Green Chemistry: Sustaining a High Technology Civilization

Terry Collins

Librarian Watch: Introduction to New Hot Areas of Chemistry
A Sustainable Civilization

- The daily activities of the people who comprise the civilization can be carried on into the indefinite future, without undermining the ability of future generations to live with at least a comparably advantageous welfare.
“All previous ethics...[have been based upon the premises]...that the human condition, determined by the nature of man and the nature of things, was given once for all; that the human good on that basis was readily determinable; and that the range of human action and therefore responsibility was narrowly circumscribed. ...[But] with certain development of our powers the nature of human action has changed, and... [given rise to]... a whole new dimension of ethical relevance for which there is no precedent in the standards and canons of traditional ethics.”

Ecospherical Responsibility of Chemists

Matter flows from ecosphere into human economy

Spent matter flows out of human economy to ecosphere

Based on ideas of Herman Daly
Themes

- Sustainability
- Ethics
- Hans Jonas
- Green Chemistry Principles
  - Anastas & Warner
- Green Metrics
  - Eissen, Metzger, Schmidt, Schneidewind
- Green Accomplishments
  - PGCCAs
- Toxicology & Ecotoxicology
  - Bernd Jastorff
- Sustainability Ethics
  - Hans Jonas
- History of the Ungreen
  - Markowitz & Rosner
Green Chemistry/Sustainability Science


Endocrine Disruption: Our Stolen Future: Are We Threatening Our Fertility, Intelligence, and Survival?—A Scientific Detective Story, Theo Colborn, Dianne Dumanoski, John Peterson Myers.


History of the Ungreen: Gerald Markowitz and David Rosner, *Deceit and Denial: the Ugly Politics of Industrial Pollution,*
The Chemical Goals for Sustainability

Safe Energy: New chemistry for solar-to-chemical & solar-to-electrical conversion technology

Renewable Feedstocks: Develop economical feedstocks for chemical and polymer industries from plants

Pollution Reduction: Move the elemental composition of technology closer to biochemistry to reduce persistent and persistent/bioaccumulative pollutants.

Achieving Sustainable Technologies through Science

- Technology invented, sustainability not an issue
- Technology grows in importance - sustainability issues become evident.
- New Technology invented to resolve sustainability issue
- Destabilizing technology becomes a defining feature of the civilization

Learn to stay in the green region
Learn how to analyze greenness

Learn to stay in the green region
Learn how to analyze greenness
The Energy Research Problem

20 days of sunlight equals the planetary reserves of oil, coal and natural gas

C20th energy research
→ nuclear fission, fossilized carbon
→ devastation of sustainability


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Selectivity

Nature
Small number of elements, supported by elaborate design, sustain the complex chemistry of life

Chemistry
Entire periodic table used to attain selectivity allowing for comparatively simple reagent design
Reducing Persistent Pollutants

**Class 1**

Elemental toxins; the prototypical persistent pollutants

**Class 2**

Particularly stable molecular species
- chlorine!

Key Concepts for Understanding How to Deal with Persistent Pollutants

- Bioaccumulation
- Atmospheric distillation
- Endocrine Disruption
- Limitations of Science
- Human Limitations
Environmental Lead is Mostly Anthropogenic

Industrial revolution

Exhaustion of Roman lead mines

Rise and fall of Athens

Use of coinage

Discovery of cupellation

Spanish production of silver in New World

Silver production in Germany

Roman republic and empire

Boutron et al. Science, 1994, 265, 1841–1843

Lead production (tons/yr)

Years

Lead concentration pg/g
Examples of The Greening of Lead Technologies—All by Replacement

- Elimination of lead from piping & solder
- Replacement of Pb reagents in synthesis
- Lead replaced in paints
- Elimination of $\text{Et}_4\text{Pb}$ from fuels
- Safer batteries

ca. 20 M tonnes of lead produced annually
Limitations of Science:
Brief History of Refrigeration

- Nicolas Carnot (1796-1832) - Carnot Theory
- Jacob Perkins - patents ether-based ice-maker
- A.C. Twinning - 1 ton/day ice machine
- DOMELRE Š - first domestic machine
- Roland and Molina - Refrigerant properties of CFCs discovered
- Farman discovers Antarctic Ozone Hole
- Montreal Protocol
- HCFCs and HFCs
- Refrigerant properties of CFCs discovered
- Different refrigerants tested in marketplace - many problems
- Jacob Perkins patents ether-based ice-maker
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
Chlorinated Dibenzodioxin
(Substituents 1-4 and 5-9 = H, Cl;
2,3- and 7-8-chlorinated species are toxic)

Chlorinated Dibenzodifuran

Our Stolen Future, Theo Colborn, Dianne Dumanoski, John Peterson Myers, Plume-Penguin, New York, 1997
• 1690s, Ulm colic outbreak—city physician, Eberhard Göckel, notes monks who abstained from wine were healthy—two visiting monks recovered upon returning to their home monastery. Göckel visited daily accepting wine—soon developed colic symptoms.

