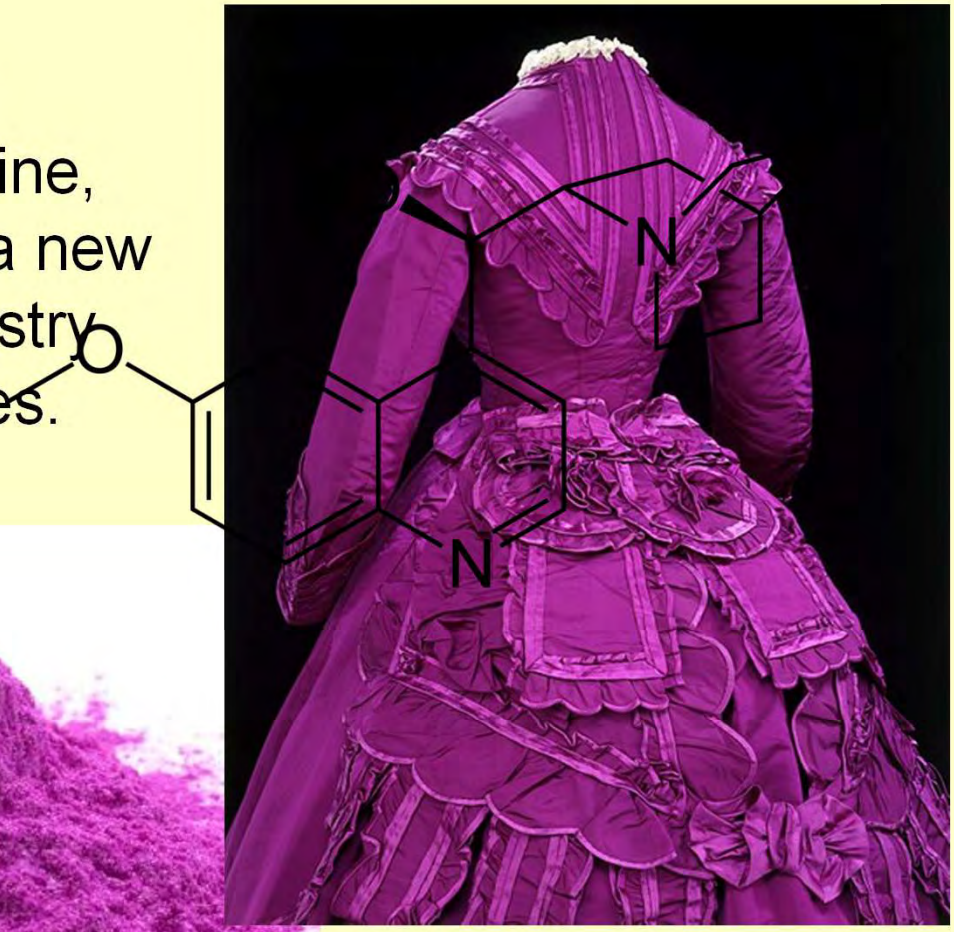
Eco-innovation & the Chemical Enterprise

Eric Beckman
Mascaro Center for Sustainable Innovation
Chemical Engineering Dept.
University of Pittsburgh

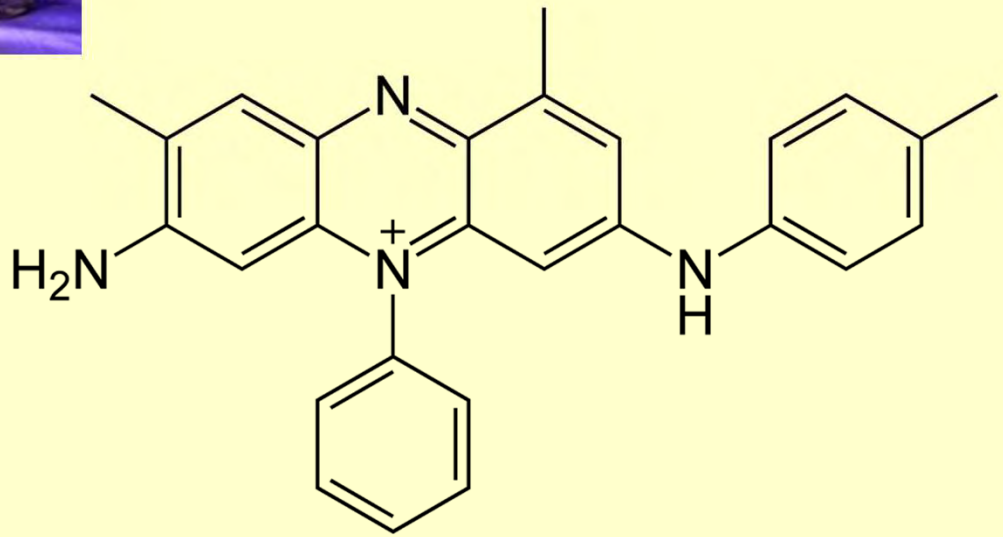
The modern synthetic chemical era begins with William Perkin in 1856 (by accident)

Not quinine, but a new industry arises.



Perkin's discovery sets off an "arms race" for new colors

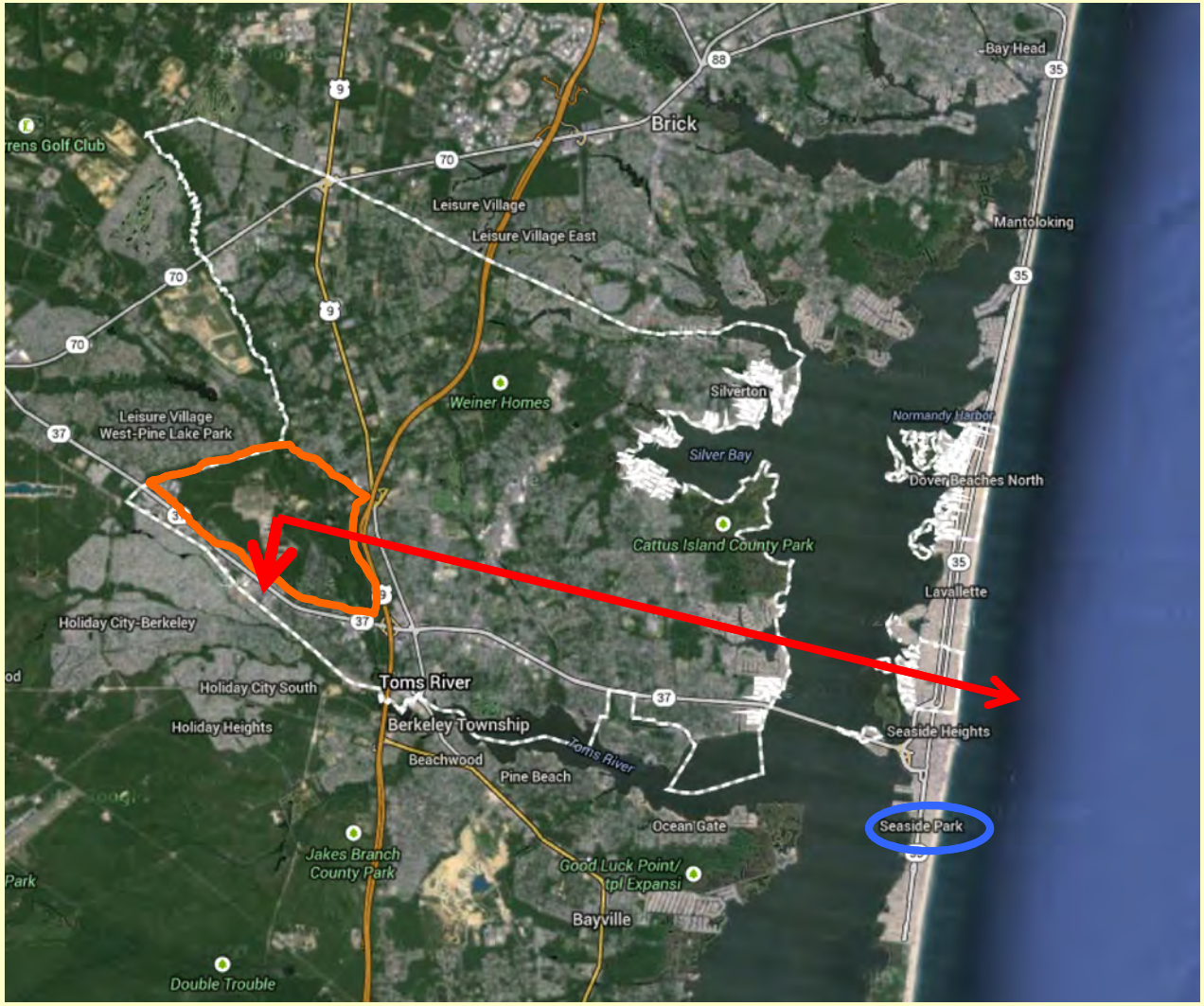
Aniline dyes: great color, but toxic ingredients & byproducts; high waste to product ratio.



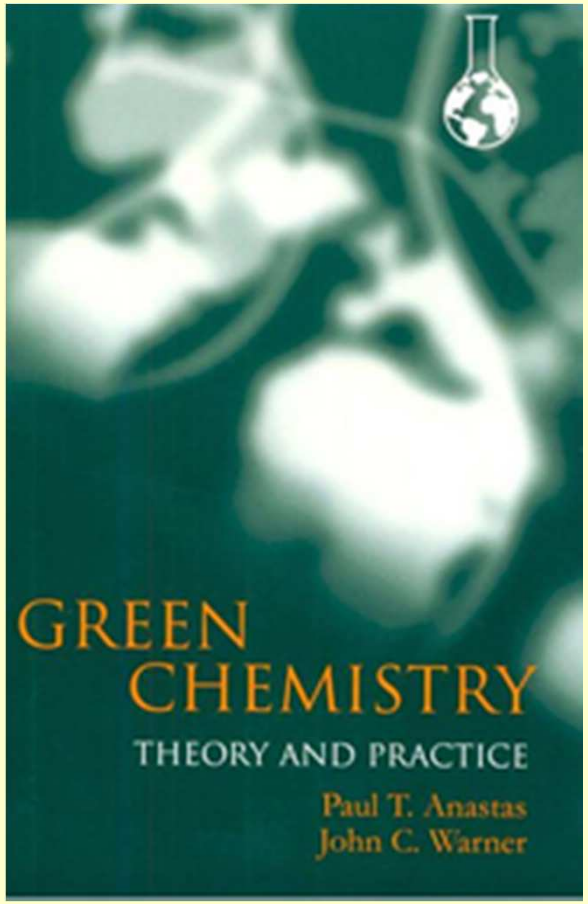
Mauveine

Tom's River: A Story of Science and Salvation (Dan Fagin, 2014 Pulitzer in non-fiction)

From 1965 to 1985, ~ 5 MM gallons per day of effluent, vat & azo dye waste (azobenzenes, nitrobenzene, benzidine, other aromatic amines)



Green Chemistry: 20 Years and counting..



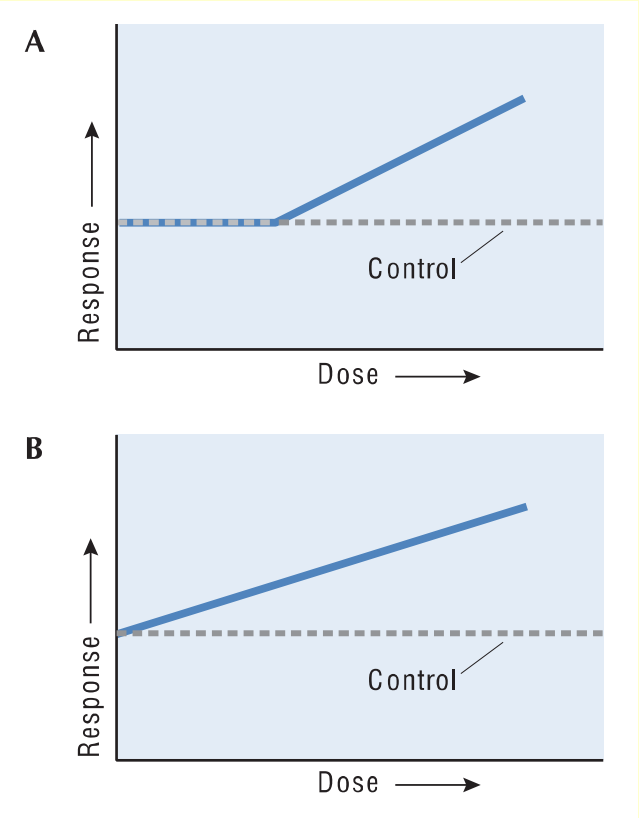
1998

Presidential Green Chemistry Awards (1996)

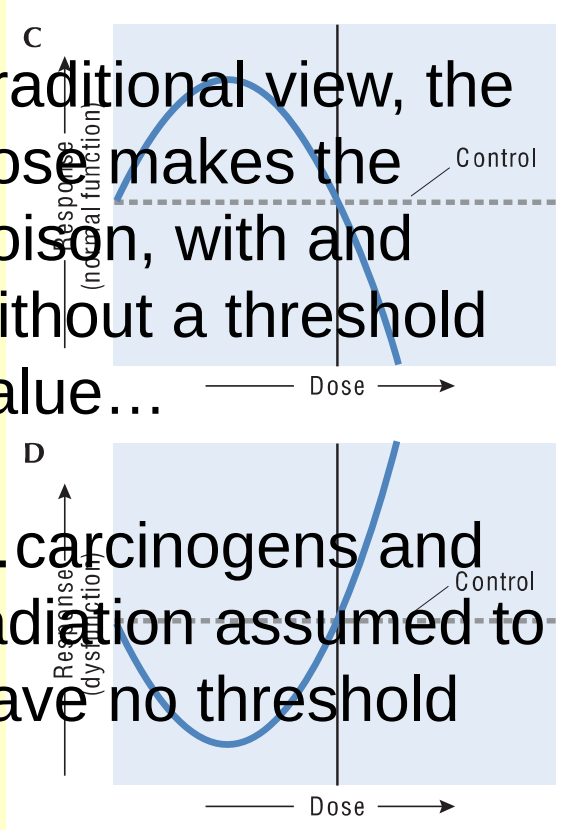
Green Chemistry: 20 Years on…

- A new way to look at chemistry & engineering
- From cleanup to pollution prevention to hazard reduction
- Along the way,
  - new ways to look at toxicity,
  - tractable tools for life cycle analysis,
  - profound changes within the business *& investment* community.
  - Green-washing: green becomes sufficiently important that it inspires cheating!

