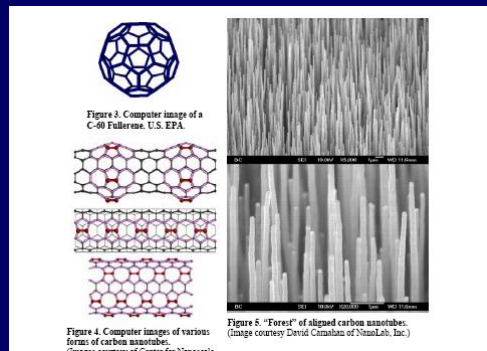
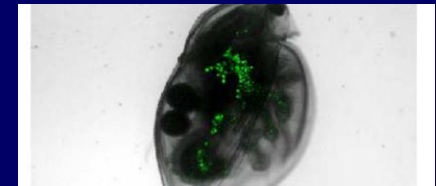
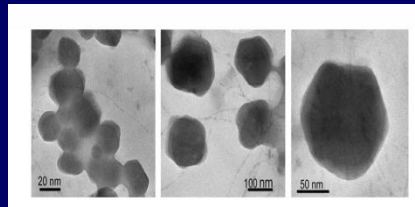
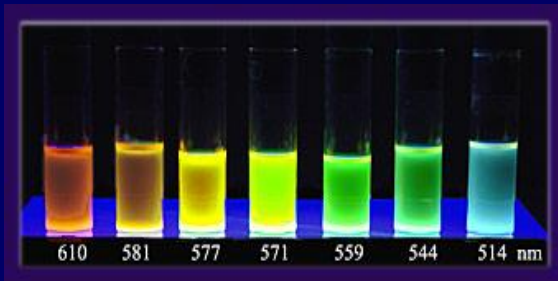


Life Cycle of Nanostructured Materials

Thomas L. Theis
Institute for Environmental Science and Policy
University of Illinois at Chicago



Why nano?

- Small amounts can have large effects
- Different physical properties as size decreases
- High specific surface areas
- Function can often be “tuned” by altering composition, size, shape, temperature, pressure
- Rich basis for new designs and applications
- Projected to generate \$1.1 trillion in economic activity by 2016 (NNI, 2001)
- Production rates $>10^5$ mT/yr by 2020 (Royal Society 2004)
- An “enabling” technology with implications for energy, materials, manufacturing, electronics, transportation, healthcare, pharmaceuticals, environmental control and purification, sensors and national security, chemical processing, and sustainable development

Nanoscale structures

- **1-D** Thin film devices, coatings (anti-reflection, corrosion), and quantum wells (stacked multiple thin films) from semiconductor, metallic and dielectric films
- **2-D** Nanofibers, nanowires, and nanorods
- **3-D** nanoparticles, single or multi-wall nanotubes, polymeric dispersions, fullerenes, dendrimers

Life Cycle Assessment

- A systems methodology for compiling information on the flow of materials and energy throughout a product chain
- LCA evolved from industry needs to understand manufacturing, and market behavior, and make choices among competing designs, processes, and products
- Defines four general sections of the product chain:
 - materials acquisition
 - manufacturing/fabrication
 - product use
 - downstream disposition of the product

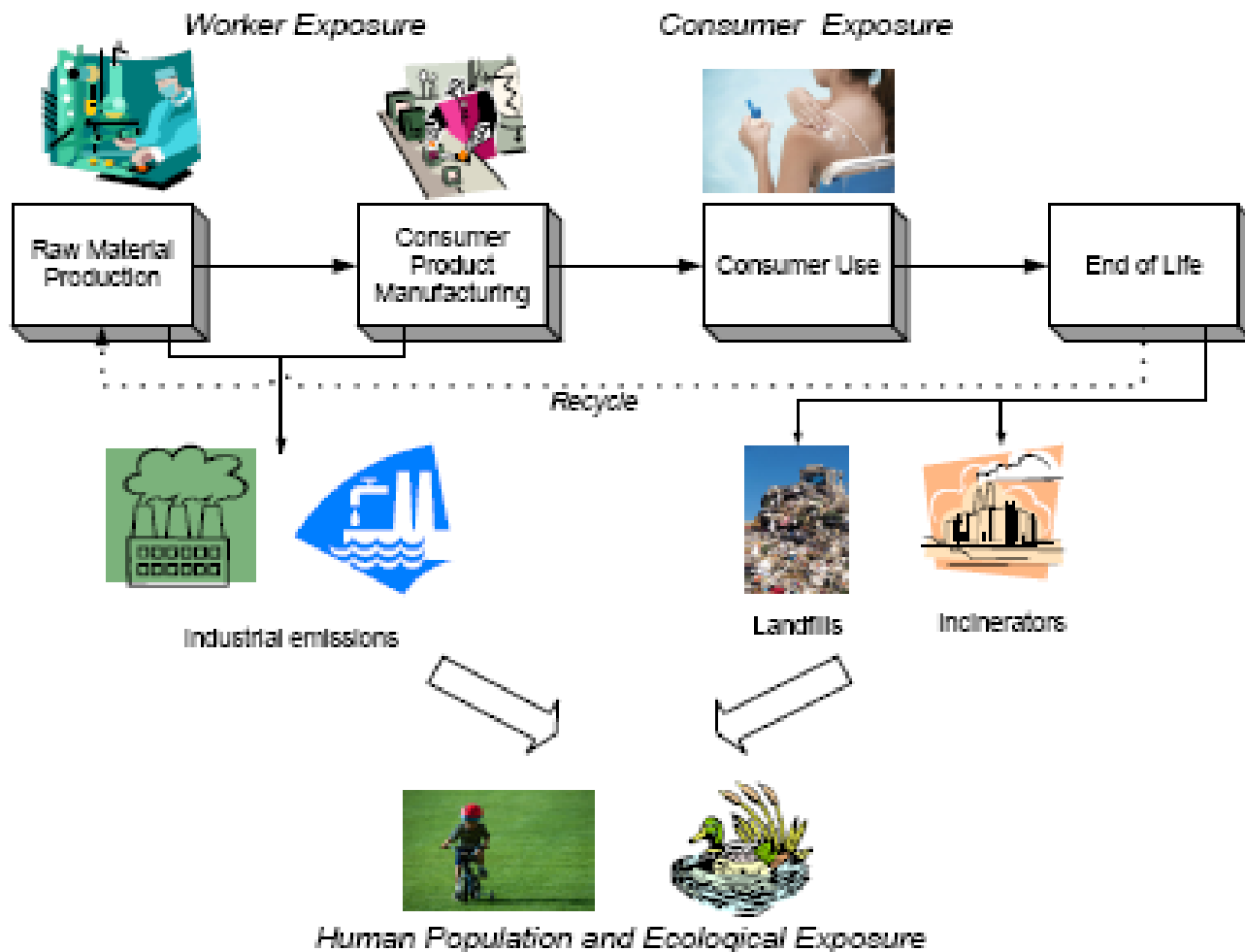
What is Life Cycle Good For?

- ID energy/material/waste hot spots
- Compare options
- Improve product/service chain
- Avoid displacing pollution
- Very good at framing policy issues

What is it not especially good for?

- Detailed risk assessments

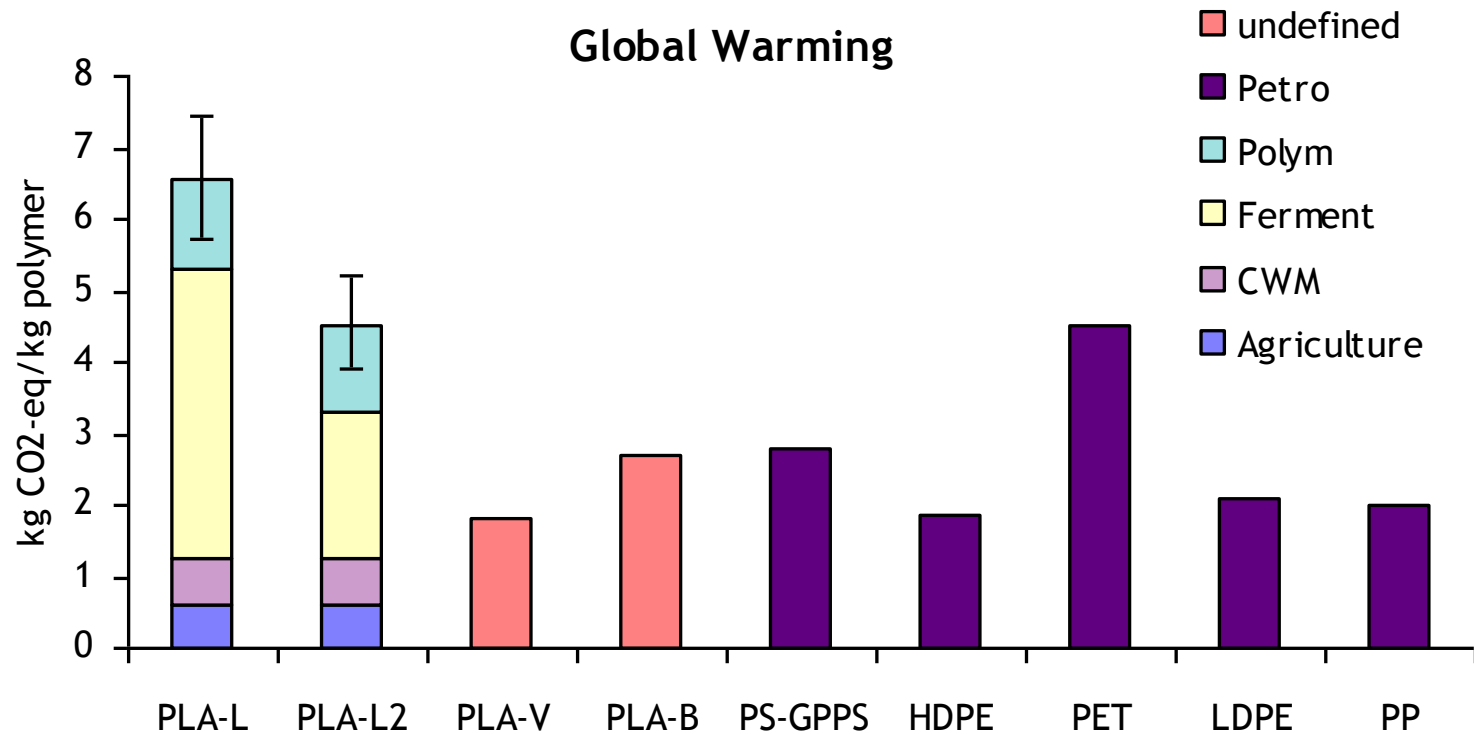
Life Cycle Assessment Stages (USEPA)



