Microbial Control

Putting you in control.

Sustainable Alternatives in Oil and Gas Water Treatment

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Introduction

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- Defining
  - Green Chemistry
  - Sustainable Chemistry
- Chemical Selection
- Differentiating Criteria for Gas and Oil Chemicals
- Hazard, Exposure and Risk
- Product Stewardship Practices
- Screening Evaluation Tools: Examples

Chemicals Used in Gas and Oil Production

- Friction reducer
- Gelling agent
- Breaker/aide
- Stabilizer
- Biocide
- Crosslinker
- Non-emulsyfier
- Corrosion inhibitor
- pH adjusting agent
- Surfactant

Hydraulic Fracturing Fluids

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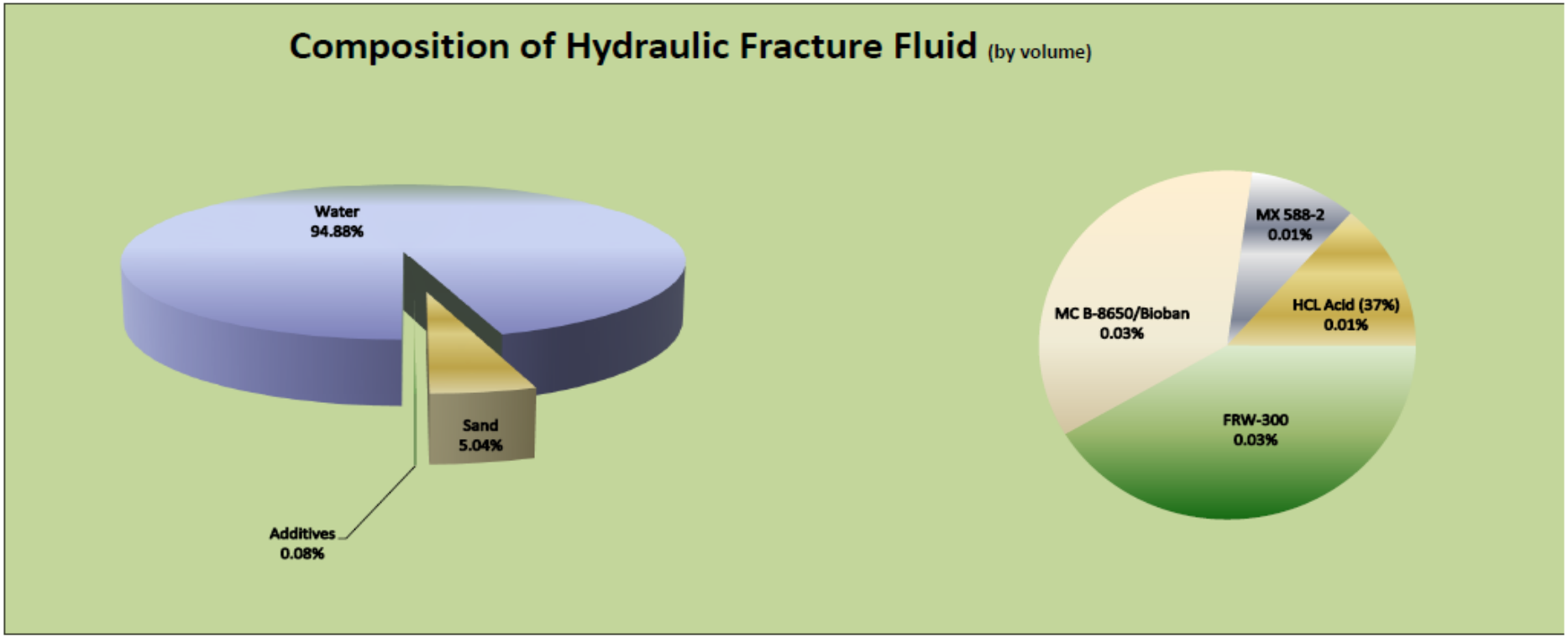
- Water + Sand + Chemicals
- Composition varies based on conditions



“Greener Alternatives”

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- Green Chemistry
- Sustainable Chemistry

- While both reflect **a journey to make something more desirable**, from an environmental and safety perspective, there are **important differences** between the two terms

