Biodegradation Mechanisms for Medium Chain Chlorinated Paraffins

Prepared for MCCP REACH Consortium

by

[redacted]

Outline

- Persistence - Why Molecules Don’t Biodegrade
- Biochemical Processes potentially involved in the Biodegradation of MCCPs
- Aerobic Biodegradation Pathways for Representative Chlorinated C_{14} Paraffins and Estimated Physical-Chemical Properties and Aquatic Toxicities of Likely Metabolites (Lower Levels of Chlorination)
- The Problem with Vicinal Substitutions
- Aerobic Biodegradation Pathways for Representative Chlorinated C_{14} Paraffins and Estimated Physical-Chemical Properties and Aquatic Toxicities of Likely Metabolites (Higher Levels of Chlorination)
- Implications of this Exercise
- Anaerobic Biodegradation – A Variation on a Theme
- Summary and Conclusions

Background - Persistence

- Enzymes deal with one bond at a time in very specific ways
  - Enzymes can have very high 3-D specificity (lock & key)
  - Substitution near a bond can affect an enzyme's ability to catalyze a reaction
    - Steric hindrance can reduce the ability of the enzyme to recognize and/or bind to the molecule
    - Effects on reactivity can increase the activation energy of a reaction
- A microorganism degrades individual molecules one at a time
  - Not all constituents in a "chemical" (even when they have only minor differences) degrade at the same rate and/or to the same extent and provide the same energetic yield

Factors Contributing to Persistence

- Inherent to the Molecular Structure
  - The needed biochemical reactions (enzymes) and pathways are not available in nature
  - While some enzymes exist, the energetic yields of the reactions that occur are insufficient to support microbial growth (co-metabolism)

- Inherent to the Molecule but Exacerbated by the Environment (Situational)
  - A molecule's low solubility and high sorptivity can render a chemical poorly bioavailable in a some situations
    - Biodegradation differs when bound to inert sediment vs emulsified in a ready biodegradation test

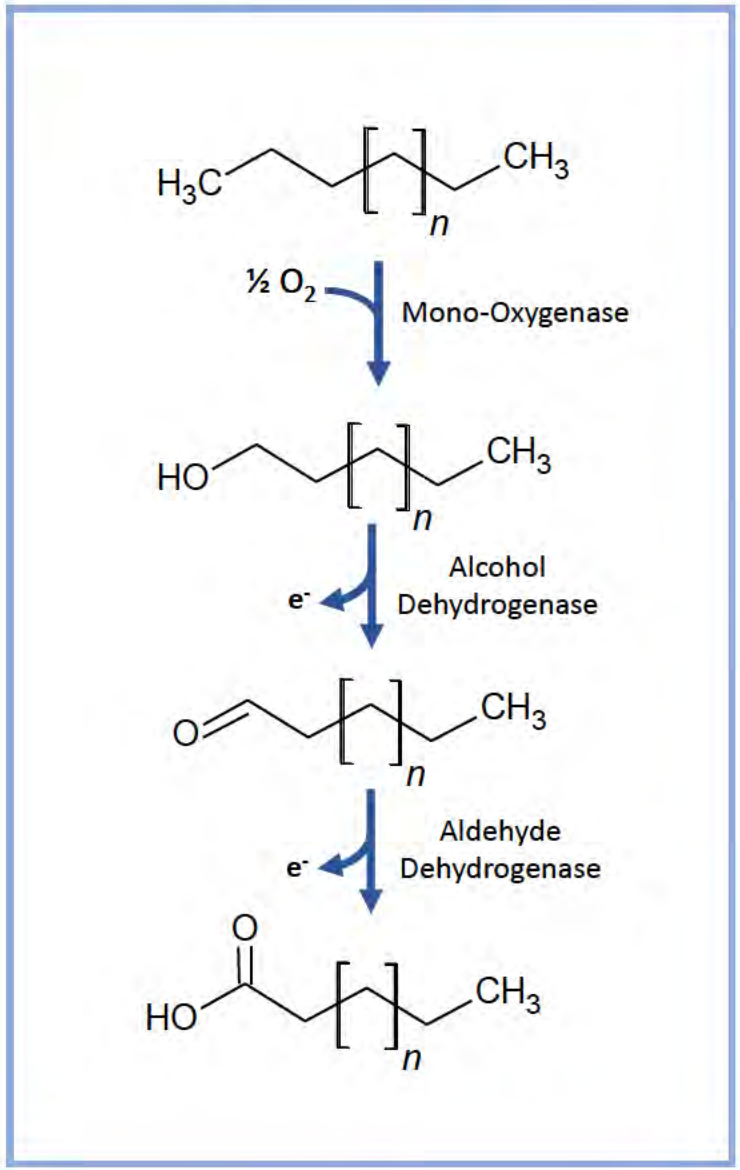
- Other Situational factors
  - Concentration is too high (inhibitory to microbes)
  - Competent degraders are absent, occur at a low levels and/or limited by time constraints
  - Other substrates are not present to fuel co-metabolic reactions
  - Environmental factors (temperature, oxygen, nutrient, cofactor limitation, etc.)

Biochemical Processes Potentially involved in the Biodegradation of MCCPs

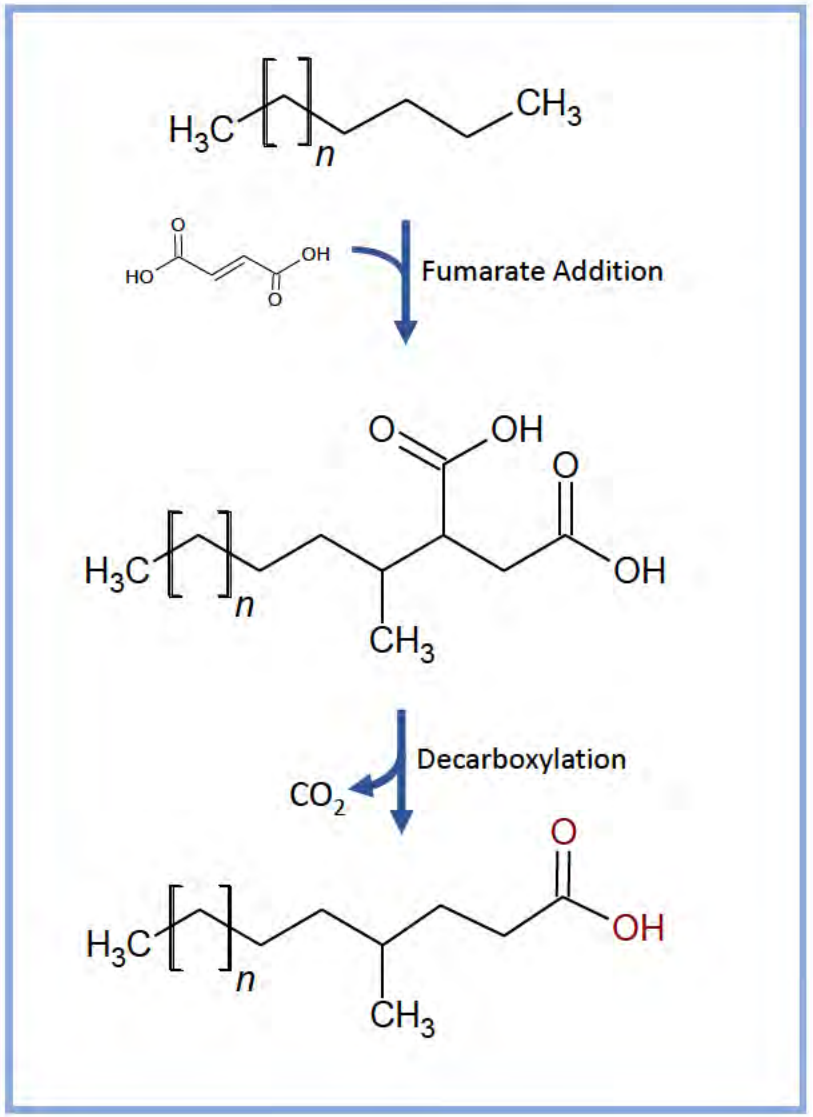
Complete Biodegradation of a MCCP Molecule Involves

- Disassembly of the Carbon Skeleton
  - Begins with oxidation of at least one of the terminal or subterminal carbons
  - Followed by chain-shortening
- Dehalogenation Reactions to remove chlorines
  - That block disassembly of the carbon backbone
  - From intermediates so they can be fully metabolized

