

Risk assessment and the cycle of natural

Organohalogenes are often perceived as man-made. In fact, chlorine is one of the most abundant elements on Earth and natural organohalogenes continue to be discovered at a rate of 100-200 per year. Currently, there are more than 4,000, of which 2,400 are organochlorines. Clearly, nature relies on chlorine as a basic building block to construct essential molecules for the survival of many organisms.

Based on current knowledge, the ocean is the greatest single source of naturally-produced organochlorines. Simple haloalkanes function as natural recyclers of halogens in the oceans, atmosphere and in the soil. Others are used as chemical defence (repellents, anti-feedants) to protect species from predators. Many organohalogenes have a powerful, beneficial biological function and are, or will be used in medicines.

Organochlorines form part of the biogeochemical chlorine cycle, fulfilling various essential roles in nature. In soil organic matter, natural chlorination is a ubiquitous phenomenon. Isotope studies suggest rapid and extensive chlorination. Recent experiments in coniferous forest soil discovered 5-20% of the soil chloride pool transformed to organically-bound chlorine within a week. The ecological role of their extensive transformation is hitherto unknown.

Biodegradation of organochlorine compounds is a key component of the natural chlorine cycle, converting chlorine back to mineral form. Micro-organisms have developed diverse strategies for degrading different types of organochlorine compounds. Many organochlorines have been shown to support energy yielding metabolisms bene-

fitting micro-organisms as the primary energy and carbon source or as electron acceptors of respiration.

Our knowledge on the formation and degradation processes of the natural chlorine cycle, including organochlorines, has expanded rapidly. Contrary to earlier assumptions, there is a wide variety of organochlorines performing essential roles in nature.

The cycle, its form, importance and quantities of substances involved are becoming better understood, resulting in unexpected findings. The coniferous top-soil layer for example is continually turning over chlorides to organochlorines and vice versa.

The occurrence of natural organochlorines poses challenges to the risk assessment process of man-made organochlorines. Around 90% of chloroform emissions originate from natural sources. Some dioxins are now recognised to have several natural sources. The first examples of natural bioaccumulative organochlorines have been discovered in seabirds and in Eskimo women's milk. Scientists and regulators are encouraged to take up the challenge to adapt risk assessment approaches to take into account this newly acquired knowledge of natural organochlorines

Organochlorines and the chlorine cycle

Gunilla Öberg (Linköping University, Sweden)

Chlorine is ubiquitous in the environment and is present as inorganic chloride (Cl_{in}) as well as in various forms of organically bound chlorine (Cl_{org}). The Cl_{in} originates mainly from the sea and is transported great distances as sea-spray and subsequently deposited on vegetation and soil as dry and wet deposition (in rain, snow, fog, etc.).

The origin of Cl_{org} compounds in soil is more complex. Anthropogenic activities such as pulp and paper bleaching, chlorination of drinking water and wastewater, production and use of solvents, plastics and pesticides may cause dispersal of Cl_{org} compounds. Some Cl_{org} substances, such as DDT, PCBs, dioxins and freons, are among those that have received considerable attention in the past due to their toxicity and persistence and their interaction with the ozone layer. It was previously believed that Cl_{org} compounds originated from anthropogenic activities only and that Cl_{in} was inert in soil, moving unchanged with the soil water. This has led to the mere presence of Cl_{org} compounds being taken as a sign of industrial activities.

Over the past 30 years, it has become clear that nature produces organochlorines in significant numbers and, in some cases, in massive quantities. Once considered to be isolation artefacts or chemical accidents of nature, the number of known natural organochlorine compounds has grown from a dozen in 1954 to more than 2,400 today. This enormous increase is both a consequence of the revitalisation of natural products chemistry in the search for novel medicinal compounds and the development of new chemical isolation, separation and identification methods.

After the first discoveries of the amazing numbers and different types of organochlorines and their various natural sources, both chemical and biological, we begin to understand some of the diverse functions of organochlorines in natural processes. With that, it has become clear that organochlorines are part of a natural biogeochemical chlorine cycle. Chlorine and halogens in general, are as natural to our ecosystems as carbon, hydrogen, oxygen, nitrogen and the other elements of life. Biogenic organohalogens are similar to the multitude of other chemicals that constitute living things. They play essential roles for the survival of organisms.

The discovery that some anthropogenic halocarbons are also made naturally requires a broader assessment of environmental risk. It is axiomatic that when the sum of natural and anthropogenic sources becomes an unacceptable risk, the human contribution must be reduced. For this determination to be made, scientists must know the proportions that come from industry and nature; a task that demands greater understanding of the biogeochemical sources and sinks of these chemicals.

In this special issue, a brief overview of the existence and function of the various organochlorines is presented. The chlorine cycle and the role of organochlorines are subsequently addressed. Their formation is explained, specifically focussing on organochlorine formation in coniferous forest soil. A brief overview of the diverse strategies developed by microorganisms to degrade organochlorines is also given. Finally, the biogeochemical cycle of chlorine is illustrated by examining a chlorine budget of a small forested catchment with additional data from other areas. The input and output fluxes and conversions of inorganic and organic chlorine are addressed. This publication aims to contribute to the recognition, understanding and



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Dr Öberg is also in charge of the group at LiU that focuses on the biogeochemistry of chlorine. She has supervised three doctoral students, six MSc and seven BSc theses in this field, of which the latest doctoral student, Teresia Svensson, will defend her thesis "Chlorine cycling in a small catchment" on May 12, 2006. Öberg reviews scientific papers on chlorine biogeochemistry for international journals such as Science, Nature, Environmental Science and Technology, Soil Biology and Biogeochemistry, Water, Air and Soil Pollution and Chemosphere.