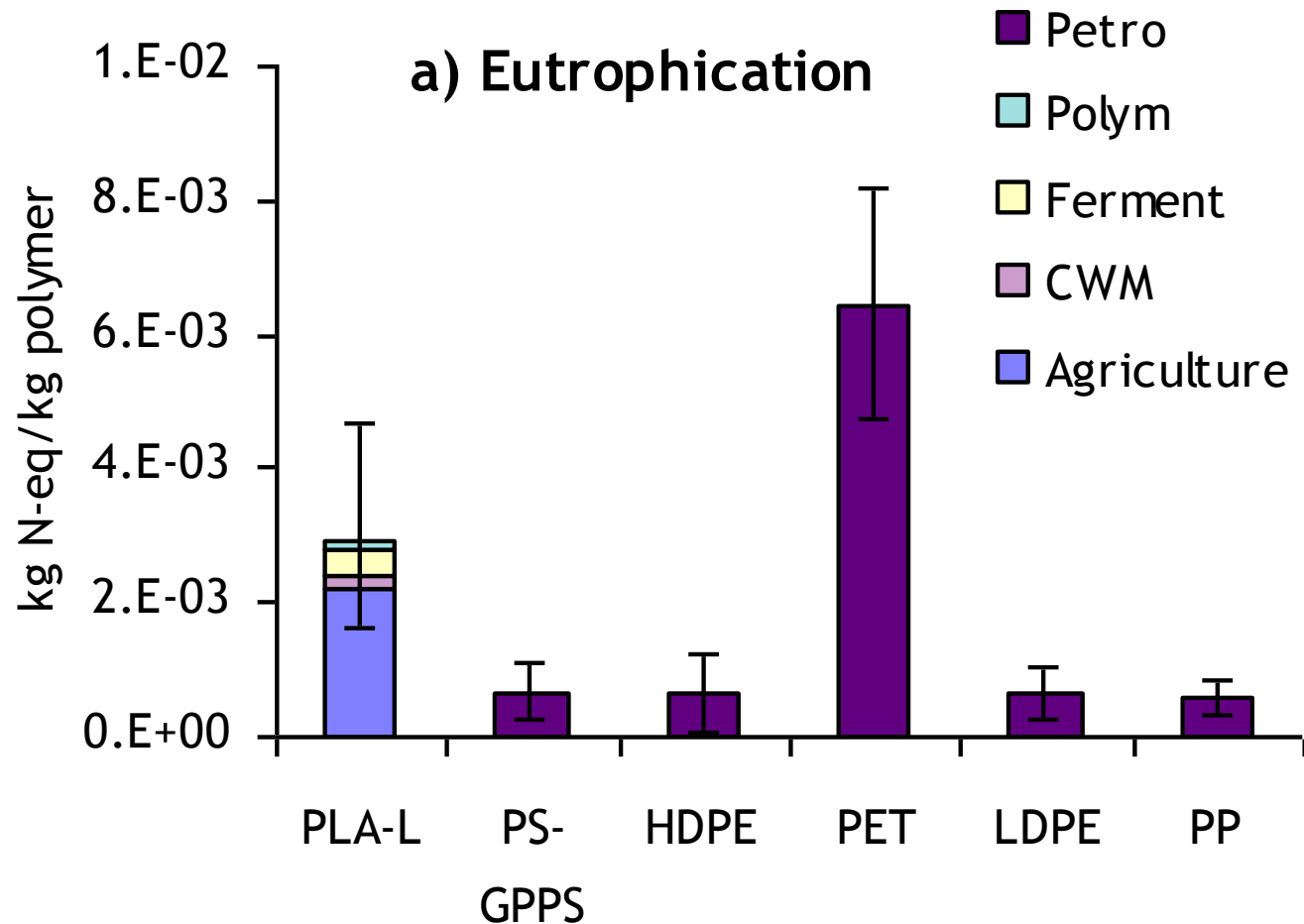
EPA Nanotech Research Focus

- Environmental Applications
 - Membranes, remediation, sensors, etc.
- Environmental Implications
 - End-of-pipe
 - Toxicity
 - Fate, transport, transformation
 - Focus on NPs already in commercial production
 - CNTs
 - Ag⁰
 - Fe⁰
 - TiO₂
 - CeO₂

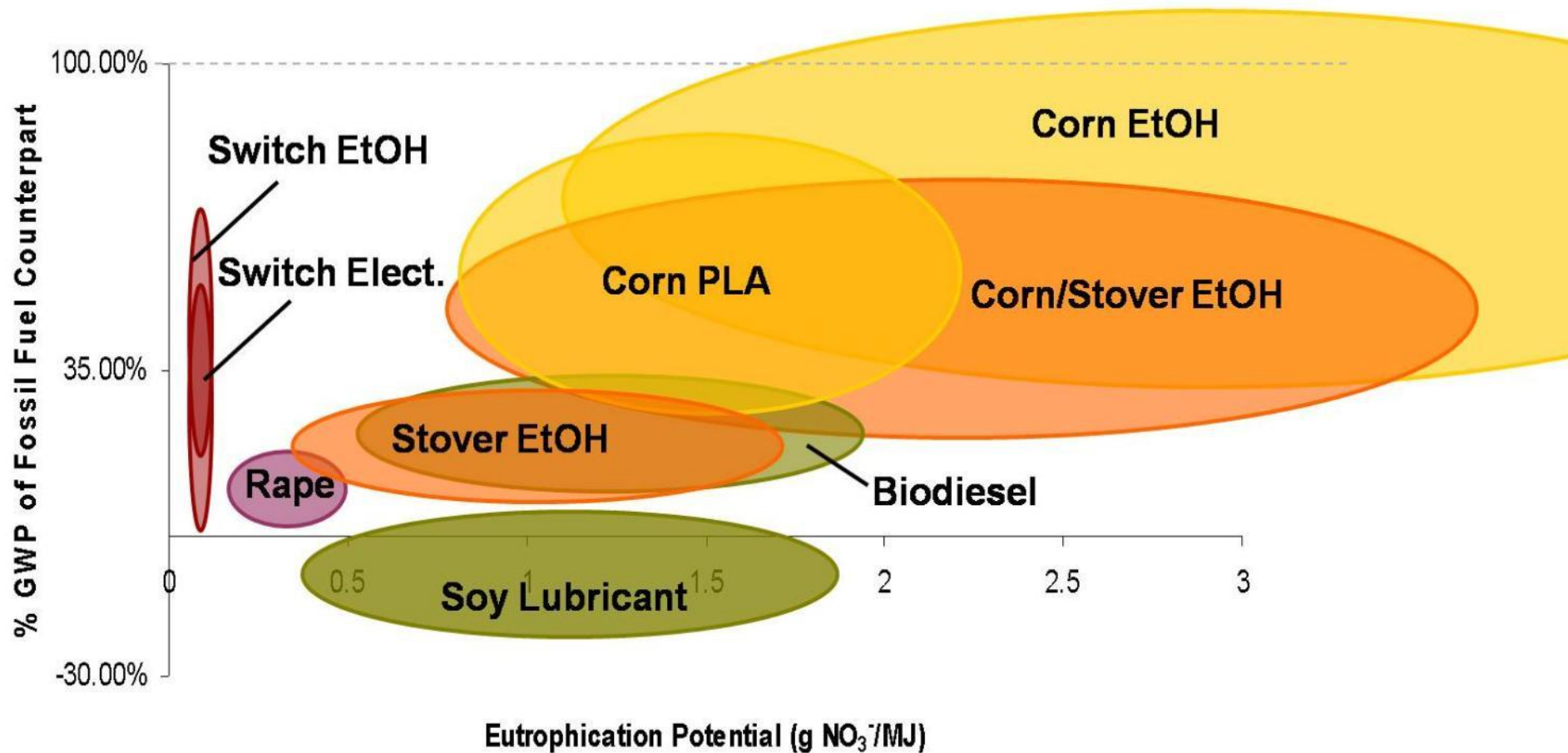
Life Cycle GWP for Polylactide vs Petro-plastics



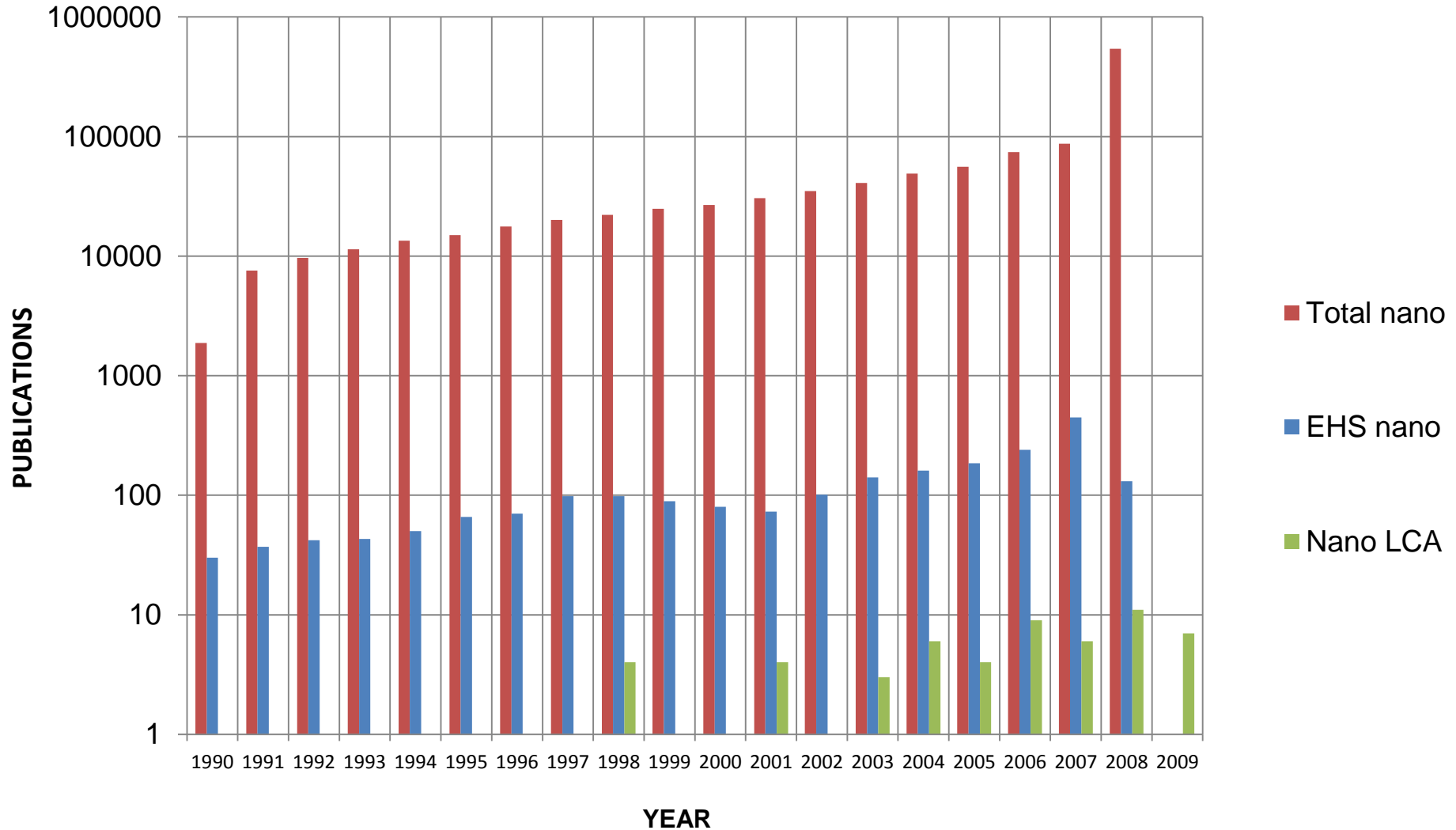
Life Cycle Comparison of Eutrophication Potential for Polylactide vs Petro-plastics



Relative C/N Profiles



Nanotechnology Publication Trends



The three nano-paradoxes...