New Ways to Look at Toxicity [from *E.J. Calabrese,* EMBO Rep. (2004), 5 (special issue), s37-s40]



Traditional view, the dose makes the poison, with and without a threshold value…

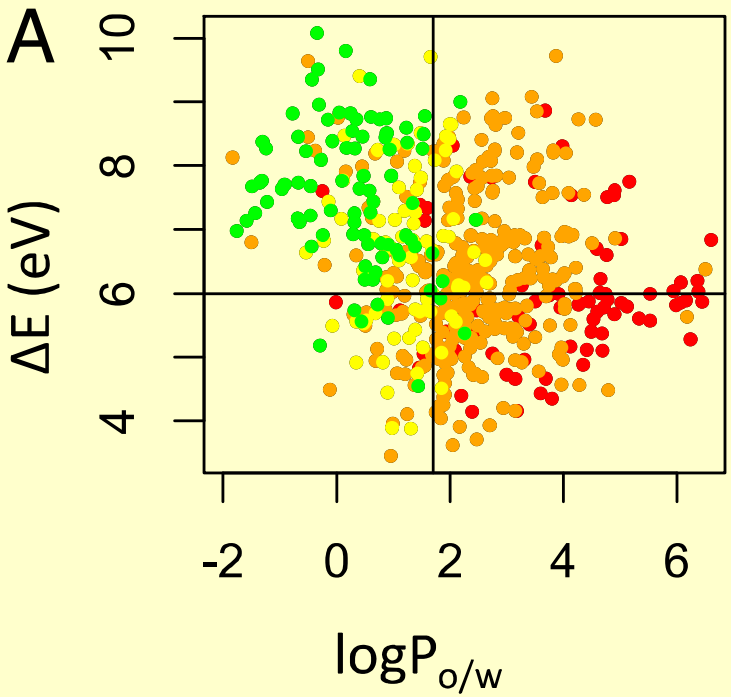


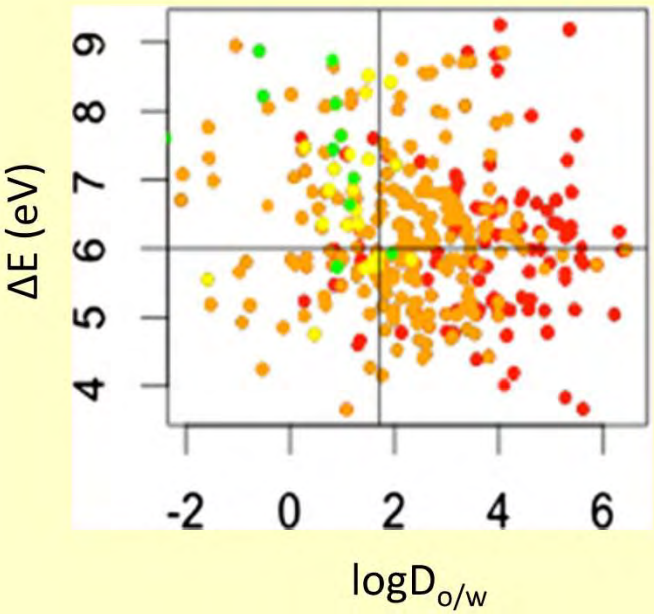
…carcinogens and radiation assumed to have no threshold

Newer ways to look at toxicity; U and J curves

Endocrine disruption, Epigenetics

Computational Toxicology: Voutchkova, et al., PNAS (2014)





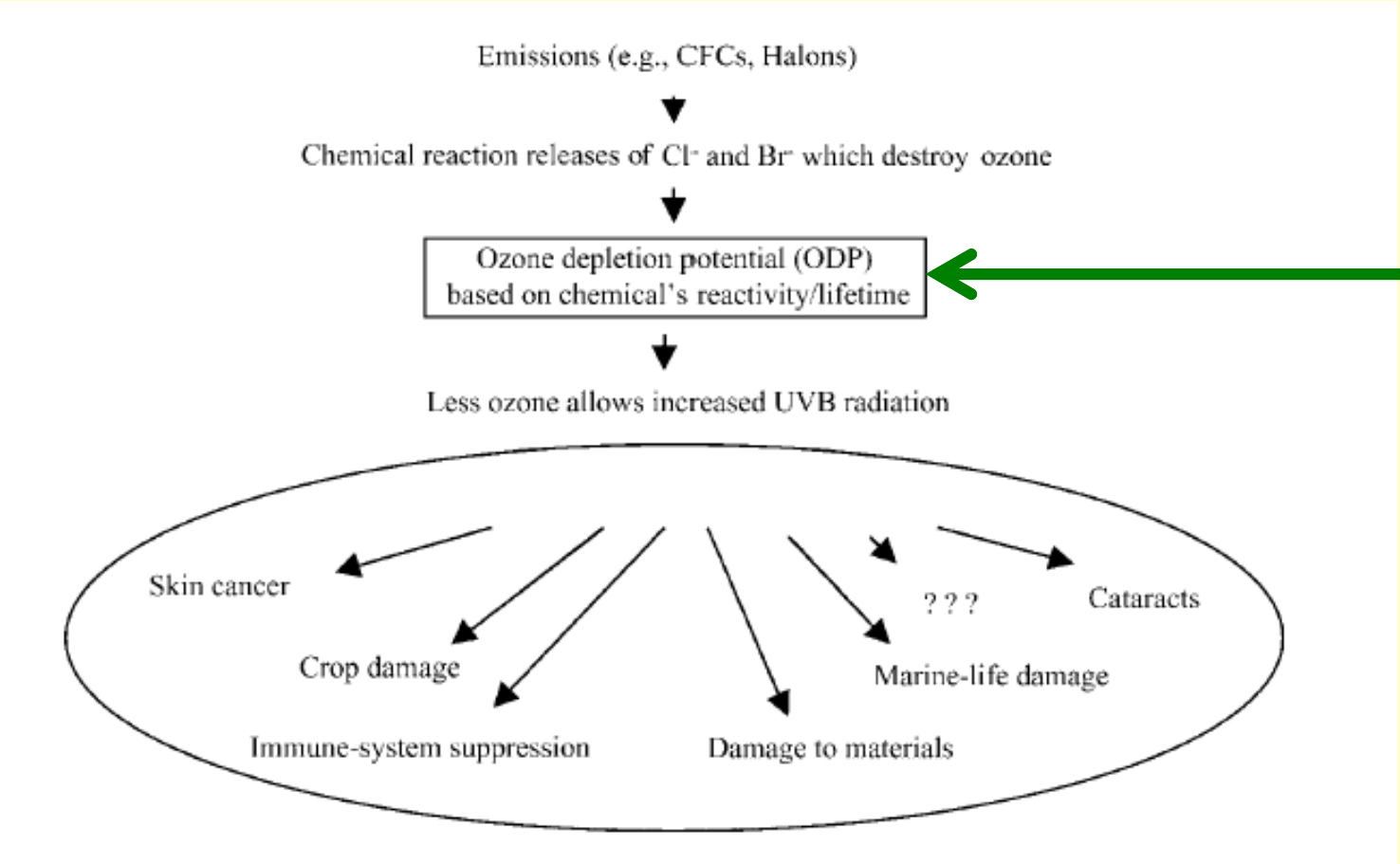
555 chemicals arranged by HOMO-LUMO difference versus LogP; colors represent degree of toxicity towards the fathead minnow

Similar plot for toxicity towards Daphnia Magna

Life Cycle Analysis Becomes a Viable Tool

TRACI: Tool for the Reduction and Assessment of Chemical and other Environmental Impacts

- C
- C
- S
- A
- E
- H
- H

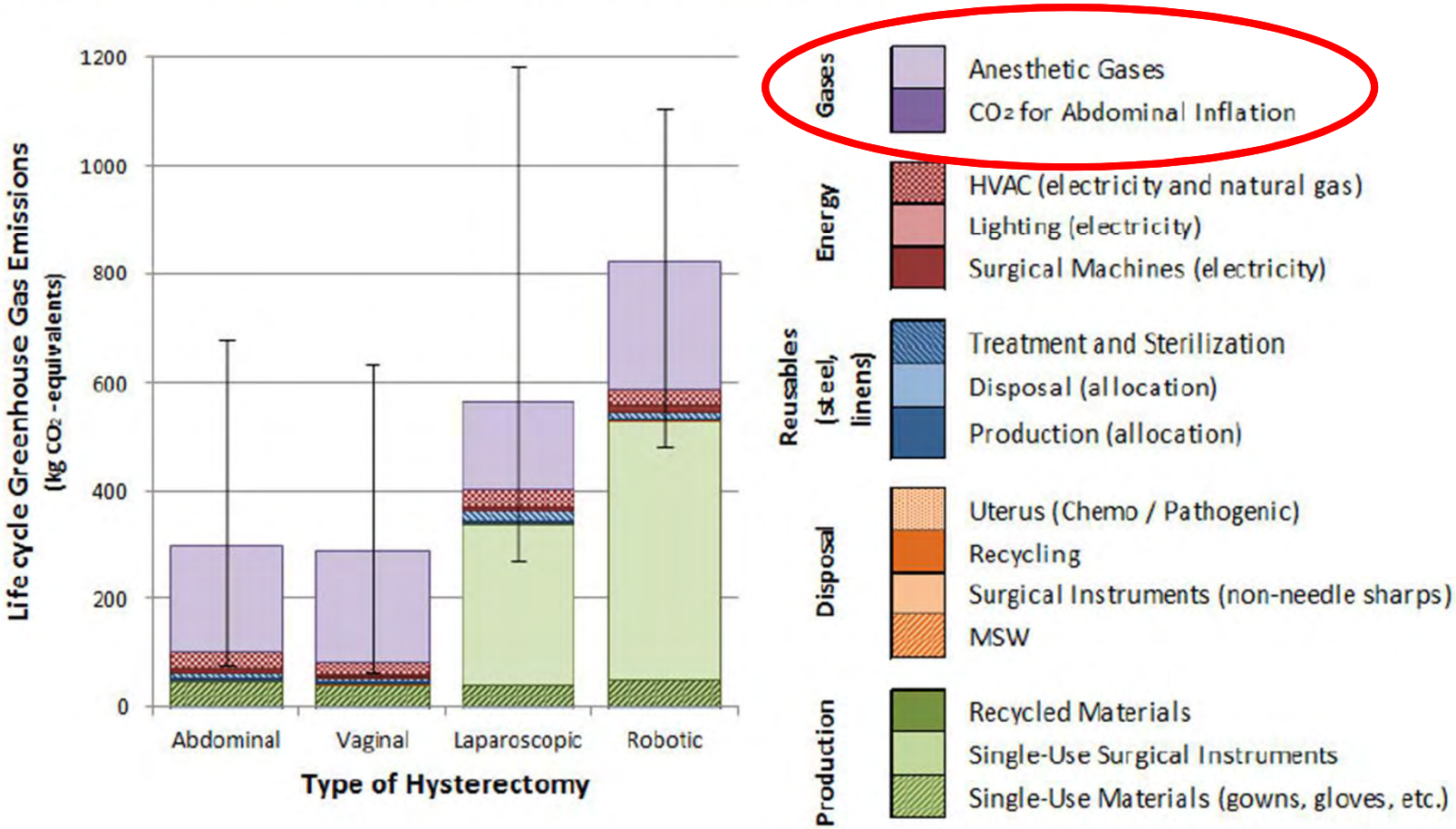


See Jane Bare, et al., *J. Industr. Ecol*. 2003, 6, 49

Melissa Bilec (UPitt, CEE): LCA applied to Healthcare

From Melissa Bilec's Group at UPitt

Figure 1: Life- Cycle Greenhouse Gas Emissions from an Average Abdominal, Vaginal, Laparoscopic, and Robotic Hysterectomy; error bars represent 90% confidence interval



Thiel, C.L., Woods, N., Landis, A.E., Eckelman, M.E., Guido, R., Sherman, J., Bilec, M.M. (2014 submitted). "Environmental Impacts of Surgical Procedures: Life Cycle Assessment of Hysterectomy in the US." Submitted to *ES&T.*

Anesthetics in Hysterectomies

Sevoflurane

130x CO_2

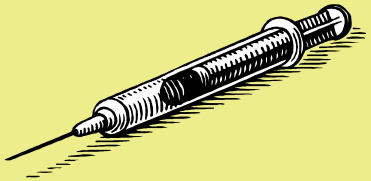
Desflurane

2500x CO_2

With Nitrous Oxide (N_2O)

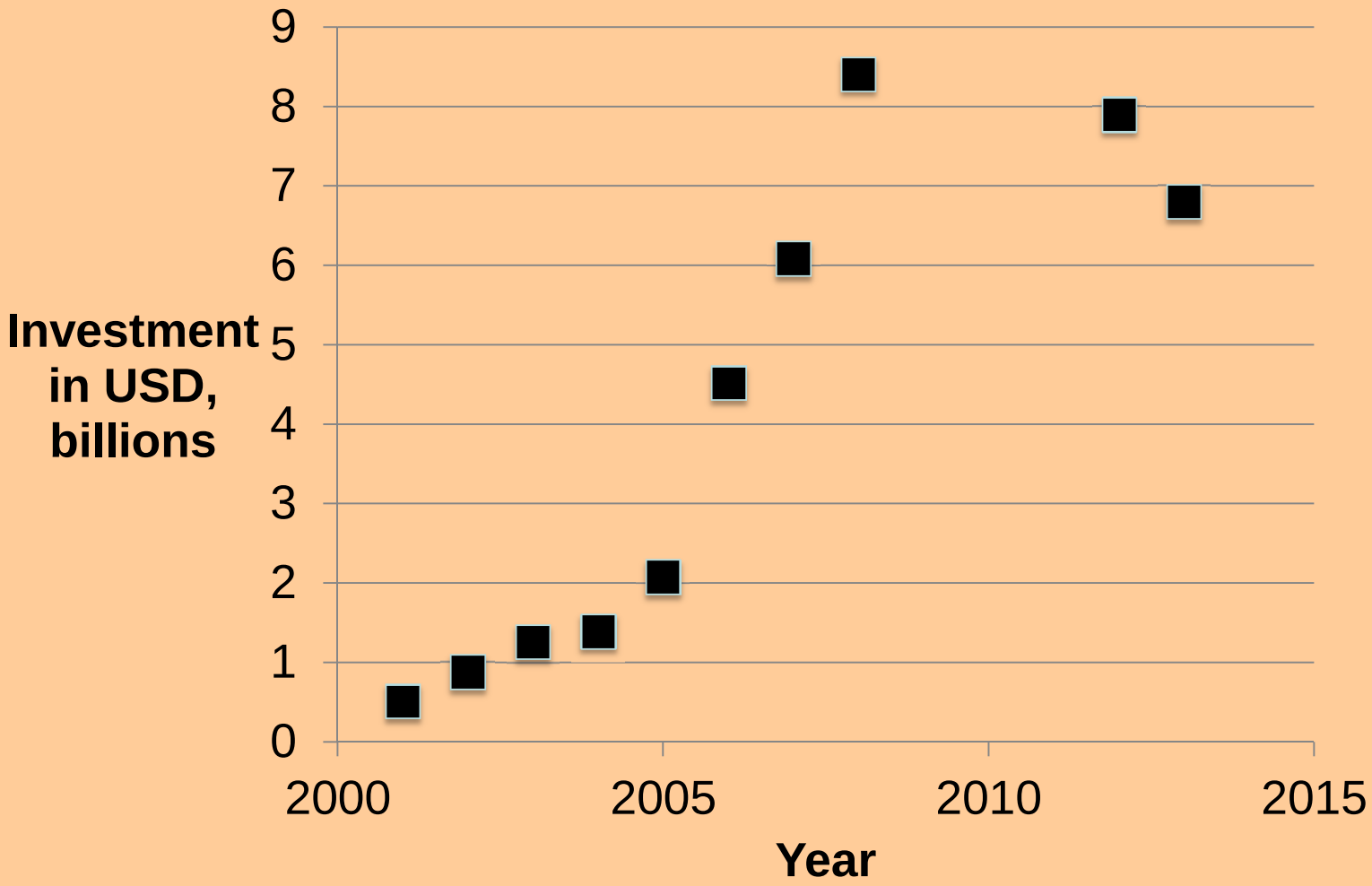
310x CO_2

Propofol



Not a GHG

The Cleantech Sector Didn't Really Exist Prior to 2000



Businesses Seeing Green Chemistry as “Good for Business”

Walmart puts product suppliers on notice about chemicals

By **Michelle Mauthe Harvey** and **Sarah Vogel**

Published February 27, 2014

Target, Wal-Mart, Whole Foods lead retail race to safer chemicals

Mark Rossi

Monday, November 18, 2013 - 6:30am

And yes, green-washing does irritate…

But it’s not anything we haven’t seen before.

