Green Chemistry and Chemical Hazard Assessment

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Green Chemistry: A System Challenge

Reagent 1 + Reagent 2 $\xrightarrow{\Delta}$ Rx Conditions $\Rightarrow$ Product + By-products

Auxiliaries (solvents, catalysts)
Chemical Makers, Chemical Choosers & Chemical Users

Chemical Makers
Synthetic Chemists

Chemical Choosers
Formulators
Compounders

Chemical Users
We are ALL chemical users
RISK = \( f(\text{Hazard}, \text{Exposure}) \)

**Hazard** = the *inherent property* of a substance having the potential to cause adverse effects when an organism, system, or (sub) population is exposed to that substance.

**Risk** = the *probability* of an adverse effect in an organism, system, or (sub) population under specified circumstances by exposure to a substance.
Exposure Controls Can - And Will - Fail

Worker exposure
Accidental spills
PPE failures
Pollution storage
Unintended usage

http://www.deathbyhealthandsafety.co.uk/safetyvalve/forgotten.html
https://studylib.net/doc/9430337/solid-and-hazardous-wastes
### Typical Hazard Endpoints Used in Chemical Hazard Assessment

<table>
<thead>
<tr>
<th>Human Health Group I</th>
<th>Human Health Group II and II*</th>
<th>Environmental Toxicity &amp; Fate</th>
<th>Physical Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carcinogenicity</td>
<td>Acute Toxicity</td>
<td>Acute Aquatic Toxicity</td>
<td>Reactivity</td>
</tr>
<tr>
<td>Mutagenicity &amp; Genotoxicity</td>
<td>Systemic Toxicity &amp; Organ Effects</td>
<td>Chronic Aquatic Toxicity</td>
<td>Flammability</td>
</tr>
<tr>
<td>Reproductive Toxicity</td>
<td>Neurotoxicity</td>
<td>Other Ecotoxicity studies when available</td>
<td></td>
</tr>
<tr>
<td>Developmental Toxicity</td>
<td>Skin Sensitization</td>
<td>Persistence</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Respiratory Sensitization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endocrine Activity</td>
<td>Skin Irritation</td>
<td>Bioaccumulation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Eye Irritation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Based on GreenScreen method
Classify Chemicals for Individual Hazards*

Table 2. Carcinogenicity Criteria for Hazard Designation

<table>
<thead>
<tr>
<th>Carcinogenicity</th>
<th>Very High</th>
<th>High</th>
<th>Moderate</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>Known or presumed human carcinogen (equivalent to GHS Category 1A and 1B)</td>
<td>Suspected human carcinogen (equivalent to GHS Category 2)</td>
<td>Limited or marginal evidence of carcinogenicity in animals (and inadequate evidence in humans)</td>
<td>Negative studies or robust mechanism-based SAR (as described above)</td>
<td></td>
</tr>
</tbody>
</table>

6.2 Carcinogenicity

Table 21. Classifications from Authoritative Lists that May Be Used to Designate Very High Hazard for Carcinogenicity

<table>
<thead>
<tr>
<th>Authoritative Body</th>
<th>Classifications for Very High Hazard Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>National Toxicology Program (NTP)</td>
<td>Known to be Human Carcinogen  Reasonably Anticipated to be Human Carcinogen</td>
</tr>
<tr>
<td>International Agency for Research on Cancer (IARC)</td>
<td>Group 1 – carcinogenic to humans  Group 2A – probably carcinogenic to humans</td>
</tr>
<tr>
<td>EU CMR List [50]</td>
<td>Category 1 – Known to be carcinogenic to humans  Category 2 – Should be regarded as if carcinogenic to humans</td>
</tr>
<tr>
<td>EU Risk Phrases [50]</td>
<td>R45: May cause cancer  R49: May cause cancer by inhalation  And all combination risk phrases containing R45 or R49.</td>
</tr>
<tr>
<td>EU Classification, Labeling, and Packaging (CLP) [50]</td>
<td>H350: May cause cancer  H350i: May cause cancer by inhalation</td>
</tr>
</tbody>
</table>

# Report Results in a Hazard Table

Table ES-1 Screening Level Hazard Summary for DecaBDE and Halogenated Flame Retardant Alternatives

This table only contains information regarding the inherent hazards of flame retardant chemicals. Evaluation of risk considers both the hazard and exposure associated with the substance including combustion and degradation by-products. The caveats listed in the legend and footnote sections must be taken into account when interpreting the hazard information in the table.

