Herder Ecotoxicology

Fate and Effects of Chemical Herders

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National Contingency Plan and Herders

- U.S. National Oil and Hazardous Substance Pollution Contingency Plan (NCP) Subpart J Product Schedule
  - Maintained by the USEPA
  - List of control devices and substances that may be used to remove or control oil discharges:
    - Dispersants (Qty: 19), bioremediation agents (e.g. enzyme additives and nutrient additives, Qty: 28), surface collecting agents (Qty: 2), surface washing agents (Qty: 58), and other misc. oil spill control substances (Qty: 17)
    - **Two Herders: Siltech OP-40 & Thickslick 6535**
  - Composition of substances is not shared on website
  - Effectiveness and toxicity testing required for listing product:
    - Data available on NCP website
    - Passing effectiveness test does not indicate product's efficacy during an oil spill
  - Listing on NCP does not indicate that device/substance will be used during a spill

Composition of Oil Spill Response Herders

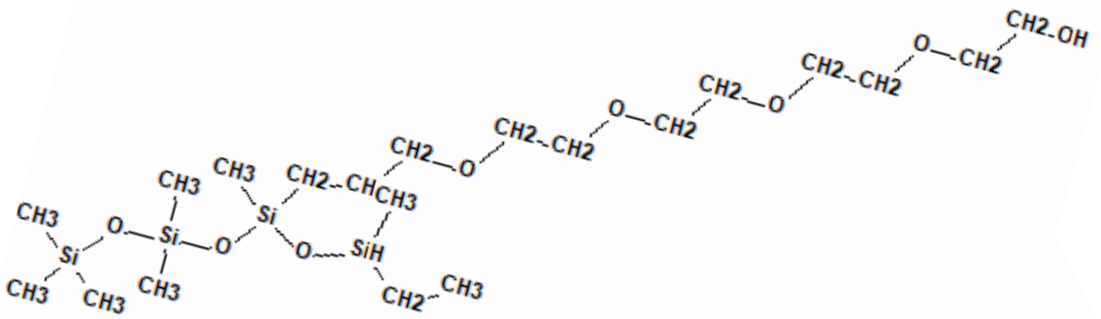
Herder	Ingredient	CAS#	Formula	Mol Wt. (g/mol)
Siltech OP-40	ethoxylated heptamethyltrisiloxane (100%)	67674-67-3	$C_{20}H_{50}O_8Si_4$	540
Thickslick 6535	sorbitan monolaurate (Span 20) (65%)	1338-39-2	$C_{18}H_{34}O_6$	347
	2-ethyl-1-butanol (35%)	97-95-0	$C_6H_{14}O$	102

- Slitech OP-40: higher molecular weight organosilicone surfactant
- Thickslick 6535: nonionic surfactant consists of two components
  - fatty ester surfactant (65%) and aliphatic alcohol solvent (35%)

Structures of Herders

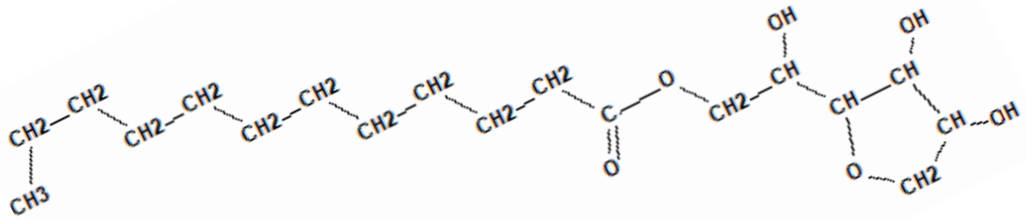
Siltech OP-40 (aka Silsurf A004-UP)

100%: ethoxylated heptamethyltrisiloxane

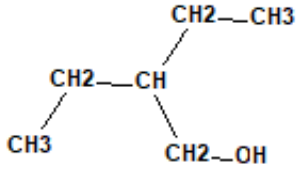


Thickslick 6535 (aka USN)

65% sorbitan monolaurate (SPAN 20)



35% 2-ethy-1-butanol



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Predicted Physical Properties and Environmental Fate of Herder Ingredients using EPISuite