Advertising is not supposed to inform, but rather to sell

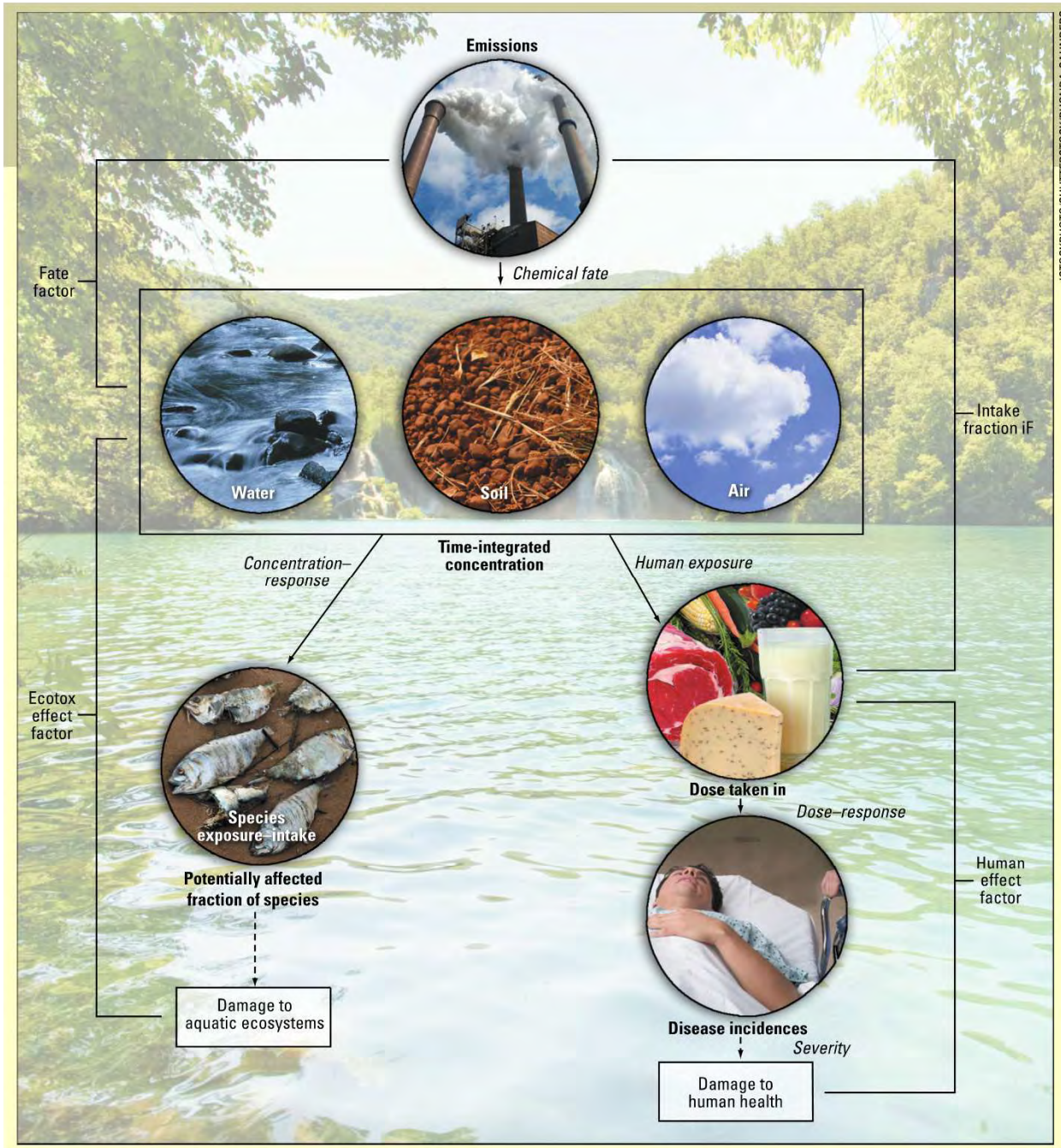
If it’s a significant business, there will be some “washing”

Themes: What Might We Accomplish in the Next 20 Years

- Resilience & Green Chemistry
- Eco-Innovation & Green Chemistry
  - Innovation by Elimination
  - Adapting Strategies from Other Industries

Resilience & Green Chemistry

Traditional Approach:



Risk = Hazard x Exposure

Minimize exposure through safety systems & *sometimes* product design. (reducing inherent hazard one of the 12 principles)

From Hauschild, et al., Envir. Sci. tech. (2008), 42, 7032

Also www.usetox.org

Reducing Risk Via Armoring

Resilience: Reducing the Consequences of Failure

***Resilience* is the capacity to adapt to changing conditions and to maintain or regain functionality and vitality in the face of stress or disturbance. It is the capacity to bounce back after a disturbance or interruption of some sort.**

From Fail-safe to Safe-fail

Ecological Resilience (Mount St. Helens, 1980)
(Photos from US Forest Service)

J. Liang, *Ecological Succession in Mount St. Helens*

Sapling breaking through ash layer (1980's)

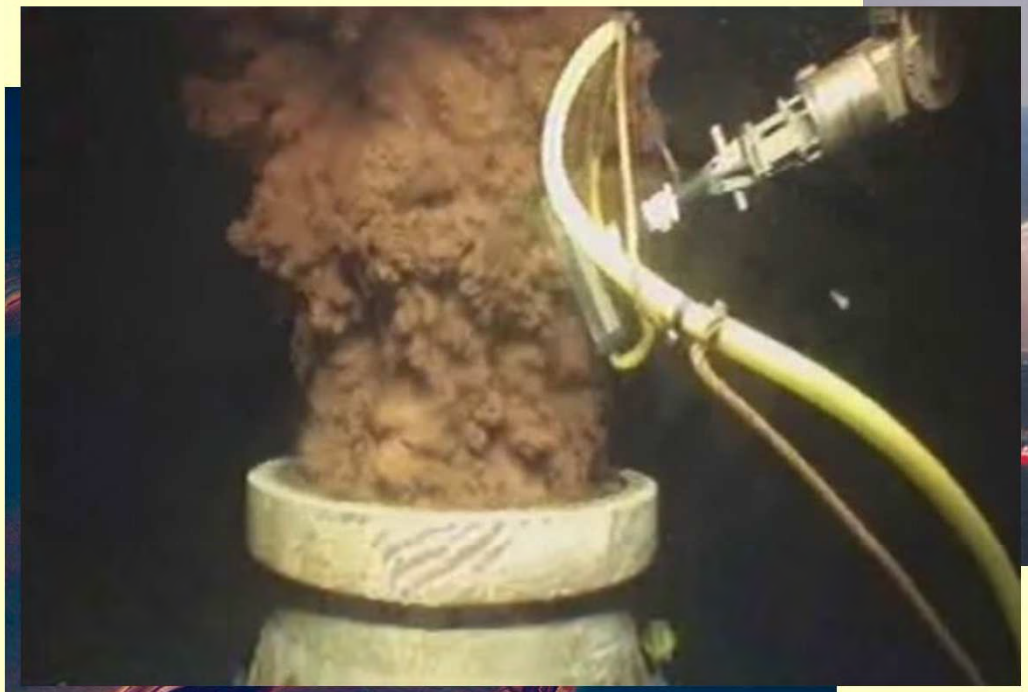
Lupines help fix nitrogen and improve soil fertility

Wildflowers re-cover pumice plain, 2004

Unfortunately, numerous examples of non-resilient (resistant) man-made systems

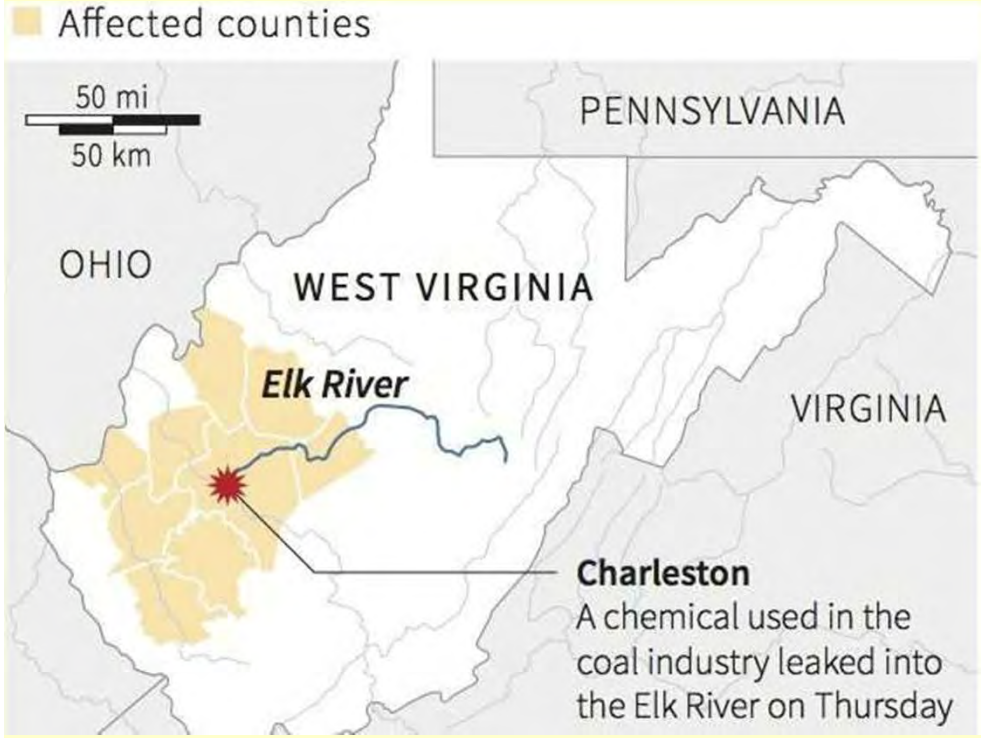
Atlanta: January, 28, 2014. Two inches of snow fall at an inopportune time (Tuesday afternoon & Wednesday morning), leading to massive gridlock

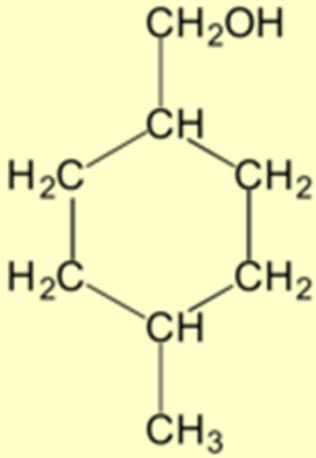
Macondo Well (Deepwater Horizon), April 20, 2010



11 dead, 4.9 million barrels of oil discharged, 87 days before well is capped

West Virginia, January 9, 2014: 48000 gallon tank of 4-methylcyclohexane methanol leaks into the Elk River (and then the Kanawha)





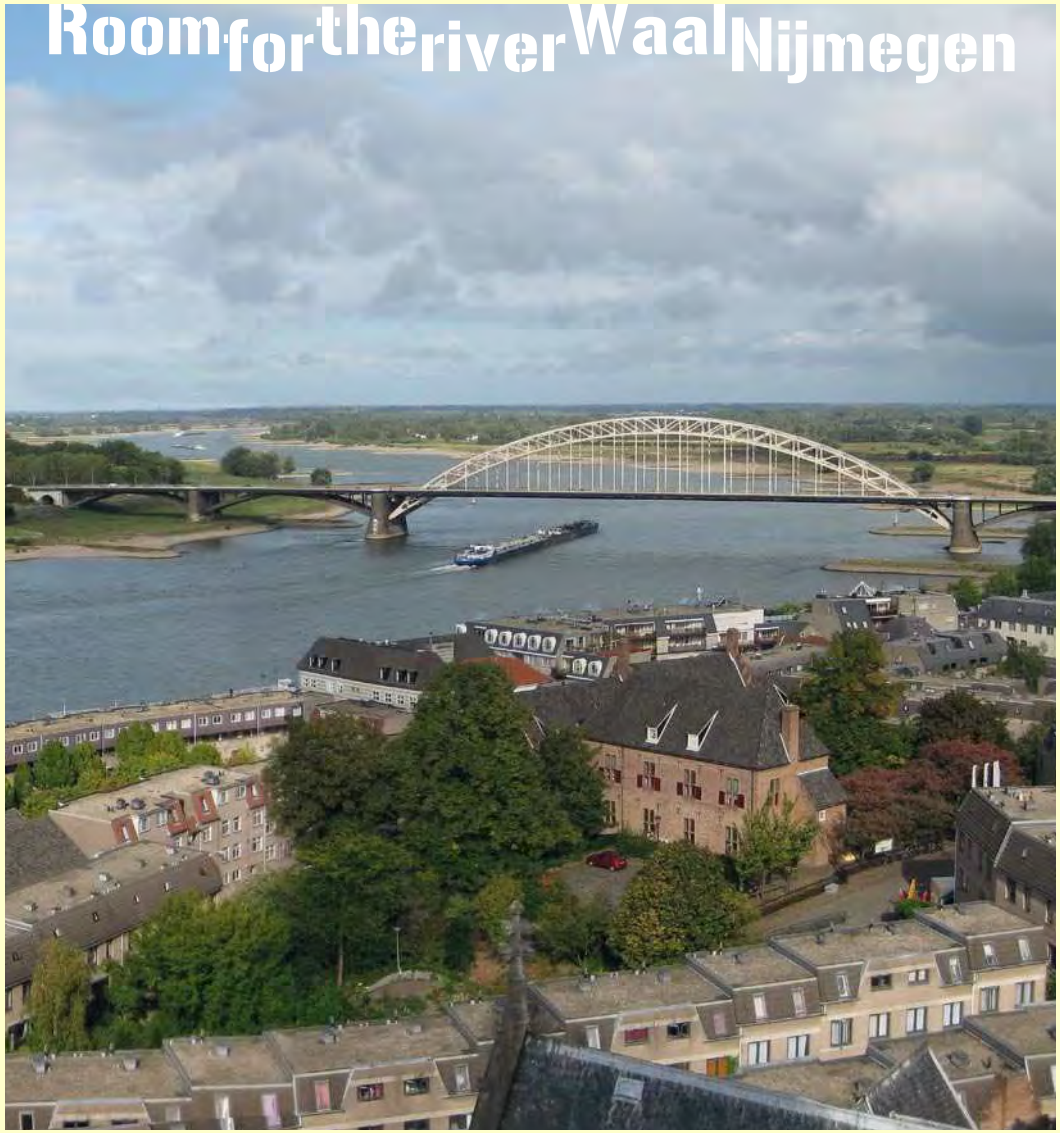
Little toxicity data available

300,000 impacted for weeks

Issues

- Traditional Fail-safe systems (try to minimize risk with armoring type systems).
- Multiple, seemingly unlikely events occur at the same time.
- Emergent behavior in complex systems makes prediction (modeling) of system behavior difficult.
- Failures in monitoring & adaptation.

Resilient Design: Dealing with Flooding in Nijmegen (Neth.)



Nijmegen: Making Room for the Waal

The present situation with the existing dike.

The dike is to be moved 350 metres inland.

An ancillary channel is to be dug in order to give the river more room. This will create an elongated island.

