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Naturally Occurring Organohalogen Compounds - A Comprehensive Update

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2 Origins

The ubiquitous abundance of the four halides (Table 2.1) has resulted in the evolution of organohalogens in all regions of our earth, both biogenic and abiotic (*73–77*).

2.1 Marine Environment

As will be seen, most naturally occurring organohalogen compounds are unique to individual marine organisms and are not widely dispersed in the environment. However, the more volatile haloalkanes, which have several marine sources, are important contributors to the atmosphere. The salinity of Earth's early ocean was probably twice that of the present value (*77*), and sea-salt spray is the major atmospheric source of reactive halogens (Cl_2, Br_2, BrCl, HOCl, HOBr) that are subsequently converted to chlorine oxide and bromine oxide. This atmosphere chemistry is exceedingly complex and beyond the scope of this review (*78–85*). The formation of reactive chlorine and bromine in sea-salt aerosols, for which there is compelling evidence, may explain the low ozone concentrations that are often observed above the oceans (*86–94*). The importance of bromine oxide to both tropospheric and stratospheric bromine-ozone chemistry has been stressed (*95–100*). Not surprising is the observation of similar bromine oxide-ozone interactions over the Dead Sea (*101*), and both bromine oxide and chlorine oxide chemical reactions with ozone over the Great Salt Lake (*102*), with concomitant ozone depletion in both areas. Although less studied, iodine in the marine boundary layer is well known and can involve the photolysis of marine biogenic organoiodine compounds (*103, 104*). Moreover, it appears that the global aerosol load has a major contribution from marine organohalogen aerosols with the inevitable formation of reactive halogens (*105*).

As abundantly illustrated in the first survey, marine organisms produce and sequester an enormous number of organohalogens. It is estimated that more than 15,000 marine natural products of all types have been described (*106*). This author

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Table 2.1 Distribution of halides/mg kg^{-1} in the environment

Halide	Oceans (*73, 74*)	Sedimentary rocks (*66, 74*)	Fungi (*75*)	Wood pulp (*218*)	Plants (*74, 76*)
Cl^-	19,000	10–320		70–2100	200–10,000
Br^-	65	1.6–3	100		
I^-	0.05	0.3			
F^-	1.4	270–740			

has determined from the published literature (1998–2005) that 15–20% of all newly discovered marine natural products are organohalogens (*107*). Given the salinity of the world's oceans, which occupy more than 70% of the earth's surface and over 90% of the volume of the crust (*108*), it is not surprising that organohalogens are plentiful in the 500,000 estimated species of marine organisms spread over 30 phyla (*109*). This figure includes 100,000 marine invertebrates (*110*), 80,000 molluscs (*111*), 15,000 sponges (*112*), and 4,000 species of bryozoa (moss animals) (*113*).

Perhaps due to their accessibility (and visibility!), sponges – the simplest and earliest multicellular organisms that evolved about one billion years ago (*114*) – have been widely examined for their chemical content, and new sponge species are still being discovered (*115*). However, to acquire significant quantities of biologically active sponge metabolites, it is necessary to develop "farming" methods (*116, 117*) or to employ cell culture and gene cluster tactics (*118*). A major sponge research area has been to explore the now well-established sponge-bacteria symbiosis (*119–123*). Such studies of sponges include *Aplysina cavernicola* (*124–126*), *Aplysina aerophoba* (*126–128*), *Theonella swinhoei* (*128*), *Rhopaloeides odorabile* (*129, 130*), and *Xestospongia muta* and *X. testudinaria* (*131*), all of which have associated active bacterial communities that may produce the metabolite.

Even older than sponges are cyanobacteria (blue-green algae, Fig. 2.1), which date back 2.8 billion years (*132*). As will be seen in Chap. 3 (Occurrence), the 2,000 species of cyanobacteria produce a multitude of organohalogen and other metabolites (*133–135*), which are often highly toxic to humans (*136–138*). The cyanobacterium *Oscillatoria spongeliae* is a common symbiont of the sponges *Dysidea herbacea* and *Dysidea granulosa* (Fig. 2.2) (*139–144*), but the actual producer of the organohalogen metabolites remains uncertain.

As will be presented in Chap. 3 (Occurrence), other marine organisms such as molluscs (*145*), sea hares (*146*), mussels (*147*), bryozoans (*148*), tunicates, and soft corals (*149*) produce a myriad of organohalogen metabolites. Interestingly, symbiotic bacteria can also be associated with these organisms (*123*). Marine phytoplankton (*150*) and macroalgae (*151, 152*) are rich sources of organohalogens, particularly volatile haloalkanes. Two relatively new areas for ocean exploration are marine bacteria and fungi (*108, 153–155, 178*). Finally, as more remote and deeper regions of the oceans are explored, new marine species are being discovered; for example, the new genus, *Osedax*, of marine worms (*156*).