Herder	Ingredient(s)	Log K_{ow}	Water Solubility (mg/L)	Vapor Pressure @25C° (Pa)	Readily Biodegradable?	Primary Biodegradation	Ultimate Biodegradation
Siltech OP-40	Ethoxylated heptamethyltrisiloxane	6.52	0.011-0.036	1.43E-08	No	weeks	months*
Thickslick 6535	Span 20 (Sorbitan Monolaurate)	3.15	< 3 mg/L*	1.25E-09	Yes	days	days-weeks
	2-ethyl-1-butanol	1.75	4000*	204*	Yes	days	weeks

*measured values

- Thickslick components:
  - higher water solubility and lower octanol water partition coefficients predicted
  - higher biodegradation potential predicted
- Thickslick expected to exhibit lower aquatic toxicity than Siltech based on Log Kow
- Surfactant components in both herders predicted to exhibit low volatility

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Aquatic Toxicity of Siltech OP-40 and Thickslick 6535: Literature Review and Model Comparison

Source of Literature:

- Peer-reviewed journal publications
- Technical Reports (ex: SINTEF Ocean, SL Ross, ACC)
- Governmental Reports (ex: NCP, EPA, ECHA dossiers)
- Included reliability assessment

Model Comparison:

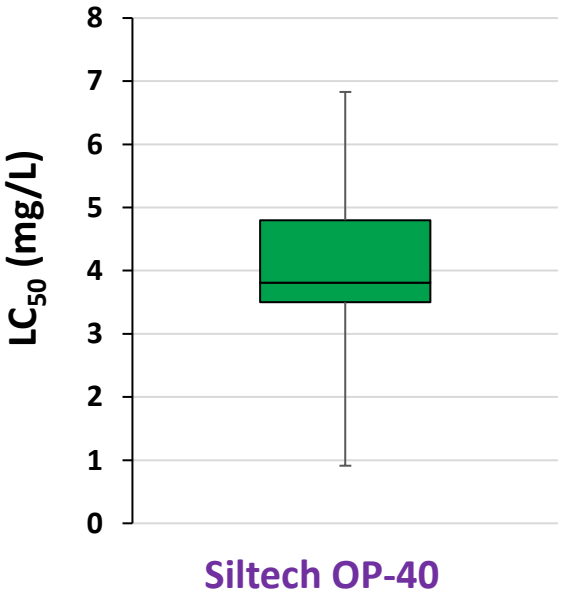
- Estimate toxicity for untested species using **measured data** and USEPA's interspecies correlation extrapolation web-based tool
- Calculate acute hazard concentrations (HCs) intended to provide 95% protection
- Compare HC5s calculated from empirical data, ICS estimates and chemical structure using gou[target site model (gTSM)

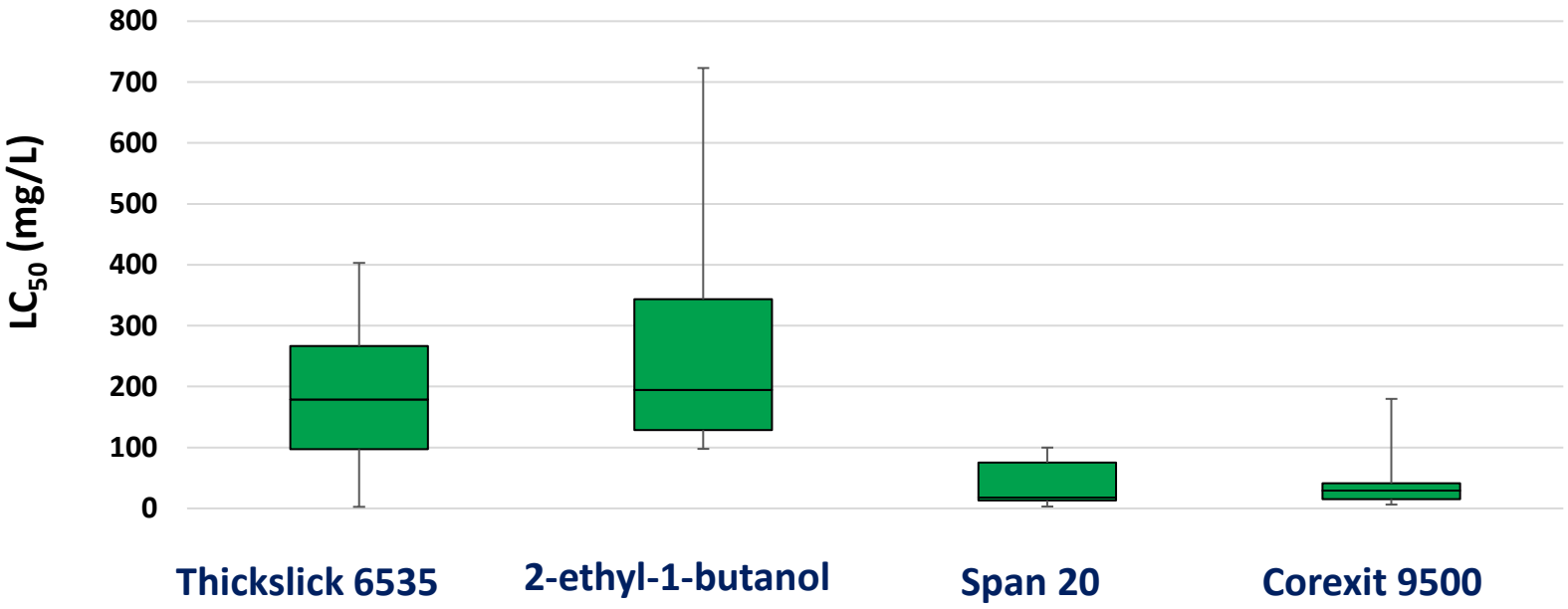
Aquatic Toxicity of Thickslick 6535: Summary of Empirical Data