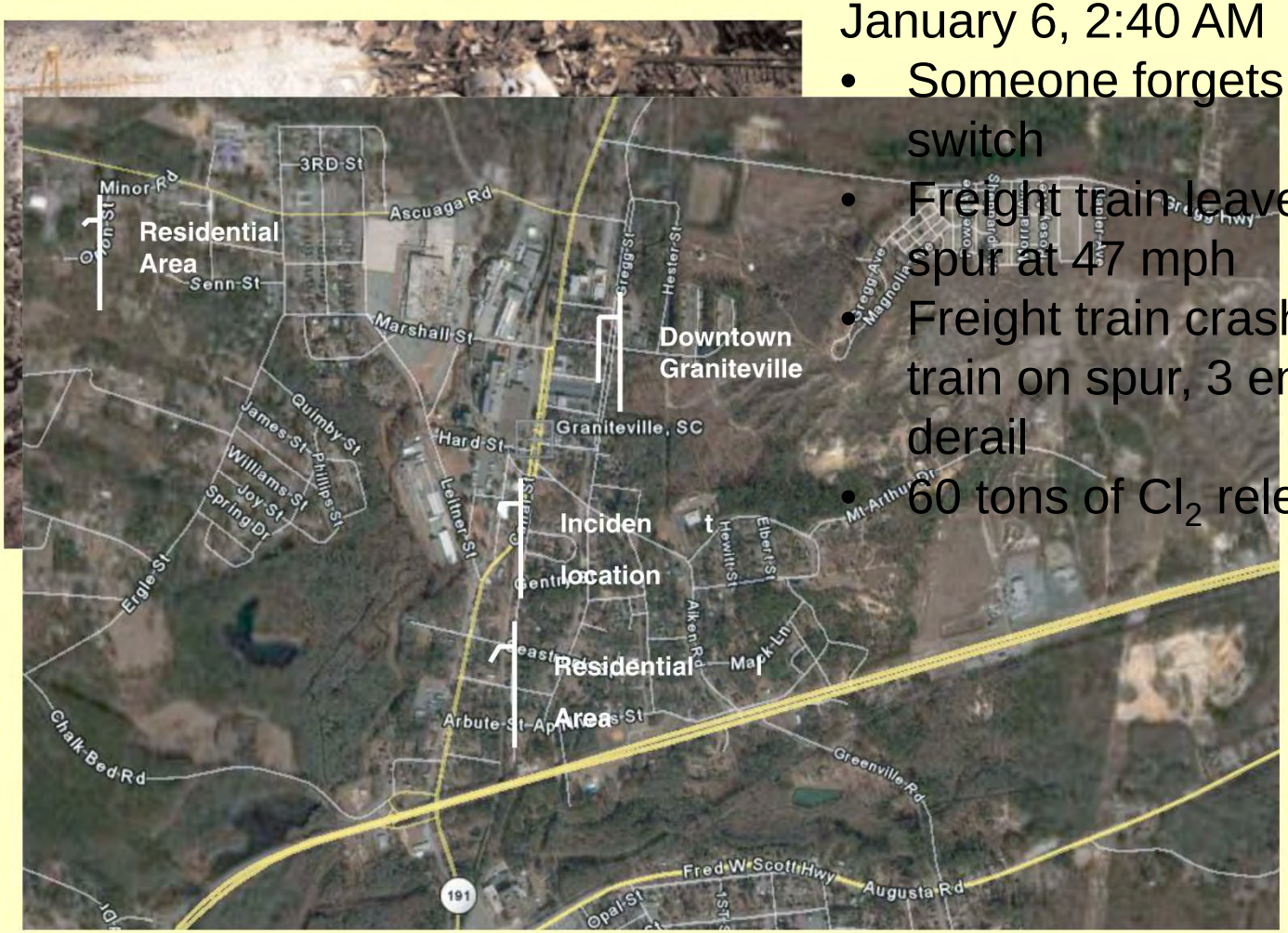
Bridges across the ancillary channel.

Resilience & Green Chemistry

- Resilience in context of green chemistry:
  - Current systems resistant – many layers of safety systems, yet often we include disruption amplifiers (highly dangerous compounds)
  - Disruption includes safety disasters & loss of critical materials (supply chain disruption)
  - To transform requires real innovation

Chlorine spill, Graniteville, SC (2005)

(Dunn & Oswalt, Northern Arizona University)



January 6, 2:40 AM

- Someone forgets to toggle a line switch
- Freight train leaves main line onto spur at 47 mph
- Freight train crashes into parked train on spur, 3 engines and 18 cars derail
- 60 tons of Cl_2 released

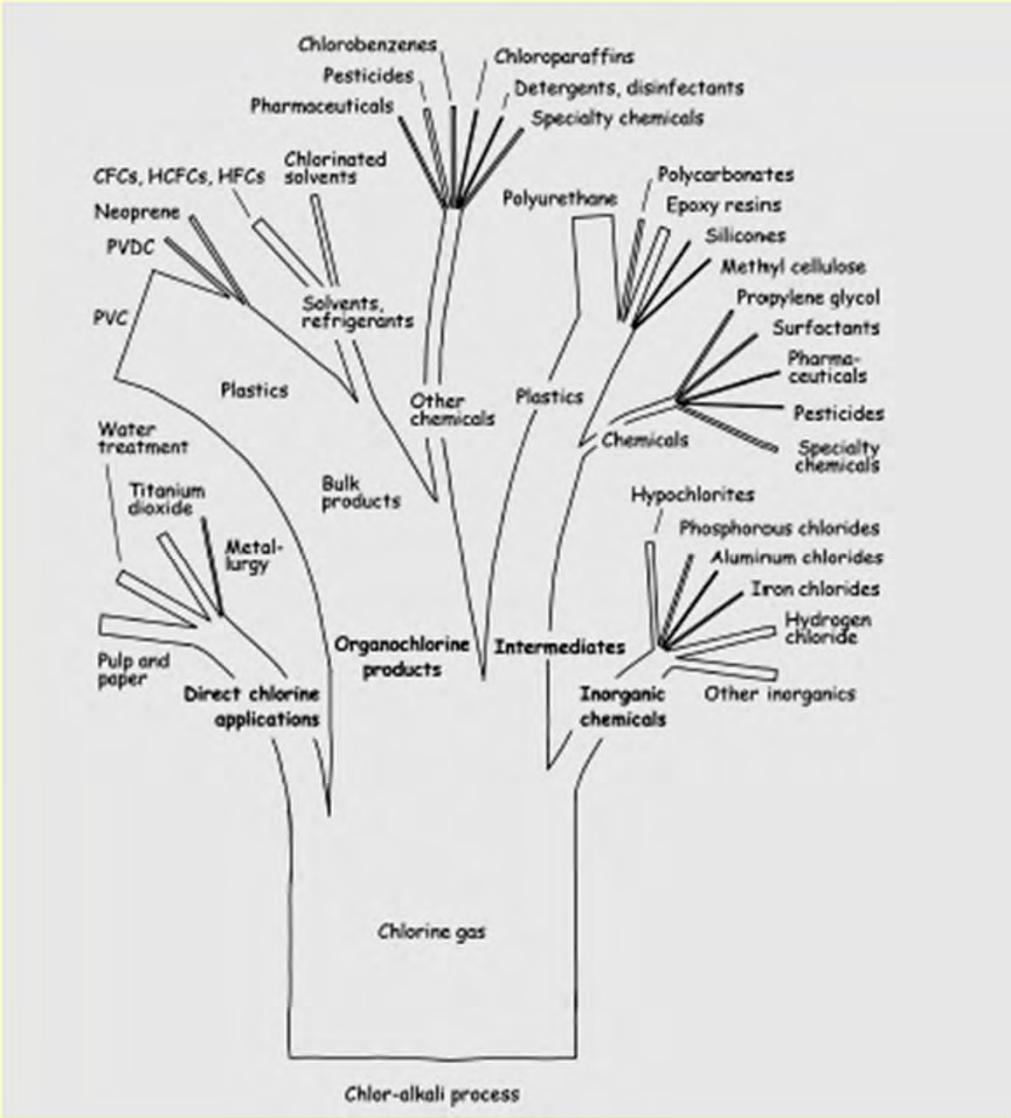
9 dead, 550 to hospitals

Chemicals that most frequently create accident risks.

Chemical	Number of Processes	Percentage of Total
Ammonia (anhydrous)	8343	32.5
Chlorine	4682	18.3
Flammable Mixtures	2830	11
Propane (industrial use)	1707	6.7
Sulfur Dioxide	768	3
Ammonia (aqueous 20% or more conc.)	519	2
Butane	482	1.9
Formaldehyde	358	1.4
Isobutane	344	1.3
Hydrogen Fluoride	315	1.2
Pentane	272	1.1
Propylene	251	1
Methane	220	0.9
Hydrogen	205	0.8
Isopentane	201	0.8
All Others	4139	16.1
Total	**25636**	**100%**

From Paul Anastas

Chlorine



~ 45 million tons of Cl_2 produced annually (using 1-2% of global electricity production), many applications

Sometimes chlorine is in the product, sometimes only in the process.

Replacing chlorine gas with better alternatives

- Liquid bleach instead of Cl_2
- Calcium Hypochlorite
- UV light
- On-site generation of Cl_2 as needed
- Elimination of Cl_2 in paper processing (H_2O_2, other methods)
- Flexys process for synthesis of 4-aminodiphenylamine via direct coupling of aniline & nitrobenzene; no chlorobenzene intermediate.
- Collins work on TAML activators & H_2O_2 to replace chlorine in oxidations.
- Alternatives to PVC

Enhancing Resiliency by Replacing Inherently Unsafe Chemicals

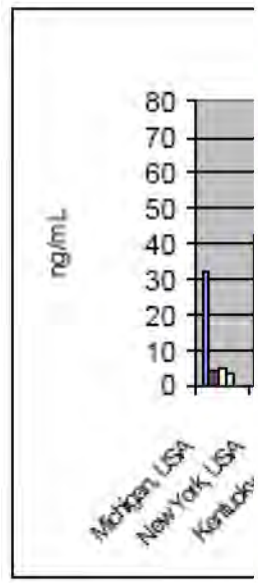
- HCN
- HF
- Phosgene
- SO_2
- Sulfuric acid
- Ammonia

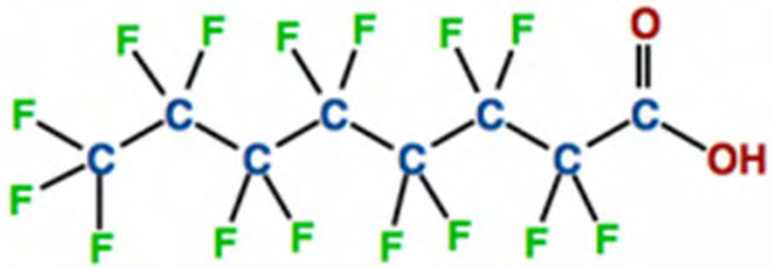
"*What you don't have, can't leak*."*

* Kletz, T.A., Chemistry and Industry, 1978: p. 287-292.

Long-term “leakage” = lack of resilience?

Figure 0.1: Human blood levels of PFOS-related substances in various countries





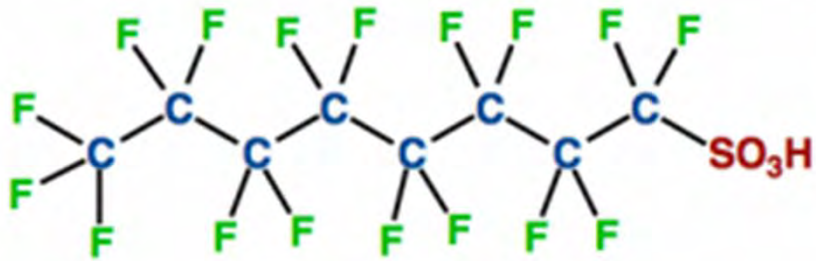


Table 6.4: max. cor
animal tissues

Species				
Marine mammals	1520 (77%)	41 (4%)	880 (15%)	86 (10%)
Mink and Otter	4900 (100%)	110 (11%)	680 (11%)	85 (10%)
Birds	2570 (60%)	440 (4%)	530 (10%)	185 (11%)
Fishes	1000 (38%)	46 (2%)	120 (9%)	20 (3%)

Miljeproject 1013, Dutch Env. Prot. Agency, “More Environmentally Friendly Alternatives to PFOS-Compounds and PFOA”, (2004)

Resilience Issues in the Business World: Complex Supply Chains

Major mobile phone rivals; both get chips from Philips plant in Albuquerque, NM.

3/17/2000; lightning strikes (literally), fire at the Philips plant.

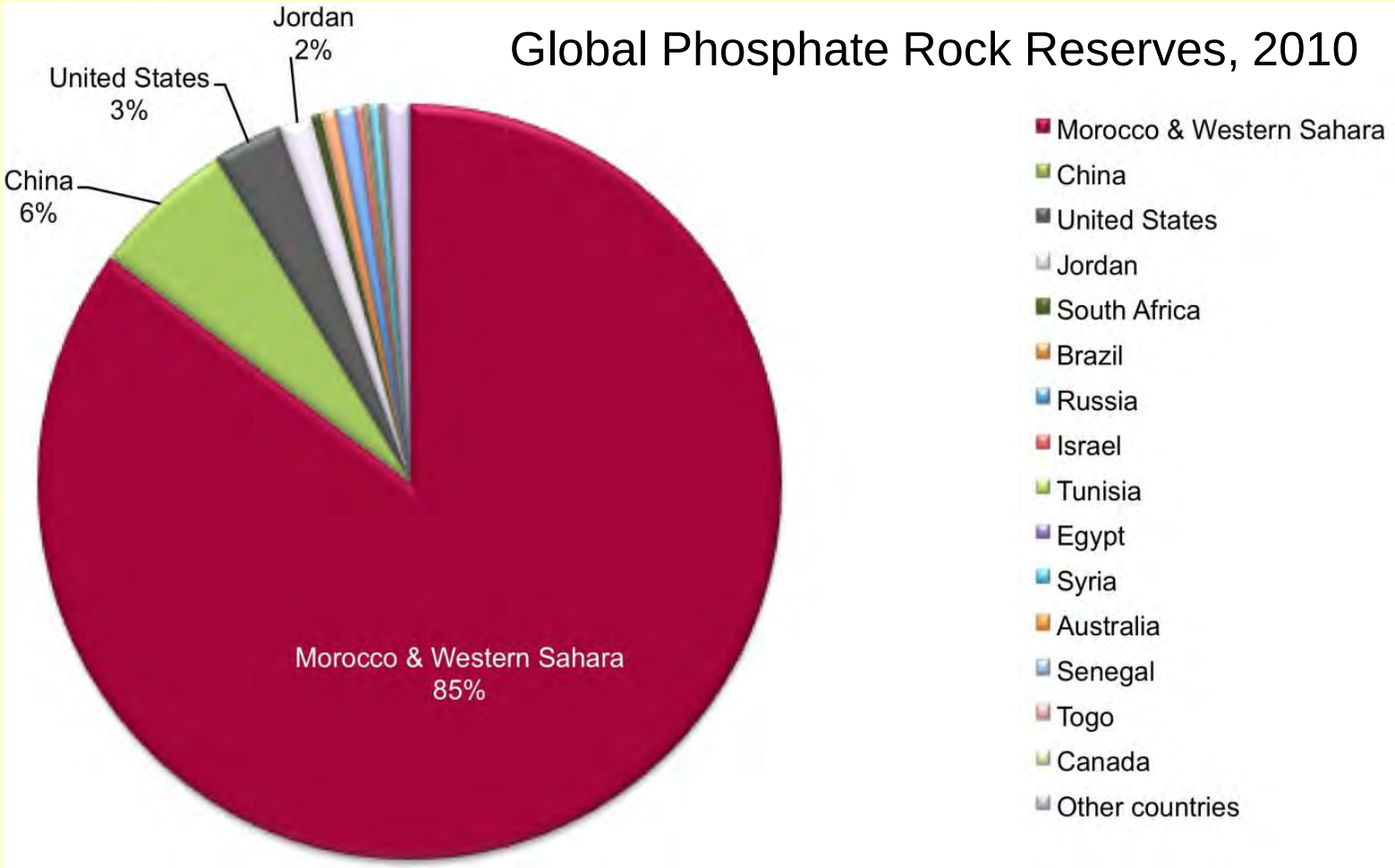
Damage to clean rooms, entire stock of chips damaged by water & smoke

