

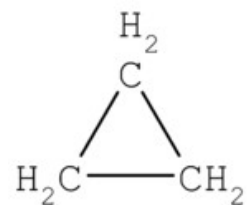
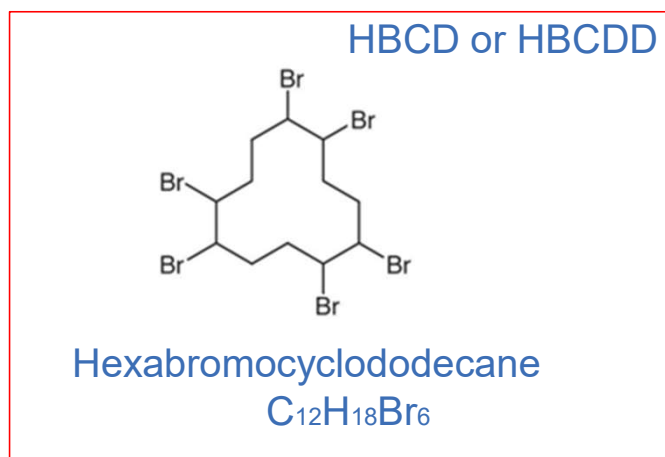


MA Flame Retardants Law, 2020

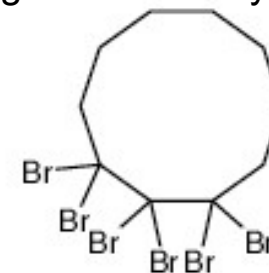
An Act to Protect Children, Families and Firefighters from Harmful Flame Retardants
Mass. Gen. Laws Ch 21A, Section 28



Subclass 3 – Polyhalogenated alicycles



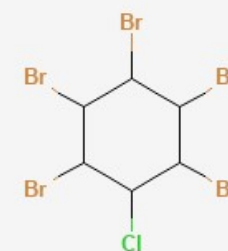
Analogue #1 – HBCyD



Hexabromocyclodecane
 $C_{10}H_{14}Br_6$

- On TURA list (never reported)
- Stockholm Convention phase out 2015
- General toxicity issues: developmental toxicity, aquatic toxicity, PBT
- Not usually used in product categories in the FR law, mostly polystyrene foam in construction.

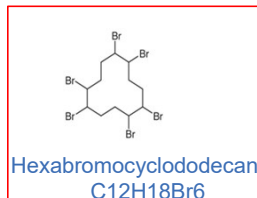
Analogue #2 - PBCC



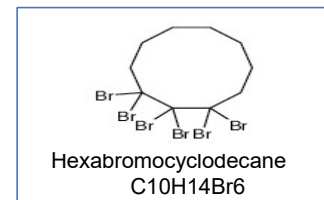
1,2,3,4,5-Pentabromo-6-chlorocyclohexane
 $C_6H_6Br_5Cl$

General information

HBCDD



Analogue #1 – HBCyD



- Confusing HBCDD and HBCyD
- CPSC 2024 Scoping Document for polyhalogenated alicycle subclass: 17 in subclass, 11 are isomers of HBCDD
- PHA subclass members have high boiling points, low vapor pressures, low water solubility, and high octanol/water partition coefficient (K_{ow}) values
- HBCDD, HBCyD and PBCC are all in the CPSC Polyhalogenated Alicycles subclass “sufficient data” to proceed with risk assessment

CompTox Data for HBCDD and Analogues 1 & 2

CompTox plus additional references as noted										
Name	CAS #	Boiling Point deg C	Vapor Pressure mmHg	Soil adsorption coeff (Koc), L/kg	Water solubility, mol/L	Octanol water coefficient, LogKow	Biodeg. Half-Life, days	Fish Biotrans. Half-Life (Km)	BCF, L/kg	BCF, L/kg Biowin (EpiSuite)
Hexabromocyclododecane (HBCDD)	25637-99-4	264	1.91E-03	2.19E+04	3.55E-07	1.35 5.625 exp (POPs doc)	10.2	2.4	26900 exp*	5019
Hexabromocyclodecane (HBCyD)	25495-98-1	372	2.85E-04	1.29E+05	2.43E-07	7	95.5	3.39	1620	16,130
Pentabromochlorocyclohexane (PBCC)	87-84-3	353	2.06E-02	1.70E+04	7.03e-6	4.59	77.6	0.49	257 ** see table to the right	604
* = average of 16 experimental values in ECOTOX										
HBCDD: Reliable experimental BCFs from two flow-through bioconcentration tests with fish are available. As a representative BCF-value 18,100 was chosen in the EU risk assessment (European Commission, 2008)										
(ECHA SVHC determination) No degradation was observed in the study of Davis et al. (2004) in aerobic soil. A half-life of 119 days was observed in Davis et al (2003b), but this value may underestimate the half-life as only disappearance of HBCDD was studied.										