Twelve Principles of Green Chemistry

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- Prevention
- Atom Economy
- Less Hazardous Chemical Syntheses
- Designing Safer Chemicals
- Safer Solvents and Auxiliaries
- Design for Energy Efficiency
- Use of Renewable Feedstocks
- Reduce Derivatives
- Catalysis
- Design for Degradation
- Real Time Analysis for Pollution Prevention
- Inherently Safer Chemistry for Accident Prevention

Sustainable Chemistry

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- Sustainable chemistry **builds upon the principles of green chemistry by integrating economic viability and social benefits across the lifecycle for a given application**.
- More sustainable products and processes must not only be more efficient in their use of materials and resources, but **must also be profitable, scaleable and useful to society**.
- This must be accomplished across the lifecycle of the product and in comparison to alternatives which could provide the same application or service.

Science Based Risk (HxE=R)

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- Conduct Hazard Assessments
  - Understand potential for harm
- Exposure Assessment
  - Use scenarios
  - Dosage
- Risk Mitigation
  - Upper label limits minimize exposure
  - Lower label limits limit ineffective usage

Environment, Health and Safety Attributes

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- Product Stewardship Principles
- Right chemical for the right use
- Ensure that products are used in a responsible/sustainable manner
- Socially responsible and Environmental Awareness
  - Disclosure of chemicals
  - Protection of water quality
  - Best practices and continuous improvement

Biocides

- Biocides are a common and necessary component in fracking fluids
- They are chemical agents used to control harmful microorganisms
  - Flow assurance
  - Protect process and product
  - Asset integrity
- Also known as antimicrobials, pesticides, algaecides, or bactericides

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Physical Property Testing

- Many tests are performed to understand the physical properties of biocides
- Stability, melting/boiling points, solubility, pH, chemical compatibility, partitioning behavior, etc.
- Data used in risk evaluations

Biocides Selection

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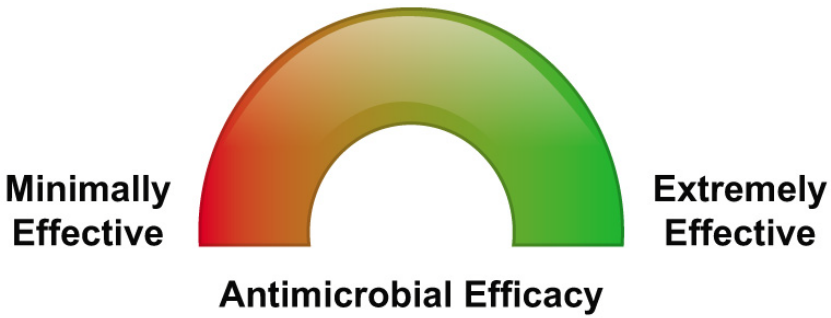

