

# BROMINATED COMPOUNDS

## FROM AN ENVIRONMENTAL VIEWPOINT

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Many of the "classical" environmental pollutants are chlorinated compounds and great efforts have been made to reduce the use and emission of such compounds. The restrictions for several of these substances are now reflected in decreasing levels of them in the environment.

Less interest has been paid to the brominated substances, probably due to lower use volumes and the knowledge of the more labile bond between bromine and carbon as compared to that between chlorine and carbon.

Bond	Bond length (pm)		Homol diss energy (kJ mol <sup>-1</sup> )	
	Prim alkyl	Aryl	Prim alkyl	Aryl
C - H	107	108	420	430
C - Cl	177	170	340	350
C - Br	190	185	290	300

Table 1. A comparison of some physical properties of C-X bonds.

Recent data, however, indicate that an increased use of some brominated aromatic substances now results in increasing levels of these in the environment. This paper will review some information on biogenic and anthropogenic brominated compounds and the scarce amount of data of the latter in our environment. Much of the available knowledge can be found in a monography of Bromine Compounds (1) and in a proceedings from a Workshop on Brominated Aromatic Flame Retardants (2).

### NATURALLY-OCCURRING BROMINATED COMPOUNDS

Many biogenic compounds containing bromine have been described both in terrestrial and aquatic environments, but they seem to be much more common in the marine environment. This is explained by the chemical composition of sea water where there is as much bromine as carbon. The concentration of chlorine is about 500 times higher but there seems to be fewer chlorinated species than brominated present in organisms. The explanation of this is probably that the enzymes involved in synthesis have to oxidize the halide ion, a process which needs much higher energy for the chloride than for the bromide ions.

One of the smaller brominated organic molecules produced in the oceans is bromoform and the yearly amount escaping up to the atmosphere has been estimated to be between 500 000 and 1 000 000 metric tonnes. A number of other brominated hydrocarbons, acids and ketones with low molecular weights have also been identified.

Polyhalogenated terpenes, both acyclic and cyclic, are also common in some algae. In this case both chlorine and bromine are often found on the molecules.

A great number of brominated aromatic compounds have been identified in marine organisms such as algae, sponges, worms and microorganisms. A few examples of the suggested structures are given in Figure 1. In some species of algae the bromine content is 2.4 mg per g tissue which corresponds to an average of 2-5 bromine atoms in every lipid molecule within the organism (3). Several "pre-dioxin" structures have been described but not the corresponding dioxins.

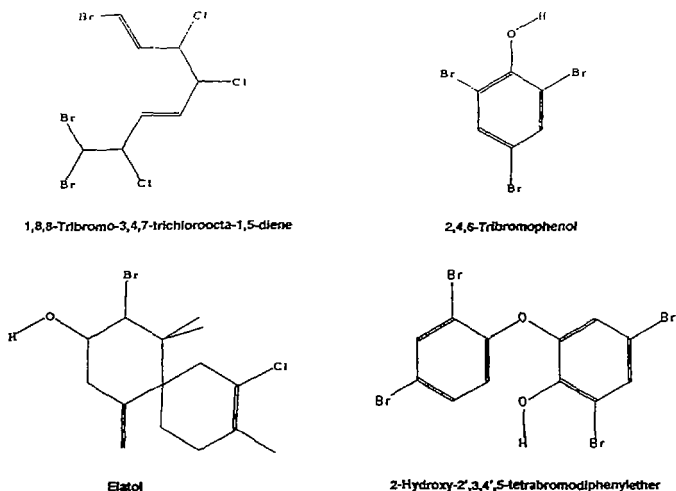


Figure 1. Some biogenic brominated compounds.

#### MAN-MADE BROMINATED COMPOUNDS

The world production of bromine seems to be rather constant or slightly increasing. The estimated production volumes were 309 000 tonnes in 1976 and 388 000 tonnes in 1984 (4).

The major use of brominated compounds has for a long time been as petroleum additives. Equimolar amounts of dichloro- (EDC) and dibromoethane (EDB) are added to leaded gasoline to take care of the lead as halide salts. During the combustion in the engine a number of both chlorinated and brominated species, including dioxins and furans, are formed (5 - 7) and 22-44 % of the bromine in the exhaust gases are found in organic compounds (8). The decreasing use of leaded gasoline decreases the demand for EDB as could be seen in the US several years ago (Figure 2).