- **VL** = Very Low hazard
- **L** = Low hazard
- **M** = Moderate hazard
- **H** = High hazard
- **VH** = Very High hazard

Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using values from predictive models and/or professional judgment.

- Based on analogy to experimental data for a structurally similar compound.
- This alternative may contain impurities. These impurities have hazard designations that differ from the flame retardant alternative, Brominated poly(phenylether), as follows, based on experimental data: HIGH for human health, HIGH for aquatic toxicity, and VERY HIGH for bioaccumulation.
- This chemical is subject to testing in an EPA consent order for this endpoint.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CASRN</th>
<th>Acute Toxicity</th>
<th>Carcinogenicity</th>
<th>Genotoxicity</th>
<th>Reproductive</th>
<th>Developmental</th>
<th>Neurological</th>
<th>Repeated Dose</th>
<th>Skin Sensitization</th>
<th>Respiratory Sensitization</th>
<th>Eye Irritation</th>
<th>Dermal Irritation</th>
<th>Aquatic Toxicity*</th>
<th>Environmental Fate</th>
</tr>
</thead>
<tbody>
<tr>
<td>DecaBDE and Halogenated Flame Retardant Alternatives</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bis(hexachlorocyclopentadiene) Cyclooctane</td>
<td>13560-89-9</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>VL</td>
<td>VL</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>VL</td>
<td>L</td>
<td>L</td>
<td>VL</td>
<td>VH</td>
</tr>
<tr>
<td>Brominated Poly(phenylether)</td>
<td>Confidential</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>VL</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>VL</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Decabromodiphenyl Ethane</td>
<td>84852-53-9</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>L</td>
<td>H</td>
<td>L</td>
<td>L</td>
<td>H</td>
<td>VL</td>
<td>VL</td>
<td>L</td>
<td>L</td>
<td>VH</td>
</tr>
<tr>
<td>Decabromodiphenyl Ether</td>
<td>1103-19-5</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>L</td>
<td>H</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>VL</td>
<td>L</td>
<td>L</td>
<td>VH</td>
<td>H</td>
</tr>
<tr>
<td>Ethylene Bis-Tetrabromophthalimide</td>
<td>32588-76-4</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>L</td>
<td>H</td>
<td>L</td>
<td>M</td>
<td>L</td>
<td>VL</td>
<td>L</td>
<td>L</td>
<td>VH</td>
<td>H</td>
</tr>
<tr>
<td>Tetrabromobisphenol A Bis(2,3-dibromopropyl) Ether</td>
<td>21850-44-2</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>M</td>
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<td>M</td>
<td>M</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>VH</td>
<td>H</td>
</tr>
<tr>
<td>Tris(tribromononyle) Phosphate</td>
<td>19180-97-1</td>
<td>M</td>
<td>M</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>Tris(tribromophenoxy) Triazine</td>
<td>25713-60-4</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>VL</td>
<td>L</td>
<td>L</td>
<td>VH</td>
<td>H</td>
</tr>
</tbody>
</table>

From https://www.epa.gov/saferchoice/design-environment-alternatives-assessments
Overall Chemical Grading System: GreenScreen®

Benchmark 1 (BM-1) criteria

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>Persistent and Bioaccumulative and Toxic (human or environment)</td>
</tr>
<tr>
<td>vPvB</td>
<td>Very Persistent and very Bioaccumulative</td>
</tr>
<tr>
<td>vPT</td>
<td>Very Persistent and Toxic (human or environment)</td>
</tr>
<tr>
<td>vBT</td>
<td>Very Bioaccumulative and Toxic (human or environment)</td>
</tr>
<tr>
<td>CMRDE</td>
<td>Carcinogen, and/or mutagen, and/or reproductive or developmental toxicant, and/or endocrine disruptor</td>
</tr>
</tbody>
</table>

From https://www.greenscreenchemicals.org
## Make More Informed Decisions:
### Which Chemical Would **YOU** Use?