Health/Materials

Energy

Consumption

The Health/Materials Paradox

Why might nanostructured materials be toxic?

size

shape

composition

photoactivity

redox activity

solubility

environmental instability

potential for exposure

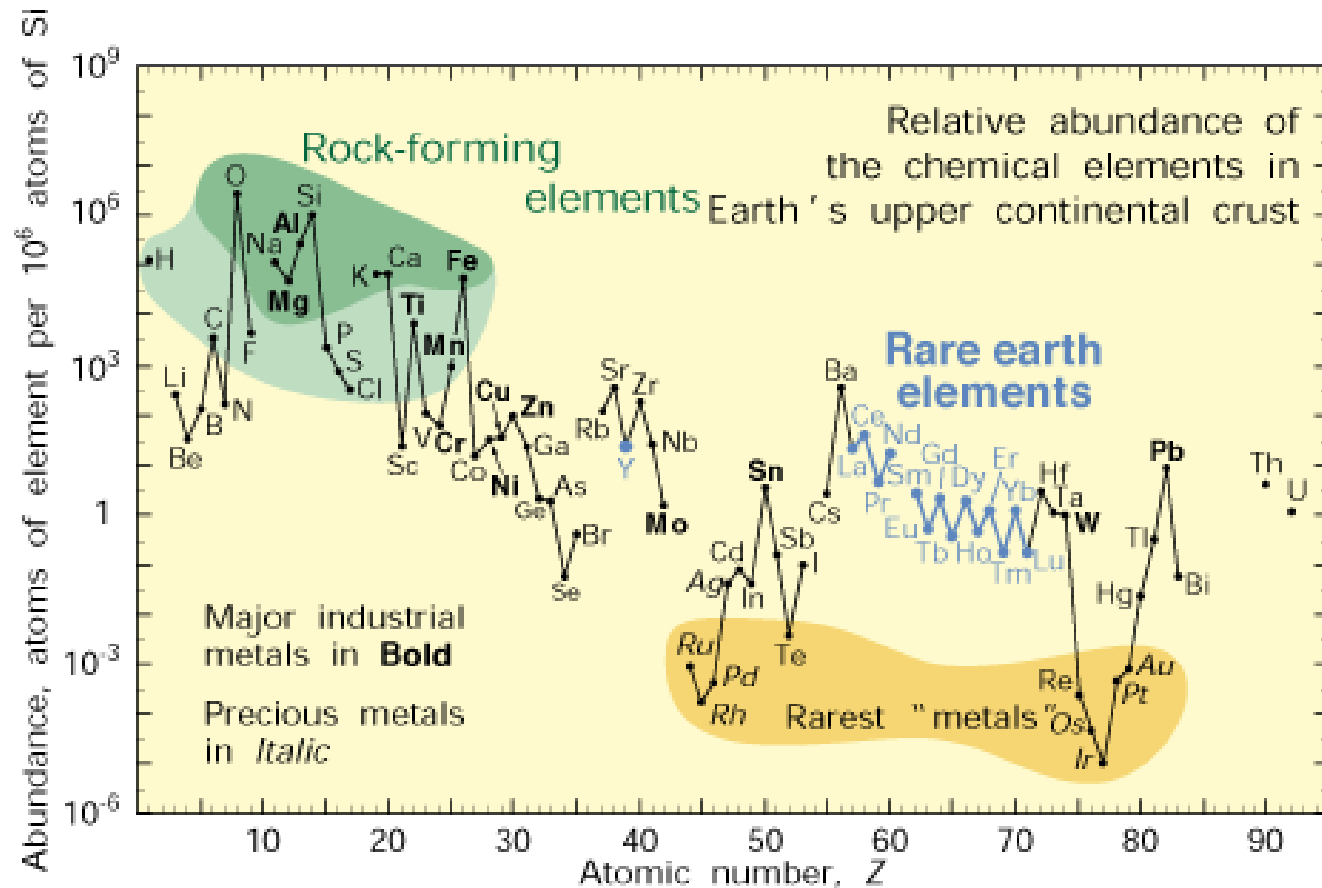
Those attributes of NSM's that are prized for commercial development and application, are the same ones that cause toxic reactions



NATIONS MOVE TO HEAD OFF SHORTAGES OF RARE EARTHS

Looming scarcities of a handful of essential elements could shake the electronics industry, unless manufacturers and mining companies develop more sources soon

R. F. Service Science 327, 1596-1597 (26 March 2010)



Source: Wikipedia

The New York Times
ON THE WEB

September 22, 2010

Amid Tension, China Blocks Vital Exports to Japan

By Keith Bradsher

HONG KONG — Sharply raising the stakes in a dispute over Japan's detention of a Chinese fishing trawler captain, the Chinese government has blocked exports to Japan of a crucial category of minerals used in products like hybrid cars, wind turbines, and guided missiles.



Chinese customs officials are halting shipments to Japan of so-called rare earth elements, preventing them from being loading aboard ships at Chinese ports, industry officials said on Thursday.

Didymium oxide is a rare earth mineral
used in delicate electronics

November 8, 2010

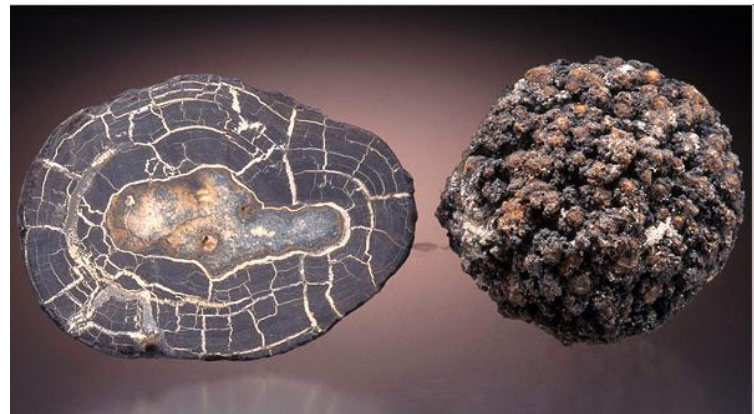
Mining the Seafloor for Rare-Earth Minerals

By William J. Broad

For decades, entrepreneurs have tried to strike it rich by gathering up ugly potato-size rocks that carpet the global seabed. Known as manganese [nodules](#), the rocks are plentiful in nickel, copper and cobalt, as well as manganese and other elements, but lie miles down

in inky darkness. Building giant machines to vacuum them up, despite much study and investment, has never proved to be economic. Now, the frustrated visionaries are talking excitedly about the possibility of belated success, and perhaps even profits.

The nodules turn out to contain so-called rare-earth minerals — elements that have wide commercial and military application but have hit a production roadblock. China, which controls some 95 percent of the world's supply, had blocked shipments, sounding political alarms around the globe and a rush for alternatives. [China ended its embargo late last month](#), but the hunt for other options continues.



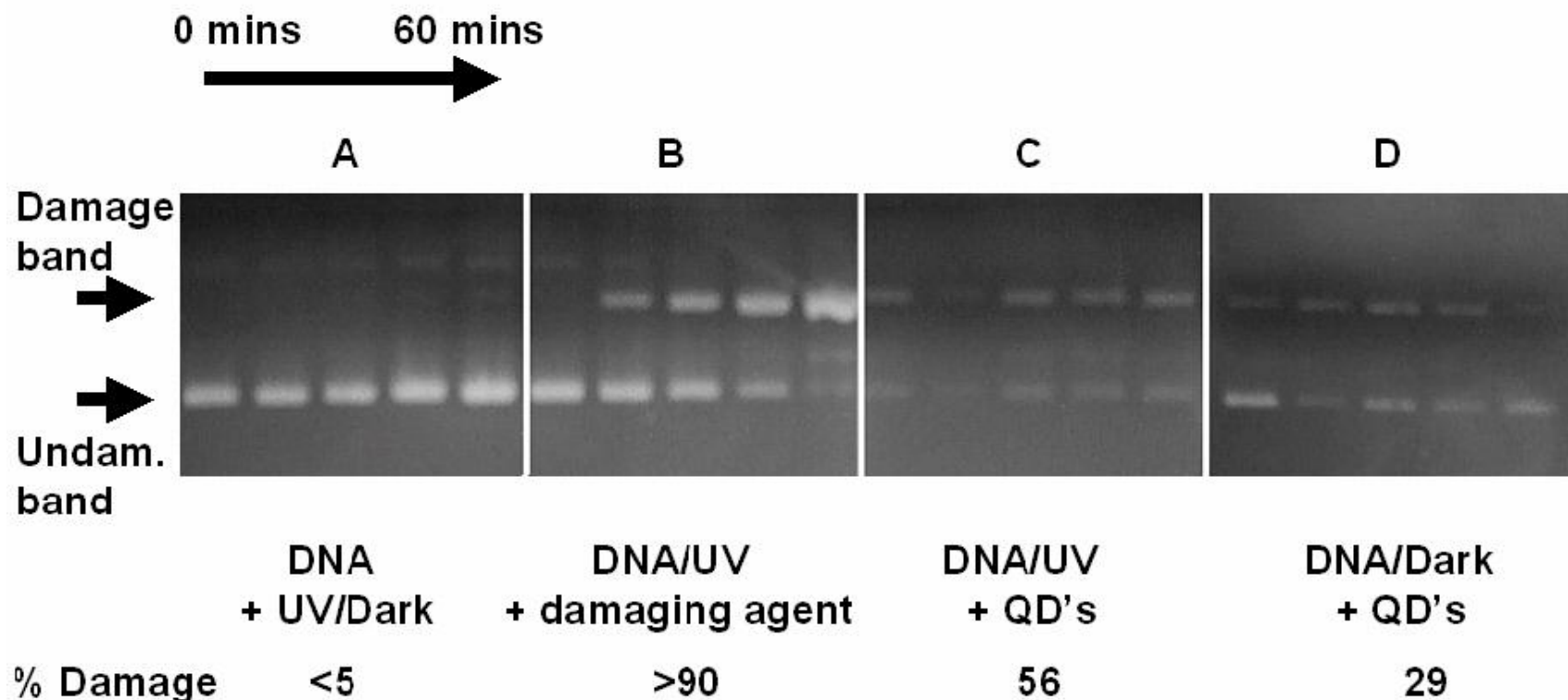
Cadmium-Free CuInS₂/ZnS Quantum Dots for Sentinel Lymph Node Imaging with Reduced Toxicity

