Organochlorines in perspective

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ABSTRACT: Efforts to classify all organochlorine compounds as toxic substances are not supported by scientific facts. These compounds are produced in vast quantities in marine environments and in soil, and 2000 naturally produced organohalogen compounds have been identified to date. Man-made organochlorines range from persistent, toxic, and bioaccumulative compounds like pesticides to beneficial substances such as pharmaceuticals, analgesics, and artificial sweeteners. It is essential to distinguish between toxic and harmless organochlorines, just as we distinguish between poisonous and edible mushrooms. Regulatory efforts can then be directed toward eliminating the discharge of persistent, toxic, and bioaccumulating substances, no matter what elements they contain.

KEYWORDS: Adsorbable organic halogen, analysis, bibliographies, chlorine compounds, natural resources, raw materials, sources.

There is a widely held perception that organochlorine compounds are solely anthropogenic in origin. However, with the identification of more than 2000 naturally produced organohalogen compounds, it is now clear that nature can both synthesize and metabolize them on a grand scale. Organochlorines are produced in vast quantities in marine environments and in soil.

Man-made organochlorines range from persistent, toxic, and bioaccumulative compounds like pesticides to beneficial substances like pharmaceuticals, analgesics, and artificial sweeteners. It is essential to distinguish between toxic and harmless organochlorines, just as we distinguish between poisonous and edible mushrooms. Efforts to classify all organochlorine compounds as toxic substances are not supported by the scientific facts.

The organochlorine spectrum

There is a wide spectrum of organochlorine compounds with a broad range of properties. The organochlorine spectrum is illustrated in **Fig. 1**. Some of these compounds are highly toxic. Indeed, chlorinated pesticides were designed to be toxic. Some organochlorine compounds are highly stable. PCBs (polychlorinated biphenyls), in particular, were selected for use because of their stability, which we now tend to characterize as "persistence."

The properties of organochlorine compounds derive from the detailed structures of the molecules and not just from presence of chlorine. For example, artificial sweeteners can be prepared from chlorine compounds (e.g., sucralose), although the majority of artificial sweeteners are nitrogen derivatives (e.g., Aspartame™, the active ingredient in Nutra Sweet®). To contend that organochlorine compounds are invariably toxic is clearly incorrect, since sucralose is licensed as a food additive in Canada. Likewise, chlorine does not have a monopoly on toxicity. Many of the most virulent poisons are nitrogen compounds (e.g., strychnine). **Figure 2** illustrates the chemical structures of chlorine-based and nitrogen-based food additives and toxins.

Organochlorine occurring naturally

Gribble *(1)* has compiled an impressive list of naturally occurring organohalogen compounds found in animals and plants. The total count of identified substances now stands at 2000 and is rising rapidly, as seen in **Fig. 3**. The following items describe only a few of the more suprising examples *(1)*:

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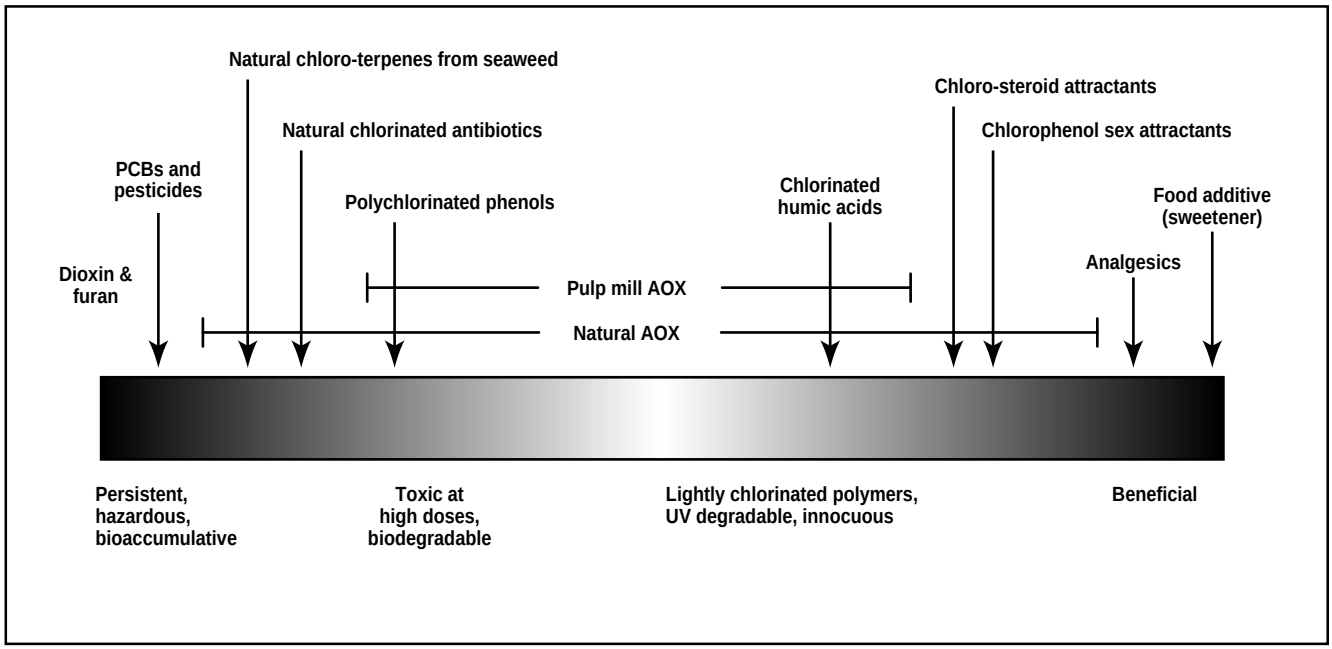
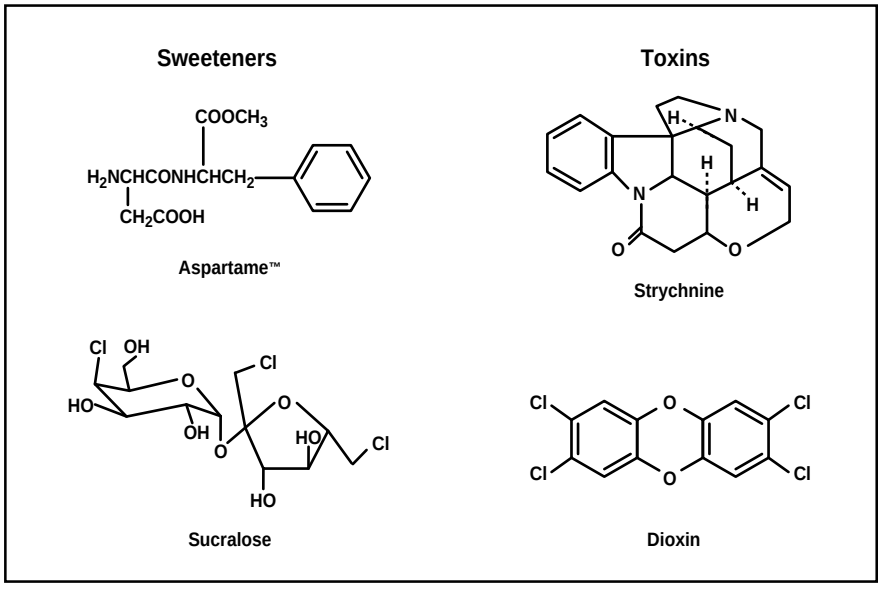
1. The organochlorine spectrum



- Grasshoppers produce 2,5-dichlorophenol as an ant repellant.
- The sex attractant (pheromone) used by several types of ticks is 2,6-dichlorophenol.
- Volcanos generate chlorofluorocarbons.
- Some chlorinated prostaglandins obtained from marine animals have potent antitumor activity.
- Some soil microbes produce antibiotics that are tetrachlorinated.
- Lentils contain chlorinated indoles.
- Oranges, lemons, and barley contain chloroform.
- A tetrabromochloro compound accounts for 1.3% of the dry weight of a marine sponge. This substance is a predioxin and is 85% halogen by weight.
- White-rot fungus degrades chlorophenols (including pentachlorophenol), DDT, and PCBs.
- Natural production of organohalogen is high. Marine and terrestrial emission of methyl chloride is 5 million tons per year, 190 times more than man-made emissions. Acorn worms in Japan were found to produce 95 lb of organohalogens per day per square kilometer.
- Rushes growing in a Mississippi salt marsh are reported to produce significant amounts of 1,2,3,4-tetrachlorobenzene.