Organism	Common Name (*Latin Name*)	Effect Endpoint	Test Duration	L/EC_{50} (mg/L)	Reference
fish	Inland silverside (*Menidia beryllina*)	mortality	96-hr	138	SL Ross & DCE, 2015
fish	Atlantic cod larvae (*Gadus morhua*)	development	24-hr	945	Huntsman Lab, 2020
fish	Atlantic cod (*Gadus morhua*)	hatching	24-hr	403	Huntsman Lab, 2020
shrimp	Mysid (*Americamysis bahia*)	mortality	48-hr	286	SL Ross & DCE, 2015
crustacean	American lobster (*Homarus americanus*)	immobilization	48-hr	195	Huntsman Lab, 2020
crustacean	American lobster (*Homarus americanus*)	mortality	24-hr	198	Huntsman Lab, 2020
crustacean	American lobster (*Homarus americanus*)	mortality	48-hr	208	Huntsman Lab, 2020
crustacean	American lobster (*Homarus americanus*)	molting	24-hr	104	Huntsman Lab, 2020
copepod	Calanoid copepod (*Acartia tonsa*)	immobilization	48-hr	368	SINTEF, 2016
copepod	Calanoid copepod (*Acartia tonsa*)	immobilization	48-hr	162	SINTEF, 2016
algae	*Skeletonema pseudocostatum*	growth rate	72-hr	2.5	SINTEF, 2016
algae	*Skeletonema pseudocostatum*	growth rate	72-hr	6.7	SINTEF, 2016
algae	*Skeletonema pseudocostatum*	growth rate	72-hr	4.3	SINTEF, 2016

Summary of Aquatic Hazard Data from Literature:

Range of measured LC_{50} results from various aquatic species





- Aquatic hazard of **Thickslick 6535** lower than **Siltech OP-40**
- Toxicity of **Thickslick 6535** dictated by surfactant, not solvent component
- Trends in toxicity consistent with estimated Log K_{ow}
- **Corexit 9500** lowest LC_{50} reported is 6.3 mg/L (early life stage Calanoid copepod) (Aurand et al., 2009)

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ThickSlick 6535 is less toxic than Siltech OP-40 and Corexit 9500