Thomas Pons,^{†,*} Emilie Pic,[‡] Nicolas Lequeux,[§] Elsa Cassette,[†] Lina Bezdetnaya,[‡] François Guillemin,[‡] Frédéric Marchal,[‡] and Benoit Dubertret[†]

[†]Laboratoire Physique et Etude des Matériaux, CNRS UPR0005, ESPCI, 10, rue Vauquelin, 75005 Paris, France, [‡]Centre de Recherche en Automatique de Nancy, Nancy-University, CNRS, Centre Alexis Vautrin, avenue de Bourgogne, 54511 Vandoeuvre-lès-Nancy Cedex, France, and [§]Laboratoire de physico-chimie des Polymères et des Milieux Dispersés, CNRS UMR7615, ESPCI, 10, rue Vauquelin, 75005 Paris, France

ACSnano VOL. 4 ▪ NO. 5 ▪ 2531–2538 ▪ 2010

DNA damage of CdSe

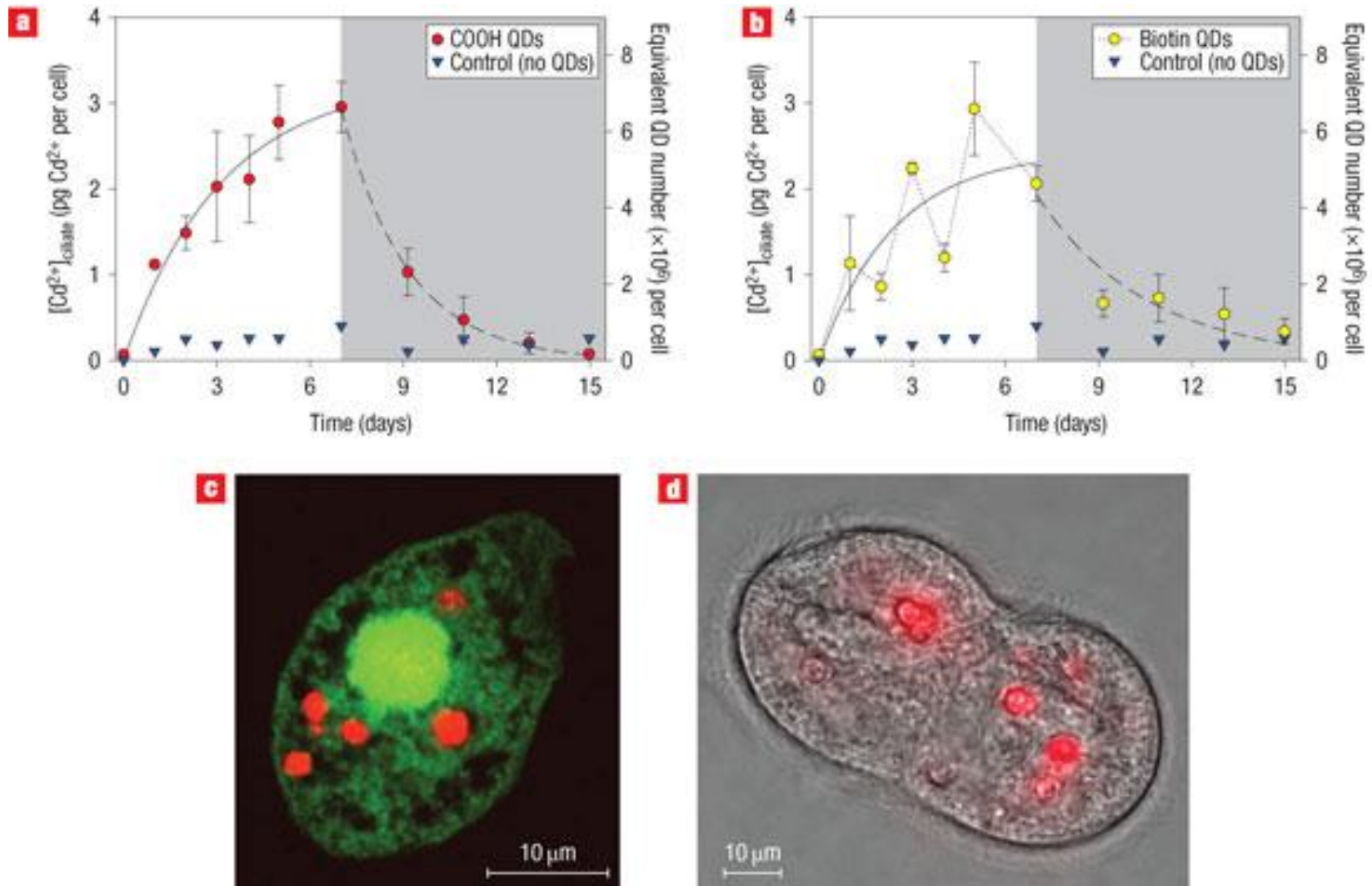


Green, M. and E. Howman

“Semiconductor quantum dots and free radical induced DNA nicking”

Chem. Commun., 2005, 121 - 123

Uptake and depuration of QDs by *T. pyriformis*

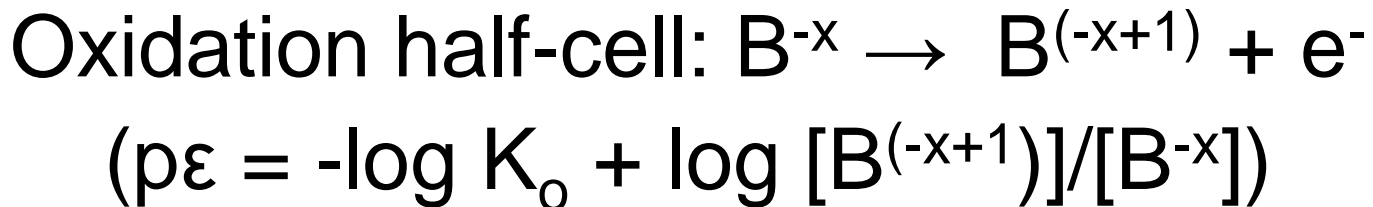
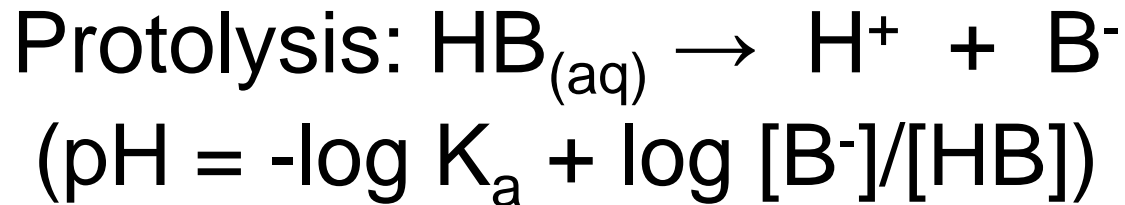
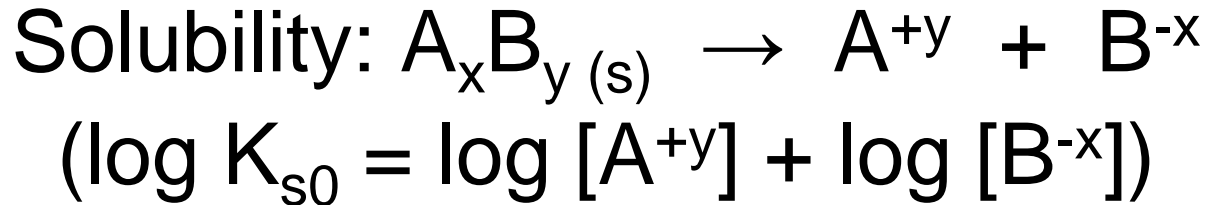


Holbrook, RD et al. "Trophic transfer of nanoparticles in a simplified invertebrate food web" NATURE NANOTECHNOLOGY 3(6): 352-355 (2008)

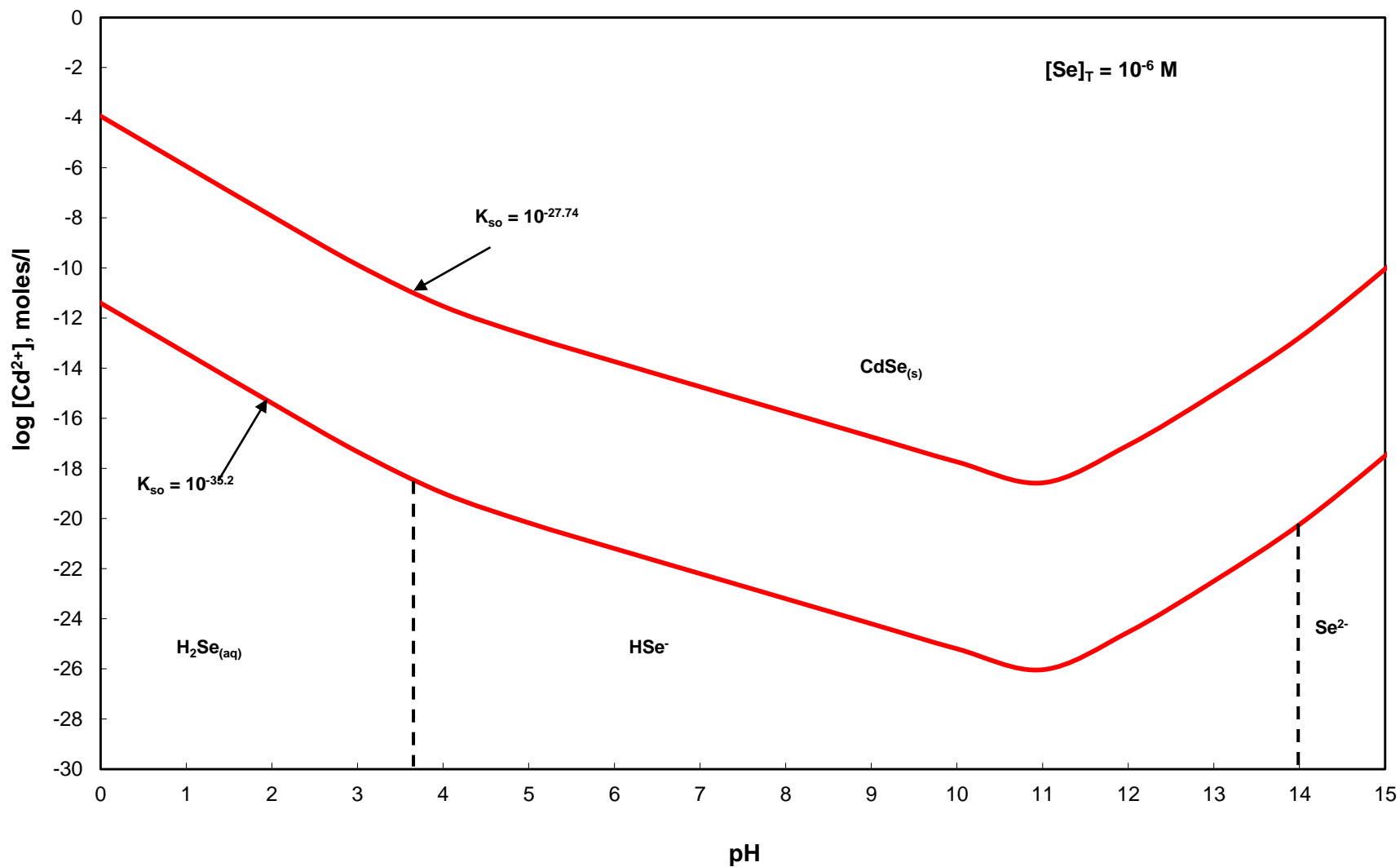
Group II-VI and III-V Semiconductors

hydrogen 1 H 1.0079																		helium 2 He 4.0026	
lithium 3 Li 6.941		beryllium 4 Be 9.0122																	
sodium 11 Na 22.990		magnesium 12 Mg 24.305																	
potassium 19 K 39.098		calcium 20 Ca 40.078																	
rubidium 37 Rb 85.468		strontium 38 Sr 87.62																	
caesium 55 Cs 132.91		barium 56 Ba 137.33		57-70 *															
francium 87 Fr [223]		radium 88 Ra [226]		89-102 **															