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proper appreciation of organochlorines and their role in nature.

Organochlorines in nature: existence, formation and function

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More than 2,400 organochlorine compounds are produced by living organisms or are formed during natural abiogenic processes such as volcanic eruptions, forest fires and geothermal processes. The ocean is the greatest source of natural organochlorines and countless marine organisms produce such compounds. Terrestrial plants, fungi, lichen, bacteria and insects also produce organochlorine compounds.

Nearly all types of organic compounds are represented, including alkanes, aromatic hydrocarbons, furans and dioxins. The mammalian immune system also contains some chlorinated by-products. Dioxins are now recognised to have several natural sources. The first examples of natural bioaccumulative organochlorines have been discovered in seabirds and in Eskimo women's milk. Nature employs chlorine as a basic building block to construct essential molecules for survival of the particular organism.

"Bioprospecting" has led chemists to discover thousands of naturally-occurring organochlorines and other organohalogens. Marine organisms are the richest sources of halocarbons, and even the "smell of the ocean" is probably caused in part by volatile alkyl halides from seaweeds. Sponges, corals, tunicates and seaweeds rely on chemical warfare for survival, using compounds that often contain halo-

gen. Numerous sponge metabolites prevent lethal barnacle fouling. The discovery of halogenated bi-pyrroles in seabirds was the first example of natural organohalogens to bioaccumulate in top-level predators.

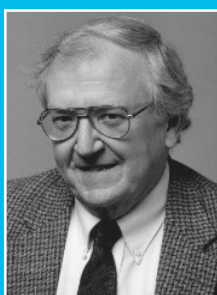
Terrestrial plants and fungi produce organochlorines. Evergreen trees and potato tubers produce methyl chloride, the most abundant chlorinated compound in the atmosphere. Other organochlorines include a growth hormone in beans and peas, seven novel chlorophenolic fungicides produced by the edible Japanese lily, and 2,4-dichlorophenol produced by a *Penicillium* mould as a growth hormone. Naturally-produced dioxins are found in peat bogs and in forest soil.

Arthropods and vertebrates also biosynthesise an array of organochlorines. Fourteen tick species produce 2,6-dichlorophenol as a sex pheromone. Termites may emit up to 15% of global atmospheric chloroform, perhaps as a waste product of the chloride naturally present in wood or as an ant repellent. The poison-arrow frog, *Epipedobates tricolor*, of Ecuador secretes epibatidine, a chlorine-containing substance with a unique chemical structure.

Epibatidine is more potent than morphine as a painkiller, and may lead to a new analgesic.

Human white blood cells containing the enzyme myeloperoxidase produce bleach and even chlorine gas to kill microbial pathogens and perhaps tumour cells. Humans deficient in myeloperoxidase are highly susceptible to bacterial infections, particularly pneumonias.

Volcanoes emit 3,000,000 tonnes of hydrogen chloride per year. High temperatures and pressures induce chemical reactions between organic matter such as peat and chloride minerals leading to organochlorines. Rock and shale also contain organo-



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After a National Cancer Institute Postdoctoral Fellowship at the University of California, Los Angeles, he joined the faculty of Dartmouth College in 1968. He served as Department Chair from 1988-91. In 2005, he was named to the newly endowed Chair as "The Dartmouth Professor of Chemistry."

Dr Gribble has published 260 papers in natural product synthesis, synthetic methodology, heterocyclic chemistry, natural organohalogen compounds and synthetic triterpenoids, one of which is currently in Phase 1 clinical trials for the treatment of leukaemia.

Dr Gribble has a long-standing interest in organic chemical toxicity, chemical carcinogenesis, chemicals in the environment and naturally occurring organohalogen compounds, and, as a home winemaker for the past 28 years, in the chemistry of wine.

chlorines, and when rocks are crushed during mining operations, small quantities of chlorinated chemicals are released.

Many naturally-occurring organochlorines exhibit important biological activity. Vancomycin is an antibiotic that is often the last line of defence against multi-drug-resistant bacteria. A chlorinated fungal metabolite called maracen is active against mycobacteria, the cause of tuberculosis. The chlorine-containing punaglandins from a South Pacific soft coral have potent antitumour activity and may soon find Clinical use, as does cryptophycin, an organochlorine compound derived from the blue-green alga, Nostoc. Spongistatin 9 is a chlorine-containing sponge metabolite that is one of the most potent compounds ever tested among 60 human tumour-cell lines.

This Focus on Chlorine Science (FOCS) is part of a series of leaflets aiming to clarify and consolidate scientific research in the field of chlorine industry. With the FOCS series, we want to facilitate the knowledge gathering of scientists, regulators and key decision makers. For further Euro Chlor science publications, please consult <https://www.eurochlor.org/resources/publications/>

Euro Chlor

Euro Chlor provides a focal point for the chlor-alkali industry's drive to achieve a sustainable future through economically and environmentally-sound manufacture and use of its products. Based in Brussels, at the heart of the European Union, this business association works with national, European and international authorities to ensure that legislation affecting the industry is workable, efficient and effective. Chlorine and its co-product caustic soda (sodium hydroxide) are two key chemical building blocks that underpin 55% of European chemical industry turnover.

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