The chemical of concern is a solvent used in cleaning products.

| Chemical Name       | Score | C | M | R | D | E | AT | ST | ST* | N  | N* | SnS* | SnR* | IrS | IrE | AA | CA | P | B | Rx | F |
|---------------------|-------|---|---|---|---|---|----|----|-----|----|----|------|------|-----|-----|----|---|---|---|---|
| Chemical of Concern | GS BM 1 | H | H | M | M | DG | vH | L  | M  | L  | M  | H   | H   | H  | H  | vH | vH | vH | vH | L | L |
| Alternative Alpha   | GS BM 2 | L | M | L | L | DG | L  | M  | M  | M  | M  | L   | M   | M  | M  | L  | M | M | M | M |
| Alternative Beta    | GS BM 2 | M | DG | L | L | M  | H  | DG | DG | M  | M  | M   | M   | H  | M  | H  | M | M | M | M |
Chemical Hazard Assessment Resources

GreenScreen for Safer Chemicals (GS)
Safer Choice / DfE AA, Cradle to Cradle
Globally Harmonized System (GHS)

Quick Chemical Assessment Tool (QCAT)

GS List Translator

SDS

Complexity
Alternatives Assessment

- Hazard
- Exposure
- Cost
- Availability
- Performance
- and/or

Life Cycle Impacts
Circularity (Waste)
Social Impacts
Alternatives Assessment Resources

**Alternatives Assessment:** process for identifying and comparing potential chemical and non-chemical alternatives that can be used as substitutes to replace chemicals or technologies of high concern. (IC2 AA Guide)


IC2: [http://theic2.org/alternatives_assessment_guide](http://theic2.org/alternatives_assessment_guide)


Picking the Right Tool for the Job

Chemical Hazard Assessment
- Evaluates hazard: The inherent potential to harm.
  *Which chemical is inherently safer?*

Risk Assessment
- Evaluates risk: The probability of adverse harm.
  *Is this product safe enough? For all uses?*

Life Cycle Assessment
- Considers multiple impacts across the life cycle and hazard from emissions. Energy usage tends to dominate results.
  *What are the overall impacts of a product from cradle to <X>?*

Alternatives Assessment
- Avoid unintended consequences. Consider hazard, exposure, cost, availability, performance, and potentially more.
  *Which product(s) are the safest, and what are the tradeoffs?*
Chemical Hazard Assessment Supports Green Chemistry and Alternatives Assessment

Safer chemicals
Safer ingredients and components
Safer products
From the life cycle perspective

http://xkcd.com/1739/
Chemical Hazard Assessment Module

- Module to help students to understand the language of chemical hazards.
- Introduce the students to various available resources to gather hazard data
- Provides an example of how one could assess and compare data

https://www.beyondbenign.org/lessons/module-chemical-hazard-awareness/
# Example Chemical Hazards

<table>
<thead>
<tr>
<th>Human Health</th>
<th>Environmental Toxicity &amp; Fate</th>
<th>Physical Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carcinogenicity</strong></td>
<td>Acute Mammalian Toxicity</td>
<td>Acute Aquatic Toxicity</td>
</tr>
<tr>
<td><strong>Mutagenicity &amp; Genotoxicity</strong></td>
<td>Systemic Toxicity &amp; Organ Effects</td>
<td>Chronic Aquatic Toxicity</td>
</tr>
<tr>
<td><strong>Reproductive Toxicity</strong></td>
<td>Neurotoxicity</td>
<td>Other Ecotoxicity studies when available</td>
</tr>
<tr>
<td><strong>Developmental Toxicity</strong></td>
<td>Skin Sensitization</td>
<td>Persistence</td>
</tr>
<tr>
<td></td>
<td>Respiratory Sensitization</td>
<td></td>
</tr>
<tr>
<td><strong>Endocrine Activity</strong></td>
<td>Skin Irritation</td>
<td>Bioaccumulation</td>
</tr>
<tr>
<td></td>
<td>Eye Irritation</td>
<td></td>
</tr>
</tbody>
</table>

**Scorecard**

- **High**
- **Medium**
- ✔️ **Low**
Hazard Activity

- Students split into groups to assess 3 reactions:
  - Lead Nitrate
  - Potassium Iodide
  - Copper Sulfate
  - Potassium Carbonate
  - Calcium Chloride
  - Sodium Carbonate

- Look at the SDS’s to identify the Hazard Statements and Toxicity Data

- Determine High, Medium or Low Hazard for each of the statements/data with the Hazard Level Guides

- Assign a Hazard Level Score for each chemical and compare reactions
Today’s Activity

- Look at the partial SDS’s for Lead Nitrate and Potassium Carbonate to identify the Hazard Statements and Toxicity Data
- Determine High, Moderate or Low Hazard for those statements with the Hazard Level Guides
- Assign Hazard Level Score based on the Health and Environmental Hazards for all 6 chemicals