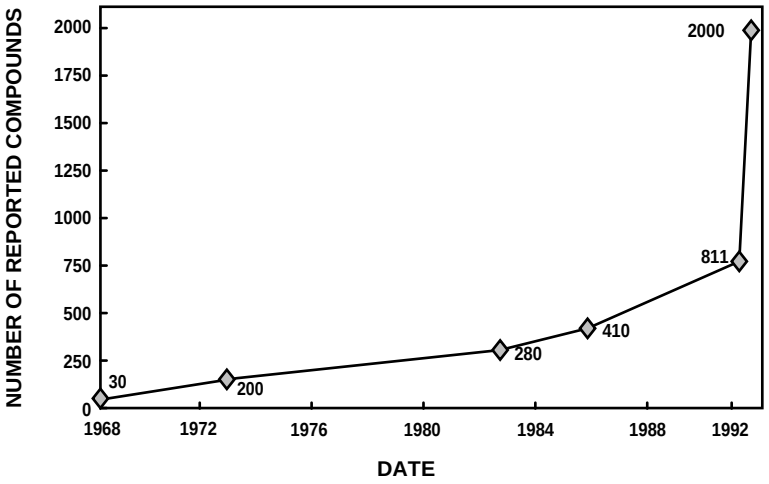
2. Structure and properties of nitrogen compounds (Aspartame™ and strychnine) and organochlorine compounds (sucralose and dioxin)



Organochlorine in rivers and lakes

In addition to the specific organochlorine compounds discussed by Gribble *(1)*, large quantities of less-well-characterized organochlorine (in the form of adsorbable organic halide, AOX) are discharged by pristine rivers and streams in Sweden *(2, 3)* and in Canada *(4, 5)*. The chlorine contents

3. Naturally occurring organohalogen compounds reported *(1)*



I. Organochlorine in animal tissue

	OX content, µg Cl/g dry material	*Literature cited*
Oysters near pulp mill, 1978	504	Leach *et al. (14)*
Oysters near same mill, 1979	85	Leach *et al. (14)*
Oysters from a nonindustrial site	53–174	Leach *et al. (14)*
Antarctic krill, Wedell Sea	10–25	Hansen *(15)*
"Unpolluted" mussels, Lake Gatow, Germany	16–23	Hansen *(15)*

of such waters are in the range 2–195 µg AOX/L, equivalent to 2–195 ppb. This translates into annual flows of thousands of tons of organochlorines into water bodies such as the Baltic Sea or Lake Superior *(5–7)*. In one study, 135 Swedish rivers and lakes were tested, and the majority had AOX concentrations of 20–60 µg/L, with some ranging up to 200 µg/L *(3)*.

While about 15 µg AOX/L is present in Swedish rainwater *(6–9)*, much of the AOX present in rivers and streams is thought to be generated in soil and peat bogs *(10, 11)*. A correlation exists between the AOX content and the amount of humic substances present in the water *(11)*. The generation of organochlorine by incubated soil samples has also been demonstrated *(12)*.

While the carbon-to-chlorine ratio of this natural AOX produced in soil is approximately 1000:1—indicating this material to be lightly chlorinated *(3)*—individual highly chlorinated compounds can be produced in soils in small amounts. For example, polychlorinated dioxins are generated during the rotting of compost *(13)* by an unknown mechanism, and soil fungus produces 2,4-dichlorophenol *(1)*.

Organochlorine in animal tissue

Leach *et al.* reported in 1985 *(14)* that oysters from a nonindustrial location on Vancouver Island had a similar organochlorine content (53–174 ppm, equivalent to 53–174 µg/g dry material) to oysters harvested near a pulp mill, as seen in **Table I**.

Since that time, Hansen *(15)* has found Antarctic krill to contain organochlorine. Since these animals are a major component in the marine food chain, it is quite likely that these substances can be found in other types of fish and in whales.

Even freshwater animals contain organochlorine. Indeed, as seen in Table I, the levels found in zebra mussels from an unpolluted lake ranged from 16 ppm to 23 ppm, i.e., in the same range as the krill *(15)*.

Organochlorine in wood and plant material

The discovery of organochlorine (OX) in unbleached kraft pulps and in effluent from an unbleached kraft mill was a surprise. However, it is now recognized that wood itself contains OX *(16)*, which produces a small OX content in the brown pulp *(17)*, often around 0.07 kg OX/ton of pulp. Because of the OX in wood, AOX levels in effluents from TCF (totally chlorine free) bleaching are not zero *(16, 18)*. However, the organochlorine structures in wood are likely to be quite different to the chlorolignin fragments present in bleach-plant effluents and humus.