• The wine had been “corrected” by adding a concoction formed by dissolving litharge, PbO, in a quantity of wine and boiling it down to a sweet extract, which Göckel noted turned the worst and sourest wine into the “best and loveliest.”

• 100s of wagon loads of wine from the Neckar River Valley arrived at Ulm’s markets daily for shipment down the Danube. The city’s economy was threatened when the people began blaming colic on wine from Ulm.

• In 1696, Duke Eberhard Ludwig issued an edict banning all lead-based wine additives—possibly the first consumer-protection legislation targeting a specific toxin—it prescribed death for perpetrators and anyone failing to whistle-blow.
Toxicity of TCDD

TCDD elicits a diverse spectrum of biological sex-, strain-, age-, and species-specific effects, including carcinogenicity, immunotoxicity, reproductive/developmental toxicity, hepatotoxicity, neurotoxicity, chloracne, and loss of body weight. These effects vary according to the age, sex, species, and strain of the animals involved.

*Veterans and Agent Orange,* Update 1996, Committee to Review the Health Effects in Vietnam Veterans of Exposure to Herbicides, Division of Health Promotion and Disease Prevention, Institute of Medicine, National Academy Press, Washington, D.C.

January 2001 - TCDD designated by USEPA as a known human carcinogen
A Timeline of Endocrine Disruption

Great Lakes; fur-farmers lose lakefish-fed minks
England; otters die off
Charles Broley, Gulf Coast, Fl; golden eagles lose instinct to mate & raise young

mid-60s

Ralph Schreider, Channel Islands of S. CA; female Western gulls co-nesting

early-70s

Mike Gilbertson, Lake Ontario; deformaties and wasting in herring gull chicks of Near Island

1980s

Lou Guilette, Lake Apopka, Fl; >60% male alligators have miniaturized sex organs

1988

Northern Europe; largest seal die-off in history

Niels Skakkeback, Copenhagen; male sperm counts dropped by almost 50% 1939-1990

1992

Mediterranean; massive die-off of striped dolphins - Alex Anguilar links to PCBs

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Our Stolen Future, Theo Colborn, Dianne Dumanoski, John Peterson Myers, Plume-Penguin, NY, 1997
Endocrine Disruption

Two important mechanisms of endocrine disruption

Human Limitations: Monsanto and TCDD

Military begins spraying agent orange in Nth. Vietnam

Spraying expands

Spraying stops – 2,4,5-T found to cause birth defects in mice

Veterans blame postwar ailments on TCDD in 2,4,5-T

Monsanto releases epidemiological studies of workers in Nitro, WV plant

Monsanto’s Chief Medical Officer concedes Nitro studies flawed

Monsanto study becomes centerpiece of Australian position towards veterans


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Biomagnification of PCB’s in the North Pacific Food Chain

- Water, 1x
- Zooplankton, 6,400x
- Lanternfish, 170,000x
- Squid, 240,000x
- Striped dolphin, 13,000,000x

US Est. Dioxin Emissions [1995]

- **Nonferrous metal smelting**: 11%
- **Power/energy generation**: 3%
- **Forest, brush & straw fires**: 3%
- **Nonincinerated municipal sludge**: 4%
- **Cement kilns**: 3%
- **Other**: 5%
- **Backyard trash burning**: 19%
- **Landfill fires**: 19%
- **Incineration**: 31%

**Total Estimated Dioxin Emissions**: 5,152 TEQ

Hydrogen Peroxide: an Ideal Green Reagent

Major industrial oxidant used primarily in non-catalyzed processes > 1.3 M tonnes annually

Key biochemical oxidant in enzymatic processes—P-450s & peroxidases

New catalyzed $\text{H}_2\text{O}_2$ processes have immense potential in green and end-of-pipe applications

New catalysts: nontoxic, inexpensive, selective, disposable, fast-acting, energy-saving
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<th>Escaping Urgency</th>
<th>Important</th>
<th>Urgent</th>
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<td>Addition: How should universities confront sustainability?</td>
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<tr>
<td>Necessity</td>
<td>Here we do what we genuinely must.</td>
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<tr>
<td>Originality</td>
<td>Here we define our authenticity and frame the original work we are capable of.</td>
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<tr>
<td>Deception</td>
<td>Here we let systems steal our chances to be authentic.</td>
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<tr>
<td>Waste</td>
<td>Here we squander our chances to be authentic.</td>
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### Urgency Addiction: Chemistry

Just as it is the bane of professional life, urgency addiction could suffocate the healthy scientific pursuit of sustainability.

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Just as it is the bane of professional life, urgency addiction could suffocate the healthy scientific pursuit of sustainability.
How should university chemists change to deal with sustainability?

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<td>• secure your dominion (tenure)</td>
<td>• focus research energy strategically on great sustainability problems</td>
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<tr>
<td>• collect adequate resources</td>
<td>• integrate sustainability ethics into research</td>
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<tr>
<td>• recruit great coworkers</td>
<td>• create new sustainable economies!</td>
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<td>• publish adequately</td>
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| • “publish or perish” in place of “do important work” | ???
| • turn green chemistry into another resource collection exercise |
Limitations of Science: The Ecosphere as a Postal Network