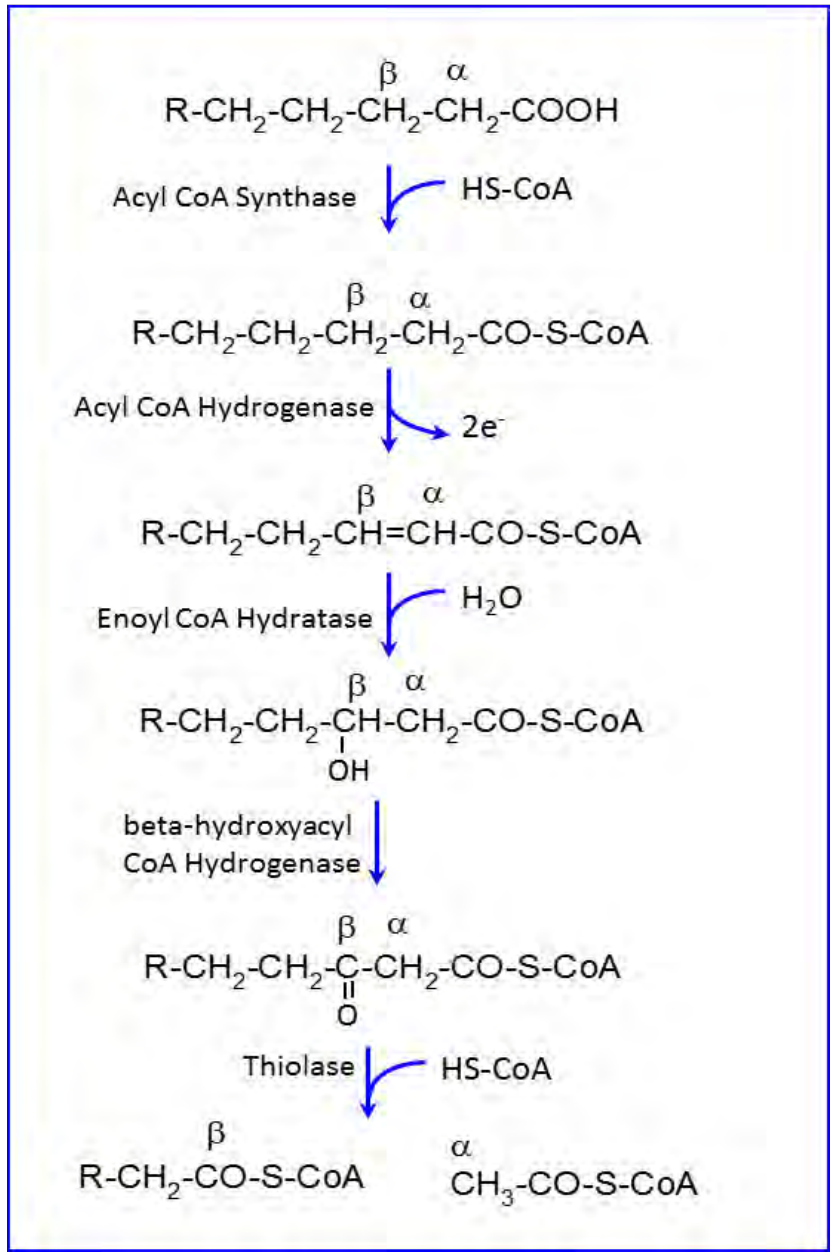
Omega Oxidation (Aerobic)



Fumarate Oxidation (Anaerobic)

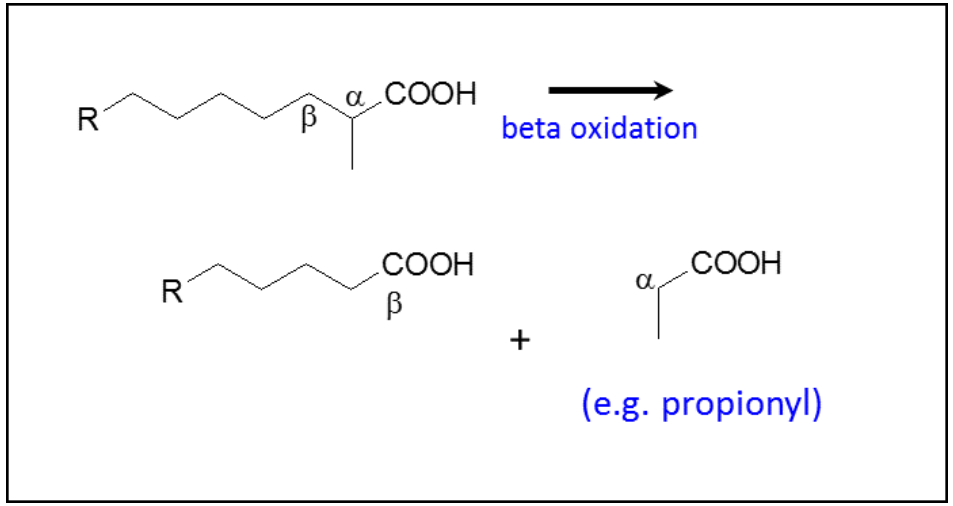


Beta Oxidation

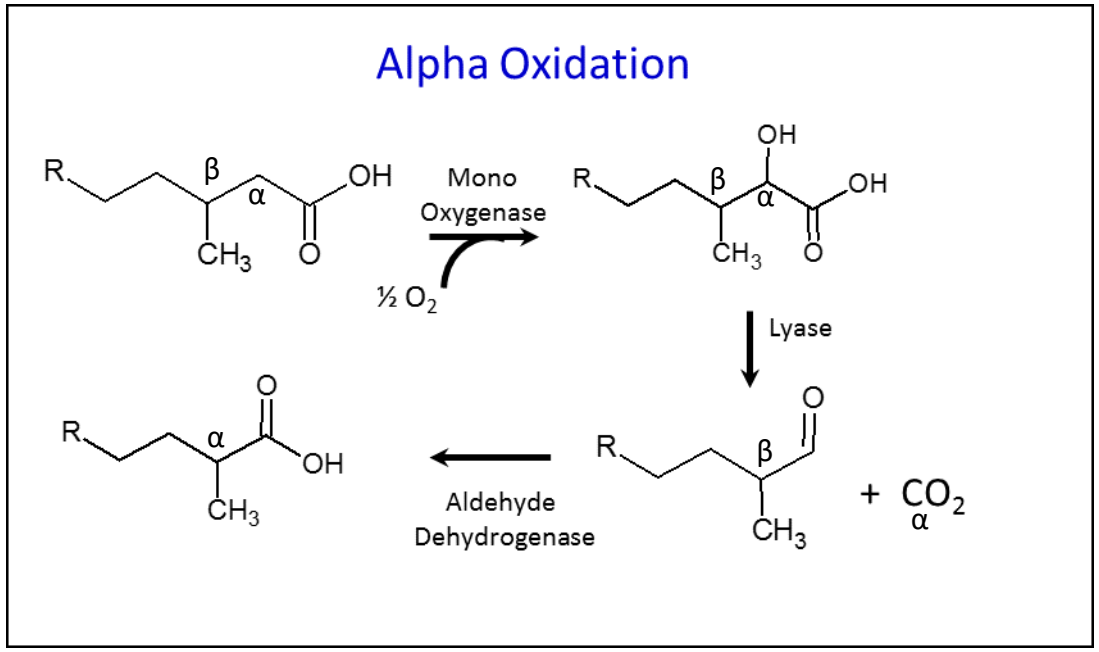


Dealing with Chain Substituents During Beta Oxidation

Alpha Substituents

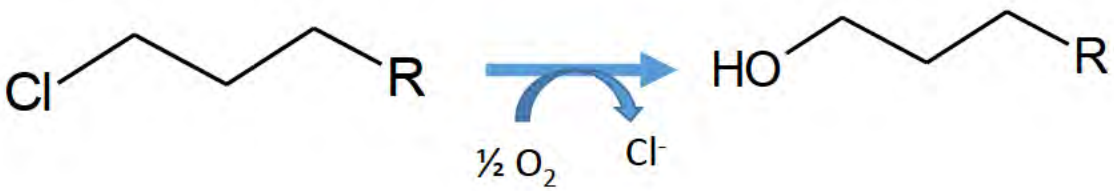


Beta (β) Substiuents

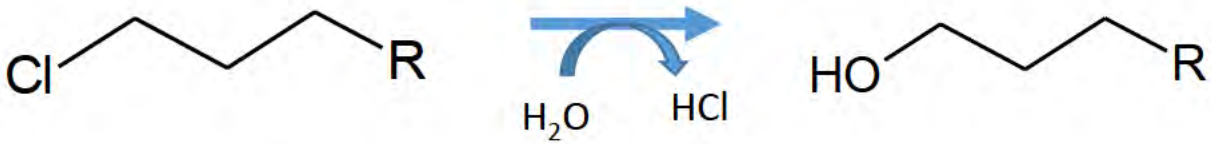


Dehalogenation Reactions

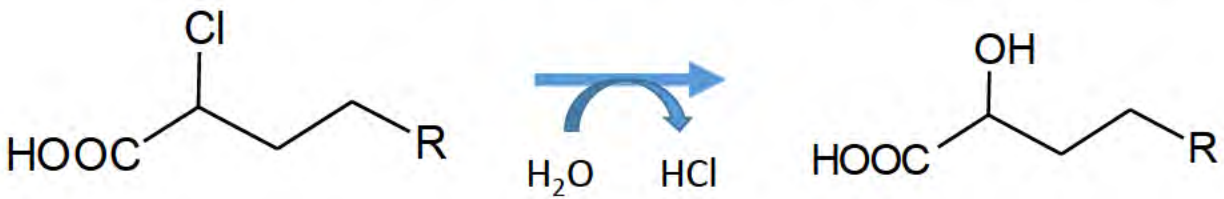
Oxygenolytic Dehalogenation (CL > 8 carbons)