Plants and trees have been known to produce specific halometabolites

II. Organochlorine content of vegetation samples *

	OX content, µg Cl/g dry material
Beech leaves	10–20
Norway spruce needles	20–60
Sphagnum moss	60–80
Grass	60–100

* Data from Kersna *et al. (20)*

III. Chlorinated fatty acids in food items [a]

	Concentration of chlorinated fatty acid, ppm [b]				
Food item	$C_{18:1}$ *(Cl, Cl)*	$C_{18:0}$ *(Cl, Cl)*	$C_{18:1}$ *(Cl, OH)*	$C_{18:0}$ *(Cl, OH)*	$C_{18:0}$ *(Cl, Cl, Cl,OH)*
Sugar cookies	47.7	10.10	42.7	20.0	38.0
Yellow cake	43.1	8.47	37.9	15.2	23.4
Biscuits	42.8	8.25	51.3	16.5	19.0
Chocolate chip cookies	40.8	8.21	26.2	15.8	n.d. [c]
Sandwich cookies	20.6	2.87	7.8	4.3	n.d.
Blueberry muffins	20.6	4.38	10.3	5.8	n.d.
Pancakes	2.7	0.63	3.4	1.2	n.d.
English muffins	1.2	0.26	2.2	2.6	n.d.

[a] Data from Heikes *(21, 22)*
[b] C_{18} fatty acids were analyzed. The number after the colon indicates the number of double bonds present. The letters in parentheses indicate the degree of chlorination.
[c] Not detected

for some time *(19)*—for example, methyl chloride is produced by cedar and cypress trees *(1)*—but only recently has total organochlorine content received attention. **Table II** shows values in the range 10–100 ppm OX for samples of leaves, moss, and grass *(20)*.

Organochlorine and people

Organochlorine in food

Two papers by Heikes *(21, 22)* report concentrations of chlorinated lipids in common foodstuffs. These data are summarized in **Table III**. When these data are recalculated as organochlorine content, the OX values range from 0.75 ppm to 30 ppm. However, OX in foodstuffs is not present only as chlorolipids. A paper by Wei *et al. (23)* indicates that chlorolipids account for only about 57% of the total organochlorine content of white flour. Applying this correction factor to the data of Heikes *(21, 22)*, one could conclude that some bakery products could contain up to 50 ppm of organochlorine.

According to Heikes, the organochlorine in bakery products comes from the flour, which can contain as much as 181 ppm OX in the form of chlorolipids *(22)*, implying a total organochlorine content of up to 318 ppm in the flour [estimating from the data of Wei *et al. (23)*].

These calculated OX numbers seemed rather high, so we measured the OX content of some food products using the method developed by PTS *(25)*. The results in **Table IV** confirm the values estimated from the work of Heikes *(21, 22)*. Surprisingly, unbleached flour also contained a significant amount of OX. We have also analyzed potatoes for organohalogen content in our laboratory. Values ranged from 0.2 ppm to 1.2 ppm on a dry basis *(26)*.

Organochlorine in laundry

Bleaching with domestic hypochlorite bleach produces significant organochlorine levels in laundry *(24)*. New cotton cloth baby diapers from two different manufacturers contained 17 ppm and 86 ppm of OX. After two washes and bleaches, they reached 82 ppm and 120 ppm OX, respectively.

A well-used cotton T-shirt contained 990 ppm OX, which fell to 350 ppm after thorough washing and solvent extraction. The presence of residual OX in the fabric after solvent extraction is an indication that carbohydrates can become chlorinated *(24)*.

Organochlorine in drinking water

Table V shows data for AOX in chlorinated drinking water in the Montreal area. The samples, taken by the author in 1990, contained 178–361 µg AOX/L. Other researchers have reported TOX (total organic halides) levels in finished drinking-water samples from 5 U.S. cities, with TOX ranging from 152 ppb to 549 ppb *(27)*. [Note that in this article, organochlorine levels in dry materials such as tissue, textiles, and food are quoted in ppm (i.e., µg/g), whereas AOX levels in drinking water and effluents are given in ppb (i.e., µg/L)].

To put this into perspective, an ECF (elemental-chlorine free) pulp mill releasing 0.25 kg AOX/ton of pulp and using 100 m^3 water/ton of pulp has an effluent containing 2500 µg AOX/L, i.e., about ten times more than drinking water. Because river dilution is normally much greater than 10:1, rivers downstream from bleached kraft mills usually contain much less AOX than does treated drinking water. Even at the time of the EPA's study of 104 mills in 1988, the majority of rivers below U.S. pulp mills contained less than 100 µg AOX/L *(28)*. The levels have decreased markedly since that time.