Philips informs both customers that the plant will be down for 1 week

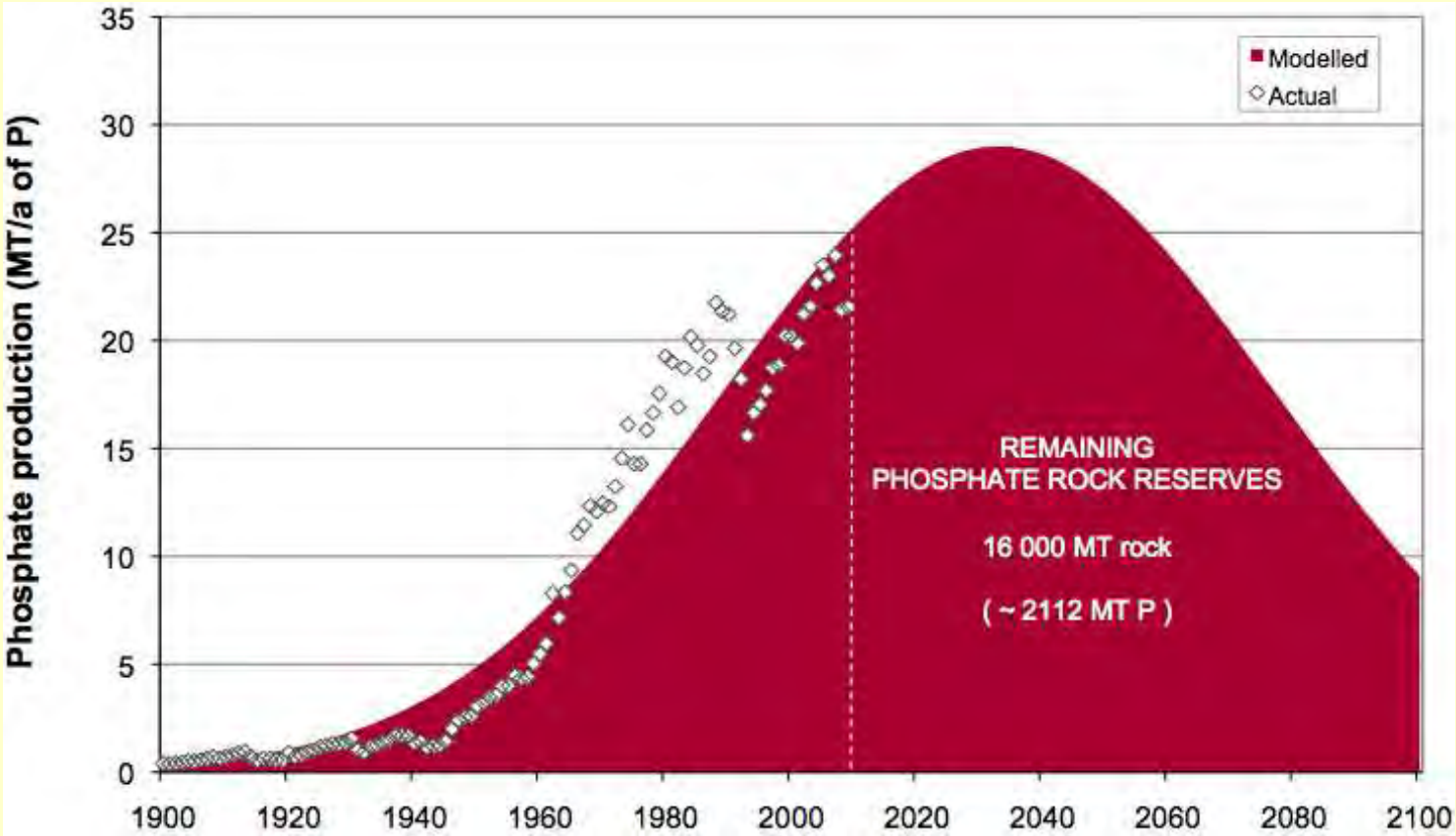
- Ericsson:
  - Accepts Philips assurances on downtime.
  - Decides to wait out the interruption.
  - Realizes too late that Philips' projection is wrong.
  - Loses market share permanently
- Nokia
  - Sent team to assess damage at Albuquerque plant.
  - Tied up spare capacity at other Philips plants.
  - Re-engineered phones to accept other chips.
  - Gained market share.

[from AS Mukherjee, *The Fire that Changed an Industry*, Financial Times 10/1/2008]

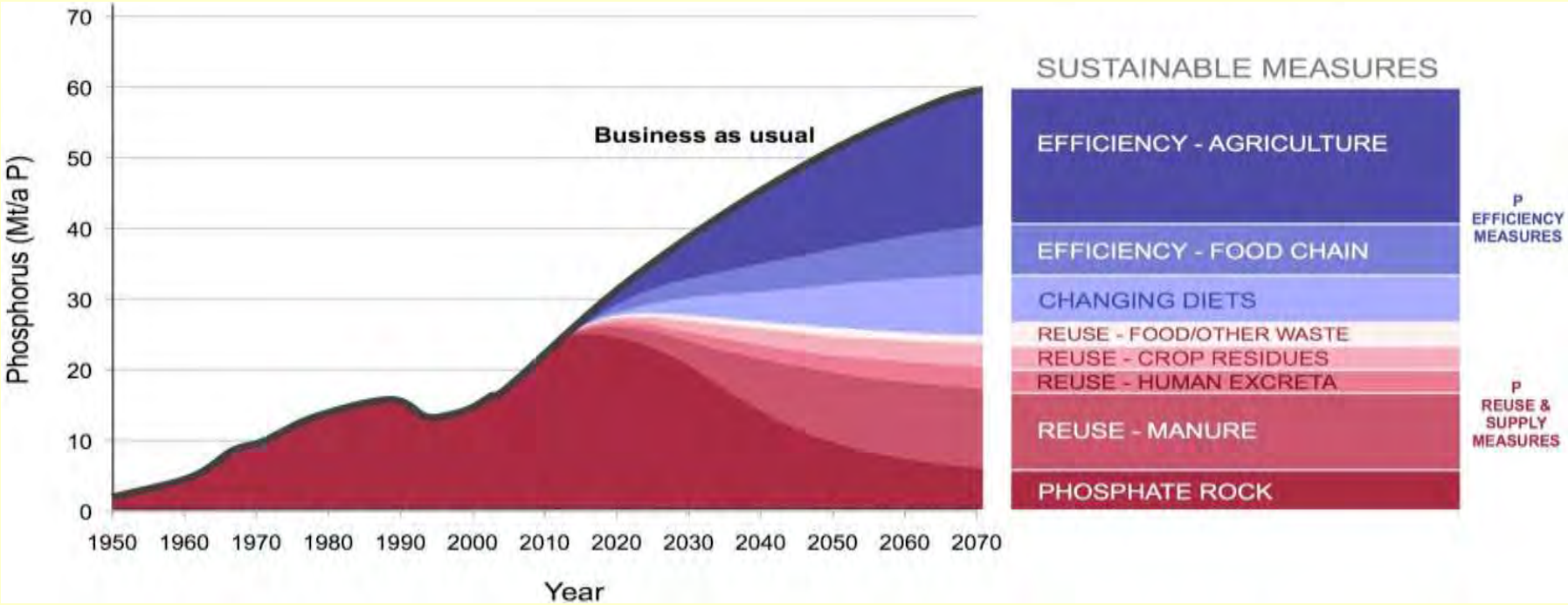
Another Challenge to Resiliency: Critical Materials



Ultimately, we will face peak phosphorous



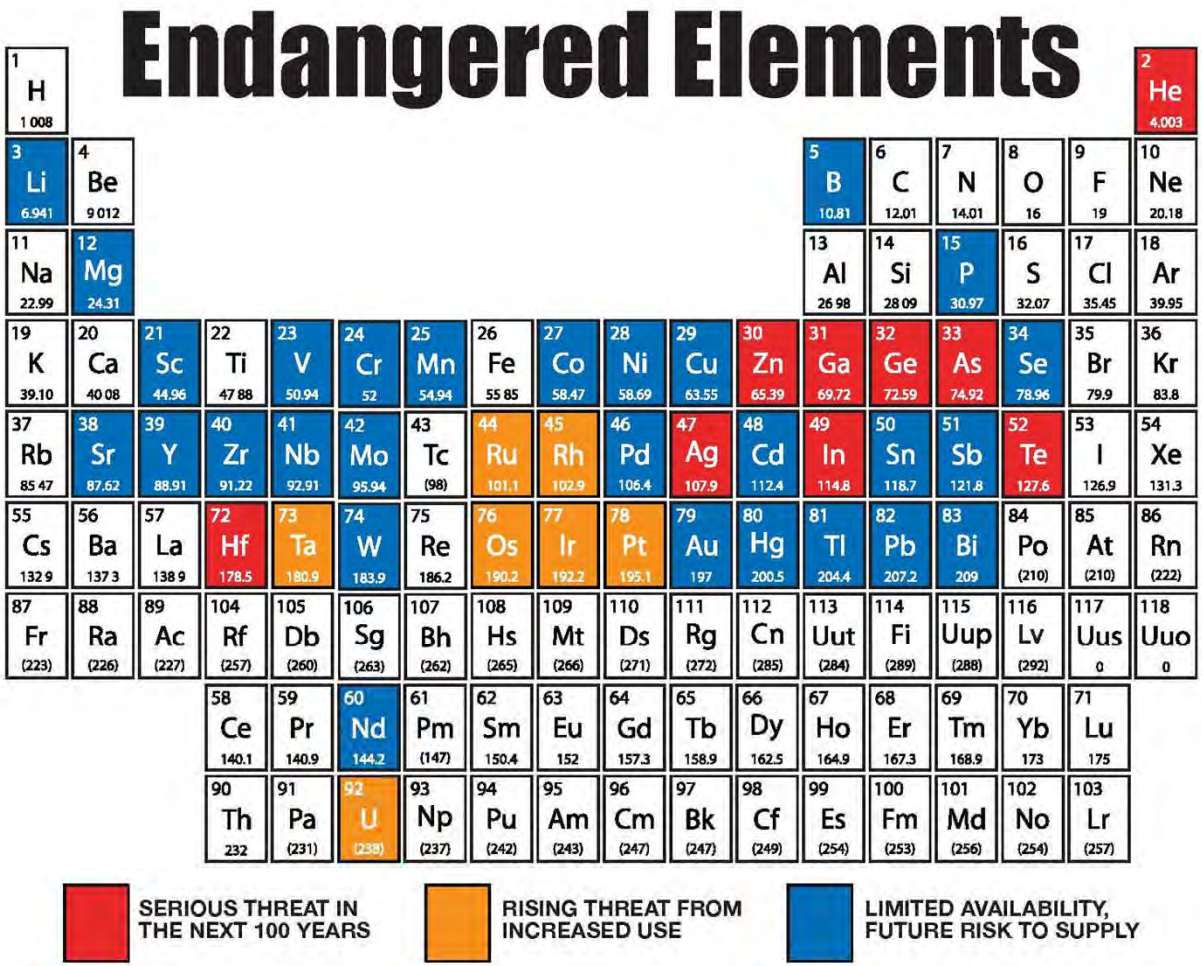
Addressing the issue will include multiple strategies



Cooper, et al, *Res., Conserv. & Recycl*. (2011), 57, 78-86

Cordell & White*, Sustainability* (2011), 3, 2027-2049

American Chemical Society Projects a Number of Endangered Elements (2014)

