Key questions

• What is exposure?
• What are the exposure sciences?
• How is exposure measured?
• How do we control (or prevent) exposure?
• How does a “focus on exposure” serve as a barrier to green chemistry?
• How can the exposure sciences inform green chemistry?
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What is exposure?
Human contact with a toxicant of concern (Ramazzini, 1688)
Risk = f (Hazard, Exposure, Vulnerability)

- Acute vs. chronic: e.g. pH, explosivity, toxicity (Carcinogen, Teratogen, Reproductive, Asthmagen, Endocrine disr, Immunotoxic, Neurotoxic, Aquatic toxicity, Organ toxicity)
- Env persistence
- Bioaccumulative potential
- Vapor pressure
- Vapor density
- Flammable range
- Specific gravity
- Boiling point
- Source
- Path
- Receiver
- Frequency
- Intensity
- Duration (of contact)
- Absorption via Inhalation, ingestion
- Bioavailability
- Dose
- Fetal & child development
- Young adult
- Adult
- Workplace
- Community
- (Env Justice)
- Product use
- Genetic variability
Risk = \( f(\text{Hazard, Exposure, Vulnerability}) \)
Risk = \( f(\text{Hazard, Exposure, Vulnerability}) \) Guiyu, China

Courtesy Basel Action Network, 2001
Flame retardants in breast milk: doubling time of 5 years

Risk = $f$(Hazard, Exposure, Vulnerability)

CDC tested for, and found, 212 substances, reported in 2009 from the NHANES cohort

287 Synthetic chemicals pollutants detected in umbilical cord blood (CDHS follow-up)

- Mercury
- Polyaromatic hydrocarbons (9)
- Polybrominated dibenzodioxins & furans (7)
- Perfluorinated chemicals (9)
- Polychlorinated dibenzodioxins & furans (11)
- Organochlorine pesticides (21)
- Polybrominated diphenyl ethers (32)
- Polychlorinated naphthalenes (50)
- Polychlorinated biphenyls (147)

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Exposure sciences as bridge between environment, broadly defined, and human health.

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White gas:
Mixture of aliphatic hydrocarbons
BP: 102 deg F  (VP = Atm Press)
Flash Point: -45 deg F  (Diesel fuel = 125 deg F)
VP: ~200 mmHg at 68 deg F  (Water: 18 mmHg at 68 deg F)
VD: 3-4  (Air = 1)
Flamm Range: 1.4% - 7.6%

Measuring exposure: source, path, receiver
Predicting the path of gasoline vapors in a container

Spatial factors

• Source
  • Mass applied
  • Physical properties of the chemical
  • Toxicity

• Path
  • Physical barriers
  • Air movement, directionality

• Receiver
  • Proximity to the source
  • Continuum of health effects
Temporal factors: Frequency, intensity, duration
Breathing zone PID measurements of total VOCs during 16 mins of brake work.

Exposure variability: Four breathing zone measurements of the same task, performed by person #1 during brake work.
Exposure variability: Five breathing zone measurements of the same task, performed by person #2 during brake work.

Exposure variability: Four breathing zone measurements of the same task, performed by person #3 during brake work.
Exposure variability: Three breathing zone measurements of the same task, performed by person #4 during brake work.

Exposure variability: Four breathing zone measurements of the same task, performed by person #5 during brake work.
Real-time, aggregate mean and median exposure profiles from 2 shops, 26 work tasks, 6 days, 9 technicians - total VOCs, mg/m$^3$ (95% CIs).
Integrated sampling characterizes exposure concentration in a single, time-weighted average measure of total inhaled dose.

Integrated breathing zone samples from 3 shops, 26 work tasks, 6 days, 9 technicians, mg/m³ (95% CIs).
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Hierarchy of Controls: Green chemistry is a long-term, definitive strategy that avoids risk-shifting.