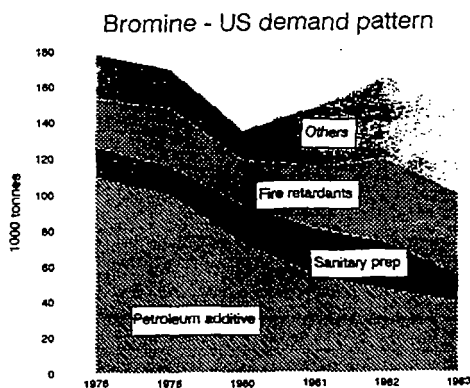


Figure 2. Use of brominated compounds in the USA during the period 1976-1986.

The decreased use of bromine in petroleum seems to have been balanced by other applications. One such application is in flame retardants, others are for pharmaceuticals, pesticides, dyestuffs and photographic chemicals.

The chlorination of water produces, in parallel with chlorinated species, some short chained brominated hydrocarbons if bromide is present. The most common product is bromoform and in a Swedish nuclear power plant, using cooling water from the sea, an emission of about 250 tonnes per year has been estimated (9). Some volatile brominated substances are used as fumigants. Dibromochloropropane and EDB have been used previously but these are banned today in several countries and now methylbromide is used (about 12 000 tonnes per year in US, 1989)

Halon is the common name for some brominated short chain compounds used in fire extinguishers. Table 2 gives the formulas, production volumes and ozone depletion factors (ODP) for the three most common Halon compounds. The ODP values are the relative effect on the ozone layer in the stratosphere compared with that of CFC 11. The Halon gases also contribute to the "green-house" effect.

Compound	Halon 1211	Halon 1301	Halon 2402
Formula	$\text{CF}_2\text{ClBr}$	$\text{CF}_3\text{Br}$	$\text{C}_2\text{F}_5\text{Br}_2$
Production 1986 (metric tonnes)	10 000	14 000	1 000
Ozone Depletion Potential	3	10	6

Table 2. The most common Halon compounds, their formulas, world production 1986 and ozone depletion factor (ODP).

A great number of brominated compounds have been used as biocides, several of which are analogues to well known chlorinated substances. In Figure 3 there is an example of this in the bromine analogue to DDT, but there are also quite different structures such as the synthetic pyrethroids deltamethrin.

An increasing amount of brominated products are used as flame retardants as can be demonstrated by the consumption in Japan, where it has increased from 2 500 tonnes 1975 to 22 100 tonnes 1987 (10). Mainly polybrominated aromatic compounds are used and some of the more common structures are shown in Figure 3.

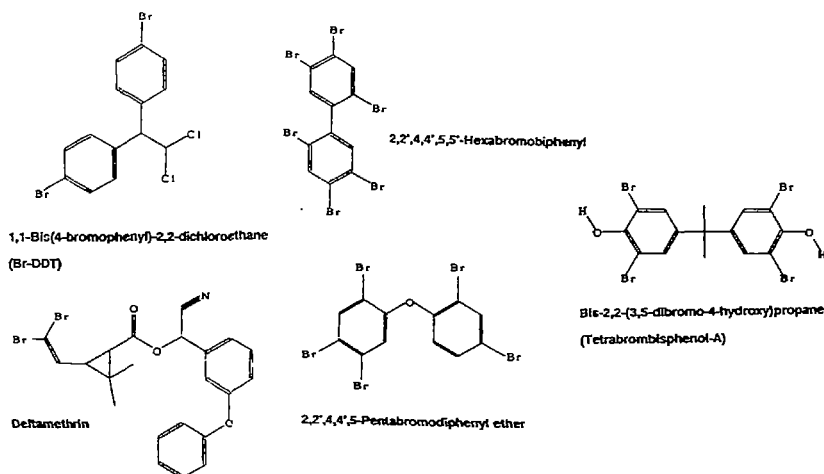


Figure 3. A few examples on man-made brominated organic compounds.

In recent years several studies have demonstrated formation of brominated dioxins (PBDD) and furans (PBDF) when some of the brominated flame retardants are heated (11-13). Especially the formation of PBDF from PBDE seems to be efficient and yields up to 30 % have been reported. The optimum temperature region seems to be 400 - 600 °C, but already at lower temperatures the reactions have been observed.

## ENVIRONMENTAL LEVELS OF MAN-MADE BROMINATED COMPOUNDS

Production of bromoform in the bleaching of paper pulp results in elevated levels of this compound downstream from these industries. The compound has in fact been used to follow the spreading of these emissions in the environment. The most volatile compounds will of course be distributed mainly to the atmosphere rapidly.