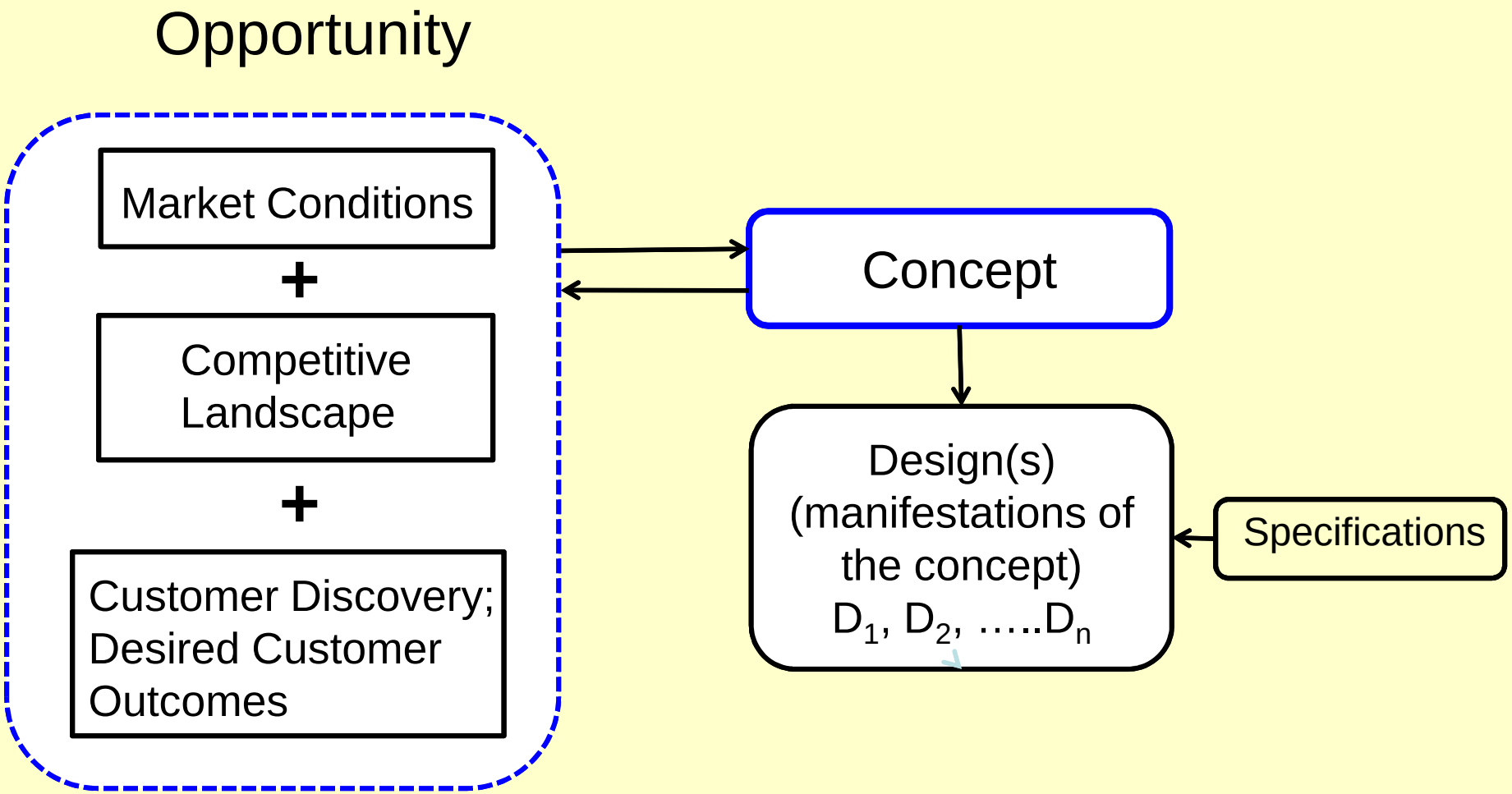


Risk Management vs. Resilience: Brief Summary

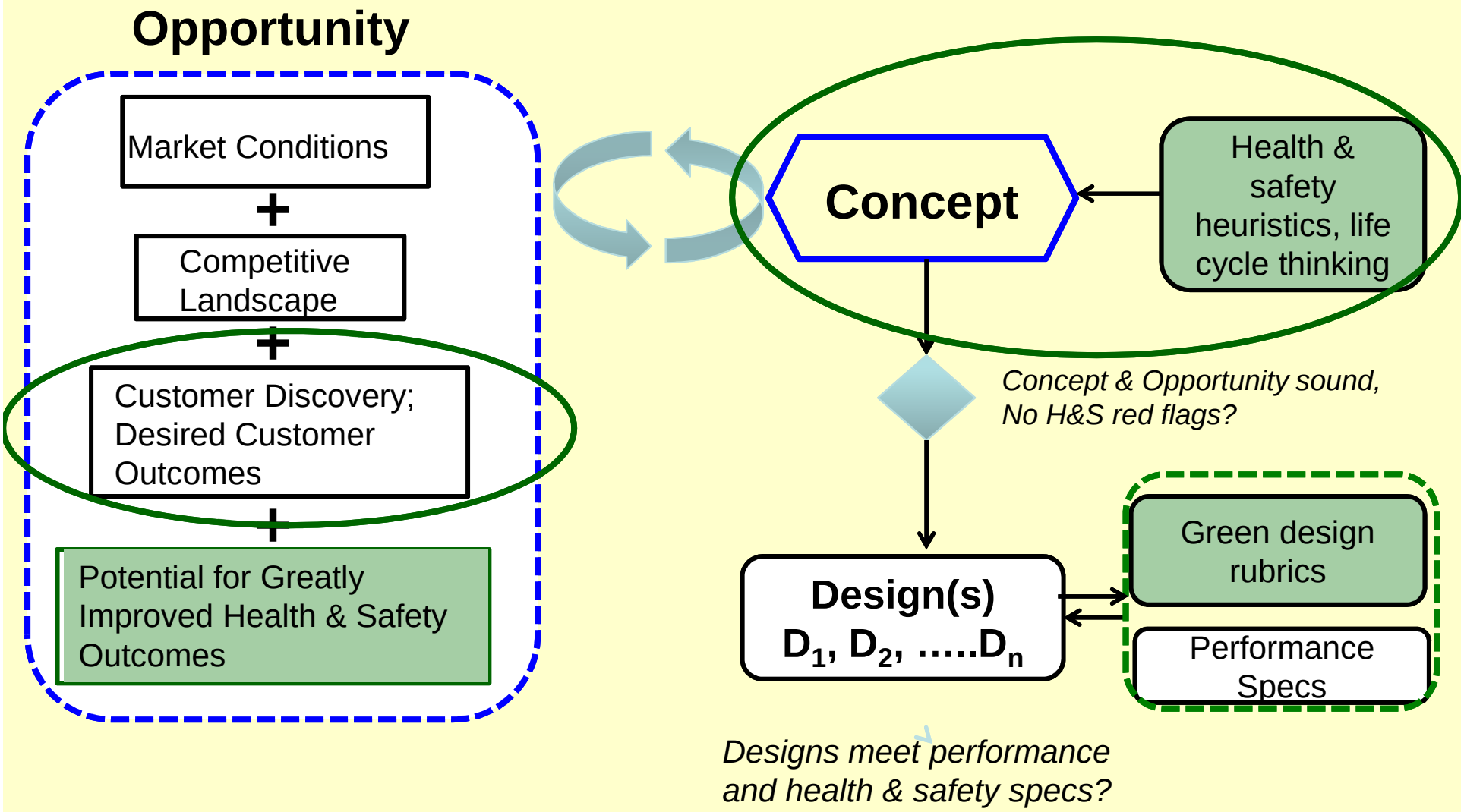
	Risk Management	**Resilience**
Design Principles	Preservation of status quo; minimize risk of failure	Adaptation to changing conditions without permanent loss of function
Design Objectives	Minimize the probability of failure	Minimize the consequences of failure
Relationship to Sustainability	Security, longevity	Recover, renewal, innovation

Eco-Innovation & Green Chemistry

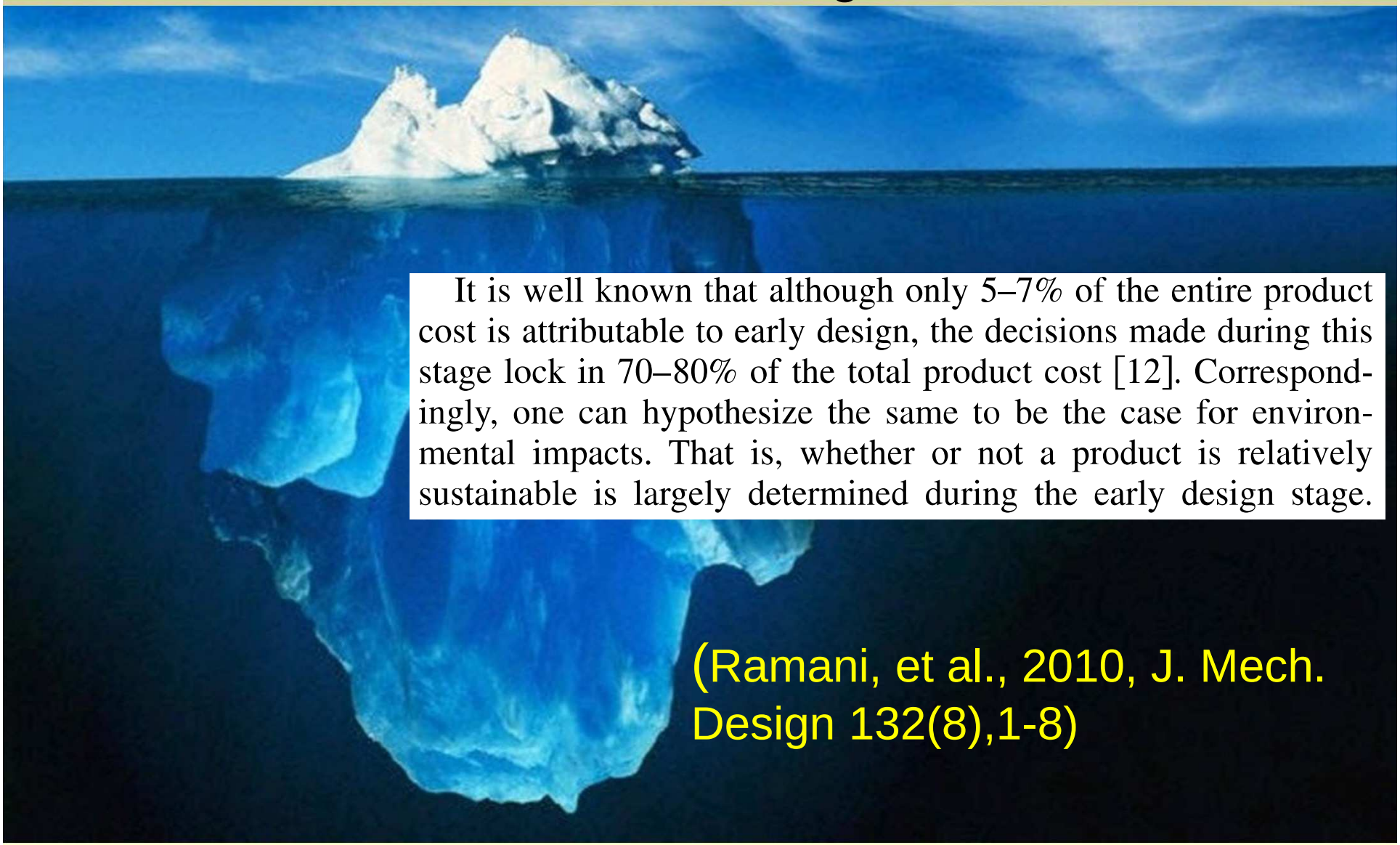
Opportunity, Concept Creation & Design



Adding "Green" Thinking to the Process



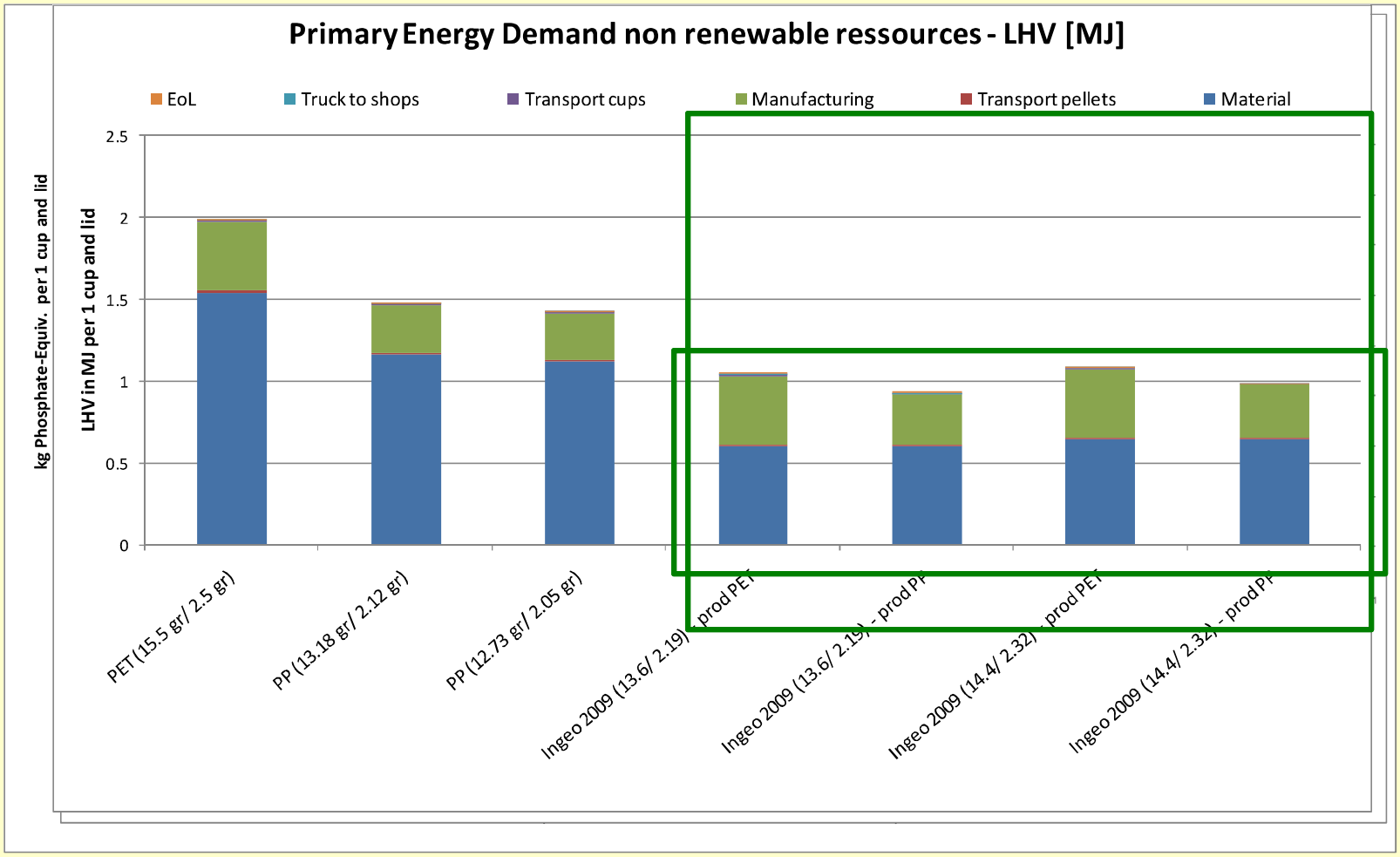
Embedded Impacts Take Shape During the Concept Formation Stage



It is well known that although only 5–7% of the entire product cost is attributable to early design, the decisions made during this stage lock in 70–80% of the total product cost [12]. Correspondingly, one can hypothesize the same to be the case for environmental impacts. That is, whether or not a product is relatively sustainable is largely determined during the early design stage.

(Ramani, et al., 2010, J. Mech. Design 132(8),1-8)

Why Innovation: Dealing with Trade-offs

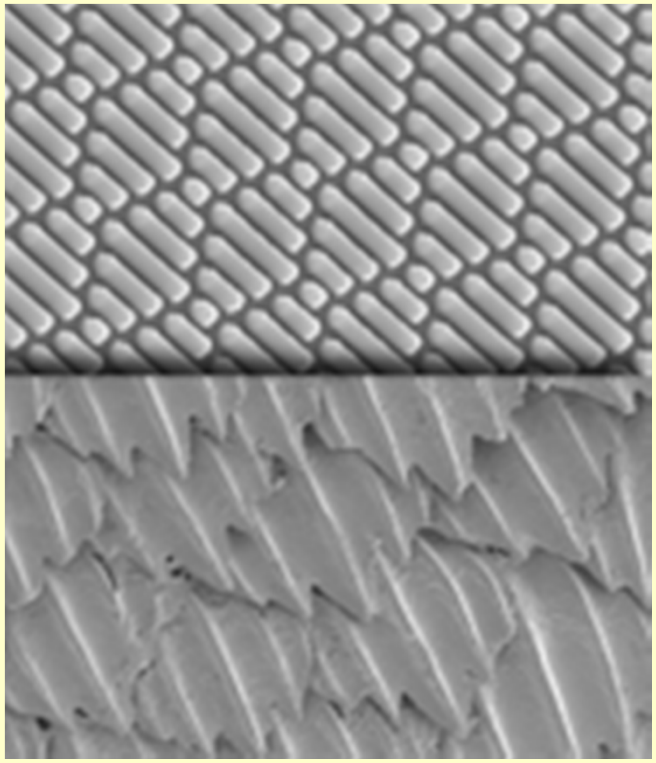


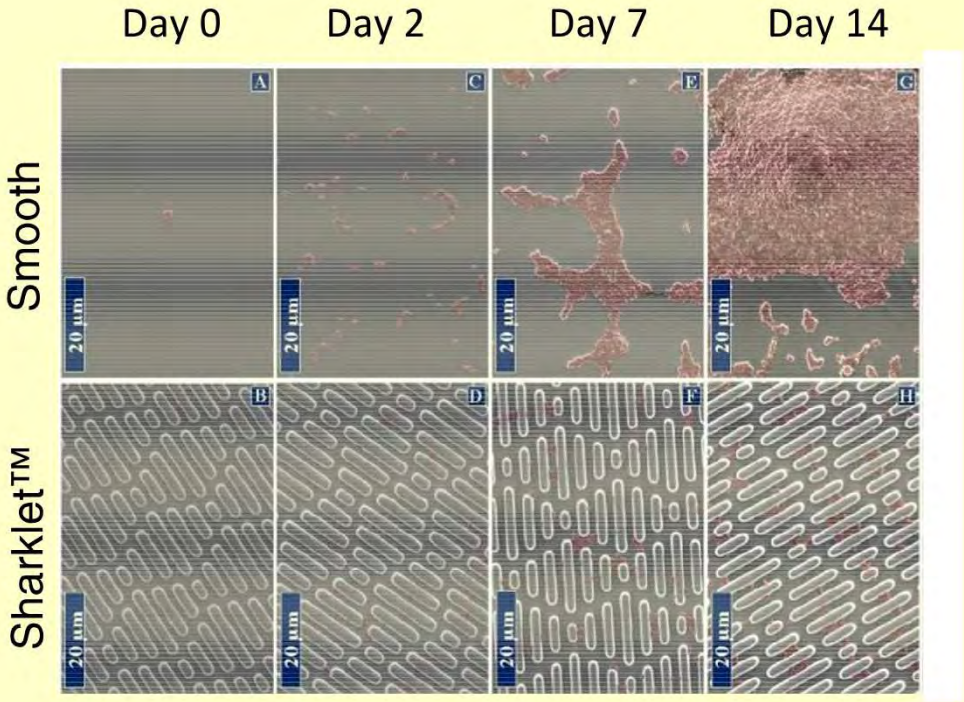
Comparative LCA: Ingeo biopolymer, PET, and PP Drinking Cups, PE Americas (2009)