- Control at the source
  (Substitute a safer chemical, enclose, reduce quantities, use a less-dispersive form, mechanize the process)

- Control along the path
  (Local and dilution ventilation, clean the process)

- Control at the receiver
  (Personal protective equipment, training in safe handling, MSDS)
Substitution – Alternatives assessment

• Assess the function the chemical is performing
  – Spraying a metal surface with degreaser

• Identify an alternative process to meet the same function
  – Flow-coating vs. spraying

• Identify safer "drop-in" substances
  – Alkaline degreasers vs. TCE or HCFCs

• Identify safer forms of the same substance
  – slurries vs. powders, liquids vs. aerosols

• Examples:
  – Water-based glues for solvent-base glues
  – Water-based paints and lacquers
  – Lead-free paints and pigments
  – Silica-free blasting agents
  – Vegetable oils for organic solvents in offset printing
  – Paper wool or polystyrene for fiberglass insulation

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• Daily U.S. chemical production & importation: 74 billion lbs
• 82,000 chemical substances, millions of products
• 3,000 High Production Volume (HPV) chemicals
• ~700 new chemicals introduced into the market each year

Global chemical production:
Growing 3% per year = doubling every 24 years
Hazardous waste

• 61 of 85 of CA largest hazardous waste sites leaking into groundwater
• 94% pose “a major threat to human health or the environment.”
• Clean-up: 400 years in California
• US EPA estimates 600 new sites needed each month until 2033

Exposure sciences in the context of scientific uncertainty and ignorance
Exposure sciences:
- A way to set priorities for existing hazards
- A means to inform green chemistry design
- Not a solution in itself.

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Exposure sciences as a bridge between green chemistry, environment, and human health.

(1) Are there properties of chemicals that can reduce exposure potential in the near field, such as vapor pressure?
(2) When green chemistry solutions are not yet developed, is it possible to implement interim control strategies to minimize or eliminate the potential for exposure to hazardous chemicals?
(3) Are there design features of chemicals that would reduce exposure potential over time and space by reducing environmental persistence and bioaccumulative potential?
Oil solubility (octanol-water coefficient)

Number of chlorine atoms on the parent hydrocarbon molecule

Butadienes: \( \text{CH}_2=\text{CH}=\text{CH}_2 \)

Methanes: \( \text{CH}_3\text{CH}_3 \)
Oil solubility (octanol-water co-efficient) vs Number of chlorine atoms on the parent hydrocarbon molecule.

For Styrenes ($C_6H_5CH=CH_2$):
- 0 chlorine atoms: ~10
- 1 chlorine atom: ~100
- 2 chlorine atoms: ~1000
- 3 chlorine atoms: ~10,000
- 4 chlorine atoms: ~100,000
- 5 chlorine atoms: ~1,000,000
- 6 chlorine atoms: ~10,000,000

For Ethanes ($CH_3CH_3$):
- 0 chlorine atoms: ~10
- 1 chlorine atom: ~100
- 2 chlorine atoms: ~1000
- 3 chlorine atoms: ~10,000
- 4 chlorine atoms: ~100,000
- 5 chlorine atoms: ~1,000,000
- 6 chlorine atoms: ~10,000,000
Oil solubility (octanol-water co-efficient)

Number of chlorine atoms on the parent hydrocarbon molecule

- **Ethylene (CH₂=CH₂)**
  - Oil solubility ranges from 10 to 1,000
  - 0 chlorine atoms: 10
  - 1 chlorine atom: 100
  - 2 chlorine atoms: 1,000
  - 3 chlorine atoms: 10,000
  - 4 chlorine atoms: 100,000
  - 5 chlorine atoms: 1,000,000

- **Benzene (C₆H₆)**
  - Oil solubility ranges from 10 to 1,000,000
  - 0 chlorine atoms: 10
  - 1 chlorine atom: 100
  - 2 chlorine atoms: 1,000
  - 3 chlorine atoms: 10,000
  - 4 chlorine atoms: 100,000
  - 5 chlorine atoms: 1,000,000
  - 6 chlorine atoms: 10,000,000

The diagrams illustrate the relationship between the number of chlorine atoms on the parent hydrocarbon molecule and the oil solubility (octanol-water co-efficient) for both ethylene and benzene.
Atmospheric persistence of some volatile organochlorine solvents