<table>
<thead>
<tr>
<th>Run #:</th>
<th>Chemical name:</th>
<th>Data Source:</th>
<th>Physical Hazard:</th>
<th>Health Hazard:</th>
<th>Environmental Hazard:</th>
<th>Hazard Level:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lead (II) Nitrate</td>
<td>SDS Data &amp; H-Statements</td>
<td></td>
<td>H302 (Medium), LD50 (oral, mouse) 1,000 mg/kg (Medium) H315, H319</td>
<td>LC50 (fish, 96 hr) 2,190 mg/l (Low), EC50 (daphnia, 24 hr) 2.7 mg/l (High- based on 48 hr criteria)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Potassium Iodide</td>
<td>SDS Data &amp; H-Statements</td>
<td>H302 (Medium), LD50 (oral, rat) – 482 mg/kg (Medium) H315, H319, LD50 (intraperitoneal, rat) – 20 mg/kg; LD50 (i.p., rat) – 43 mg/kg; LD50 (intravenous, rat) – 48.9 mg/kg</td>
<td></td>
<td>H410 (High), LC50 (fish, 96 hr) – 1-2.5 mg/l (High), EC50 (daphnia, 48 hr) – 0.024 mg/l (High)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Copper (II) Sulfate</td>
<td>SDS Data &amp; H-Statements</td>
<td>H319</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Potassium Carbonate</td>
<td>SDS Data &amp; H-Statements</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calcium chloride</td>
<td>SDS Data &amp; H-Statements</td>
<td>LD50 (oral, rat) – 2,301 mg/kg (Low) H319</td>
<td></td>
<td>LC50 (fish, 96 hr) – 10,650 mg/l (Low), EC50 (daphnia, 48 hr) – 2,400 mg/l (Low)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium carbonate</td>
<td>SDS Data &amp; H-Statements</td>
<td>LD50 (oral, rat) – 4,090 mg/kg (Low), LC50 (oral, rat 2 hr) – 5,750 mg/l (Low) H319</td>
<td></td>
<td>LC50 (fish, 96 hr) – 300 mg/l (Low), EC50 (daphnia, 48 hr) – 265 mg/l (Low)</td>
<td></td>
</tr>
</tbody>
</table>
## Example (Lead (II) Nitrate): Looking up SDS H statements

<table>
<thead>
<tr>
<th>Hazard Level</th>
<th>Health Hazard</th>
<th>Environmental Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>H350, H340, H360, H301, H311, H331, H310, H330, H300</td>
<td>H400, H401, H410</td>
</tr>
<tr>
<td>Medium</td>
<td>H351, H341, H361, H302, H312, H332</td>
<td>H402</td>
</tr>
<tr>
<td>Low</td>
<td>H303, H313, H333 or No H-Phrases</td>
<td>No H-Phrases</td>
</tr>
</tbody>
</table>

### 2. Hazards Identification

#### 2.1 Classification of the substance or mixture

- GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)
  - Oxidizing solids (Category 2), H272
  - Acute toxicity, Oral (Category 4), H302
  - Acute toxicity, Inhalation (Category 4), H332
  - Serious eye damage (Category 1), H318
  - Carcinogenicity (Category 1B), H350
  - Reproductive toxicity (Category 1A), H360
  - Specific target organ toxicity - repeated exposure (Category 2), H373
  - Acute aquatic toxicity (Category 1), H400
  - Chronic aquatic toxicity (Category 1), H410
## Example (Lead (II) Nitrate): Looking up SDS H statements

<table>
<thead>
<tr>
<th>Chemical name:</th>
<th>Data Source:</th>
<th>Physical Hazard:</th>
<th>Health Hazard:</th>
<th>Environmental Hazard:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (II) Nitrate</td>
<td>SDS Data &amp; H-Statements</td>
<td>H272</td>
<td>H302 (<em>Medium</em>), H332 (<em>Medium</em>), H350 (<em>High</em>), H360 (<em>High</em>), IARC Group 2A: Probably carcinogenic to humans (<em>High</em>)</td>
<td>H400 (<em>High</em>), H410 (<em>High</em>)</td>
</tr>
</tbody>
</table>

### 2.1 Classification of the substance or mixture

GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)