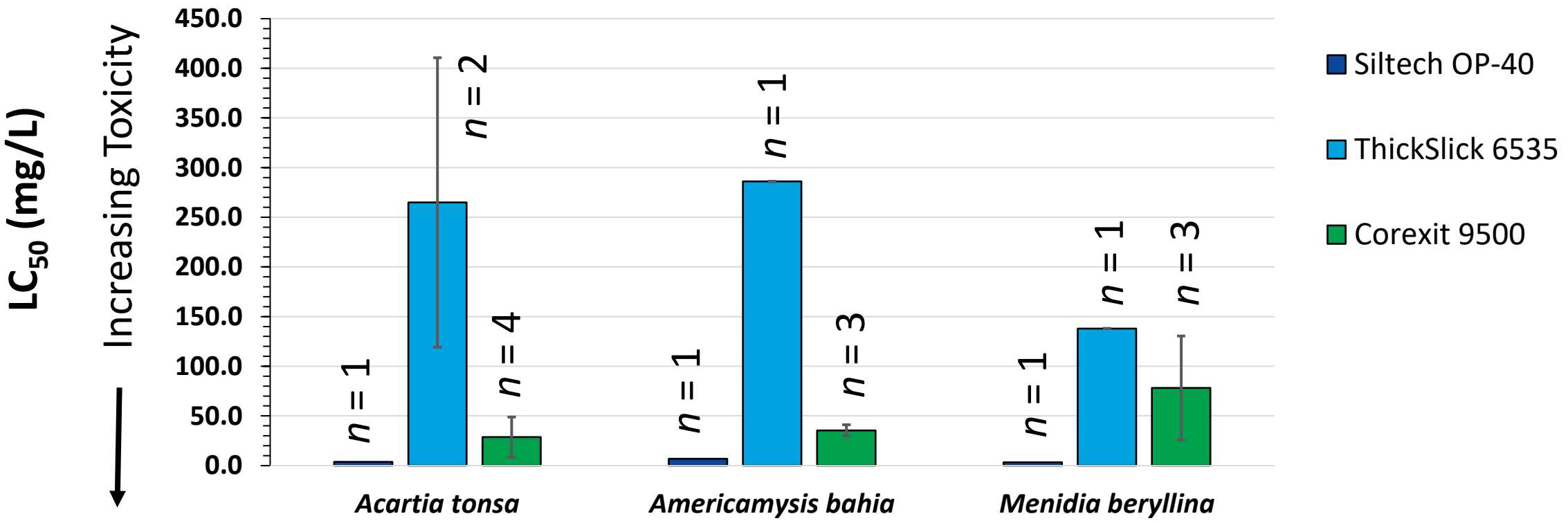

Figure 1. Mean LC_{50} (mg/L) values for *Acartia tonsa*, *Americamysis bahia*, and *Menidia beryllina* in response to Siltech OP-40, ThickSlick 6535, and Corexit 9500, including standard deviations and the number of tests (*n)*. Tests within the same species were conducted following similar EPA or ISO guidelines.

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Summary

- Key Messages
  - Herder application results in very low and short duration water column exposures
  - Herders not persistent and are subject to degradation
  - Considerable aquatic toxicity data are available that provide technical basis to establish water quality objectives to protect aquatic life
  - Predicted herder concentrations expected to pose *de-minimis* risk to aquatic resources

- Research Priorities
  - Develop analytical method w/ppb level sensitivity for Span 20 & Siltech OP-40 surfactants
  - Field monitoring of herder concentrations to calibrate/validate model predictions
  - Exposure and effects of burned residue (esp. to benthos) following ISB field application
  - Comparative risk assessment of oil spill response scenarios with and w/o herder use

Questions

Cooper et al. (2017)

Backup

Aquatic Hazard Assessment

- Compile aquatic toxicity data for 2EB, Span20, ThickSlick and Slitech into excel database
- Include reliability assessment … see below format:

Test Species	Taxonmonic Classification (Order)	Common name	Habitat[a]	Life Stage[b]	Temp. (°C)	Exposure Duration (d)	Exposure Type[c]	Chemical Measurement[d]	Acute Effect	Acute Value LC50/EC50 (mg/L)	95% Confindence Interval (mg/L)	Chronic Endpoint	Chronic Value (mg/L)	Reliability Ranking	Notes	Reference[e]
Calanus hyperboreus	Calanoida	copepod	marine	NR	2	2	S	N	Survival	12	NR			2	field collected test organisms	Fritt-Rasmussen et al. 2021
Calanus hyperboreus	Calanoida	copepod	marine	NR	5	4	S	N	Fecal Production Rate		NR	NOEC	0.3	2	field collected test organisms	Fritt-Rasmussen et al. 2021
Calanus hyperboreus	Calanoida	copepod	marine	NR	2	25	S	N	Survival		NR	LC50	27.4	3	field collected test organisms	Fritt-Rasmussen et al. 2021
Menidia beryllina	Atheriniformes	inland silverside	marine	NR	24	4	S	N	Survival	138	121-157			2		Buist et al 2018
Americamysis bahia	Mysida	mysid shrimp	marine	NR	24	2	S	N	Survival	286	226-363			2		Buist et al 2018
Menidia beryllina	Atheriniformes	inland silverside	marine	9–14 d	25	4	S	N	Survival	53.7	30.3-77.1			2		Alloy et al. 2022
Pimephales promelas	Cypriniformes	fathead minnow	freshwate	9–14 d	25	4	S	N	Survival	126.4	35.6-217.2			2		Alloy et al. 2022