<table>
<thead>
<tr>
<th>Substance</th>
<th>Atmospheric half-life, years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloromethane</td>
<td>1.0</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>0.4</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.4</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>24.3</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>31.2</td>
</tr>
<tr>
<td>Dichlorodifluoromethane</td>
<td>69.3</td>
</tr>
<tr>
<td>Bromochlorodifluoromethane</td>
<td>11.1</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td>0.4</td>
</tr>
<tr>
<td>Trichloroethane</td>
<td>3.3</td>
</tr>
<tr>
<td>Dichlorotetrafluoroethane</td>
<td>152.5</td>
</tr>
<tr>
<td>Trichlorotrifluoroethane</td>
<td>58.9</td>
</tr>
<tr>
<td>Chloropentafluoroethane</td>
<td>381.2</td>
</tr>
<tr>
<td>Tetrafluoroethylene</td>
<td>0.3</td>
</tr>
<tr>
<td>Dichlorofluoromethane (HCFC-22)</td>
<td>8.3</td>
</tr>
<tr>
<td>Dichlorotrifluoroethane (HCFC-123)</td>
<td>1.2</td>
</tr>
<tr>
<td>Chlorotetrafluoroethane (HCFC-124)</td>
<td>4.8</td>
</tr>
<tr>
<td>Dichlorofluoroethane (HCFC-141b)</td>
<td>6.2</td>
</tr>
<tr>
<td>Chlorodifluoroethane (HCFC-142b)</td>
<td>13.2</td>
</tr>
<tr>
<td>Dichloropentafluoropropane (HCFC-225ca)</td>
<td>1.9</td>
</tr>
<tr>
<td>Dichloropentafluoropropane (HCFC-225ca)</td>
<td>5.5</td>
</tr>
</tbody>
</table>

A half-life is the amount of time needed for a substance to degrade to half its original concentration.
Persistence of some volatile organochlorine solvents in water

<table>
<thead>
<tr>
<th>Substance</th>
<th>Estimated half-life, years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>1,850</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>40</td>
</tr>
<tr>
<td>1,1-dichloroethane</td>
<td>61</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>72</td>
</tr>
<tr>
<td>1,1,2-trichloroethane</td>
<td>139</td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>1</td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane</td>
<td>&lt;1</td>
</tr>
<tr>
<td>1,1,1,2-tetrachloroethane</td>
<td>47</td>
</tr>
<tr>
<td>Pentachloroethane</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Hexachloroethane</td>
<td>1,800,000,000</td>
</tr>
<tr>
<td>1,3-dichloropropane</td>
<td>2</td>
</tr>
<tr>
<td>2,2-dichloropropane</td>
<td>&lt;1</td>
</tr>
<tr>
<td>1,1,2,3-tetrachloropropane</td>
<td>&lt;1</td>
</tr>
<tr>
<td>1,1,2,3,3-pentachloropropane</td>
<td>&lt;1</td>
</tr>
<tr>
<td>1,1-dichloroethylene</td>
<td>120,000,000,000</td>
</tr>
<tr>
<td>1,2-dichloroethylene</td>
<td>21,000,000,000</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>1,300,000</td>
</tr>
<tr>
<td>Perchloroethylene</td>
<td>990,000,000,000</td>
</tr>
</tbody>
</table>

A half-life in water is calculated from experimentally-determined rate constants.

24 hours ~ 80,000 seconds
0.6 seconds out of 24 hours ~ 100 years of chemical production in 14 million years of human evolution.

Global chemical production: doubling every 24 years = every 0.15 seconds.
“All substances are poisons: there is none which is not a poison. The right dose differentiates a poison from a remedy.”

*Paracelsus*, 1493-1541

“The dose of the mixture makes the poison, but differently for different individuals and differently at different times during growth and development.”

*Peter Montague*, 2002

“Exposure provides the dose that makes the poison.”

*Lioy*, 2010

“The only way we have of studying the unknown is by pretending that it is like the known.

That the unknown is like the known makes science possible; that it is also unlike the known makes science necessary.

This conflict is the reason that all theories are eventually proven to be wrong, limited, irrelevant, or inadequate.”

*R. Levins*, 1995

“Truth emerges more readily from error than confusion.”

*Francis Bacon*, 1561-1626
Green chemistry, toxicity, and exposure

“Understanding principles of exposure sources and pathways will facilitate green chemical and product design, safe use, and prevention of adverse health consequences to people and to the environment.”

Anastas, 2010