- Oxidizing solids (Category 2), H272
- Acute toxicity, Oral (Category 4), H302
- Acute toxicity, Inhalation (Category 4), H332
- Serious eye damage (Category 1), H318
- Carcinogenicity (Category 1B), H350
- Reproductive toxicity (Category 1A), H360
- Specific target organ toxicity - repeated exposure (Category 2), H373
- Acute aquatic toxicity (Category 1), H400
- Chronic aquatic toxicity (Category 1), H410
Example (Lead (II) Nitrate): Looking up Toxicological and Ecological Effects

11.1 Information on toxicological effects

- **Acute toxicity**
  No data available
- **Inhalation**
  No data available
- **Dermal**
  No data available
- **LD50 Intravenous - Rat**
  93 mg/kg
- **LD50 Intraperitoneal - Mouse**
  74 mg/kg
- **Skin corrosion/irritation**
  No data available
- **Serious eye damage/eye irritation**
  No data available
- **Respiratory or skin sensitisation**
  No data available
- **Germ cell mutagenicity**
  No data available
- **Carcinogenicity**
  IARC: 2A - Group 2A: Probably carcinogenic to humans (Lead nitrate)

12. ECOLOGICAL INFORMATION

12.1 Toxicity

- **Toxicity to fish**
  LC50 - Oncorhynchus mykiss (rainbow trout) - 1.5 mg/l - 96.0 h
  Sigma-Aldrich - 11520

- **Toxicity to daphnia and other aquatic invertebrates**
  LC50 - Cyprinus carpio (Carp) - 0.4 - 1.3 mg/l - 96.0 h
  EC50 - Daphnia magna (Water flea) - 0.5 - 2.0 mg/l - 48 h
### Example (Lead (II) Nitrate):
Looking up Toxicological and Ecological Effects

<table>
<thead>
<tr>
<th>Chemical name:</th>
<th>Data Source:</th>
<th>Physical Hazard:</th>
<th>Health Hazard:</th>
<th>Environmental Hazard:</th>
<th>Hazard Level:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (II) Nitrate</td>
<td>SDS Data &amp; H-Statements</td>
<td>H272</td>
<td>H302 (Medium), H332 (Medium), H350 (High), H360 (High), IARC Group 2A: Probably carcinogenic to humans (High)</td>
<td>H400 (High), H410 (High), LC50 (fish, 96 hr) – 1.5 mg/l (High), LC50 (fish, 96 hr) – 0.4-1.3 mg/l (High), EC50 (daphnia, 48 hr) – 0.5-2.0 mg/l (High)</td>
<td>High</td>
</tr>
</tbody>
</table>
Potassium Carbonate

• Look at the partial SDS handout to identify the Hazard Statements and Toxicity Data

• Determine High, Medium or Low Hazard for the statements with the Hazard Level Guides

• Assign a Hazard Level Score

<table>
<thead>
<tr>
<th>Potassium Carbonate</th>
<th>SDS Data &amp; H-Statements</th>
<th>H302 (Medium), LD50 (oral, rat) – 1,870 mg/kg (Medium)</th>
<th>LC50 (fish, 96 hr) &lt; 510 mg/l (Low)</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H315, H319, H335</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Chemical Hazard Assessment Module

