NATURALLY-OCCURRING ORGANOCHLORINES

The perception that all chlorinated compounds are man-made and environmentally hazardous is incorrect. Natural organochlorines are numerous and chemically diverse: some 2,200 have been identified to date (2003), made by biological, physical and chemical processes. Sources range from bacteria, fungi, plants, marine organisms, insects and other animals (including humans) to forest fires, volcanoes and other geothermal events. Overall, the oceans are the main source of natural organochlorines (they contain 26 quadrillion tonnes of chloride), followed by soil (the earth's crust contains one quadrillion tonnes of chloride). Lightning-triggered forest fires produce 900,000 tonnes of methyl chloride per year. Minor sources of organochlorines include sediments, precipitation, surface- and groundwaters.

SOURCES OF ORGANOCHLORINES

Within the **oceans**, marine organisms such as seaweeds, sponges, corals and sea slugs produce chlorinated substances (such as methyl chloride, dichloromethane, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, alkenes, terpenes, steroids, fatty acids and glycopeptides). Several million tonnes of methyl chloride are released into the **atmosphere** each year, much of it apparently made by marine algae and phytoplankton.

Sea spray aerosols are a major source of atmospheric chlorine. Via chemical processes, which are not well understood, the chloride in sea aerosol is transformed into inorganic chlorinate substances, including hydrogen chloride. These react with hydroxyl radicals present in air to form chlorine atoms, which react again with volatile organic compounds to produce organochlorines. This route is thought to be an important source of methyl chloride, the most abundant organochlorine in the lower atmosphere, and a major natural source of stratospheric chlorine.

Sea spray carried in the atmosphere is also thought to be the major source of chloride ions in the **soil**. Many organisms, including fungi, plants and insects can convert chloride to organic chlorine. About 300 natural chlorine-containing compounds have been isolated from terrestrial fungi and plants, ranging from simple molecules such as methyl chloride to more complex, heavily-chlorinated ones. Wood-rot fungi play a key role in plant decay and recycling. They produce hypochlorite to degrade lignin which indirectly produces many organochlorines. One species of *Penicillium* produces 2,4-dichlorophenol as a growth hormone. The edible Japanese lily makes seven chlorinated fungicides to protect it from attack by a pathogenic fungus, *Fusarium*.

Sediments contain chlorinated organic compounds known to have been deposited before man-made sources existed. For example, pentachlorophenol occurs in lake bottom sediments dating back to the 17th century, whilst dioxins and furans have been found in lake sediments from 1860. Plants are the main source of high molecular weight halogenated organic compounds in sediments. Certain algae, marine organisms and terrestrial lichen and fungi also make organochlorines by chlorinating organic matter using haloperoxidase enzymes.

In Europe, concentrations of organochlorines average 10µg Cl/l in **rain and snow**, and range from 5-50µg Cl/l in **surface waters** and 1-15 µg Cl/l in **groundwater**. Analysis of glacier ice known to have been deposited in the pre-industrial era suggests that significant natural sources exist. Only a small proportion of the organochlorines found in surface waters can be explained by industrial activities. In most lakes and rivers, natural plant decay processes account for the majority of organically bound chlorine compounds. Levels of chlorinated substances in groundwater are higher in spruce forests than in farm-land; natural processes account for more chlorinated substances in groundwater than use of pesticides.

THE NATURAL CHLORINE CYCLE: MECHANISMS FOR PRODUCTION AND DEGRADATION

An important pathway for recycling organic plant matter involves biochlorination. Some 63,000 million tonnes of plant material degrades each year to humic acid. This is biochlorinated by the ubiquitous soil enzyme, chloroperoxidase, to give chlorinated humic acid, which in turn yields chlorophenols, chloroacetic acids and chloroform. Chlorophenols can dimerize to form dioxins, a process which has been shown to occur in soil in Swedish Douglas fir forests and New Brunswick peat bogs. Chlorinated humic acids have been found in groundwaters dating back 5,200 years, and in organic matter 35,000 years old.

Little is known about the extent and role of dechlorination of organically bound chlorine. However, numerous microbes use organochlorines as a food source and biodegrade them in this way. Most naturally-occurring organochlorines degrade readily in the environment.

CHLORINE INVENTORY

The movement of volatile chlorine-containing organic compounds between the ocean and the atmosphere can be measured, and provides a helpful perspective on the relative contributions of nature and human activities.

Table 1.

RELATIVE IMPORTANCE OF CHLOROFORM EMISSIONS (total flux 660,000 t/y)	
Oceans 44%	Water treatment 3%
Soil 26%	Other anthropogenic 2%
Termites 13%	Forests 0.7%
Paper manufacturing 4%	Peatlands 0.6%
Rice fields 3%	Biomass burning 0.3%
Microalgae 3%	Macroalgae 0.02%

More than 90% of the chloroform emitted into the atmosphere is from natural sources. Less than 10% comes from man-made sources (Paper manufacturing, water treatment and others).

BENEFITS TO HUMANS

Many natural organochlorines are highly biologically active, with potential to benefit humans. Examples include medicines such as penicillin, morphine, quinine, and the life-saving antibiotic, vancomycin. Chlorine-containing punaglandins, derived from a South Pacific soft coral, have potential in stopping tumour growth. Maracen, a chlorinated fungal metabolite, is active against the mycobacteria that cause tuberculosis. A chlorinated seaweed metabolite, telfarine, may help stop the spread of diseases such as malaria by killing mosquito larvae.

INTERESTING FACTS

- Around 3,800 natural organohalogens exist, of which 2,200 are natural organochlorines, made by biological, physical and chemical processes.
- Mammalian white blood cells transform chloride in blood into hypochlorite (bleach) to kill invading bacteria, tumour cells, etc.
- Several chlorinated dioxins and furans can be produced naturally in peat bogs.
- Up to 100,000 t/y of chloroform are produced by termites worldwide.
- Volcanoes emit three million tonnes of hydrogen chloride per year.
- One species of fungus is estimated to produce 160,000 t/y of methyl chloride.
- Methyl chloroform (1,1,1-trichloroethane) and HCFC-22 have no natural sources.
- About 25% of dichloromethane, 10% of trichloroethene and 5% of tetrachloroethene appear to be emitted from the oceans.
- Since monitoring began in 1985, the European chlor-alkali industry has reduced emissions of 20 chlorinated organic compounds by 90% to air and by 98% to water.

KEY SCIENCE INFORMATION SHEET
One of a new series Euro Chlor is publishing to improve understanding by non-scientists of scientific issues. Each publication focuses on health or environmental aspects of the production, use and disposal of chlorine and its derivatives. Other information sheets available include dioxins, POPs and PBTs, marine risk assessments and children and exposure to highly-chlorinated chemicals.
Naturally-Occuring Organochlorines and other publications can be found on the Internet at chlorine online (http://www.eurochlor.org).