There is scientific interest in discovering if there are any ill effects

IV. Organochlorine content of food products

Food product	OX content, µg Cl/g dry material
Apple pie crust	34
Yellow cake mix	210
Unbleached flour	29

V. AOX in water samples from the Montreal area [a]

Sample type	Location	No. of samples taken	AOX content, µg/L
Drinking water	Pierrefonds	1	361
Drinking water	Pointe Claire	5	249–313
Drinking water	Ste. Anne	2	178–302
Well water	West Island	2	n.d. [b]
Ottawa River	Lake of 2 Mountains	1	27
Urine sample	Ste. Anne resident	1	362

[a] Samples gathered in Sept./Oct. 1990 and analyzed by Paprican

[b] Not detected; detection limit 10 µg/L

from AOX produced by chlorination of drinking water. Studies are presently being conducted *(29, 30)*, but there is no need for precipitate action to change water-treatment procedures. Chlorination of water is one of the great public health successes of the past century, and the dangers of waterborne disease resulting from underchlorination seem far greater than the risks of cancer from small amounts of chloroform and such substances.

Two recent events have underlined the need for continued vigilance in water purification. One was the outbreak of waterborne *Cryptosporidium* infections in Milwaukee in 1993, which caused several deaths *(31)*. The other was the return of cholera epidemics to Latin America. Sadly, the current campaign against chlorine in North America and Europe, and the concern about chlorination by-products, led some South American authorities to decrease or shut off the chlorine flow in water-purification plants, with resulting severe loss of life *(32)*.

Organochlorine in humans

A pioneering study in Finland showed that urine contains AOX in an amount that correlates with the AOX content of the local drinking water *(33)*, but the extrapolated data indicate that urine contains a background level of about 100 µg AOX/L in excess of the contribution from drinking water. The single urine sample that was analyzed from the Montreal area (Table V) is consistent with the Finnish study, in that the urine had a higher AOX concentration than associated drinking-water samples. Three explanations have been suggested for this extra AOX content of urine:

1. Some of the AOX is organo-iodine products from the thyroid gland *(33)*.
2. Some of the AOX comes from food *(33)*.
3. Some AOX is a by-product of the body's defense mechanism against infection *(34)*. It is thought that white blood cells employ a chlorination step to kill off invading cells *(35–38)*.

To my knowledge, there are no reports of AOX levels in blood. However, if the kidneys can extract it into urine, then AOX clearly must also be present in the blood stream.

It is interesting to note that the AOX concentration in human effluent is roughly 1/10th that of a modern ECF pulp mill producing 0.2 kg AOX/ton of pulp.

Degradation of organochlorine

Laboratory studies of AOX degradation date from the report by Amy *et al.*, who noted that pulp-mill AOX was adsorbed by biomass *(39)*. They later discovered that a portion of the AOX was mineralized (i.e., converted to chloride) by microorganisms in an aerated lagoon *(40)*. More recently, Roy-Arcand and Archibald reported that part of the pulp-mill AOX can be destroyed by exposure to daylight *(41)* or ultraviolet (UV) irradiation *(42)* in the laboratory. Significantly, UV radiation is not essential, because substantial AOX removal was achieved with a blue–green light source having no UV component *(42)*.

Studies of AOX degradation in a more natural setting are now underway. Saski *et al. (43)* diluted treated effluent from a Finnish pulp mill with lake water and retained it outdoors in floating enclosures for 9–13 months. Up to 64% of the AOX in the treated effluent was destroyed in these conditions.

In a Canadian study *(44)*, undiluted biotreated effluents from three modern kraft mills were placed 20 cm and 120 cm below the surface of a remote lake in sealed plastic bags, permitting free passage of gases and light. Over 132 days, most of the ef-

fluents' AOX was mineralized, and the effluents remained nontoxic (by an acute-toxicity assay). Each mill effluent supported a distinct photosynthesis-based microbial community inside the bags. Each community had a high species diversity, which is typical of a healthy ecosystem. These communities were nearly as rich and diverse as those found on the outside surfaces of the bags, which were exposed only to lake water. This ability of undiluted biotreated kraft effluents to promote the growth of a wide variety of microflora and fauna over many generations indicates a complete lack of toxicity under receiving-water conditions.

These findings call into question the Greenpeace statement, "Enough is known about the persistence and toxicity of organochlorines as a class to justify an outright ban" *(45)*.

Concluding remarks

Organochlorine molecules come in all shapes and sizes. The organochlorine spectrum is a continuum ranging from toxic substances to food additives.

Organochlorine compounds occur naturally in all locations: in oceans, rivers, plants, and inside both marine and freshwater animals. Some of the organochlorine appearing in human urine may have a natural origin within our own bodies, though it is important to realize that we ingest organochlorine at ppb levels in drinking water and at ppm levels in some foods.

In view of the widespread distribution of natural sources of organochlorine, it makes no sense to try to ban the industrial use of chlorine in an effort to eliminate this class of compounds. However, it does make sense to eliminate the discharge of persistent, toxic, and bioaccumulating substances, no matter what elements they contain. ■

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