1-Haloalkane Halidohydrolase (CL ≤ 8 carbons)

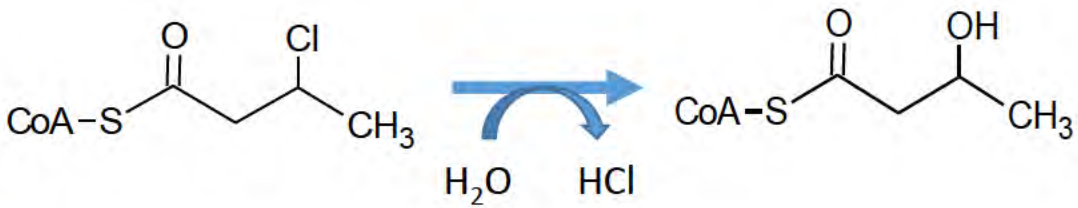


2-Halo-Alkanoic Acid Hydrolytic Dehalogenase



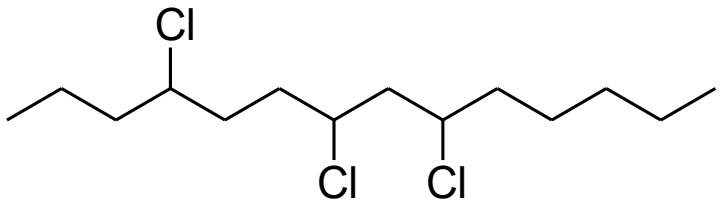
Anaerobic Reductive Dehalogenation

3-Haloacyl-CoA Hydrolytic Dehalogenase



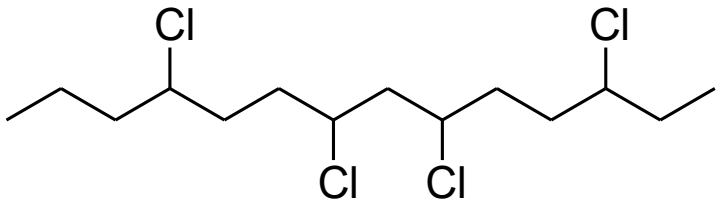
Biodegradation Pathways of Representative Chlorinated C_{14} Paraffins

Representative MCCP Homologs (UK 2013 Assessment)



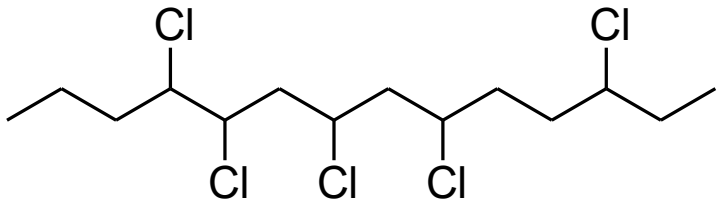
$C_{14}H_{27}Cl_3$

4,7,9 Trichloro Tetrdecane



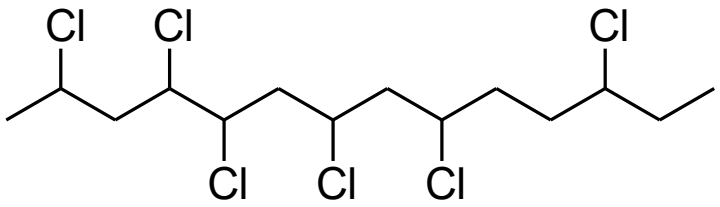
$C_{14}H_{26}Cl_4$

3,6,8,11 Tetrachloro Tetradecane



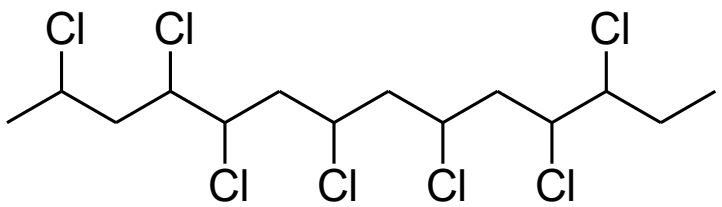
$C_{14}H_{25}Cl_5$

3,6,8,10,11 Pentachloro Tetradecane



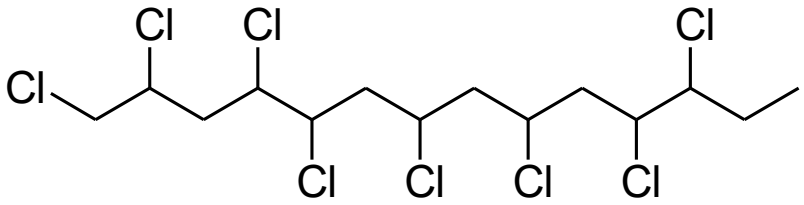
$C_{14}H_{24}Cl_6$

2,4,5,7,9,12 Hexachloro Tetradecane



$C_{14}H_{23}Cl_7$

2,4,5,7,9,11,12 Heptachloro Tetradecane



$C_{14}H_{22}Cl_8$

1,2,4,5,7,9,11,12 Octachloro Tetradecane

Estimated Properties of Representative Chlorinated C_{14} Paraffins

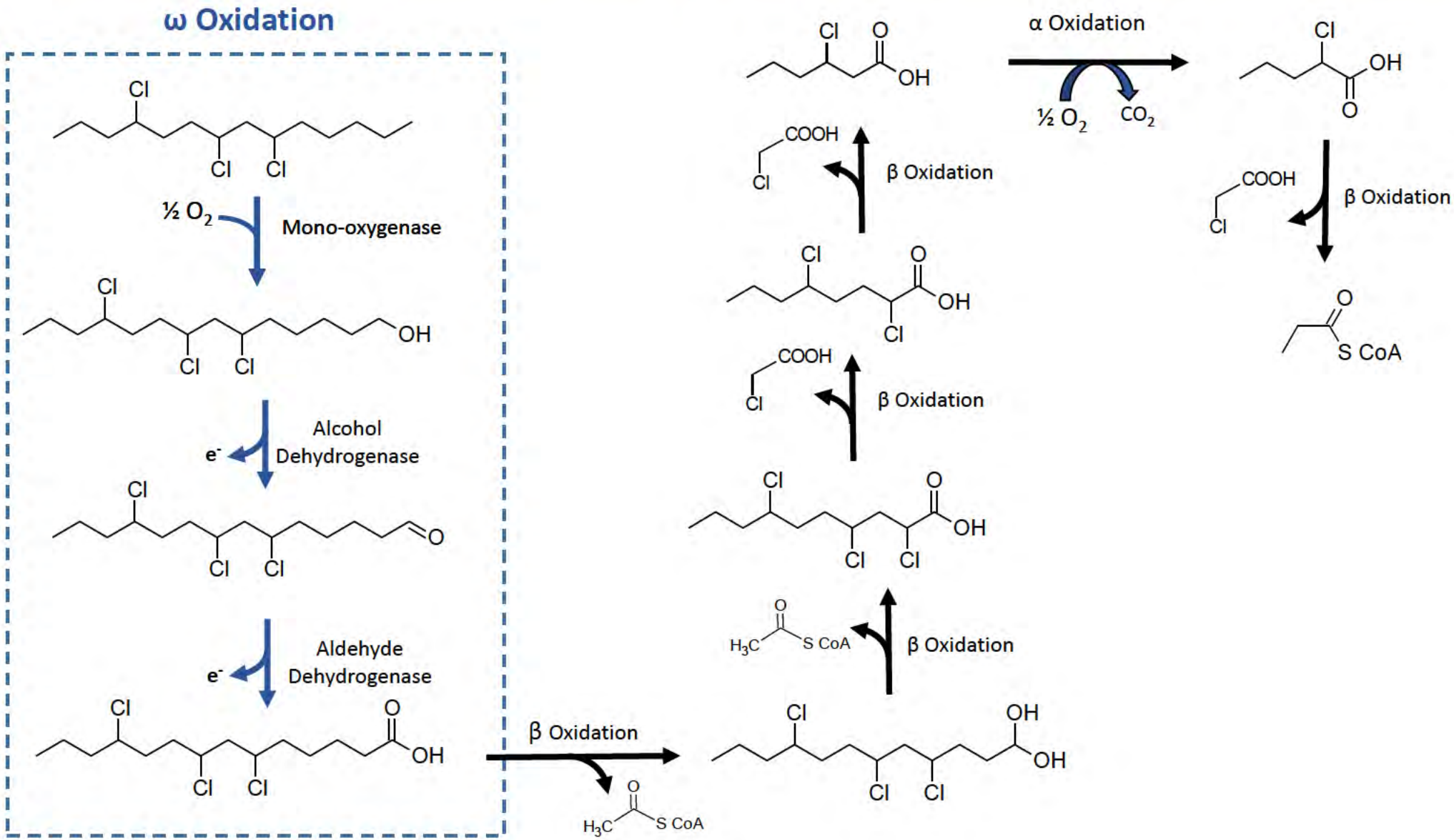
	Log K_{ow}	Log K_{oc}	Solubility (µg/L)	Fish ChV (µg/L)	Daphnid ChV (µg/L)
$C_{14}H_{27}Cl_3$ (35.3% Cl) 4,7,9 Trichloro Tetradecane	7.76	4.82	2.84	0.306	0.691
$C_{14}H_{26}Cl_4$ (42.3.3% Cl) 3,6,8,11 Tetrachloro Tetradecane	7.94	5.03	1.25	0.239	0.565
$C_{14}H_{25}Cl_5$ (47.9% Cl) 3,6,8,10,11 Pentachloro Tetradecane	8.12	5.24	0.541	0.185	0.456
$C_{14}H_{24}Cl_6$ (52.6% Cl) 2,4,5,7,9,12 Hexachloro Tetradecane	8.30	5.42	0.233	0.142	0.366
$C_{14}H_{23}Cl_7$ (56.5% Cl) 2,4,5,7,9,11,12 Heptachloro Tetradecane	8.48	5.63	0.094	0.108	0.291
$C_{14}H_{22}Cl_8$ (59.9% Cl) 1,2,4,5,7,9,11,12 Octachloro Tetradecane	8.73	5.92	0.037	0.071	0.203