<table>
<thead>
<tr>
<th>Rank #</th>
<th>Chemical name</th>
<th>Data Source:</th>
<th>Physical Hazard:</th>
<th>Health Hazard:</th>
<th>Environmental Hazard:</th>
<th>Hazard Level:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lead (II) Nitrate</td>
<td>SDS Data &amp; H-Statements</td>
<td>H272</td>
<td>H302 (Medium), H332 (Medium), H350 (High), H360 (High), IARC Group 2A: Probably carcinogenic to humans (High)</td>
<td>H400 (High), H410 (High), LC50 (fish, 96 hr) 1.5 mg/l (High), EC50 (fish, 96 hr) 0.4-1.3 mg/l (High), EC50 (daphnia, 48 hr) 0.5-2.0 mg/l (High)</td>
<td>High</td>
</tr>
<tr>
<td>2</td>
<td>Potassium Iodide</td>
<td>SDS Data &amp; H-Statements</td>
<td>H315, H319</td>
<td>LD50 (oral, mouse) 1,000 mg/kg (Medium)</td>
<td>LC50 (fish, 96 hr) 2.190 mg/l (Low), EC50 (daphnia, 24 hr) 2.7 mg/l (High: based on 48 hr criteria)</td>
<td>High</td>
</tr>
<tr>
<td>3</td>
<td>Copper (II) Sulfate</td>
<td>SDS Data &amp; H-Statements</td>
<td>H315, H319, LD50 (intraperitoneal, rat) 20 mg/kg; LD50 (oral, rat) 43 mg/kg; LD50 (intravenous, rat) 48.9 mg/kg</td>
<td>H410 (High), LC50 (fish, 96 hr) 1-2.5 mg/l (High), EC50 (daphnia, 48 hr) 0.024 mg/l (High)</td>
<td>LC50 (fish, 96 hr) &lt; 510 mg/l (Low)</td>
<td>High</td>
</tr>
<tr>
<td>4</td>
<td>Potassium Carbonate</td>
<td>SDS Data &amp; H-Statements</td>
<td>H319, H319</td>
<td>LD50 (oral, rat) 1,870 mg/kg (Medium)</td>
<td>LC50 (fish, 96 hr) 10,650 mg/l (Low), EC50 (daphnia, 48 hr) &lt; 2,400 mg/l (Low)</td>
<td>Medium</td>
</tr>
<tr>
<td>5</td>
<td>Calcium chloride</td>
<td>SDS Data &amp; H-Statements</td>
<td>H319</td>
<td>LD50 (oral, rat) 2,301 mg/kg (Low)</td>
<td>LC50 (fish, 96 hr) 300 mg/l (Low), EC50 (daphnia, 48 hr) 265 mg/l (Low)</td>
<td>Low</td>
</tr>
<tr>
<td>6</td>
<td>Sodium carbonate</td>
<td>SDS Data &amp; H-Statements</td>
<td>H319</td>
<td>LD50 (oral, rat) 4,090 mg/kg (Low), LC50 (inb, rat, 2 hr) 5,750 mg/l (Low)</td>
<td>LC50 (fish, 96 hr) 300 mg/l (Low), EC50 (daphnia, 48 hr) 265 mg/l (Low)</td>
<td>Low</td>
</tr>
</tbody>
</table>
Quotes from Teachers

Students “felt empowered to make good choices in lab where they are normally just told what to use for chemicals”

“I was pleasantly surprised when students (unprompted by me) asked for access to hazard information about the products of each reaction as well to ensure that they were not going to have safety or disposal issues at the end of their procedures”
Green Chemistry and Chemical Hazard Assessment

Session: Towards Safer Design Strategies: Using Toxicology Tools & Concepts within Chemistry Courses & Programs

PRESENTED AT THE GREEN CHEMISTRY AND ENGINEERING CONFERENCE
JUNE 20, 2018

MARGARET H. WHITTAKER
TOXSERVICES LLC
Overview

• Definitions: Toxicity, Safer, Sustainable
• Concepts to guide tool selection
• Comparative hazard assessment in action!
• Essential tool kit for the green chemist and/green toxicologist
• Resources
Big Picture: Safer is Part of the Sustainability Puzzle

- **Safer** – Less likely to harm

- **Sustainability** – Meeting the needs of the present generation without compromising the needs of future generations

- **UN Sustainable Development Goals** – The UN has identified 17 goals to achieve by 2030...SDG 12 underscores the importance of hazard reduction and green chemistry
Characteristics of a 21st-Century Tool Box

- Formulating chemicals, materials, or products that are safe and sustainable requires:
  - (1) Knowledge of the chemicals (or biological/radiological/physical) substances present
  - (2) Knowledge of hazards, risks, and life cycle attributes, and
  - (3) Robust methods to reduce and eliminate chemicals of concern
Before We Get to the Tools - What is a CofC? What is Toxicity?

**A chemical of concern displays one or more of the following traits:**

- Carcinogenicity, mutagenicity, reproductive or developmental toxicity
- Potential concern for children’s health
- Used in children’s products
- Neurotoxic
- Persistent, bioaccumulative, and toxic (PBT)
- Very persistent or very bioaccumulative in the environment (vPvB)
- Ozone depleting
- Detected in biomonitoring programs

**Chemicals of concern are challenging to phase out:**

- Switching to a chemical with unknown hazards may result in a chemical that is more hazardous

*Toxicity* is the degree to which a substance or mixture of substances can harm living organisms.
A majority of green chemists and toxicologists around the world manage chemicals with the same tools used 30 years ago:

- Restricted substances lists (RSL)
- Chemical analysis to confirm absence of chemicals on RSL or other priority chemicals - e.g., California Prop 65 chemicals, EU Substances of Very High Concern (SVHCs)
- Requesting Safety Data Sheets from suppliers without mandating that SDS be GHS compliant
- Relying on a patchwork of ecolabels
Tools for Screening: Don’t Forget to Assess Multiple Endpoints!