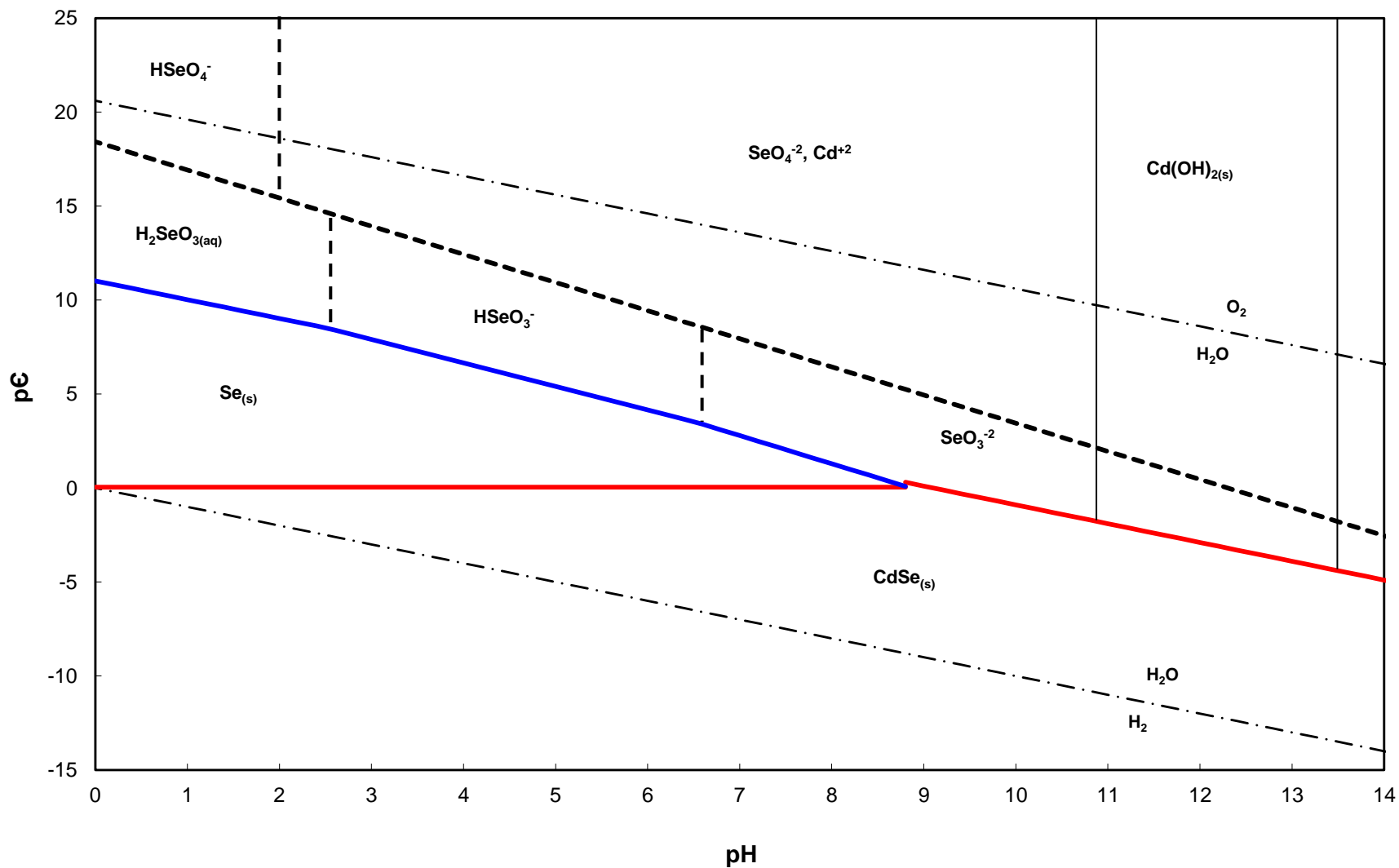
Aquatic reactions



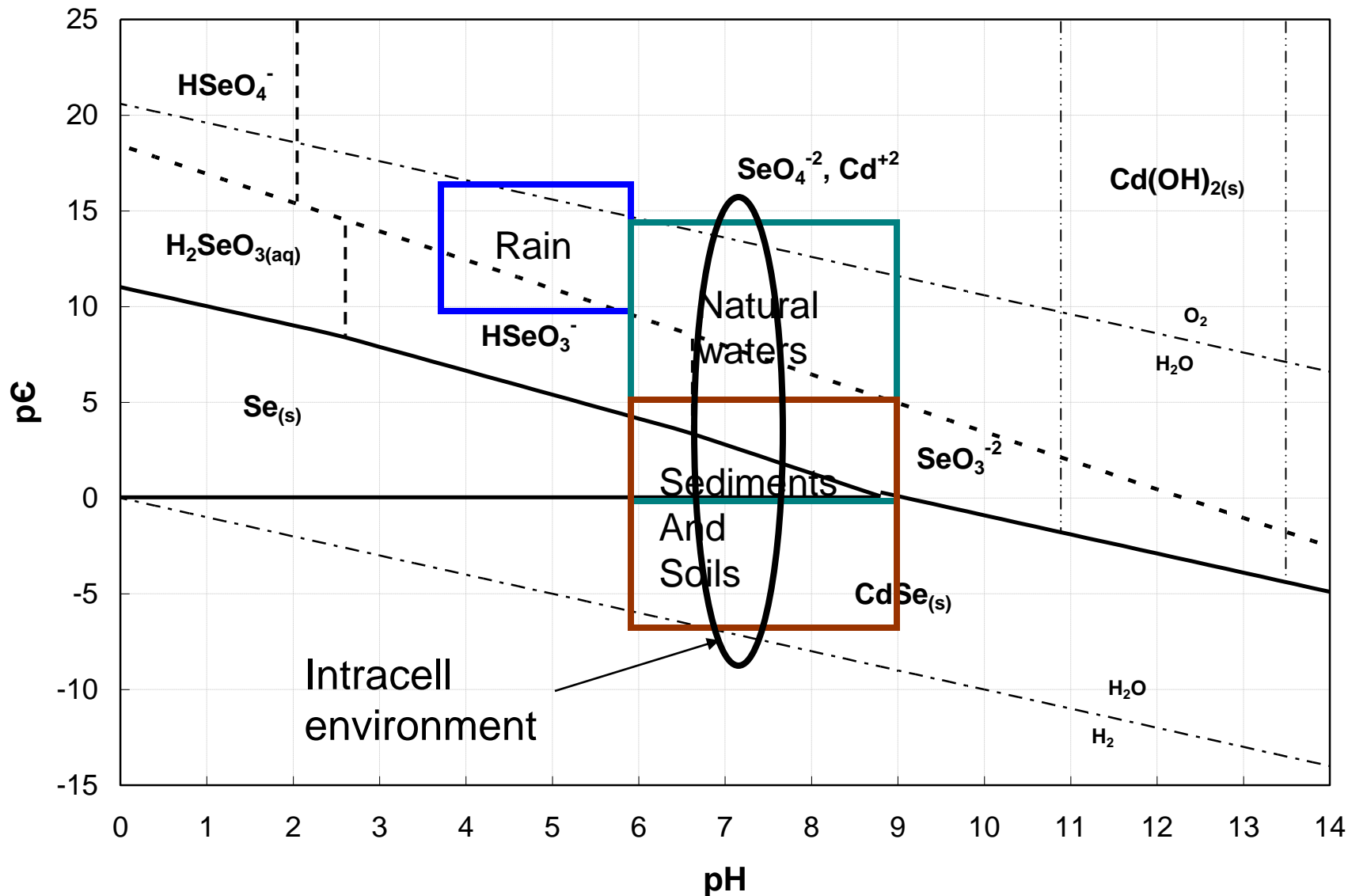
Solubility of CdSe in water



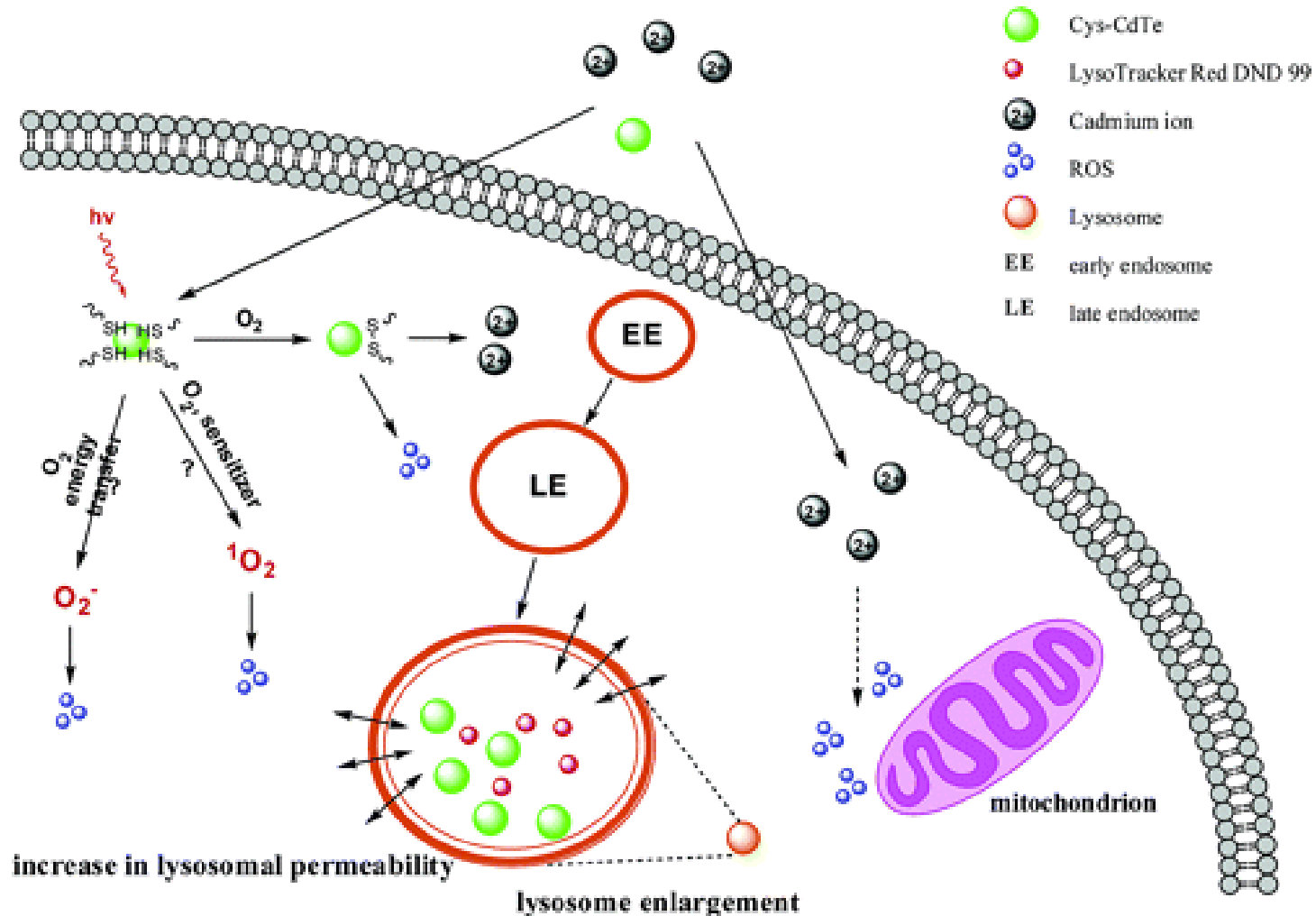
$p\varepsilon$ -pH diagram for CdSe



CdSe in aquatic environments



Mechanism of toxicity



Schematic representation of the mechanistic pathways implicated in the cytotoxicity of CdTe QDs in live cells, highlighting the salient changes in cellular morphology, the chemical species involved, and the chemical reactions that can lead to ROS and free Cd²⁺ ion release (Cho et al. (2007).

Limited experience suggests that composite materials are not recycled

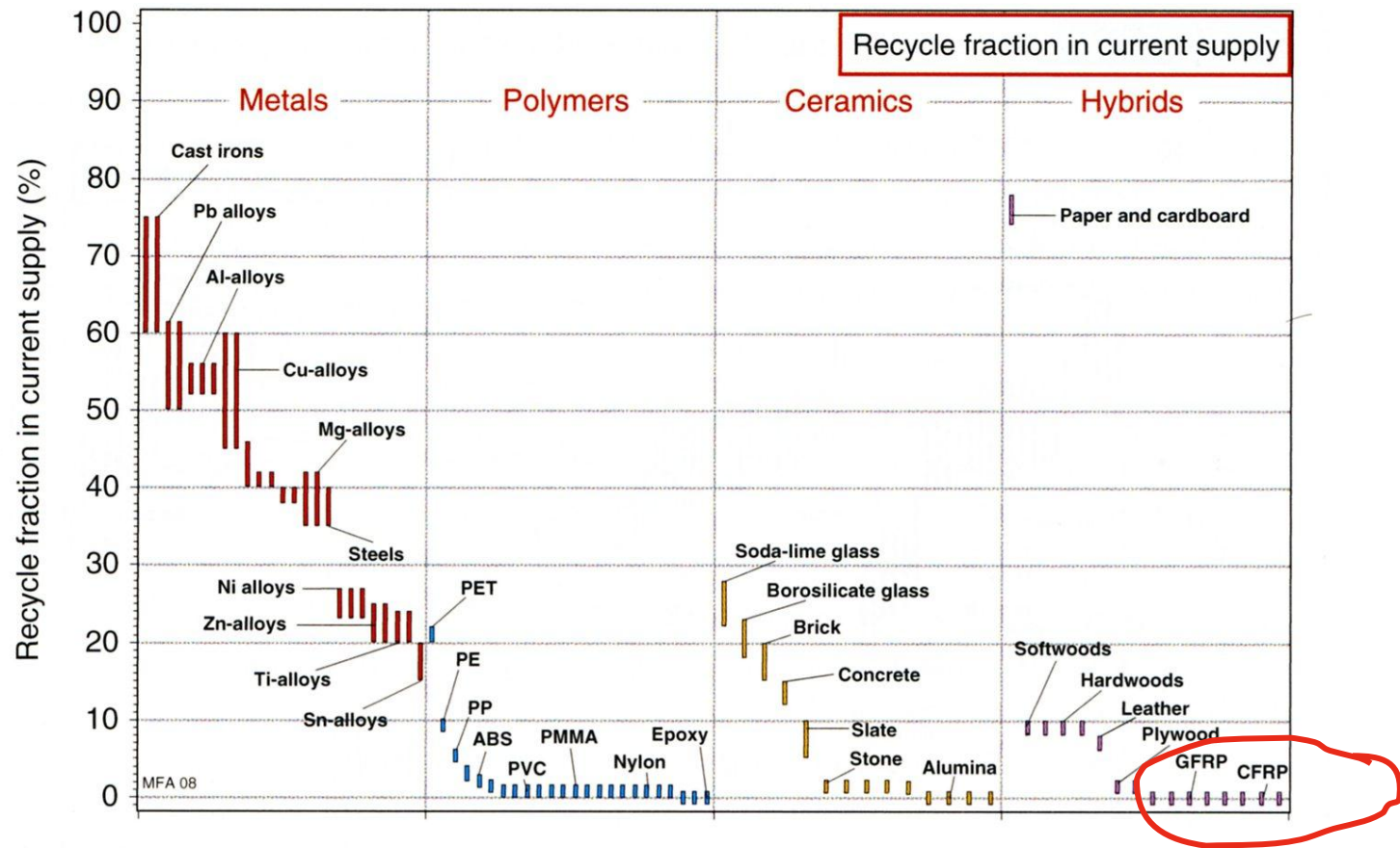
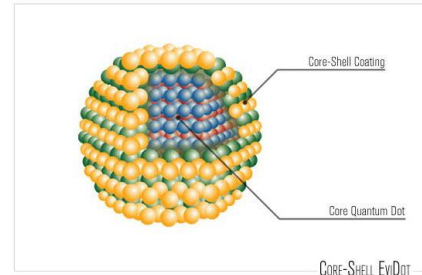
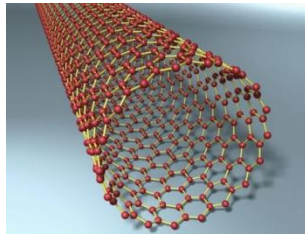


FIGURE 6.13 *Recycle fraction bar chart.*

Ashby, M.F. *Materials and the Environment*, Elsevier (2009)

The Energy Paradox

- Some of the most energy intensive materials known, but...



- Less than 1% (currently) of the mfg cost

(Healy & Isaacs, 2008)

Nano-based Energy Savings

Table 3. Potential U.S. Energy Savings from Eight Nanotechnology Applications
(Adapted from Brown, 2005 a)

Nanotechnology Application	Estimated Percent Reduction in Total Annual U.S. Energy Consumption**
Strong, lightweight materials in transportation	6.2 *
Solid state lighting (such as white light LED's)	3.5
Self-optimizing motor systems (smart sensors)	2.1
Smart roofs (temperature-dependent reflectivity)	1.2
Novel energy-efficient separation membranes	0.8
Energy efficient distillation through supercomputing	0.3
Molecular-level control of industrial catalysis	0.2
Transmission line conductance	0.2
Total	14.5

*Assuming a 5.15 Million BTU/ Barrel conversion (corresponding to reformulated gasoline – from EIA monthly energy review, October 2005, Appendix A)

**Based on U.S. annual energy consumption from 2004 (99.74 Quadrillion Btu/year) from the Energy Information Administration Annual Energy Review 2004

Estimate of embodied energy for SWNT =
 Synthesis + purification + infrastructure + utilities + input
 + materials $\approx 1.0 - 0.1$ TJ/kg