BIOWIN predicts that all three chemicals are NOT readily biodegradable

TABLE 2-3
BCF Estimations for Pentabromochlorocyclohexane

Equation	Calculated BCF	Reference
$\text{Log BCF} = 0.76 \log K_{ow} - 0.23^a$	15,000	Veith et al., 1980
$\text{Log BCF} = 2.791 - 0.564 \log WS^b$	618	Kenaga and Goring, 1978
$\text{Log BCF} = 0.935 \log K_{ow} - 1.495^a$	8,470	Kenaga and Goring, 1978

^aLog K_{ow} = log octanol-water partition coefficient

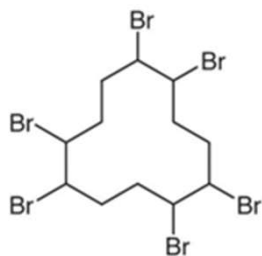
^bWS = water solubility in ppm (1 ppm)

HBCyD

Tech University of Denmark (2016) brominated FR category approach (<https://core.ac.uk/download/pdf/84595605.pdf>). The cycloalkanes were ID'ed as a “preliminary” read-across grouping:

- “This is chemically a broad structural group, which need thorough consideration before possible read-across between members. The two HBCDDs are chemically the closest analogues, although the different positions (alpha/beta vs. alpha/gamma) of the bromine atoms may give different activities. According to the rough (Q)SAR-based clusterings the two HBCDDs have similar profiles for carcinogenicity, endocrine activity and skin sensitization. HBCDD (CAS 3194-55-6), DBEDBCH, TBCO and HBCYD all have bromine in alpha/beta position (however with HBCYD having two bromines at the same carbon) and these substances have according to the rough (Q)SAR based clusterings similar profiles for reproductive toxicity effects. HBCDD (CAS 3194-55-9) and TBCO have similar (Q)SAR-based profiles for carcinogenicity, genotoxicity, reproductive toxicity and skin sensitization. HBCDDs and HBCYD were predicted to be vPvB. HBCDD (CAS 3194-55-6) is included in training sets for DTU models with negative experimental results for Ames, AR antagonism and ER agonism.”
- “Where the models could make robust predictions, all members had a number of positive indications for genotoxicity. Especially DBE-DBCH had many positive genotoxicity indications. HBCDDs, DBEDBCH and TBCO were positive within AD in a number of cancer models. HBCDD (CAS 3194-55-6), DBE-DBCH, TBCO and HBCYD had a few positive hits for reproductive toxicity and cardio toxicity.”

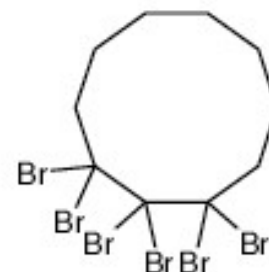
Subclass 3 – Polyhalogenated alicycles



Hexabromocyclododecane
 $C_{12}H_{18}Br_6$

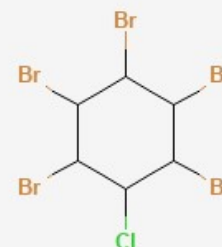
Q3b: Is each proposed analogue (#1,2) sufficiently similar to at least one chemical identified in the law (HBCDD) such that the proposed analogue would be reasonably anticipated to have similar concerns re: toxic hazard, persistence, bioaccumulation?

Analogue #1



Hexabromocyclodecane
 $C_{10}H_{14}Br_6$

Analogue #2



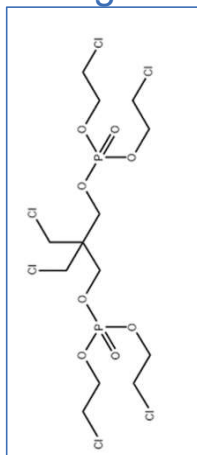
1,2,3,4,5-Pentabromo-6-chlorocyclohexane
 $C_6H_6Br_5Cl$

Which subclasses remain?

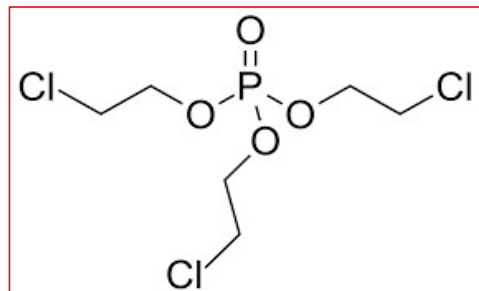
- **Subclass 1 – Polyhalogenated organophosphates**
- Subclass 2 – Polyhalogenated diphenyl ethers
- Subclass 3 – Polyhalogenated alicycles
- Subclass 4 – Polyhalogenated phthalates/benzoates/imides
- Subclass 5 – Polyhalogenated bisphenol aliphatics
- **Subclass 6 – Polyhalogenated aliphatic chains**
- Subclass 7 – Inorganic (not a NAS subclass)