- We learned earlier that tools that screen a chemical should assess multiple hazard endpoints based on human health, environmental, and physical attributes.

<table>
<thead>
<tr>
<th>Human Health Group I</th>
<th>Human Health Group II</th>
<th>Environmental Toxicity &amp; Fate</th>
<th>Physical Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carcinogenicity</td>
<td>Acute Toxicity</td>
<td>Acute Aquatic Toxicity</td>
<td>Reactivity</td>
</tr>
<tr>
<td>Mutagenicity &amp; Genotoxicity</td>
<td>Systemic Toxicity &amp; Organ Effects</td>
<td>Chronic Aquatic Toxicity</td>
<td>Flammability</td>
</tr>
<tr>
<td>Reproductive Toxicity</td>
<td>Neurotoxicity</td>
<td>Other Ecotoxicity Studies (Terrestrial Toxicity)</td>
<td></td>
</tr>
<tr>
<td>Developmental Toxicity</td>
<td>Skin Sensitization</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Respiratory Sensitization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endocrine Activity</td>
<td>Skin Irritation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Eye Irritation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Inventory  Screen  Assess  Optimize
Quick Refresher!

- GHS classifies health, physical, and environmental hazards
- There are three main components of GHS:
  - Hazard classification, Chemical labelling, and Safety data sheets
- For hazard classification, GHS assigns hazard class and hazard category
  - **GHS hazard class** represents the nature of a chemical hazard, e.g., flammable liquids, carcinogen
  - **GHS hazard category** is numerical classification within each hazard class. e.g., Acute toxicity has 5 hazard categories, with Cat 1 being worst
Tools for Screening: Caveat Emptor w/ SDS!

Warning! Disclosure on SDS is incomplete, so use these “tools” carefully!
Case in point: environmental hazards do not have to be disclosed on OSHA-Compliant SDS!

GHS is implemented in only 72 countries (green shading)

GHS is not implemented in many countries (blue shading)
- Most of Africa
- India (still in process of implementing)
- Bangladesh
Tools for Screening: How to Decipher GHS

- GHS describes the nature and severity of hazard class and hazard category
  - There are 29 hazard classes (left columns below)
  - Hazard class and category are summarized in H statements
    - H2xx: Physical hazards
    - H3xx: Health hazards
    - H4xx: Environmental hazards

<table>
<thead>
<tr>
<th>GHS Hazard Classifications by Endpoint</th>
</tr>
</thead>
<tbody>
<tr>
<td>GHS Health Hazards</td>
</tr>
<tr>
<td>Acute Toxicity</td>
</tr>
<tr>
<td>Skin Corrosion/Irritation</td>
</tr>
<tr>
<td>Serious Eye Damage/Eye Irritation</td>
</tr>
<tr>
<td>Respiratory or Skin Sensitization</td>
</tr>
<tr>
<td>Germ Cell Mutagenicity</td>
</tr>
<tr>
<td>Carcinogenicity</td>
</tr>
<tr>
<td>Reproductive Toxicity</td>
</tr>
<tr>
<td>Specific Target Organ Toxicity Single Exposure</td>
</tr>
<tr>
<td>Specific Target Organ Toxicity Repeated Exposure</td>
</tr>
<tr>
<td>Aspiration Hazard</td>
</tr>
</tbody>
</table>

Free on-line tool to look up all 107 H statements:
http://www.chemsafetypro.com/Topics/GHS/GHS_hazard_statement_code_signal_word_finder.html
Tools for Screening Chemicals: Comparison of Hazard Data on SDS

• What is on a Safety Data Sheet?

• As we learned previously during the session, SDS is a 16-section document that discloses hazards, provides information about proper transportation, disposal, exposure controls, and chemical composition.

• Sections 12 through 15 of an SDS are required under GHS, but they are not mandatory under the revised OSHA Hazard Communication Standard:
  • Ecological Information
  • Disposal Considerations
  • Transport Information
  • Regulatory Information

Voluntary sections of an OSHA HCS-compliant SDS
**HEALTH HAZARD**

- Glyoxal (CAS #107-22-2)
  - Crosslinker; Used as an intermediate in wrinkle-resistant textile formulations
- Mutagenic (among other hazards)
  - H341: Suspected of causing genetic defects
  - GHS Category 2

**ENVIRONMENTAL HAZARD**

(NOT LEGALLY REQUIRED ON U.S. SDS!!)