Ecosar Class: Neutral organics

Disclaimers

- These are not proven pathways but they are largely consistent with results from actual biodegradation tests and output from pathway simulation tools.
- They involve biochemical reactions and pathways that have previously been documented in some context.
- They should be seen as working hypotheses to help explain the existing data and evaluate future test results until proven wrong
- Although the various enzymatic reactions have been documented to occur, their actual occurrence may be more limited due to unknowns regarding the specificity of the enzymes involved
- Some reaction and sequences were favored over others that would have similar outcomes
- Reactions that progressed biodegradation were assumed to take place unless there was specific evidence to the contrary.

Postulated Biodegradation Pathway for 4,7,9 Trichloro Tetradecane (Option1)



ECOSAR Estimates of Aquatic Toxicity of Metabolites (Option 1)

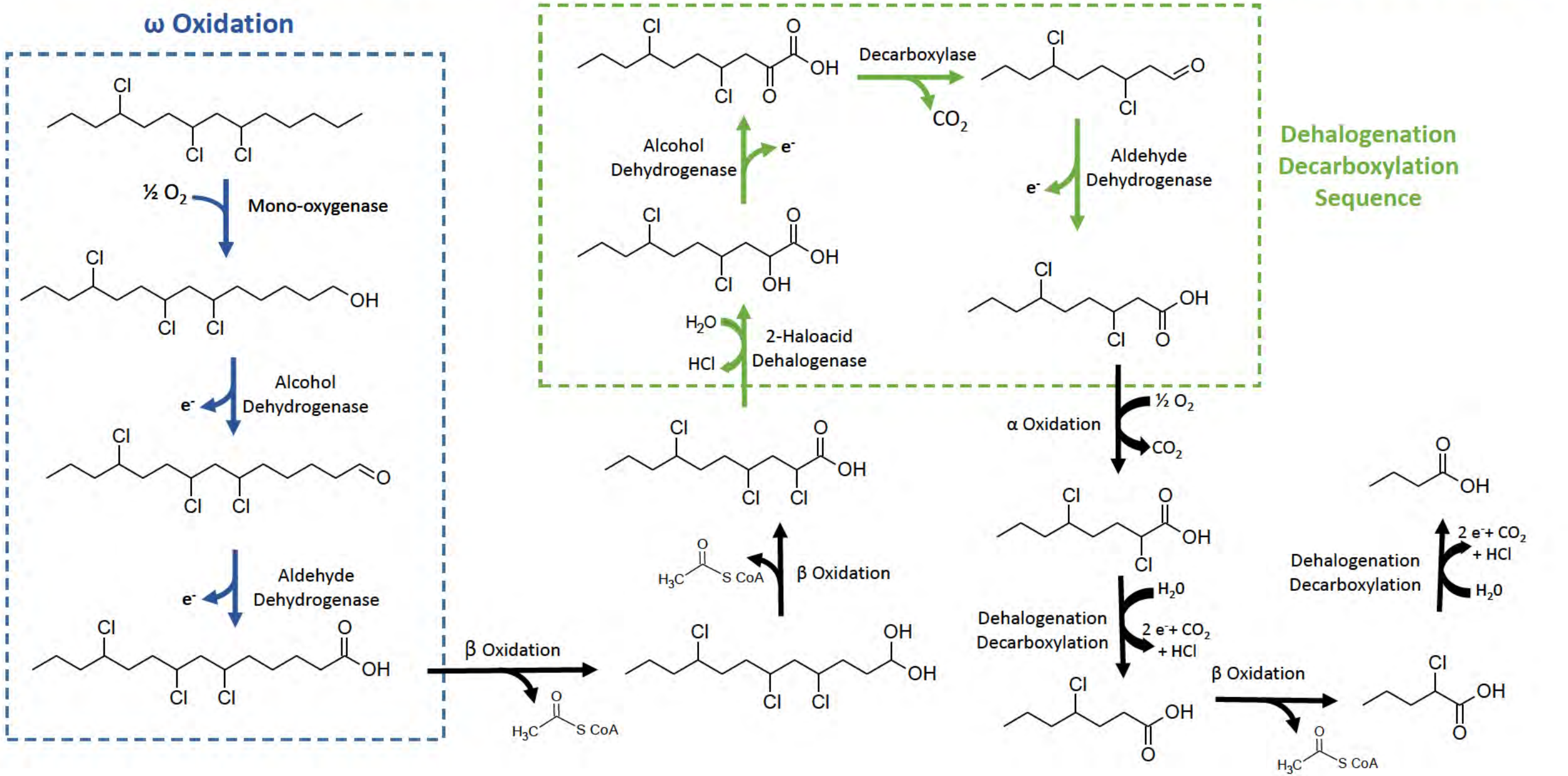
4,7,9 Trichloro Tetradecane

Chemical Formula	SMILES	Log Kow	Fish Chronic Value (mg/L)	Daphnid Chronic Value (mg/L)	Formation
C14 H27 Cl3	CCCC(Cl)CCC(Cl)CC(Cl)CCCCC	7.76	0.00031[a]	0.00069[a]	Parent
C14 H27 CL3 O1	CCCC(Cl)CCC(Cl)CC(Cl)CCCCCO	6.29	0.006[a]	0.009[a]	Oxygenase
C14 H25 CL3 O1	CCCC(Cl)CCC(Cl)CC(Cl)CCCCC=O	6.27	0.006[a] (0.003[b])	0.009[a] (0.007[b])	Alcohol Dehydrogenase
C14 H25 CL3 O2	CCCC(Cl)CCC(Cl)CC(Cl)CCCCC(=O)O	6.52 (2.71)[salt]	0.038 (0.047[c])	0.064 (0.047[c])	Aldehyde Dehydrogenase
C12 H21 CL3 O2	CCCC(Cl)CCC(Cl)CC(Cl)CCC(=O)O	5.54 (1.73)[salt]	0.238 (0.399[c])	0.315 (0.399[c])	Beta Oxidation
C10 H17 CL3 O2	CCCC(Cl)CCC(Cl)CC(Cl)C(=O)O	4.56	0.148 (0.168[d])	0.155 (0.106[d])	Beta Oxidation
C8 H14 CL2 O2	CCCC(Cl)CCC(Cl)C(=O)O	3.39	1.11 (1.33[d])	0.883 (0.529[d])	Beta Oxidation
C6 H11 CL2 O2	CCCC(Cl)CC(=O)O	2.23	76.8	46.0	Beta Oxidation
C5 H9 CL1 O2	CCCC(Cl)C(=O)O	1.74	18.2 (23.1[d])	9.70 (4.84[d])	Alpha Oxidation
C3 H17 CL3 O2	CCC(=O)O	0.58	965	388	Beta Oxidation

Omega Oxidation Sequence

ECOSAR Model: Neutral Organic Acid except, [a]Neutral Organic (Baseline), [b]Aldehyde , [c]Surfactant, [d]Halo Acid, [e]Halo Alcohol-Acid