As for the chlorinated compounds, the lipophilic brominated substances will cause special environmental problems due to bioaccumulation. This puts the brominated aromatic compounds into focus. As was described above the main application of this group is as flame retardants. Close to production and user sites these have been found both in sediment and biological samples (14).

The development of new analytical techniques have made it possible to detect organic brominated compounds with a high specificity and sensitivity. The chromatograms in Figure 4 represent the brominated compounds in an extract of a Sea Eagle sample. The extract had been treated with concentrated sulfuric acid so a great deal of the biogenic substances have been removed. Unfortunately the methodology used does not give much information of the identity of the separated compounds so the identification is very difficult. So far a number of the brominated flame retardants (PBDE and PBB) have been found in the sample and also in all other samples analyzed for these substances. Analysis of different levels in a sediment core also indicates that the concentrations are increasing (14).

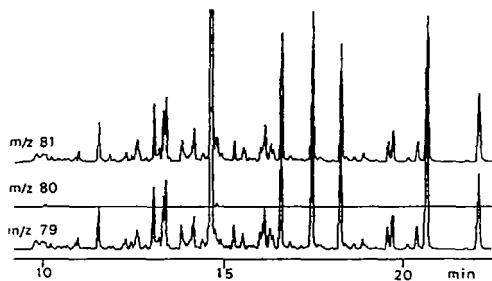


Figure 4. Gas chromatographic/mass spectrometric analysis of a Sea Eagle sample from the Baltic. The three curves describe the negative ions  $m/z = 79, 80$  and  $81$ , where  $79$  and  $81$  represent the bromide ions formed from the brominated substances (15).

The brominated dibenzo-p-dioxins and furans have been found in city air and snow samples but, to my knowledge, not in any biological samples so far. Some brominated polyaromatic hydrocarbons have also been found in air samples but the exact structures of these are not yet known (16).

## BIOLOGICAL EFFECTS OF BROMINATED COMPOUNDS

Some of the naturally-occurring brominated compounds are used as chemical weapons by the organisms and thus have biological effects. A relation between total amount of bromine metabolites and antimicrobial activity has also been demonstrated (3).

An accident in Michigan in 1973 started a study of polybrominated aromatic compounds (17). About 450 kg of a flame retardant based on polybrominated biphenyls (PBB) was mixed into cattle feed which was then distributed to farms throughout the state. About 34 000 cattle, 1 500 000 poultry and several thousand swine and sheep were killed. The main component of the flame retardant was a hexabromobiphenyl, but a number of other PBB congeners were found in the product. The studies revealed that the effects of PBB seems to be very like the effects of PCB. The 3,3',4,4'-substituted congeners without or with one ortho-substituent are most potent, induce 3-methylcholanthrene-type microsomal enzymes and interact with the TCDD receptor. Another parallel with PCB is that congeners with vicinal hydrogen, especially in 3,4-positions, are more easily metabolized. An action level from the authorities in the state was in 1977 set to 0.02 ppm (fat weight basis) in milk and meat.

In a recent assessment of brominated diphenyl ethers the US EPA found that there were no data available for environmental effects of PBDE (18). High doses of decabromodiphenyl ether to rats have shown some evidence of carcinogenicity. The same compound didn't show any malformations in fetuses of rats given up to 1000 mg/kg on gestation days 6 - 15. Increased xenobiotic metabolism was the result of penta- and octabromodiphenyl ether at a dose of 0.78 mg/kg/day to rats during 90 days. These results have been the base for the ADI suggested by US EPA, which are 0.031 mg/day/70 kg for the pentabromohomologues, the value for octabromodiphenyl ether is 0.043 and for decabromodiphenyl ether 0.7 mg/day/70 kg.

There are some studies on effects of PBDD/F, especially regarding enzyme induction potency, described in the literature. The results indicate the same mechanisms as for PCDD/F even if there are differences in magnitude. 2,3,7,8-TeBDD is reported to have between 10 and 108 % of the AHH induction effect the TCDD (19,20). Some results indicate significantly higher potency for the 2,3,7-TeBDD than for the corresponding chlorine compound.

#### CONCLUSION

Our knowledge of the brominated organic compounds is limited but indicates that we can expect behaviours and properties alike the corresponding chlorinated substances. We also know that some of the anthropogenic brominated compounds are present in the environment, in some cases at increasing levels. This must alert us to be careful with the use of some of these substances and try to find safer alternatives. This is the only way to avoid new "PCB and dioxin problems".

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