Subclass 1 – Polyhalogenated Organophosphates

Analogue #5

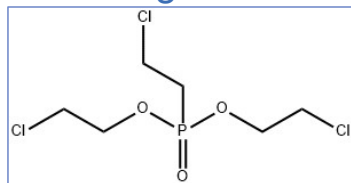


2,2-bis(chloromethyl)-propane-1,3-diyltetrakis(2-chloroethyl)bisphosphate

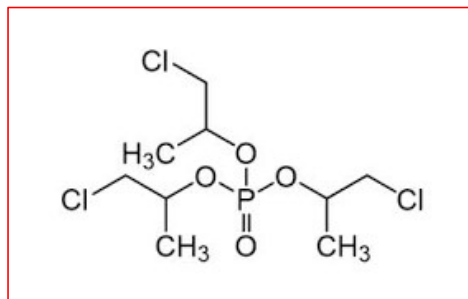
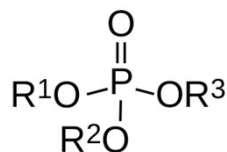


Tris(2-chloroethyl)phosphate (TCEP)

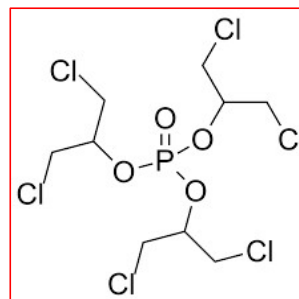
Analogue #4



Bis(2-chloroethyl)2-chloroethylphosphonate

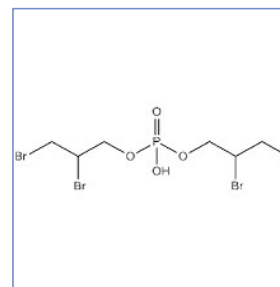


Tris(1-chloro-2-propyl)phosphate (TCPP)



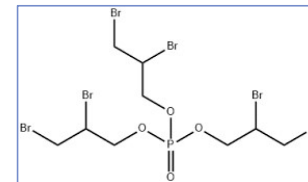
Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)

Analogue #3



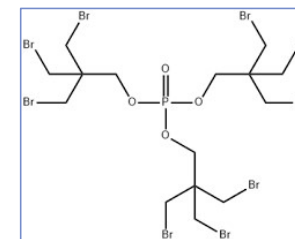
Bis(2,3-dibromopropyl)phosphate

Analogue #1



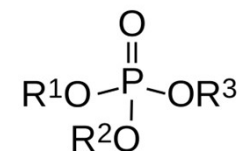
Tris(2,3-dibromopropyl)phosphate (TDBPP)
“Brominated tris” or “Tris”

Analogue #2



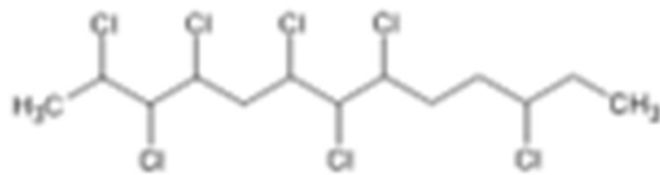
Tris(tribromoneopentyl)phosphate

The Phosphate FRs



- Many! 101 of EPA's full FR inventory (797) are phosphates; largest NAS subclass (22)
- Many are non halogenated (e.g., triphenyl phosphate)
- TCEP, TDCPP, TCPP part of EPA's Chlorinated Phosphate Ester Cluster FRs (Workplan 2015)
- General toxicity issues: carcinogenicity, reproductive toxicity, aquatic toxicity, respiratory sensitizer (due to being organophosphates), endocrine disruptors, persistent
- TCEP and TDCPP included in TRI in 2022 due to TURI petition, will be adopted under TURA

Category 6 – Polyhalogenated Aliphatic Chains



Chlorinated paraffins
85535-84-8
 $C_xH_{(2x-y+2)}Cl_y$
(where $x = 10-13$; $y = 3-12$)

The Parrafin FRs

- Short chain – C10-13; Medium chain – C14-17; Long chain C>17
- Exist as a mixture of chain lengths
- General toxicity issues SCCPs: carcinogenicity, PBT, aquatic toxicity
- EPA TSCA Action Plan for SCCPs (2009)
- SCCP on TURA list as "polychlorinated alkanes, C10-13" (never reported)
- EPA TSCA review (2015) of medium and long note aquatic toxicity and vP, vB
- Short chain – POPs 2017; Medium chain recommended for POPs 2023, currently under evaluation