- 1,2-Benzisothiazol-3(2H)-one (CAS #2634-33-5)
  - Preservative
  - Aquatically toxic (acute)(among other hazards)
  - H400: Very toxic to aquatic life
  - GHS Category 1 acute aquatic toxicity

### SECTION 2. Hazards identification

#### 2.1 Classification of the substance or mixture

**Classification (REGULATION (EC) No 1272/2008)**

- Skin irritation, Category 2, H315
- Eye irritation, Category 2, H319
- Skin sensitisation, Category 1, H317
- Germ cell mutagenicity, Category 2, H341

For the full text of the H-Statements mentioned in this Section, see Section 16.
SDS Bike Lubricant Comparison: Eco-Sheep vs. ProGold

• Eco-Sheep is a bike lubricant that is lanolin-based
• Lanolin is also known wool wax or wool grease, is a wax secreted by the sebaceous glands of wool-bearing animals (including sheep)
• Eco-Sheep formulations are U.S. EPA Safer Choice Certified
• All ingredients assessed by U.S. EPA for human health and environmental hazards!!
Eco-Sheep Bike Lubricant

- Section 2 of the SDS for Eco-Sheep Mountain Sheep discloses no classified hazards
- Not all ingredients are disclosed on SDS, though!
- Let’s do some digging into the SDS!!
Eco-Sheep Bike Lubricant SDS

Section 12 of an SDS comprises the environmental disclosure (remember: U.S. SDS don’t legally have to disclose environmental hazards!)

<table>
<thead>
<tr>
<th><strong>12.1. Toxicity</strong></th>
<th>Ecology - general</th>
<th>The product is not considered harmful to aquatic organisms or to cause long-term adverse effects in the environment.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>12.2. Persistence and degradability</strong></td>
<td>Eco Sheep</td>
<td>Biodegradable.</td>
</tr>
<tr>
<td></td>
<td>Persistence and degradability</td>
<td>Biodegradable.</td>
</tr>
<tr>
<td></td>
<td>Eco Sheep</td>
<td>Bioaccumulative potential</td>
</tr>
<tr>
<td></td>
<td>Bioaccumulative potential</td>
<td>Not bioaccumulative.</td>
</tr>
<tr>
<td><strong>12.4. Mobility in soil</strong></td>
<td>No additional information available</td>
<td></td>
</tr>
<tr>
<td><strong>12.5. Other adverse effects</strong></td>
<td>Other information</td>
<td>No other effects known.</td>
</tr>
</tbody>
</table>
Eco-Sheep Bike Lubricant SDS

- Section 15 and 16 of the SDS discloses minimal or slight hazards.
ProGold Chain Lubricant

• Section 2 of the SDS discloses many hazards with this bike lubricant

• Also, this bike lubricant is not EPA Safer Choice Certified

• Side-note:
  • H statements on U.S. SDS do not include their corresponding H statement numbers (not a legal requirement in the U.S.)
Does no disclosure mean no hazards?!

Short Answer: No!!
TIME TO VOTE: WHICH BIKE LUBRICANT WOULD YOU SAY IS SAFER?

**PROGOLD**
- This bike lubricant has hazards for many endpoints:
  - Flammable
  - Hazardous to human health
  - No hazard statements disclosed for environmental endpoints

**ECOSHEEP**
- No hazards disclosed in Section 2 of SDS
- What if there were data gaps in the hazards disclosed? How would you conclude this is safer?
Tools to Optimize: Putting it Together

- ChemSec outlines six steps for informed substitution as part of a December, 2017 Best Practices in Chemicals Management Guide (https://t.co/oXZLLf4l1Z)
  - Define the function, use, and need of the substance you want to replace
  - Define criteria for the alternative
  - Search for available alternative solutions
  - Evaluate and compare alternatives
  - Test on a pilot scale
  - Implement substitution
Conclusion

• The pursuit of safer chemicals, materials, and products is a dynamic process

• Identifying “safer” formulations is part detective work and part science!
  • Start first by identifying chemicals used in formulations....then...
  • Classify hazards for a broad spectrum of endpoints to protect both human health and the environment

• The two formulation comparison in this presentation highlights challenges identifying “safer” formulations....GHS is not perfect, but makes the comparison process much easier thanks to hazard classification!
Thank You

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Thank you!

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