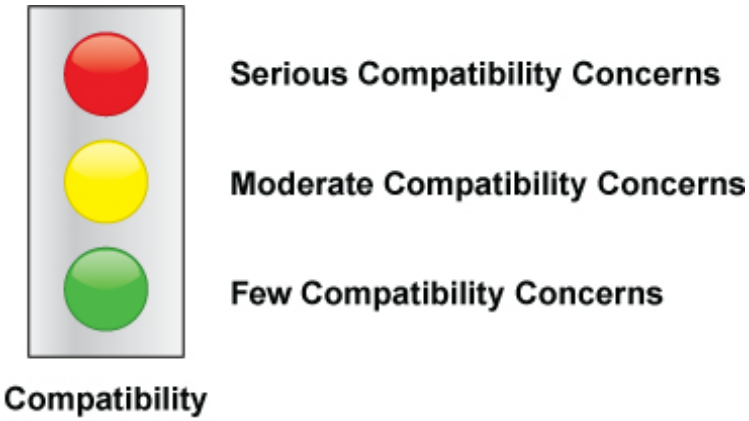

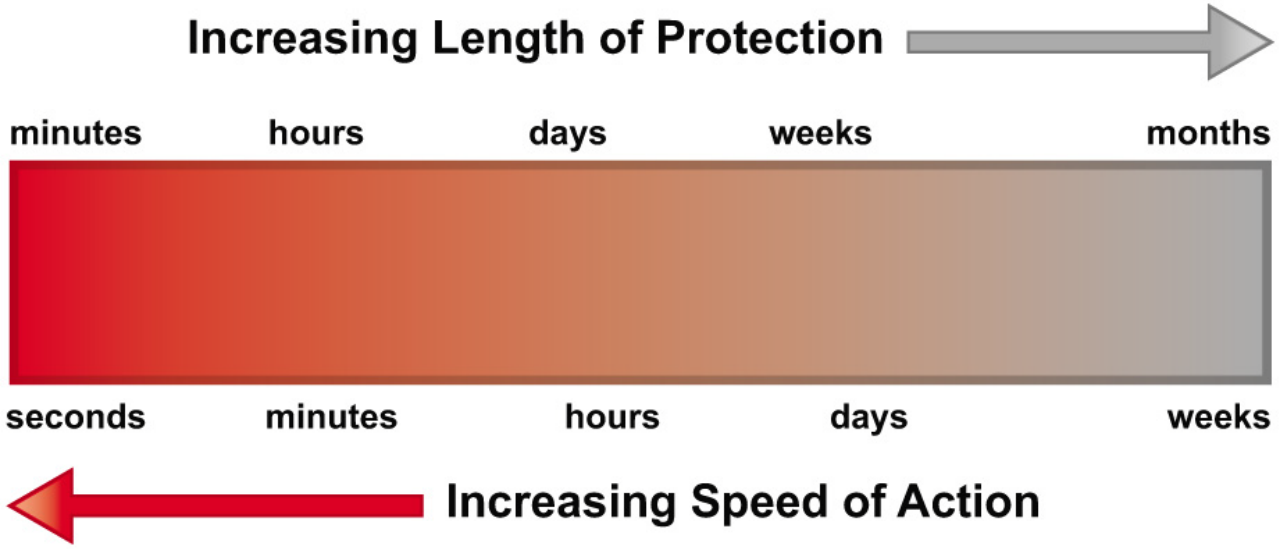

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Data Requirements to Support Registration

- Biocides are thoroughly tested to meet regulatory requirements
- EPA requires over 100 different studies for registration
- Testing includes:
  - Physical properties
  - Environmental fate
  - Ecotoxicology
  - Mammalian toxicology

Chemical Selection: Criteria for Fracking

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- Persistence
  - Readily biodegradable
- Bioaccumulation
  - Octanol / Water Partition Coefficient
- Toxicity
  - Aquatic
  - Avian
- Use Rate/Pattern
  - Efficacy / Efficiency

Ecotoxicological Testing

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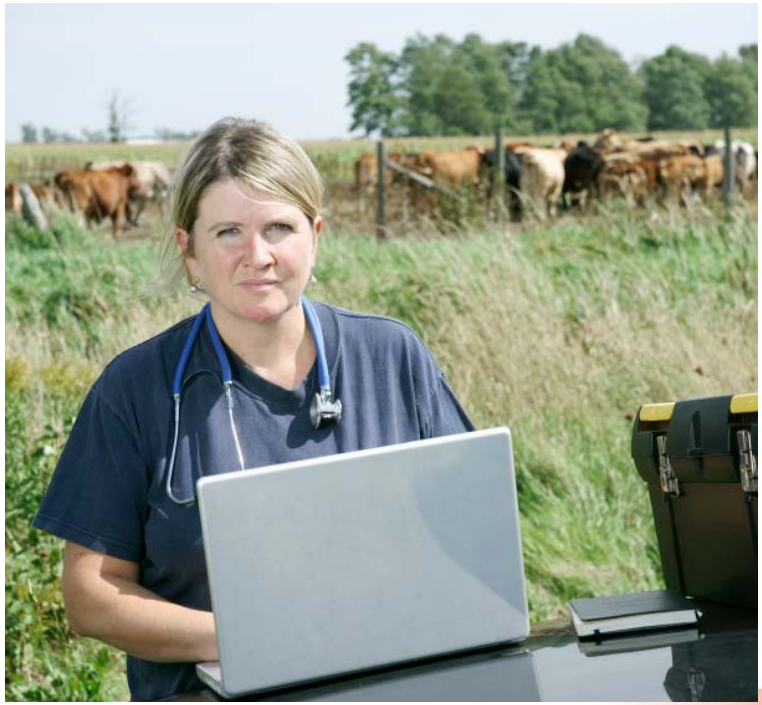
- Acute hazard testing determines a chemical's effect on a variety of organisms
- Information gathered on a variety of terrestrial, aquatic, and marine organisms
- Data used in risk evaluations