- Use measured data to estimate toxicity for untested species using USEPA 's interspecies correlation extrapolation web-based tool
- Use empirical data alone and in combination with ICE predictions to construct species sensitivity distributions
- Use *SSD tools* R package to estimate acute hazard concentrations (HC_5) intended to provide 95% protection
- Estimate HC_5 directly from structure using group target site model (gTSM) developed by Boone et al. (2023)
- Compare HC_5 determined for ThickSlick with HC_5 computed from components assuming additivity

$$HC_{5,\text{ThickSlick predicted}} = 1/\ [0.35/HC_{5,2EB} + 0.65/HC_{5,span}\ ]$$

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Acute Hazard Concentrations (HC5) Intended to Protect Aquatic Life

Substance	Basis for SSD Derivation	Number of Species	Acute HC_5 (mg/L)
2-ethyl butanol	Empirical toxicity data	16	48.3 [28.0-93.3]*
	Empirical data + ICE predictions	21	18.9 [8.3-47.5]
	gTSM prediction	38	13.3
Span 20	Empirical toxicity data	7	5.2 [1.0-38.0]
	Empirical data + ICE predictions	16	5.6 [2.5-16.5]
	gTSM prediction	38	2.5
ThickSlick6535	Empirical toxicity data	17	3.0 [1.3-8.5]
	Empirical data + ICE predictions	31	3.1 [2.1-7.8]
	Empirical calculated from components	16/7	7.5 [1.5-47.9]
	Empirical + ICE predictions calculated from components	21/31	7.4 [3.3-21.4]
	gTSM prediction calculated from components	38	3.5
Slitech OP-40	Empirical toxicity data prediction	16	0.92 [0.68-1.27]
	Empirical data + ICE predictions	30	0.45 [0.31-0.73]
	gTSM prediction	38	0.62

gTSM = group target site model (Boone et al. 2023); *values in brackets denote 95% confidence intervals

- HC_5 predicted from chemical structure in agreement with value derived using empirical herder toxicity data
- HC_5 for Thickslick driven by Span 20 toxicity; HC_5 derived from components assuming additivity in agreement
- Predicted water concentrations & exposure duration orders of magnitude lower than HC_5 (see earlier slide)
- Conclude BOTH herders pose *de-minimis* risk to aquatic resources

Global Hazard Classification

Substance	Siltech OP-40		Sorbitan Monolaurate		2-Ethyl 1-Butanol	
CAS#	CAS# 67674		1338-39-2		97-95-0	
	Category/Code	Statement	Category/Code	Statement	Category/Code	Statement
Relevant Hazards to Wildlife	Eye Dam. 1	H318				
	Eye Irrit. 2	H319	Eye Irrit. 2	H319		
	Acute Tox. 3, 4	H331, H332			Acute Tox. 4	H302, H312
	Aquatic Chronic 2,3	H411, H412				
			Skin Irrit. 2	H315		
					Flam. Liq. 3	H226

H226 = Flammable liquid and vapour
H302 = Harmful if swallowed or in contact with skin
H312 = Harmful in contact with skin
H315 = Causes skin irritation
H318 = Causes serious eye damage
H319 = Causes serious eye irritation

H331 = Toxic if inhaled
H332 = Harmful if inhaled
H411 = Toxic to aquatic life with long lasting effects
H412 = Harmful to aquatic life with long lasting effects

- Limited hazards for wildlife identified
- Fewer hazards for ThickSlick consistent with use of Span 20 as feed additive

Future Work / Next Steps:

Develop Water Quality Objectives to Support Herder Risk Assessment

- Define species sensitivity distributions (SSDs) for herders and herder components using two independent approaches:
  - USEPA's Interspecies Correlation Extrapolation Model (ICE)
    - Uses limited measured toxicity data to estimate toxicity for untested species
  - Target Lipid Model (TLM)\
    - Uses estimated partitioning properties to predict toxicity for multiple species
- Use SSDs to derive a 5th percentile hazard concentration (HC_5)
  - Provides concentration that is intended to provide 95% protection level under constant exposure conditions, i.e. water quality objective
- Evaluate results:
  - Assess consistency in HC_5 estimates using ICE and TLM approaches
  - Compare HC5s to empirical hazard data to confirm protective
- Publish in Peer-Reviewed Journal!