Bacteria on surfaces; desired outcome is no bacteria on surfaces

Desired outcome is no bacteria

Sharklet Technologies (Aurora, CO) patterned surface





Shark skin: Very low surface frictional drag;
B. Dean & B. Bhushan, *Phil. Trans. Roy. Soc. A* (2010); 368, 4775-4806

Concept versus Design

Example: Desired customer outcome = “no bacteria on surfaces”

Concept 1: = “anti-bacterial spray”

Design 1A = spray of triclosan + ethanol
Design 1B = spray of lactic acid/water

Concept 2: “Anti-bacterial surface”

Design 2A = ammonium chloride-functional acrylic coating
Design 2B = Coating impregnated with silver nanoparticles
Design 2C = shark scale mimic (Sharklet, Aurora, CO)

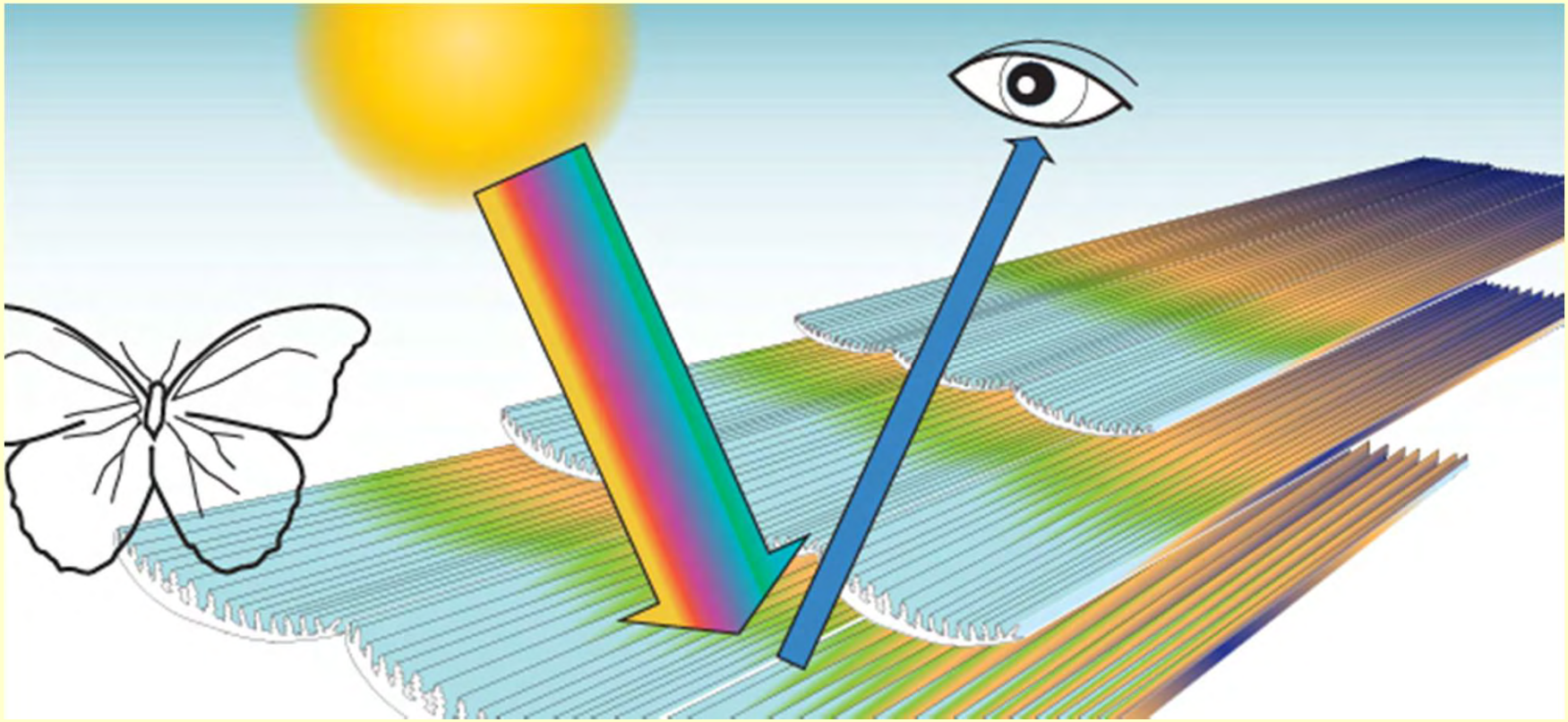
Concepts can be chemical or “non-chemical”

Xenex’s “Violet” robot in an OR at the University of Pittsburgh Medical Center.

Desired outcome is “color”; current method is to use pigments

Synthetic organic dyes, mixed-metal pigments (Fe, Cr, Ni, Sb, Ti, Co, Zn)

The Morpho Butterfly



MorphoTex (Teijin Fibers)

Bio-based Ethanol

Switchgrass or waste cellulose

Corn as feedstock

Employ Cyanobacteria to Generate Ethanol

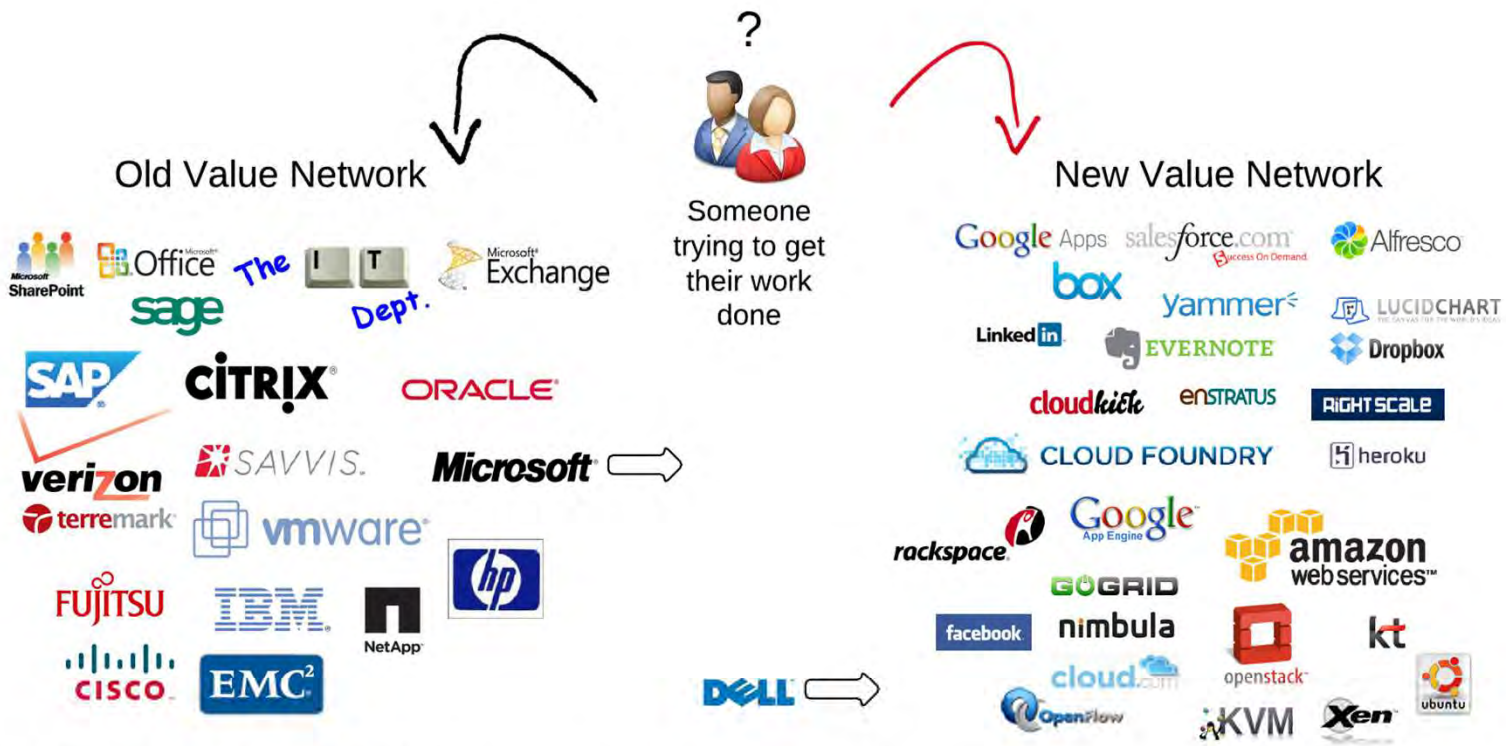
Cyanobacteria 40 μm

Bacteria employ CO_2 & sunlight as feedstocks;

Joule Unlimited (Bedford, MA) is in process of plant scale-up.

Eco-Innovation & Green Chemistry: Can we adapt trends from “non-chemical” businesses?

Products Become Services: Transformation of the Digital Economy



- Perception of value: infrastructure is very important
- Infrastructure/Operations centric
- Serves established markets (Enterprise IT dept)
- Commercialises sustaining technologies
- Built around: Products (hardware, licenses, contracts)
- Typical cost structures: high margin
- Dominant technology stack: Purpose-built, integrated
- Design practices: Scale Up, N+1
- Typical App Delivery: Private Network

- Perception of value: infrastructure should be invisible
- Application centric
- Serves emerging markets (developers/startups)
- Commercialises disruptive technology
- Built around: Services (Utilities, Subscriptions)
- Typical cost structures: low margin
- Dominant technology stack: Commodity, Open Source
- Design practices: Scale Out, Design for Failure
- Typical App Delivery: Internet

One’s personal music library was once a product; now it is primarily a service

Can a Molecule be a Service?

Some metals are becoming services: Aluminum

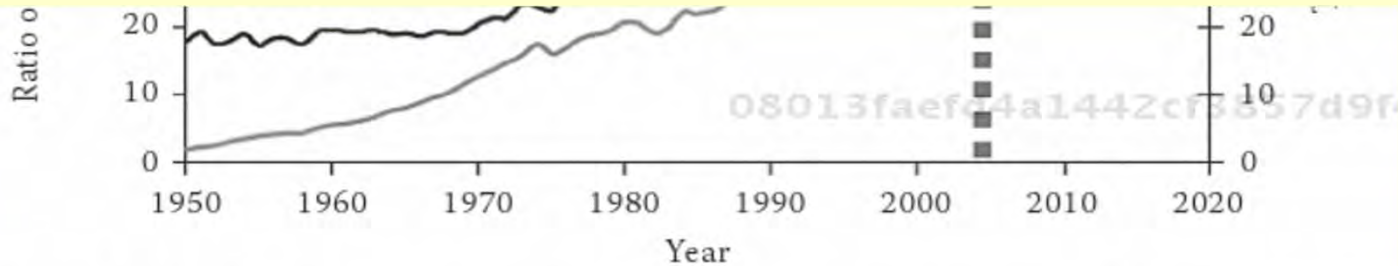
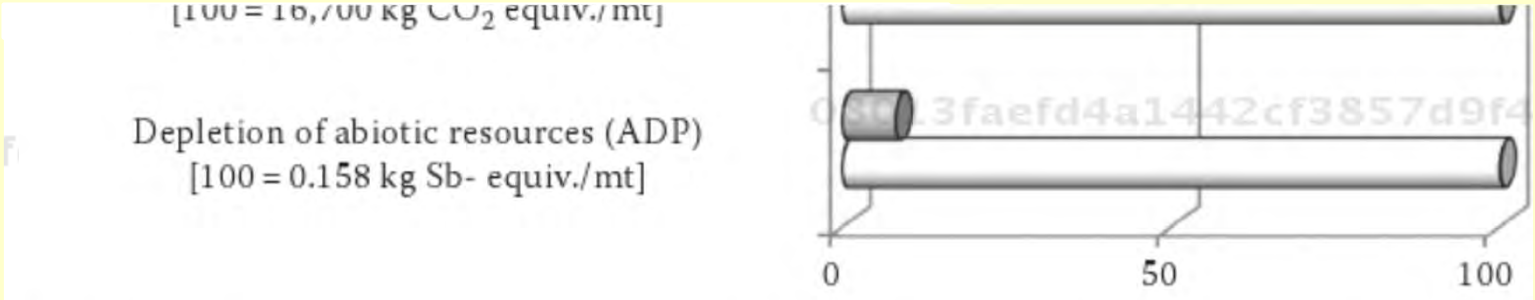


FIGURE 1.1 Total aluminum production and percent from primary and secondary sourc
(From Organization for Economic Cooperation and Development [OECD], Materi
case study 2: Aluminium, in *OECD Global Forum on Environment*, October 25, 20
http://www.oecd.org/environment/resourceproductivityandwaste/46194971.pdf.)