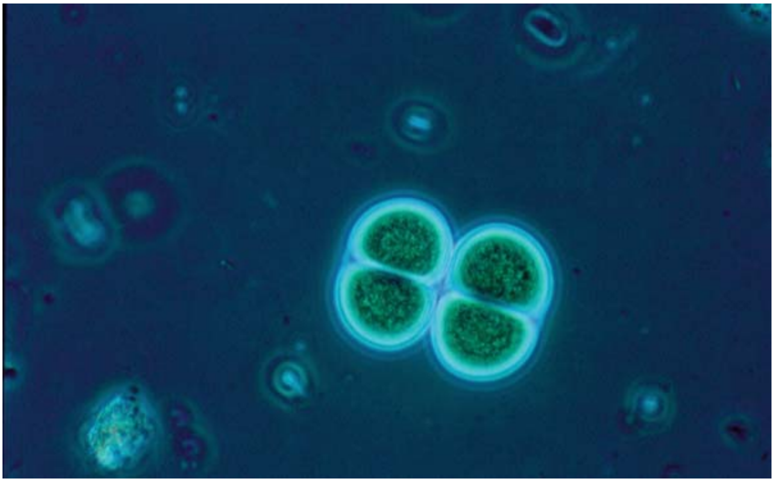

Fig. 2.1 *Chroococcus turgidus*, a species of cyanobacteria, which are prolific producers of organohalogens (Photo: A. D. Wright)

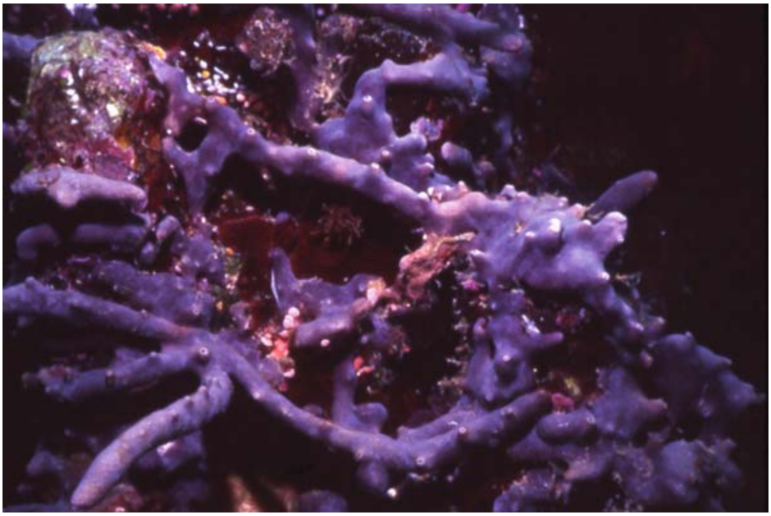

Fig. 2.2 *Dysidea granulosa*, a cyanobacterium containing sponge (Photo: F. J. Schmitz)

2.2 Terrestrial Environment

Organohalogens are present in many terrestrial environments: sediments, soils, plants, fungi, lichen, volcanoes, biomass combustion, bacteria, insects, and higher organisms. The high concentration and dispersal of chloride in minerals, soils, and plants results in a multitude of both biogenic and abiotic organochlorine compounds in these terrestrial environments (*37, 157–167*). Humic forest lake sediments (*168*) and peatlands (*169–171*) contain large quantities of organohalogens, including organoiodines that form during humification in peatlands (*171*). Peatlands that comprise 2% of the earth's continental surface are a major reservoir of organically bound iodine in the terrestrial environment (*171*), accumulating 280–1,000 million tons of organochlorines during the postglacial period (*169*). Likewise, 91% of the bromine found in peat is organically bound (*170*).

X-ray absorption spectroscopy has revealed the formation of organochlorine compounds from chloride and chloroperoxidase in "weathering" plant material (*172–174*). Moreover, this technique has uncovered the bromide-to-organobromine conversion in environmental samples (*174*). In addition to chloroperoxidase mediated chlorination, the abiotic chlorination in soils and sediments involving the alkylation of halides during Fe(III) oxidation of natural organic phenols in soils and sediments has been discovered (*175–177*).