Aquatic Toxicity of 2-ethyl-1-butanol: Summary of Empirical Data and Read Across

Substance	Organism	Common Name (*Latin Name*)	Effect Endpoint	Test Duration	L/EC_{50} (mg/L)	Reference
2-ethyl-1-butanol	algae	*Skeletonema pseudocostatum*	growth rate	72-hr	321	SINTEF, 2016
1-hexanol	fish	Common Bleak (*Alburnus alburnus*)	mortality	96-hr	120	Bengtsson et al., 1984
4-methyl-2-pentanol	fish	Goldfish *(Carassius auratus)*	mortality	24-hr	360	Bridie et al., 1979
1-hexanol	fish	Zebrafish *(Danio rerio)*	mortality	96-hr	144	Wellens, 1982
2-hexanol	fish	Zebrafish *(Danio rerio)*	mortality	96-hr	340	Wellens, 1982
1-hexanol	fish	Ide *(Leuciscus idus melanotus)*	mortality	24-hr	131	Juhnke & Ludemann, 1978
2-hexanol	fish	Ide *(Leuciscus idus melanotus)*	mortality	24-hr	287	Juhnke & Ludemann, 1978
3-hexanol	fish	Ide *(Leuciscus idus melanotus)*	mortality	24-hr	353	Juhnke & Ludemann, 1978
1-hexanol	fish	Fathead minnow *(Pimephales promelas)*	mortality	96-hr	98	Brooke et al., 1984
1-hexanol	fish	Fathead minnow *(Pimephales promelas)*	mortality	96-hr	122	Broderius & Kahl, 1985
3-methyl-3-pentanol	fish	Fathead minnow *(Pimephales promelas)*	mortality	96-hr	672	Geiger et al., 1988
1-hexanol	fish	Japanese rice fish *(Oryzias latipes)*	mortality	24-hr	166	Ikemoto et al., 1992
1-hexanol	copepod	Water Flea *(Daphnia magna)*	mortality	96-hr	151	Ikemoto et al., 1992
1-hexanol	algae	*Chlorella vulgaris*	growth rate	120-hr	723	Ikemoto et al., 1992
1-hexanol	algae	*Scenedesmus vacuolatus*	growth rate	24-hr	224	Fu et al., 2015
1-hexanol	algae	*Pseudokirchneriella subcapitata*	growth rate	72-hr	115	Fu et al., 2015

Aquatic Toxicity of Span 20 (Sorbitan Monolaurate): Summary of Empirical Data

Organism	Common Name (*Latin Name*)	Effect Endpoint	Test Duration	L/EC_{50} (mg/L)	Reference
fish	Zebrafish (*Danio rerio)*	mortality	96-hr	≥ 13.2	ECHA dossier
copepod	Calanoid copepod (*Acartia tonsa*)	immobilization	48-hr	≥ 100	ECHA dossier
algae	*Skeletonema costatum*	growth rate	72-hr	17.9	ECHA dossier
algae	*Skeletonema costatum*	growth rate	72-hr	3.1	SINTEF, 2016

Aquatic Toxicity of Siltech OP-40: Summary of Empirical Data

Organism	Common Name (*Latin Name*)	Effect Endpoint	Test Duration	L/EC_{50} (mg/L)	Reference
fish	Inland silverside (*Menidia beryllin*)	mortality	96-hr	3.3	SL Ross & DCE, 2015
fish	Atlantic cod larvae (Gadus morhua)	development	24-hr	4.8	Huntsman Lab, 2020
fish	Atlantic cod (*Gadus morhua*)	hatching	24-hr	6.8	Huntsman Lab, 2020
crustacean	American lobster (*Homarus americanus*)	immobilization	48-hr	3.5	Huntsman Lab, 2020
crustacean	American lobster (*Homarus americanus*)	mortality	48-hr	3.6	Huntsman Lab, 2020
crustacean	American lobster (*Homarus americanus*)	molting	24-hr	>3.2 (<6.0)	Huntsman Lab, 2020
shrimp	Brine shrimp (*Artemia*)	mortality	48-hr	0.91	Huntsman Lab, 2020
shrimp	Mysid (*Americamysis bahia*)	mortality	48-hr	6.8	SL Ross & DCE, 2015
copepod	Calanoid copepod (*Acartia tonsa*)	immobilization	48-hr	3.8	SINTEF, 2016
algae	*Skeletonema pseudocostatum*	growth rate	72-hr	4.3	SINTEF, 2016