Postulated Biodegradation Pathway for 4,7,9 Trichloro Tetradecane (Option 2)



ECOSAR Estimates of Aquatic Toxicity of Metabolites (Option 2)

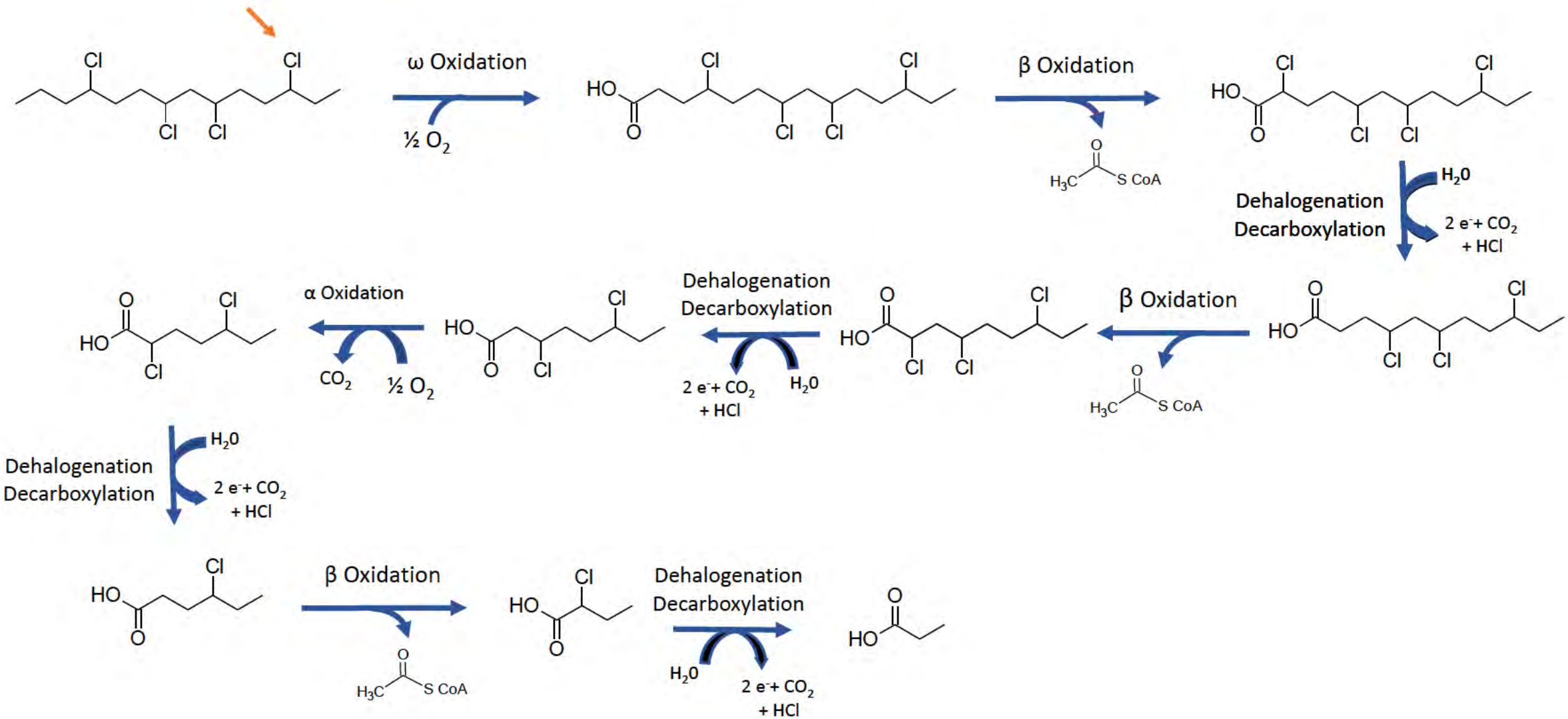
4,7,9 Trichloro Tetradecane

Chemical Formula	SMILES	Log Kow	Fish Chronic Value (mg/L)	Daphnid Chronic Value (mg/L)	Formation
C14 H27 Cl3	CCCC(Cl)CCC(Cl)CC(Cl)CCCCC	7.76	0.0003[a]	0.00069[a]	Parent
C14 H25 CL3 O2	CCCC(Cl)CCC(Cl)CC(Cl)CCCCC(=O)O	6.52 (2.71)[salt]	0.038 (0.047[c])	0.064 (0.047[c])	Aldehyde Dehydrogenase
C12 H21 CL3 O2	CCCC(Cl)CCC(Cl)CC(Cl)CCC(=O)O	5.54 (1.73)[salt]	0.238 (0.399[c])	0.315 (0.399[c])	Omega Oxidation
C10 H17 CL3 O2	CCCC(Cl)CCC(Cl)CC(Cl)C(=O)O	4.56	0.148 (0.168[d])	0.155 (0.106[d])	Beta Oxidation
C10 H18 CL2 O3	CCCC(Cl)CCC(Cl)CC(O)C(=O)O	3.15	2.171 (6.28[e])	1.622 (9.67[e])	Dehalogenase
C10 H16 CL2 O3	CCCC(Cl)CCC(Cl)CC(=O)C(=O)O	2.56	6.90	4.47	Alcohol Dehydrogenase
C9 H16 CL2 O1	CCCC(Cl)CCC(Cl)CC=O	3.63	0.692[a] (0.134[b])	0.580[a] (0.239[b])	Decarboxylase
C9 H16 CL2 O2	CCCC(Cl)CCC(Cl)CC(=O)O	3.89	4.54	4.04	Aldehyde Dehydrogenase
C8 H14 CL2 O2	CCCC(Cl)CCC(Cl)C(=O)O	3.39	1.11[a] (1.32[d])	0.883[a] (0.529[d])	Alpha Oxidation
C7 H13 CL1 O2	CCCC(Cl)CCC(=O)O	2.72	32.1	21.6	Dehalogenation Decarboxylation
C5 H9 CL1 O2	CCCC(Cl)C(=O)O	1.74	18.2[b] (23.1[d])	9.70[b] (4.84[d])	Beta Oxidation
C4 H8 O2	CCCC(=O)O	1.069	438	198	Dehalogenation Decarboxylation

Dehalogenation Decarboxylation Sequence

ECOSAR Model: Neutral Organic Acid except, [a]Neutral Organic (Baseline), [b]Aldehyde , [c]Surfactant, [d]Halo Acid

Postulated Biodegradation Pathway for 3,6,8,11 Tetrachloro Tetradecane



ECOSAR Estimates of Aquatic Toxicity of Metabolites

3,6,8,11 Tetrachloro Tetradecane

Chemical Formula	SMILES	Log Kow	Fish Chronic Value (mg/L)	Daphnid Chronic Value (mg/L)	Formation
C14 H26 CL4	CCCC(Cl)CCC(Cl)CC(Cl)CCC(Cl)CC	7.94	0.00024[a]	0.00057[a]	Parent
C14 H24 CL4 O2	OC(=O)CCC(Cl)CCC(Cl)CC(Cl)CCC(Cl)CC	6. 7052 (2.71)[salt]	0.029	0.052	Omega Oxidation
C12 H20 CL4 O2	OC(=O)C(Cl)CCC(Cl)CC(Cl)CCC(Cl)CC	5.72	0.019[a] (0.020[b])	0.026[a] (0.020[b])	Beta Oxidation
C11 H19 CL3 O2	OC(=O)CCC(Cl)CC(Cl)CCC(Cl)CC	5.05	0. 593	0.699	Dehalogenation Decarboxylation
C9 H15 CL3 O2	OC(=O)C(Cl)CC(Cl)CCC(Cl)CC	4.07	0.367[a] (0.425[b])	0.342[a] (0.221[b])	Beta Oxidation
C8 H14 CL2 O2	OC(=O)CC(Cl)CCC(Cl)CC	3.39	11.1	8.83	Dehalogenation Decarboxylation
C7 H12 CL2 O2	OC(=O)C(Cl)CCC(Cl)CC	2.90	25.3[a] (3.30[b])	15.6[a] (1.09[b])	Alpha Oxidation
C6 H11 CL1 O2	OC(=O)CCC(Cl)CC	2.23	76.8	46.0	Dehalogenation Decarboxylation
C4 H7 CL1 O2	OC(=O)C(Cl)CC	1.25	42.8[a] (55.2[b])	20.2[a] (9.6[b])	Beta Oxidation
C2 H4 O2	OC(=O)CC	0.087	732	778	Dehalogenation Decarboxylation

ECOSAR Model: Neutral Organic Acid except [a]Neutral Organic (Baseline), [b]Halo Acid