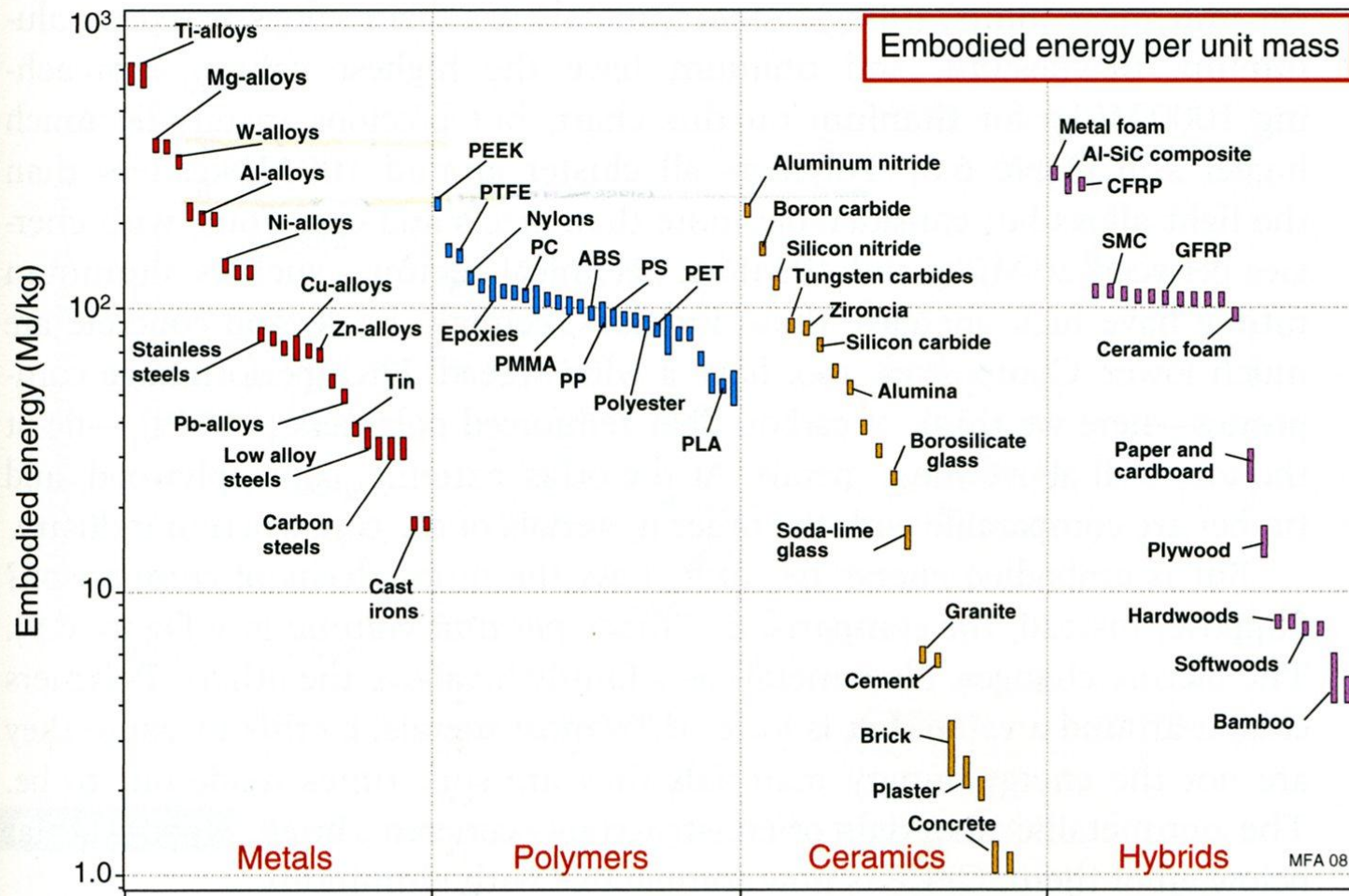
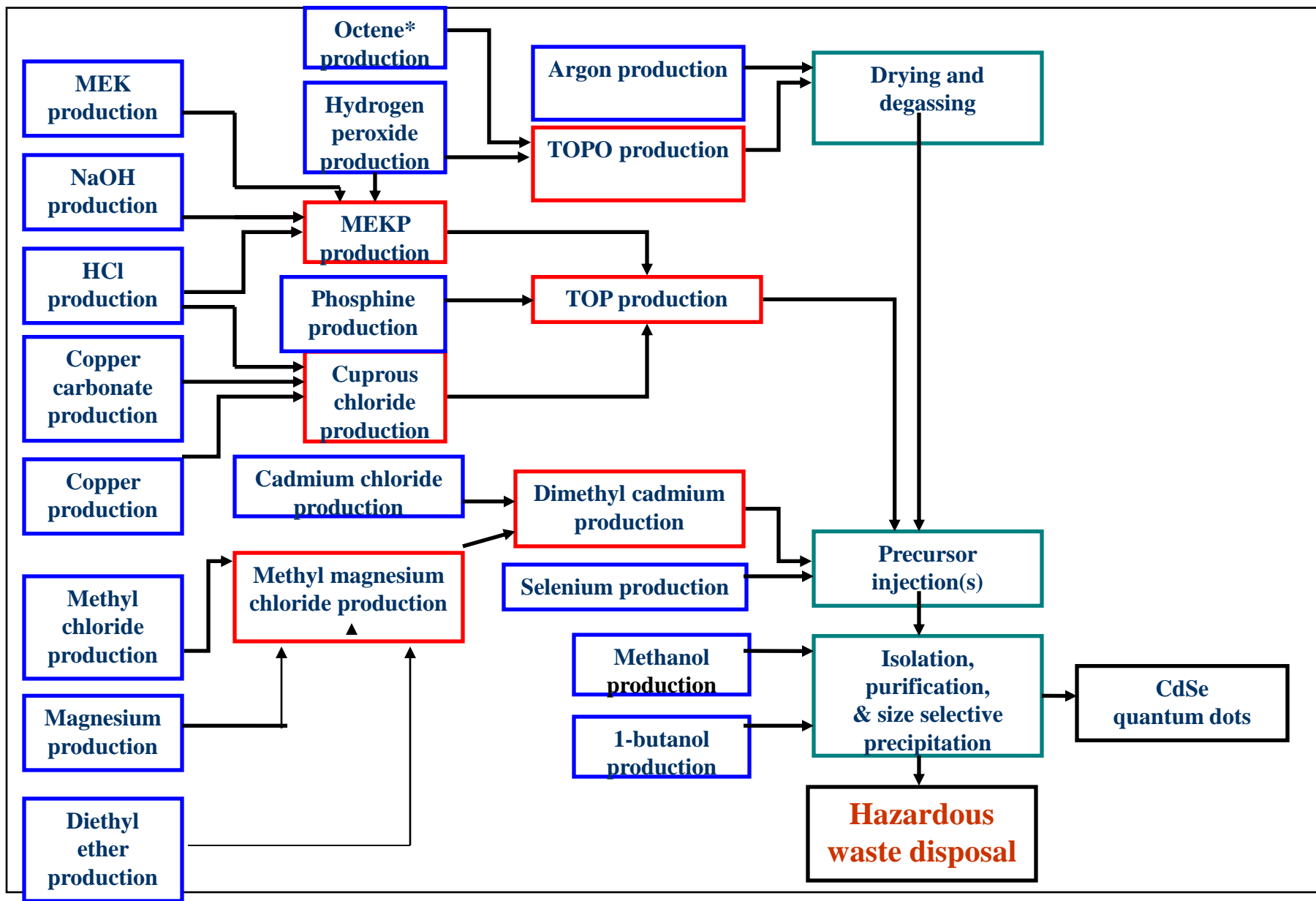


FIGURE 6.8 A bar chart of the embodied energies of materials per unit mass.

Ashby, M.F. *Materials and the Environment*,
 Elsevier (2009)

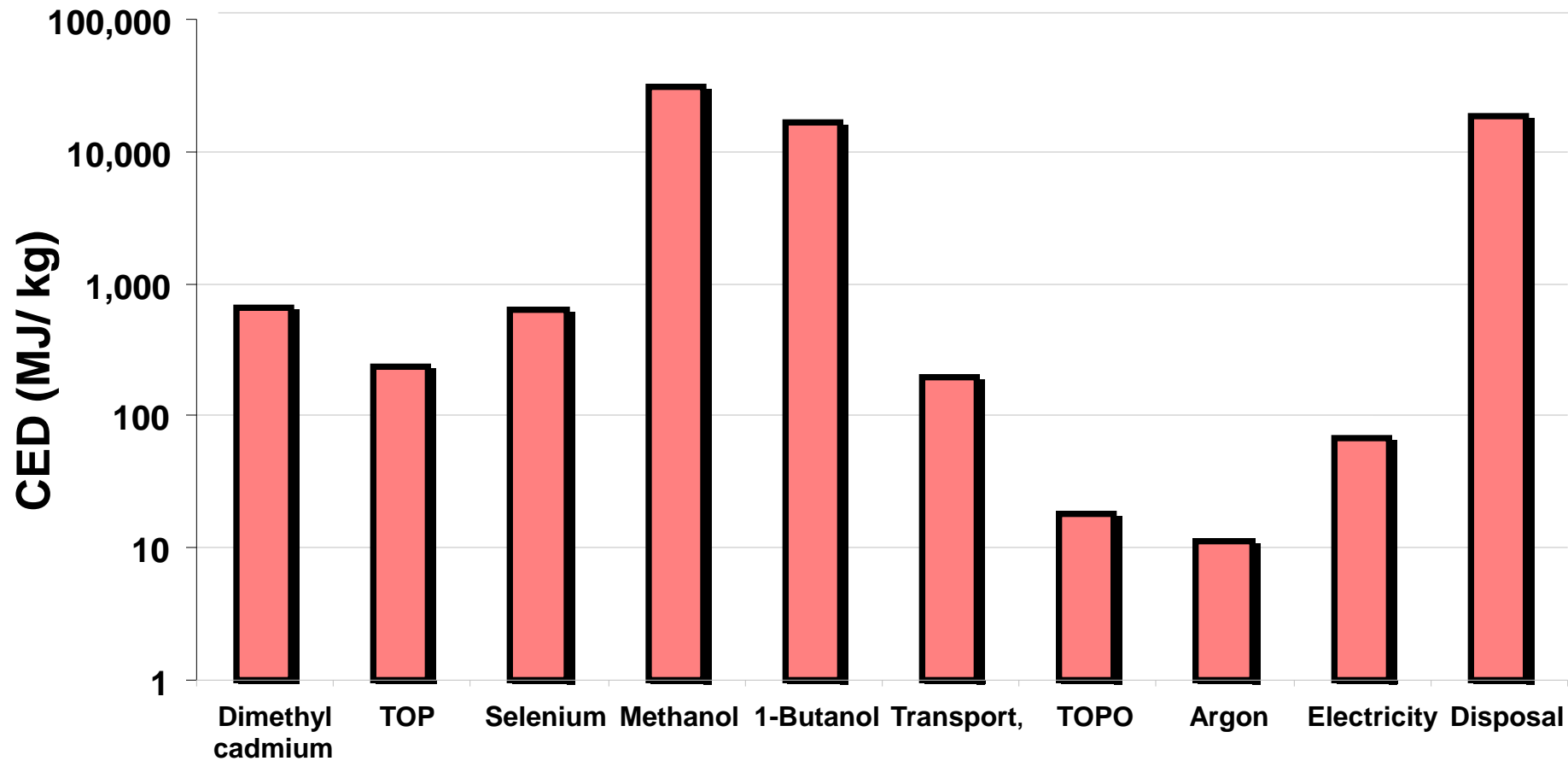
Sources of Impacts During Manufacturing of NSMs

- Strict purity requirements and less tolerance for contamination during processing (up to “nine nines”)
- Low process yields
- Significant energy requirements
- Batch processing (post-processing, reprocessing), or very low-yield continuous processing
- Use of toxic/basic/acidic chemicals and organic solvents
- High (or low) temperatures, pressures
- High water consumption