Mammalian Toxicology Testing

- Provides information on how chemicals affect mammals
- Both acute (short term) and chronic (long term) data gathered to meet regulatory requirements
- Data used in risk calculations



Environmental Fate Testing

The *environmental fate* of a chemical describes the processes by which it moves through and is transformed in the environment.

Studies performed under controlled, standard conditions

- Partitioning behavior
- Chemical degradation
- Biodegradation
- Photodegradation
- Transport phenomena

Risk Analysis

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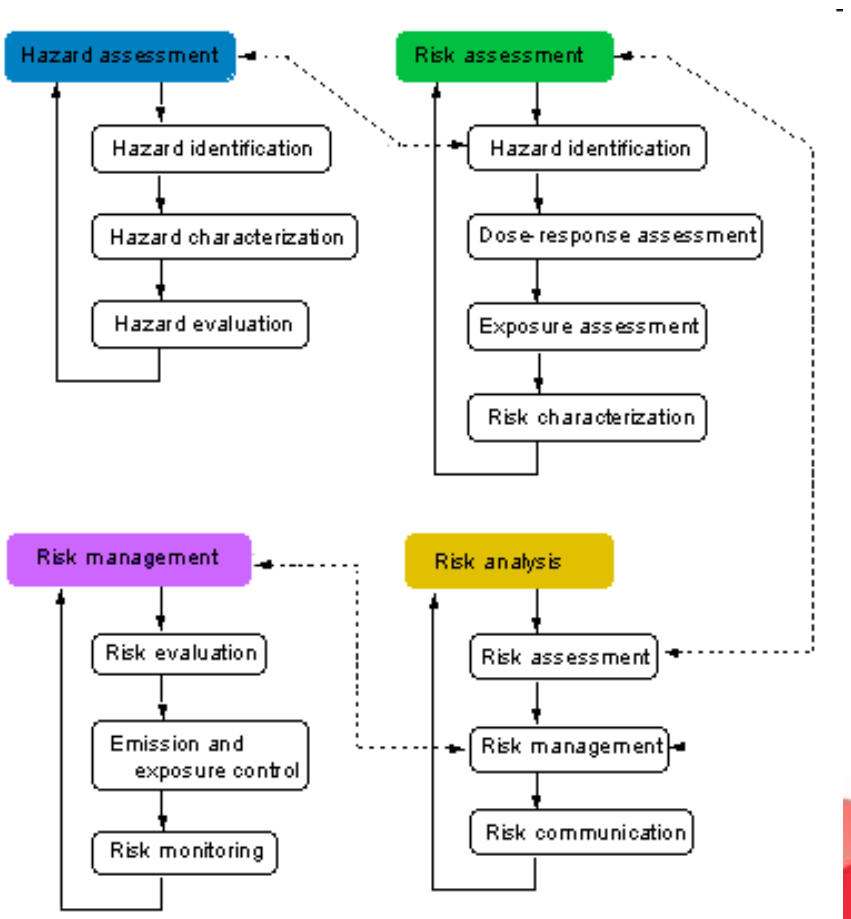
- Attempts to model real-world conditions
- Evaluates the risk of using a specific chemical in a specific application
- Uses physical property, environmental fate, and toxicology data from chemical
- Applies safety factor to worst-case scenarios
- When properly used, biocides can effectively control microbial contamination without adversely affecting the environment



Risk Assessment Methods – North Sea

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- Chemical Hazard and Risk Management Model (CHARM)
  - Predicted environmental concentration (PEC)
    - application-specific
    - “realistic worst case”
  - Hazard quotient (HQ)
    - ratio of PEC to predicted no-effect concentration