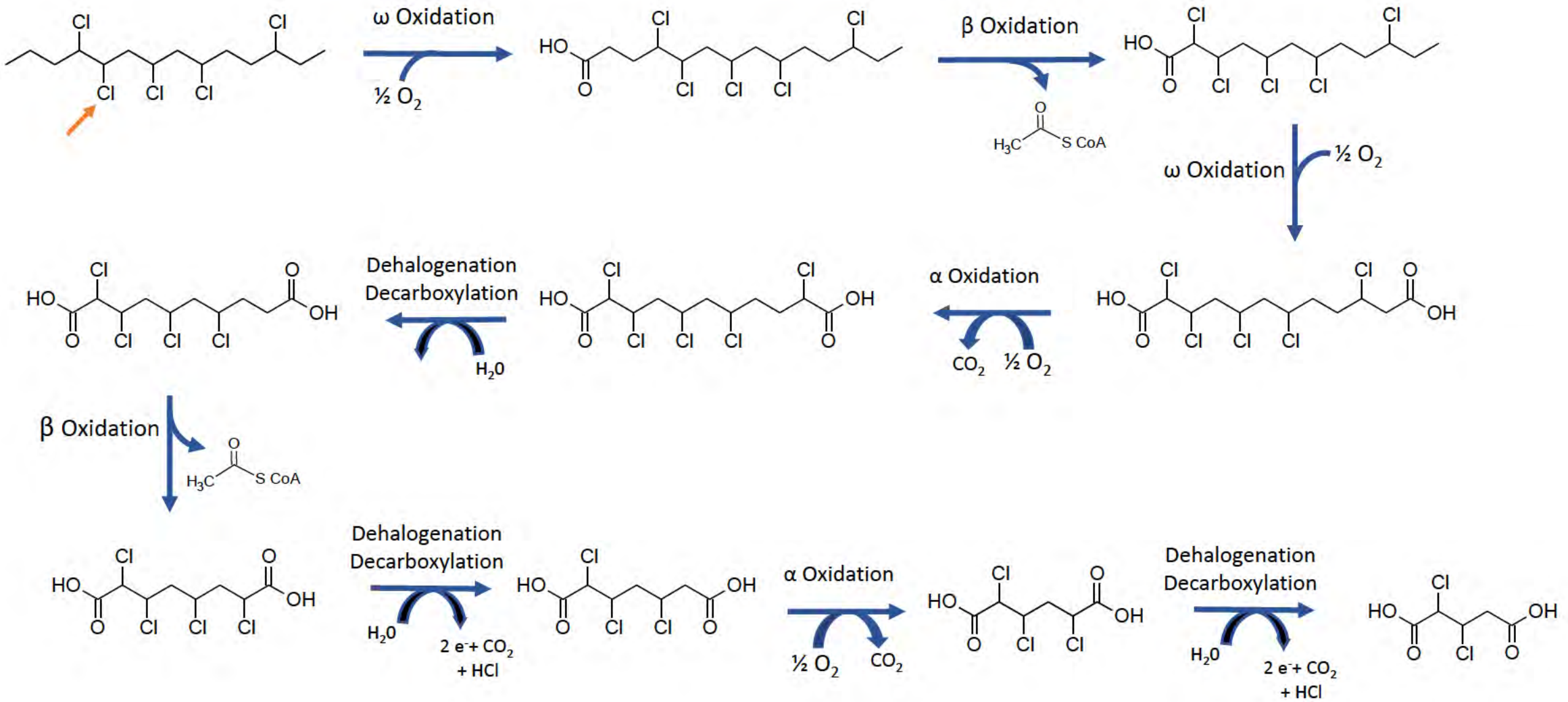
Dechlorination of Vicinal Chlorines

- It is well established that vicinal methyl substitutions stop beta oxidative shortening of alkyl chains from either direction.
- Biodegradation of chlorinated alkanes and their commercial mixtures by Pseudomonas sp. strain 27
  (Heath et al. J Ind Microbiol Biotechnol (2006) 33: 197–207)

Substrate	% Theor Chloride Released	% Parent Recovered	Incubation Time
1-Chlorodecane	90	<1	8
1-Chloro hexadecane	102	1	22
1,10-Dichlorodecane	100	>1	5-17
1,2-Dichlorodecane	54*	2–10%	50
5,6-Dichlorodecane	1	2 flasks 100% 3 flasks 0%	35
1,2,9,10-Tetrachlorodecane	<1	100	35
1,2,5,6,9,10-Hexachlorodecane	<1	>89	35
Cereclor S52	<1	ND	>120
Cereclor S52 (Emulsified)	27	ND	30

*attributed to abiotic lactone formation

Postulated Biodegradation Pathway for 3,6,8,10,11 Pentachloro Tetradecane



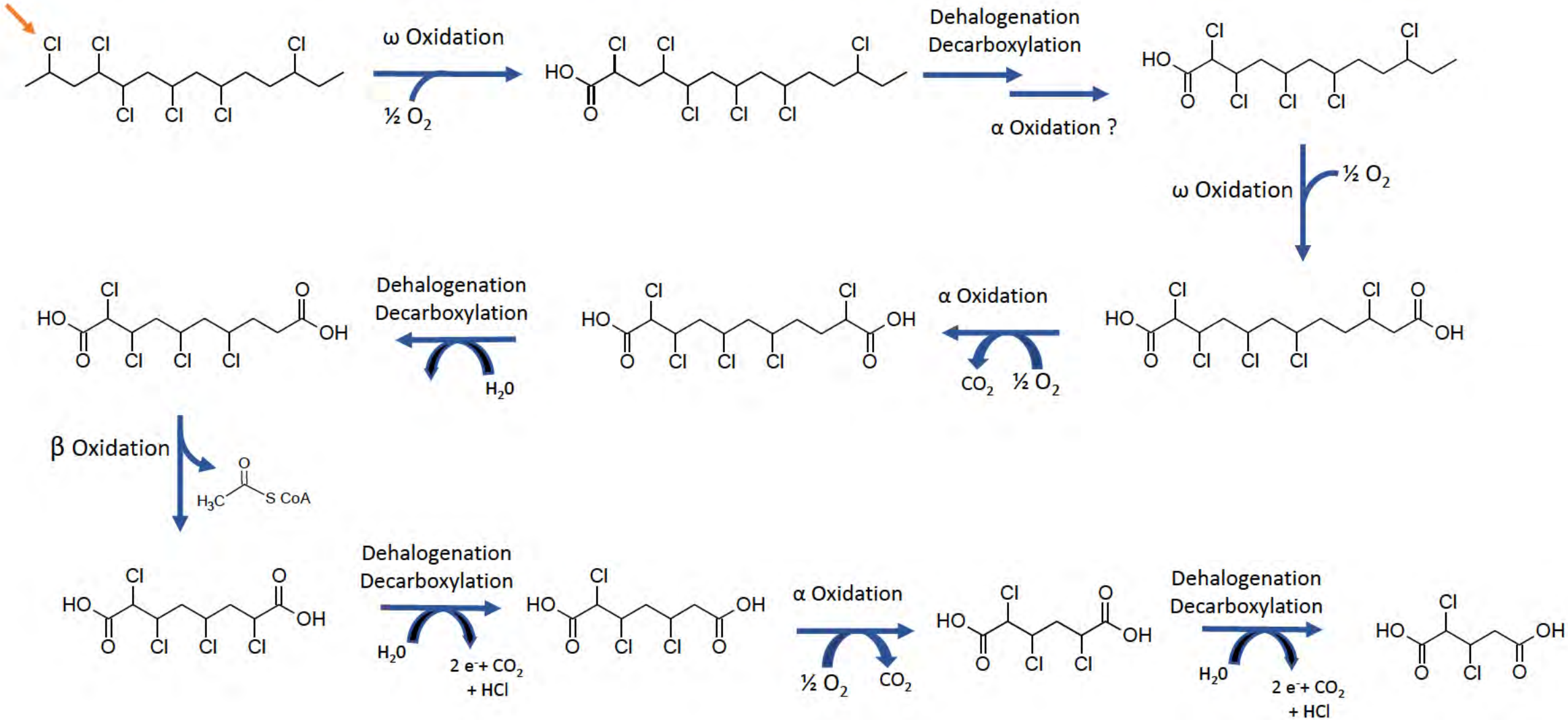
ECOSAR Estimates of Aquatic Toxicity of Metabolites