Global

This book will lead readers through the sequence used for recycling scrap a
minum. It will start with a description of the *minerals* (aluminum alloys) that
contained in the ore body and describe the various locations where aluminum scr
is found. It will then describe the practice te inum
other materials with which it is mixed and the means for purifying it of coatings a
other impurities. Subsequent chapters will describe the furnaces used for remelti
the recovered scrap and the refining techniques used for improving its purity a

Aluminum Recycling Saves Money & Reduces Life Cycle Impacts



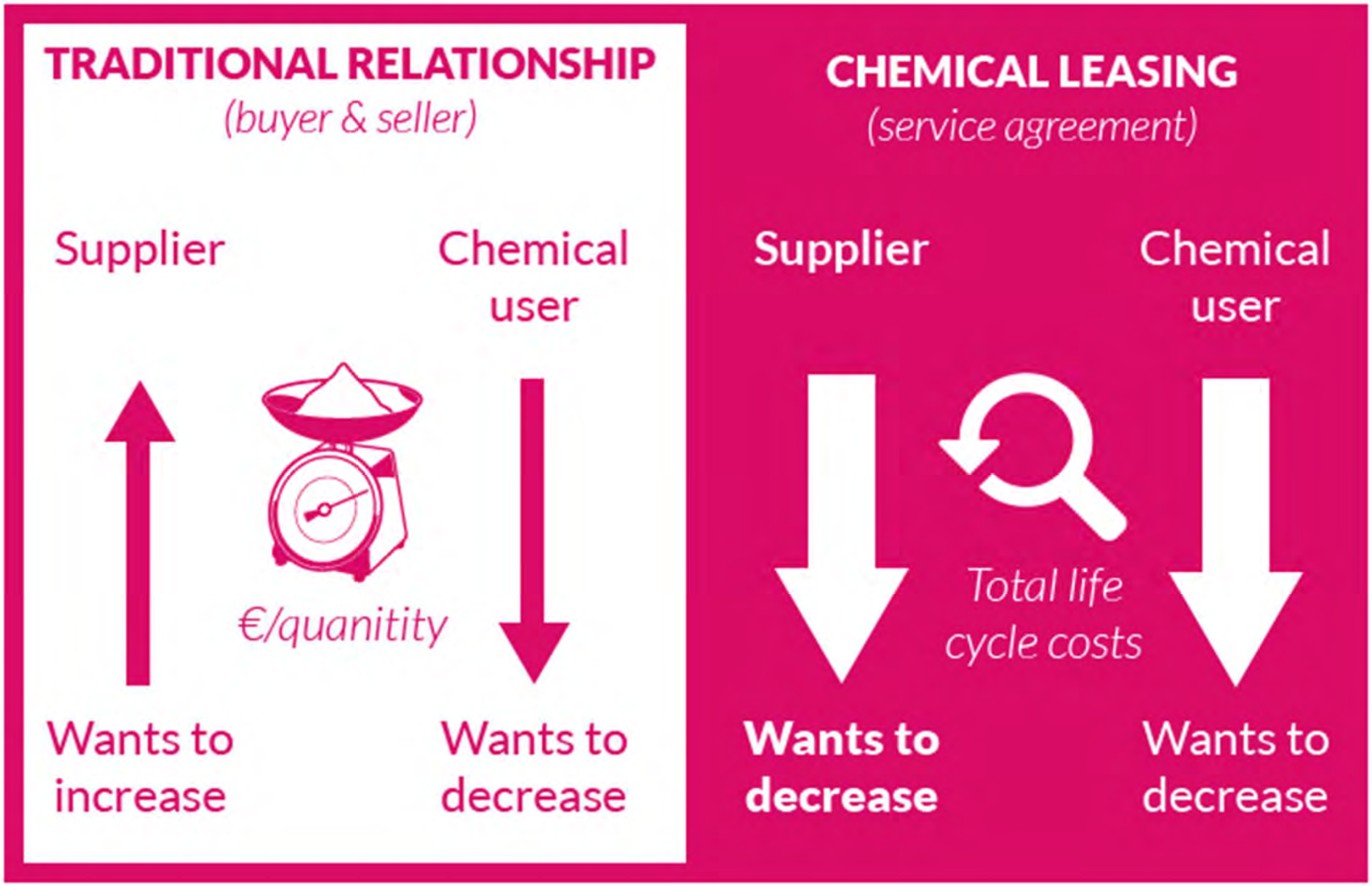
IGURE 1.7 Environmental effect of primary and secondary aluminum production. (Aft
ing, N. et al., *Procedia Eng.*, 27, 465, 2012.)

ocation. As a result, its collection can be a problem. This is particularly true for ol
crap, as will be seen in Chapter 3. The cost of collecting and processing old scra
an make this type of recycling uneconomic.

Emission control: While gaseous emissions fr
nuch lower than for primary production, secondar
rs are more likely to be located in urban areas (Anderson, 1931), making the
ubject to tighter emissions standards (Martchek, 1997). Furthermore, the pote
ial emissions from secondary producers are much different than those of primar

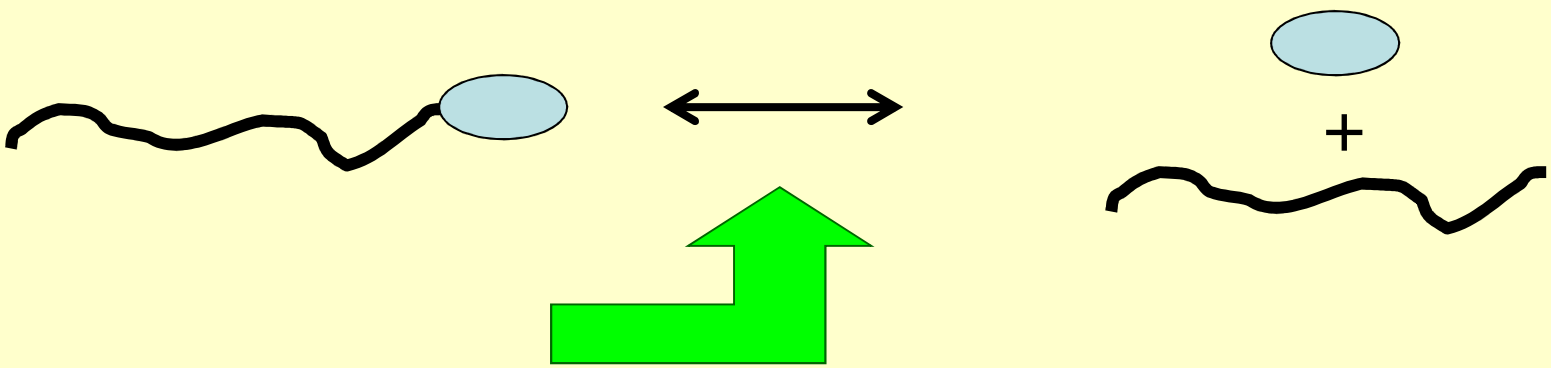
From M.E. Schlesinger, Aluminum Recycling (2014), CRC Press

Molecules as Services?



Molecular Triggers: "Reversible" Surfactants

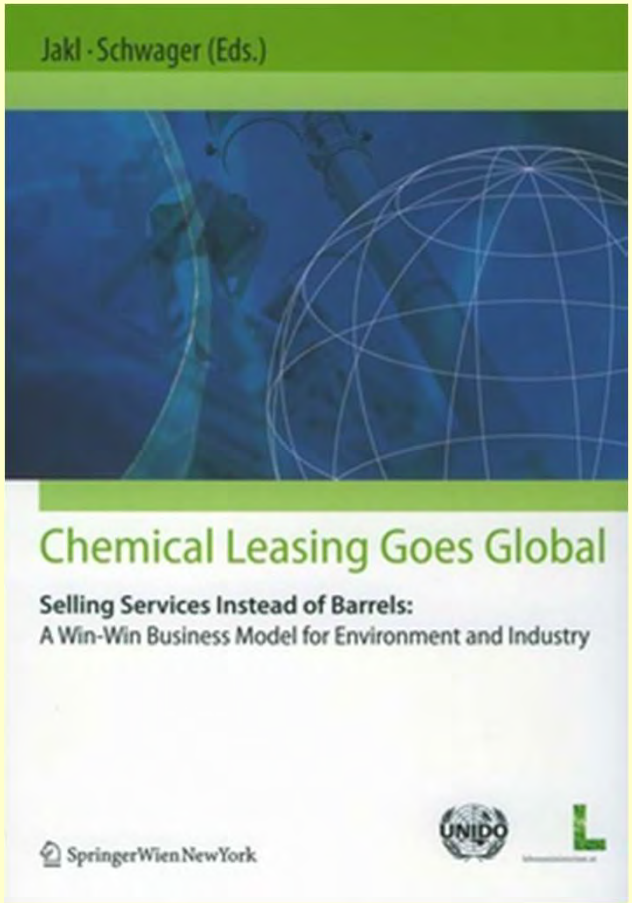
- Surfactants are useful in that they allow mixing of two immiscible phases, but emulsions are hard to break.



Trigger (light, CO_2/N_2)

Use of amidines by Phil Jessop's group (Queens Univ.)

Chemical Leasing moving forward slowly

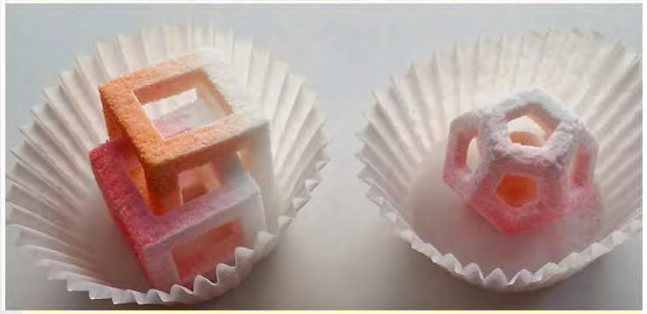


Distributed Manufacturing & Green Chemistry?

Power Generation: Kids, don't try this at home

3D Printing – The Ultimate Distributed Manufacturing?

Applied to aviation, apparel, & artificial organs



3D Printing (aka Additive Manufacturing): Distributed production – no shipping or packaging?

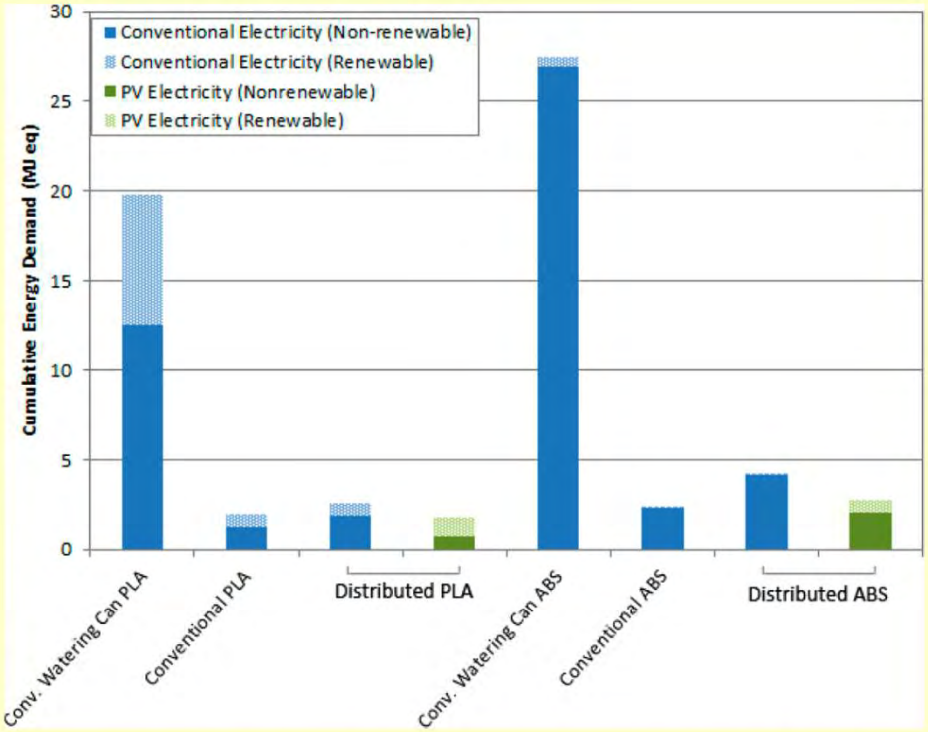
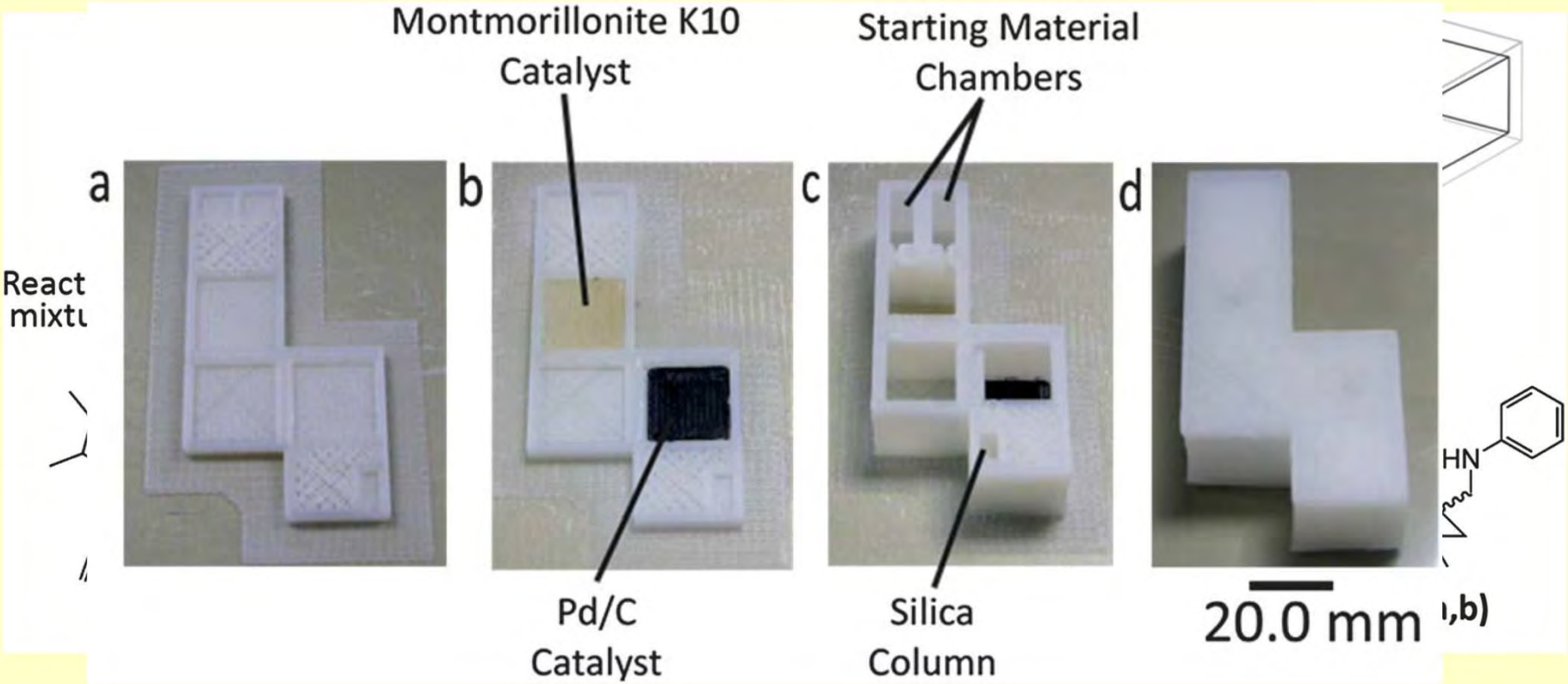


Figure 6. CED showing a typical watering can in PLA and ABS, and values for the spout in conventional PLA and ABS at 100% fill and distributed PLA and ABS at 100% fill, along with the effect of PV electricity.

M. Krieger & J.M. Pearce, *ACS Sust. Chem.& E*ng. (2013)
dx.doi.org/10.1021/sc400093k

Cronin's Group: *Printed Labware [Kitson, et al.,* Chem. Sci. (2013), 4, 3099-3103]



A molecular analog to 3D printing?

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Summary

- The first 20 years (or so) of green chemistry have seen a sea change in the way the chemical enterprise operates.
- It's not just about chemistry anymore – we're overlapping other disciplines whether we like it or not.
- Just as radical & disruptive innovation has driven changes in our digital & home lives, the same should hold true for green chemistry in the next 20 years.
- The educational enterprise needs to keep pace with the chemical (business) enterprise.

“It's tough to make predictions, especially about the future.”

Yogi Berra

Thank you!