Hazard Quotient Bands

HQ range	Band Color
0-1	Gold
1-30	Silver
30-100	White
100-300	Blue
300-1000	Orange
>=1000	Purple

increasing hazard

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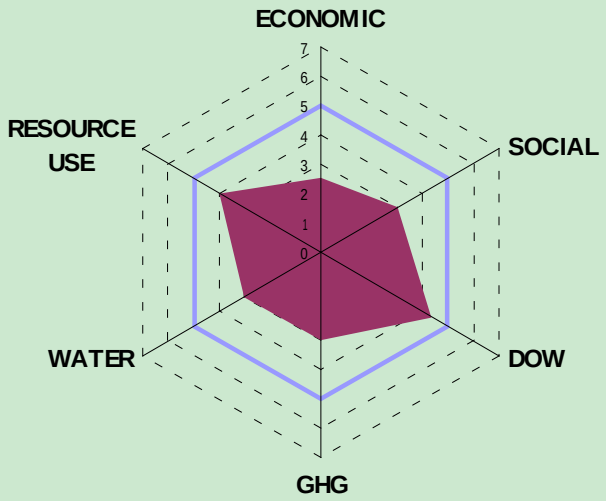
Sustainability Footprint Tool

A qualitative tool developed for Sustainable Chemistry/Life Cycle Analysis experts with grounding through a common review system.



Addressing 6 dimensions of sustainability:

- Economic
- Social
- Life Cycle – Environment
- Greenhouse Gas Emissions
- Water
- Resource Use
  - Energy, Raw Material

A Sustainable Technology Chemical Screening Tool

- Initial Screening
  - Evaluates up to forty four Data points
  - Hazard Ranking = Higher Score from Environmental and Human Health Hazards
  - Exposure endpoints, Efficacy and Dose Levels
    - Use rates + PBT rating + Use patterns
- Leading to an Industry Accepted Risk based Screening Tool
  - That can differentiate sustainable chemistry endpoints of Hydraulic Fracturing chemicals

Sustainability Chemistry Screening Tool

Hazard & Exposure Criteria for Screening Tool

HAZARD

Environment and Human Health Classifications based upon GHS

Environmental:

From GHS classification guidance document:

Table 4.1.2: Classification scheme for substances hazardous to the aquatic environment

Classification categories			
Acute hazard (*Note 1*)	Long-term hazard (*Note 2*)		
	Adequate chronic toxicity data available		Adequate chronic toxicity data not available (*Note 1*)
	Non-rapidly degradable substances (*Note 3*)	Rapidly degradable substances (*Note 3*)	
Category: Acute 1 $L(E)C_{50} \leq 1.00$	**Category: Chronic 1** NOEC or $EC_x \leq 0.1$	**Category: Chronic 1** NOEC or $EC_x \leq 0.01$	**Category: Chronic 1** $L(E)C_{50} \leq 1.00$ and lack of rapid degradability and/or BCF $\geq$ 500 or, if absent log $K_{ow} \geq 4$
Category: Acute 2 $1.00 < L(E)C_{50} \leq 10.0$	**Category: Chronic 2** $0.1 <$ NOEC or $EC_x \leq 1$	**Category: Chronic 2** $0.01 <$ NOEC or $EC_x \leq 0.1$	**Category: Chronic 2** $1.00 < L(E)C_{50} \leq 10.0$ and lack of rapid degradability and/or BCF $\geq$ 500 or, if absent log $K_{ow} \geq 4$
Category: Acute 3 $10.0 < L(E)C_{50} \leq 100$		**Category: Chronic 3** $0.1 <$ NOEC or $EC_x \leq 1$	**Category: Chronic 3** $10.0 < L(E)C_{50} \leq 100$ and lack of rapid degradability and/or BCF $\geq$ 500 or, if absent log $K_{ow} \geq 4$
	Category: Chronic 4 (*Note 4*) Example: (*Note 5*) No acute toxicity and lack of rapid degradability and BCF $\geq$ 500 or, if absent log Kow $\geq$ 4, unless NOEC$_x$ > 1 mg/l		

Human Health:

As above, based upon GHS

EXPOSURE

Use Elements - based upon IUR

intermediate — consumed during industrial processing
industrial (not intermediate) - used in an industrial setting
commercial — occupational use in nonindustrial setting
consumer — general population residential use

Persistence:

Volatile substance (VP > 1000 Pa): Not Persistent if air half life < 2 days
Nonvolatile (VP < 1000 Pa): Not Persistent if:
a) ready biodegradability (OECD 301)
b) inherent biodegradability (OECD 301, 302, 306)
c) read across from measured data on a related substance.
d) equivalent degree of degradation (i.e. >20% in 28 days) via an abiotic degradation mechanism such as photolysis (OECD 316) or hydrolysis (OECD 111)
OR, a substance is Not Persistent if:
e) evaluation of simulation data from transformation in soil, marine water/sediment, brackish water/sediment, surface water/sediment, oceanic water die away (e.g., OECD 308/309) have half lives below 180 days.
OR, if data are lacking:
f) evaluation via BIOWIN model (EPIWEB 4)

Bioaccumulation:

A substance is not bioaccumulative if:
a) measured TMF < 1 (field study)
b) measured fish BMF < 1 (lab study)
c) measured fish BCF < 5000 (lab study)
d) predicted BCF < 5000 using the BCFBAF model included in EPIWIN 4
The above order reflects the preference for use in decision-making
NOTE -- P&B CRITERIA ARE FOR ORGANICS

Tonnage - based upon IUR reporting ranges

< 25,000 lbs (below IUR site reporting limit)
25,000 - <1 MM lbs national aggregate
1MM - <100 MM lbs national aggregate
≥100 MM lbs national aggregate

Sustainability Chemistry Screening Tool

Hazard x Exposure = Risk

Exposure Elements				
Use Pattern	intermediate	industrial - not intermediate	commercial	consumer
Use Score	1	2	3	4
Persistence / Bioaccumulation (PB)	not P, not B		P & not B OR B & not P	P&B
PB Score	1		3	5
Tonnage	<25,000 lbs (below IUR site reporting limit)	25,000 - <1MM lbs IUR aggregate	1MM- <100MM lbs IUR aggregate	≥ 100MM lbs IUR aggregate
Tonnage Score	1	2	3	4
SUM (Use + PB + Tonnage Scores)	**range 3 -13**			

SIEVE RANKING = Hazard + Exposure Rankings				Exposure Ranking = Based on Sum (Use + PB + Tonnage Scores)				
				3-4	5-6	7-8	9-10	11-13
				low	med-low	medium	med-high	high
Hazard Ranking = Higher Score from Environmental and Human Health Hazards				1	2	3	4	5
		Environmental Hazard	Human Health Hazard					
1	low	not classified	Not carcinogen/mutagen/repro/develop; OR Repeat Dose >1000 mg/kg/day (oral); > 2000 mg/kg/day (dermal); > 1000 ppm/6hr/day (gas inhalation); >5.0 mg/l/6h/day (vapour inhalation); > 1.0 mg/l/6h/day (dust mist fume inhal).	2	3	4	5	6
2	medium	Acute III OR Chronic III/IV ; [not acutely toxic and no chronic data]	Not carcinogen/mutagen/repro/develop;OR Repeat Dose 100 - 1000 mg/kg/day (oral); 200 - 2000 mg/kg/day (dermal); 250 - 1000 ppm/6hr/day (gas inhalation); 1.0 - 5.0 mg/l/6h/day (vapour inhalation); 0.2 - 1.0 mg/l/6h/day (dust mist fume inhal).	3	4	5	6	7
3	med-high	Acute II or Chronic II	GHS CMR Cat 2; OR GHS Repeat Dose Cat 2: Repeat Dose 10 - 100 mg/kg/day (oral); 20 - 200 mg/kg/day (dermal); 50 - 250 ppm/6hr/day (gas inhalation); 0.2 - 1.0 mg/l/6h/day (vapour inhalation); 0.02 - 0.2 mg/l/6h/day (dust mist fume inhal).	4	5	6	7	8
4	high	Acute I OR Chronic I OR insufficient information to classify	GHS CMR Cat 1a, 1b; OR GHS Repeat Dose Cat 1: Repeat Dose </= 10 mg/kg/day (oral); </= 20 mg/kg/day (dermal); </= 50 ppm/6hr/day (gas inhalation); </= 0.2 mg/l/6h/day (vapour inhalation); </= 0.02 mg/l/6h/day (dust mist fume inhal). OR insufficient information to classify	5	6	7	8	9