3,6,8,10,11 Pentachloro Tetradecane

Chemical Formula	SMILES	Log Kow	Fish Chronic Value (mg/L)	Daphnid Chronic Value (mg/L)	Formation
C14 H25 CL5	CCCC(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)CC	8.12	0.00019[a]	0.00046[a]	Parent
C14 H23 CL5 O2	OC(=O)CCC(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)CC	6.88 (3.07)[salt]	.023	.041	Omega Oxidation
C12 H19 CL5 O2	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)CC	5.90	0.014[a] (0.016[b])	0.021[a] (0.016[b])	Beta Oxidation
C12 H17 CL5 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(=O)O	4.08	0.553[a] (0.640[b])	0.516[a] (0.330[b])	Omega Oxidation Other Terminus
C11 H15 CL5 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)C(=O)O	3.59	1.40[a] (1.65[b])	1.16[a] (0.709[b])	Alpha Oxidation
C10 H14 CL4 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)CCC(=O)O	2.91	4.55[a] (5.51[b])	3.21[a] (1.83[b])	Dehalogenation Decarboxylation
C8 H10 CL4 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)C(=O)O	1.93	28.6[a] (35.9[b])	16.0[a] (8.13[b])	Beta Oxidation
C7 H9 CL3 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(=O)O	1.26	90.1[a] (116[b])	42.7[a] (20.2[b])	Dehalogenation Decarboxylation
C6 H7 CL3 O4	OC(=O)C(Cl)C(Cl)CC(Cl)C(=O)O	0.769	223[a] (293[b])	94.1[a] (42.1[b])	Alpha Oxidation
C5 H6 CL2 O4	OC(=O)C(Cl)C(Cl)CC(=O)O	0.098	223[a] (293[b])	94.1[a] (42.1[b])	Dehalogenation Decarboxylation
C4 H4 CL2 O4	OC(=O)C(Cl)C(Cl)C(=O)O	-0.393	1630[a] (2240[b])	520[a] (205[b])	Alpha Oxidation

ECOSAR Model: Neutral Organic Acid except [a]Neutral Organic (Baseline), [b]Halo Acid

Postulated Biodegradation Pathway for 2,4,5,7,9,12 Hexachloro Tetradecane



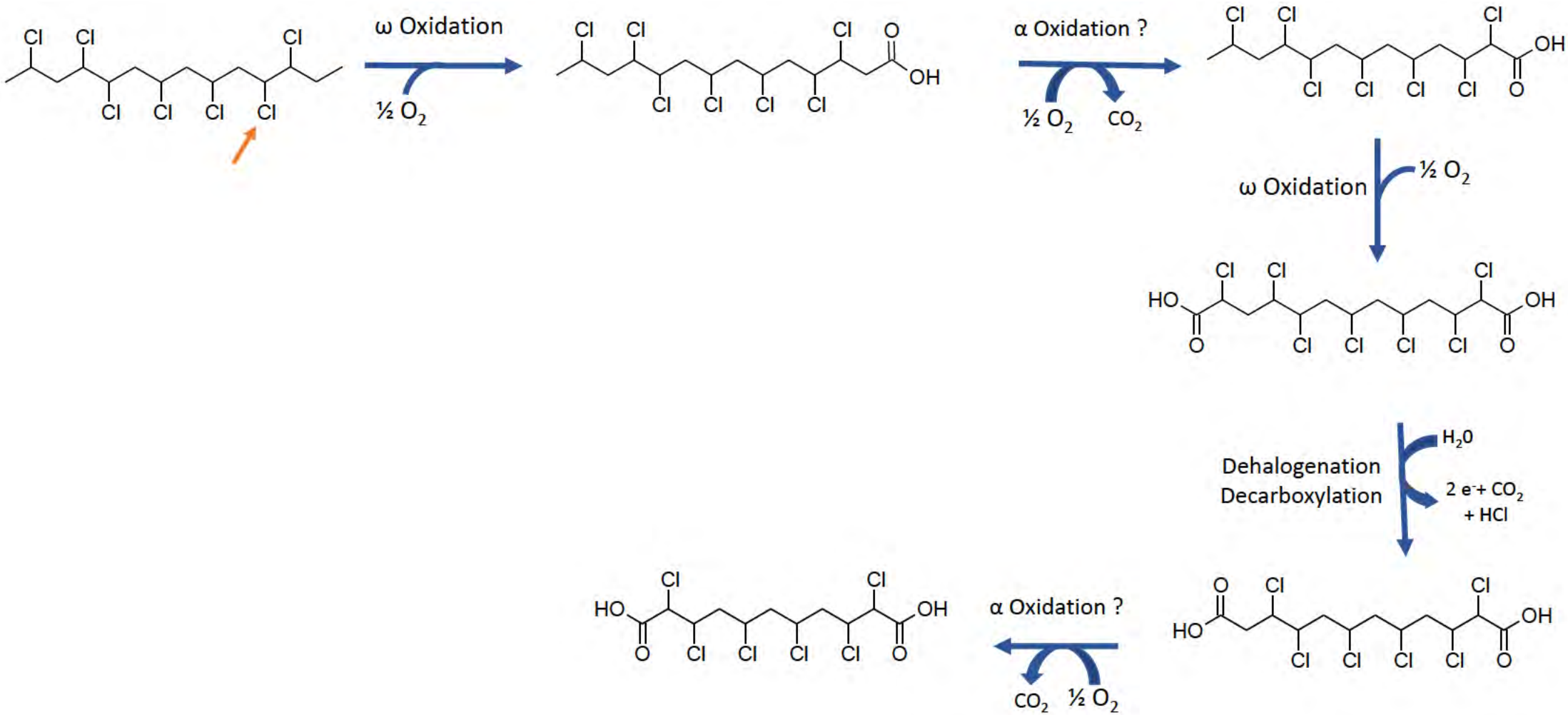
ECOSAR Estimates of Aquatic Toxicity of Metabolites

2,4,5,7,9,12 Hexachloro Tetradecane

Chemical Formula	SMILES	Log Kow	Fish Chronic Value (mg/L)	Daphnid Chronic Value (mg/L)	Formation
C14 H24 CL6	CC(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)CC	8.30	0.00014[a]	0.00036[a]	Parent
C14 H22 CL6 O2	OC(=O)C(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)CC	7.07 (3.25)[salt]	0.0017[a] (0.0018[b])	0.003[a] (0.003[b])	Omega Oxidation
C13 H20 CL5 O2	OC(=O)CC(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)CC	6.39	0.057	0.093	Dehalogenation Decarboxylation
C12 H19 CL5 O2	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)CC	5.90	0.0017[a] (0.016[b])	0.003[a] (0.016[b])	Alpha Oxidation
C12 H17 CL5 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)CC(=O)O	4.08	0.553[a] (0.640[b])	0.516[a] (0.330[b])	Omega Oxidation Other Terminus
C11 H15 CL5 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)CCC(Cl)C(=O)O	3.59	1.40[a] (1.65[b])	1.16[a] (0.709[b])	Alpha Oxidation
C10 H14 CL4 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)CCC(=O)O	2.91	4.55[a] (5.51[b])	3.21[a] (1.83[b])	Dehalogenation Decarboxylation
C8 H10 CL4 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)C(=O)O	1.93	28.6[a] (35.9[b])	16.0[a] (8.13[b])	Beta Oxidation
C7 H9 CL3 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(=O)O	1.26	90.1[a] (116[b])	42.7[a] (20.2[b])	Dehalogenation Decarboxylation
C6 H7 CL3 O4	OC(=O)C(Cl)C(Cl)CC(Cl)C(=O)O	0.769	223[a] (293[b])	94.1[a] (42.1[b])	Alpha Oxidation
C5 H6 CL2 O4	OC(=O)C(Cl)C(Cl)CC(=O)O	0.098	223[a] (293[b])	94.1[a] (42.1[b])	Dehalogenation Decarboxylation
C4 H4 CL2 O4	OC(=O)C(Cl)C(Cl)C(=O)O	-0.393	1630[a] (2240[b])	520[a] (205[b])	Alpha Oxidation

ECOSAR Model: Neutral Organic Acid except [a]Neutral Organic (Baseline), [b]Halo Acid

Postulated Biodegradation Pathway for 2,4,5,7,9,11,12 Heptachloro Tetradecane



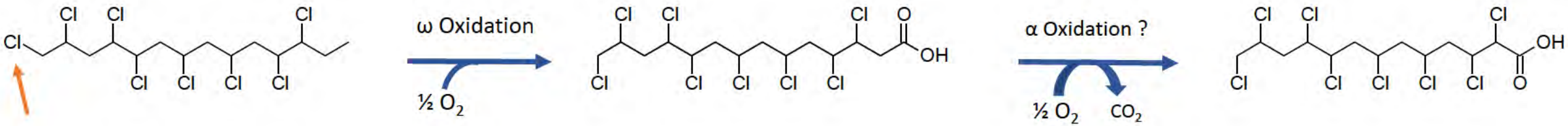
ECOSAR Estimates of Aquatic Toxicity of Metabolites