Other terrestrial organisms frequently contain organohalogens. Lichens dating back 400 million years are a rich source of chlorinated phenolics (*1, 178, 179*). The even older fungi, which date back one billion years (*180*), perhaps number 1.5 million species of which only 70,000 are described (*181*). Basidiomycetes fungi are ubiquitous producers of organohalogens (*182*), and fungi, bacteria, and lichen engage in symbiosis (*183, 184*). Tundra fungi under snow-cover (*185*) and insect pathogenic fungi (*186*) are of recent interest and undoubtedly will yield novel natural products. Slime molds (myxomycetes) (*187*) and bryophytes (liverworts, mosses, hornworts) (*188, 189*) possess a rich assortment of natural products, including organohalogens, but terrestrial bacteria remain king of the biosynthesizers (*190*).

Volcanoes have been comparatively little studied for their chemical content. However, a few studies have provided some astonishing results as will be described later in Chap. 3 (Occurrence) (*1*). The origin of volcanic organohalogens may simply be a result of the halides present in sediments and minerals reacting with organic matter within the volcano at the high temperatures and pressures during eruptions and outgassing. The four halides are known to be entombed in rocks and sediments (*190–199*), and also in the ocean mantle (*200, 201*). Volcanic emissions invariably contain massive quantities of HCl and HF (*1*). Recent studies of Mt. Etna (*202–205*), Mt. Pinatubo (*206*), Soufriere Hills (*207, 208*), Popocatépetl (*209*), Villarrica (*210*), Satsuma-Iwojima (*211*), Sakurajima (*212*), and Laki (*213*) confirm their ubiquity of gaseous HCl and HF. Reactive bromine (BrO) and iodine emissions are also reported (*206, 208, 211, 212*). The largest known point source of both HCl and HF is the 1997 Mt. Etna eruption, with emission rates of 8.6 and 2.2 kg s^{-1}, respectively (*203*). Newer detection techniques such as solar occultation spectroscopy (*203*) and remote infrared spectroscopy (*214*) will obviously lessen the hazards of sampling. The role that these halogens play in depleting ozone has been discussed (*215*).

Only two studies of organohalogen volcanic gases were reported since the last survey, those of Vulcano (Fig. 2.3) (*216*) and Kuju, Satsuma-Iwojima, Mt. Etna,

Fig. 2.3 A volcano on Stromboli, an island in the Tyrrhenian Sea off the north coast of Sicily (Photo: F. M. Schwandner)

and Vulcano (*217*). These results will be described in Chap. 3 (Occurrence). The mysterious chemistry that occurs in volcanoes has been addressed with regard both to halogen (*218*) and hydrocarbon formation (*219*). An interesting personal account of the Kamchatka hot springs, which are a rich source of organohalogens (*1, 218*), has appeared (*220*). A novel volcanic source of HCl stems from the heating and evaporation of seawater by molten lava from the Hawaiian volcano Kilauea, which has been in continuous eruption since 1986, leading to highly acidic plumes ("acid rain") estimated at 3–30 tons of HCl daily (*221*).

A related pyrolytic source of HCl, HBr, and low molecular weight haloalkanes is biomass combustion. Human controlled fires may date back 790,000 years (*222*), but natural forest and grass fires presumably date from the time vegetation first appeared on earth (350–400 million years ago), and continue unabated today (*223–225*). Recent massive fires include those in Indonesia 1997 (*226*), Northern Alberta 1998 (*227*), Alaska 2004 (*228*), and Russia 2002–2005 (*229*). In Canada alone some 10,000 forest fires occur annually (*230*), and forest fires have plagued the Western United States for decades (*225, 231*). The 1988 Yellowstone fire, which burned more than 3 months, consumed 600,000 ha (*225*). Interestingly, a model study revealed that heating a mixture of methane, hydrogen chloride, and oxygen forms haloalkanes, chlorinated aromatics, dioxins, and many other organochlorines (*232*), indicating the plausibility of finding such compounds in volcanic plumes and biomass combustion fires. Cigarette smoke contains 30–66 mg kg^{-1} of unidentified organochlorines (*233*).

2.3 Extraterrestrial Environment

Although both HCl (*234*) and HF (*235*) are present in interstellar space, it came as a stunning surprise when meteorites were found to contain organohalogen compounds (*236*). The several earlier claims of meteoritic organochlorines were only cautiously advanced and perhaps even viewed with skepticism (*237–240*). In various forms, chlorine has been detected in and around Io, Jupiter's largest moon (*241–245*).

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