online, there are a few of you who may have read the March 2009 issue of *P&SF* before April 3. In the paper by Donohue, *et al.*, there were two mislabeled figure captions:

On page 42, Figure 5, parts a and b were reversed, and the caption should read:
"XSTEM and EDX interface analysis of (a) argon glow-treated and (b) HIPIMS steel coupons."

On page 43, Figure 8, parts a and b were reversed, and the caption should read:
"Plots of Me-DLC and C-DLC Raman spectra: (a) visible light and (b) UV."

With apologies to the authors, *P&SF* regrets the errors.