2,4,5,7,9,11,12 Heptachloro Tetradecane

Chemical Formula	SMILES	Log Kow	Fish Chronic Value (mg/L)	Daphnid Chronic Value (mg/L)	Formation
C14 H23 CL7	CC(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)CC	8.48	0.00011[a]	0.00029[a]	Parent
C14 H21 CL7O2	CC(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)CC(=O)O	7.24 (3.43)[salt]	0.013	0.026	Omega Oxidation
C13 H19 CL7 O2	CC(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(=O)O	6.75	0.014[a] (0.003[b])	0.021[a] (0.005[b])	Alpha Oxidation
C13 H17 CL7 O4	OC(=O)C(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(=O)O	4.93	0.126[a] (0.141[b])	0.144[a] (0.102[b])	Omega Oxidation Other Terminus
C12 H16 CL6 O4	OC(=O)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(=O)O	4.26	0.421[a] (0.485[b])	0.411[a] (0.271[b])	Dehalogenation Decarboxylation
C11 H14 CL6 O4	OC(=O)C(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(=O)O	4.1	0.534[a] (0.618[b])	0.501[a] (0.325[b])	Alpha Oxidation

ECOSAR Model: Neutral Organic Acid except [a]Neutral Organic (Baseline), [b]Halo Acid

Postulated Biodegradation Pathway for 1,2,4,5,7,9,11,12 Octachloro Tetradecane



ECOSAR Estimates of Aquatic Toxicity of Metabolites

<1

Chemical Formula	SMILES	Log Kow	Fish Chronic Value (mg/L)	Daphnid Chronic Value (mg/L)	Formation
C14 H22 CL8	C(Cl)C(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)CC	8.73	0.000071[a]	0.00020[a]	Parent
C14 H21 CL8 O2	C(Cl)C(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)CC(=O)O	7.50 (3.69)[salt]	0.009	0.018	Omega Oxidation
C13 H18 CL8 O2	C(Cl)C(Cl)CC(Cl)C(Cl)CC(Cl)CC(Cl)CC(Cl)C(Cl)C(=O)O	7.06	0.002[a] (0.002[b])	0.004[a] (0.004[b])	Alpha Oxidation

ECOSAR Model: Neutral Organic Acid except [a]Neutral Organic (Baseline), [b]Halo Acid

Implications

Probability of Vicinal Chlorines in Chlorotetradecane

assuming equal reactivity of hydrogens

Number of Chlorines	Percent Chlorine	p of at least one vicinal	p of a terminal vicinal on one end	p of a terminal or α-β vicinal on one end	p of a terminal vicinal on both ends	p of a terminal or α-β vicinal on both ends
1	15.2	0.00	0.00	0.00	0.00	0.00
2	26.5	0.05	0.03	0.05	0.00	0.00
3	35.2	0.15	0.08	0.14	0.00	0.00
4	42.2	0.29	0.17	0.28	0.00	0.01
5	47.8	0.49	0.28	0.46	0.01	0.05
6	52.5	0.66	0.34	0.62	0.03	0.13
7	56.5	0.86	0.41	0.80	0.07	0.27
8	59.8	1.00	0.48	0.97	0.11	0.48
9	62.8	1.00	0.55	1.00	0.18	0.77
10	65.3	1.00	0.62	1.00	0.28	1.00

Not All Sites Are Equal
Relative Reactivity of Alkyl Hydrogens
(Jensen et al (2007)*

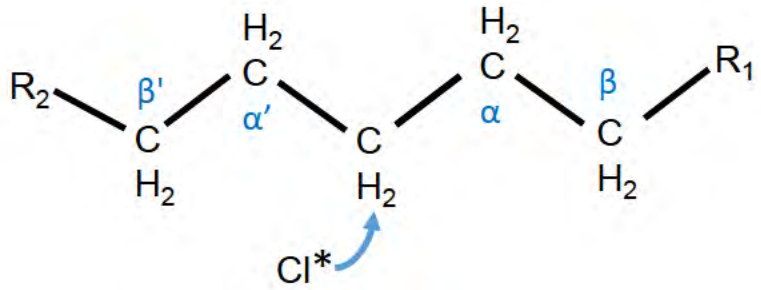


Table 2 Relative reactivity for hydrogen atoms for hydrogen atoms located on secondary carbon atoms

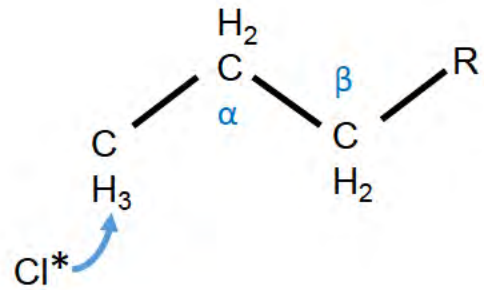
Values shown in bold font are experimentally determined values; values shown in regular font are interpolated values; values shown in parenthesis are from the literature [14]

[a] See naming convention on Fig. 8

Total # chlorine atoms on β- and β'-carbon[a] atom	# chlorine atoms on secondary carbon atom bound to the hydrogen atom of interest	Total # chlorine atoms on α- and α'-carbon[a] atoms				
		0	1	2	3	4
0	0	**1.000** (0.93–1.00)	**0.500**	**0.111**	0.025	0.025
	1	**0.095**	**0.067**	0.030	0.007	0.007
1	0	**0.720**	**0.410**	0.090	0.025	0.025
	1	0.080	0.052	0.028	0.007	0.007
2	0	0.600	0.350	0.081	0.025	0.025
	1	0.070	0.042	0.026	0.007	0.007
3	0	0.540	0.320	0.077	0.025	0.025
	1	0.065	0.037	0.025	0.007	0.007
≥ 4	0	0.540	0.320	0.077	0.025	0.025
	1	0.065	0.037	0.025	0.007	0.007

Table 1 Relative reactivity for hydrogen atoms located on terminal carbon atoms

# chlorine atoms on β-carbon[a] atom	# chlorine atoms on terminal carbon atom bound to the hydrogen atom of interest	# chlorine atoms on α-carbon[a] atom		
		0	1	2
0	0	**0.370** (0.37–0.40)	**0.067**	0.021
	1	**0.074**	0.022	0.011
	2	0.037	0.020	0.011
1	0	**0.310** (0.30)	**0.067**	0.021
	1	0.062	0.022	0.011
	2	0.033	0.020	0.011
2	0	0.279	0.067	0.021
	1	0.062	0.022	0.011
	2	0.033	0.020	0.011



**Characterization of polychlorinated alkane mixtures – a Monte Carlo approach.*

Implications of Reactivity Differences

- In a tetradecane molecule there are four carbons (3,6,9,12) that have the highest probability of being chlorinated, because their hydrogens are twice as reactive as those on any adjacent carbon
- There are also two other carbons (1,14) that are ~10% more likely to chlorinated than any adjacent carbon.
- As these carbons become chlorinated, chlorination of adjacent carbons becomes increasingly more favored.
- Consequently, the incidence of vicinal chlorines is lower than predicted for low chlorination levels and higher than predicted for higher chlorination levels.

How Biodegradation Differs under Anaerobic Conditions

- *Omega* oxidation will not occur but terminal oxidation may occur by fumarate addition resulting in formation of longer chain chlorinated fatty acids
- All beta oxidation reactions should occur but energetic yields will be less, likely resulting in slower microbial growth and slower degradation rates
- 1-Haloalkane halidohydrolase and 2-Halo-alkanoic acid hydrolytic dehalogenase reactions will likely continue.
- Alpha oxidation, and oxygenolytic dechlorination reactions will not occur.
- Some reductive dechlorination of vicinal chlorines may become possible but will occur slowly.
- Anaerobically recalcitrant metabolites will likely be more abundant and larger in molecular weight than those formed under aerobic conditions.
- These metabolites likely will be more polar and less toxic to aquatic organisms than the parent.
- Moreover, because of their increased polarity and solubility, some of these metabolites have the potential to migrate out of anaerobic compartments (sediment) and enter aerobic compartments, where they will be subject to aerobic biodegradation processes.

Summary and Conclusions

- Multiple biodegradation pathway options may exist for a chlorinated paraffin molecule.
- All pathway options involve conversion of the paraffin to a chlorinated fatty acid, shortening of the carbon chain and dechlorination.
- Each homolog will be degraded by a somewhat different pathway but overall these pathways lead to increasingly polar and less toxic metabolites.
- Pathway options decline as chlorination levels and occurrence of vicinal chlorine substitutions increase.
- Existing evidence indicates that vicinal chlorines block chain shortening reactions and are resistant to aerobic dechlorination.

Summary and Conclusions

- Internal vicinal chlorines are likely to result in the formation of recalcitrant mono and/or dioic chlorinated acids.
- Terminal and alpha-beta vicinal chlorines will likely limit terminal oxidation of chlorinated paraffins and when present on both ends may result in persistence of the parent molecules.
- The incidence of vicinal chlorines increases with the level of chlorination and increases more rapidly as more reactive hydrogens have been exchanged.
- While anaerobic biodegradation is possible, it will be more limited than that under aerobic conditions likely resulting in slower and less extensive biodegradation with more terminal metabolites that are higher molecular weight.
- While anaerobic dechlorination of vicinal carbons is a possibility, it is likely very slow and unlikely to result in sufficiently short half-lives to meet regulatory criteria.