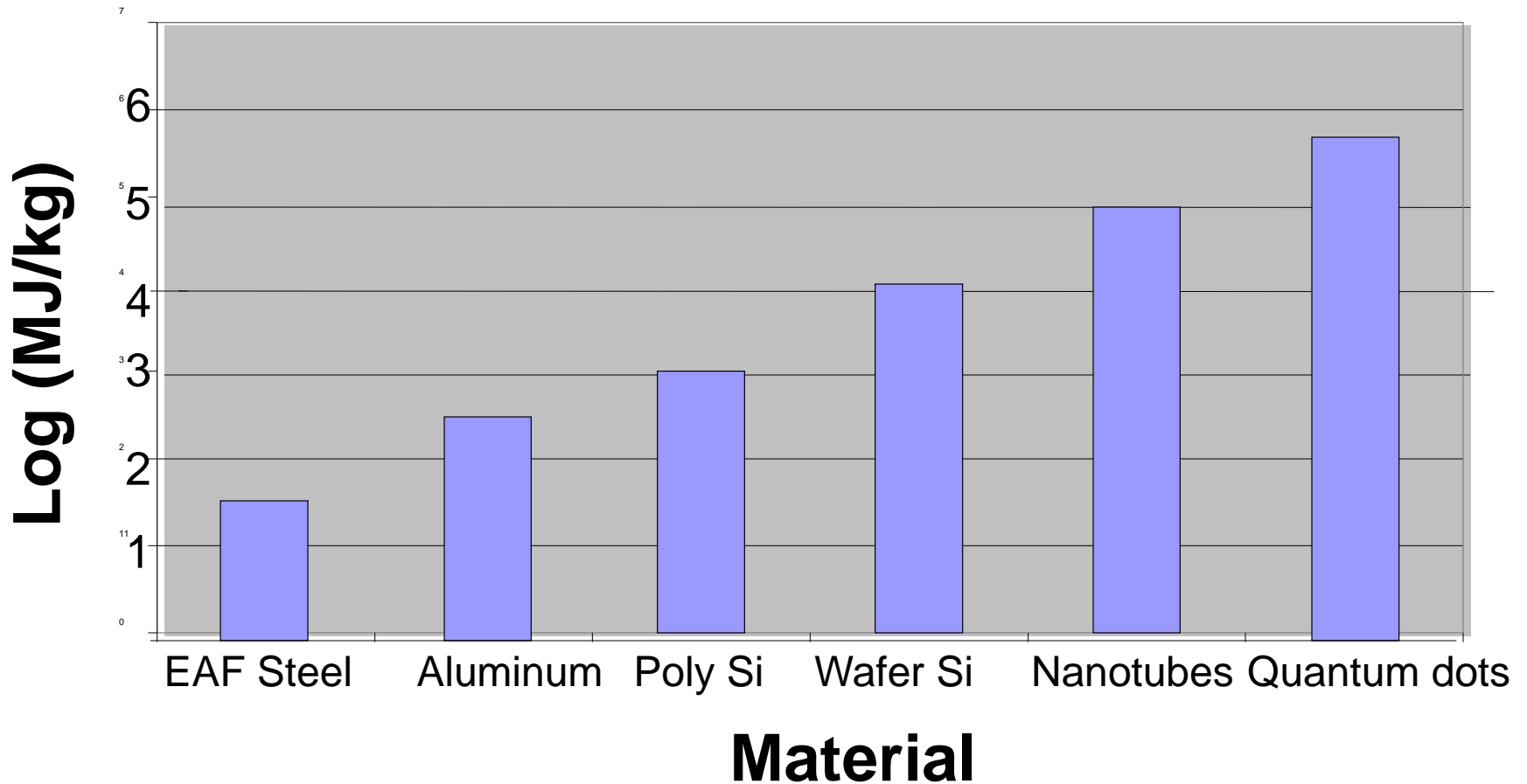


Material flows for the synthesis of CdSe quantum dots using sol-gel

Cumulative energy demand (embodied energy) CdSe q-dots

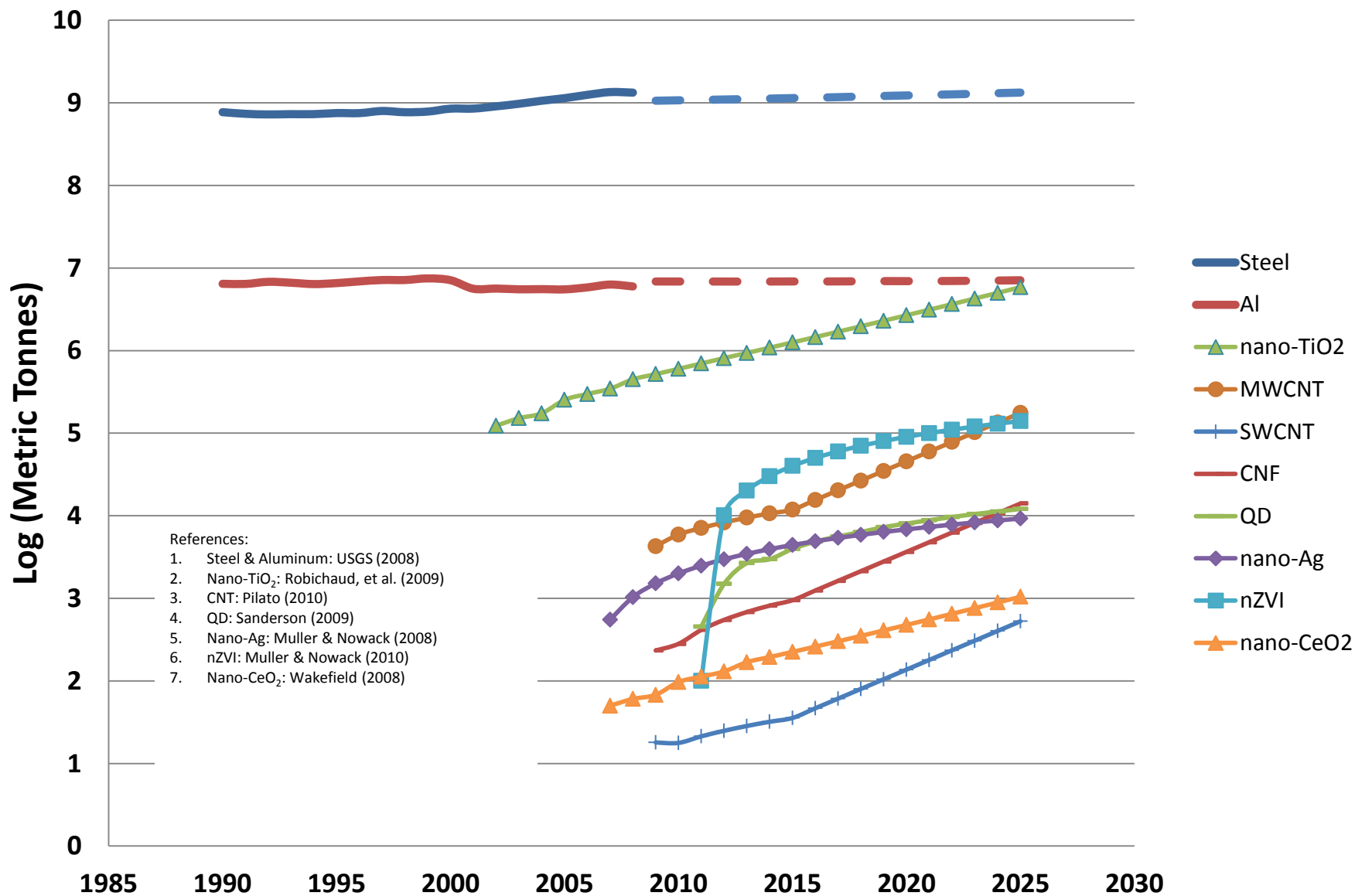


Embodied Energy (Cradle-to-Gate)



Adapted from Gutowski et al. 2007, and Sengul and Theis 2008.

Current and Forecast World Production of Various Materials



So, how much of the nanostructured materials we make will directly impact the environment?

Qualitative ranking based on type of use (high to low probability of direct entry to environment)

HIGH



LOW

Food/Beverage
Biomedical/Health Care
Paints and Coatings
Agricultural/Gardening
Children's Goods
Appliances
Computers
Lighting/Solar
Fitness
Automotive
Composite Structural Components

“Greening” product chains

Product conceptualization, development, manufacturing, distribution, marketing, use, and post-use disposition that incorporate

- Design for the environment principles
- Green engineering
- Green chemistry
- Business practices built upon the concepts of systems thinking and “eco-efficiency”

And the Consumption Paradox

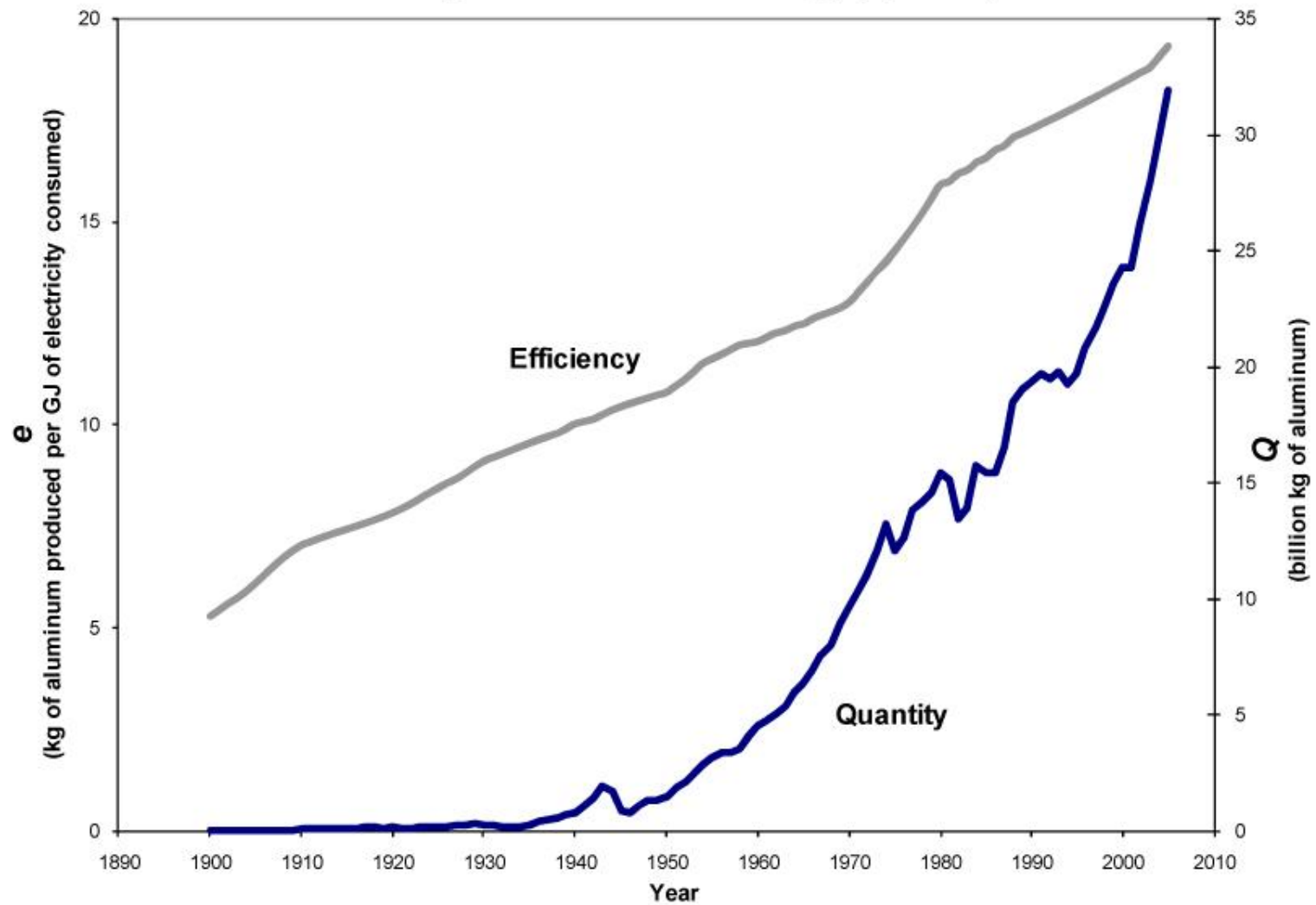
If “greening” principles and practices can become widespread enough, then better material and energy efficiencies will result, effectively “decoupling” environmental impacts from the consumptive habits of the human population

If a greater variety of more efficient and environmentally-conscious products and services are made available, usually at lower costs, societal benefits will necessarily result, thereby moving toward at least partial fulfillment of the sustainability paradigm

Rebound Effect?

- Through improved efficiency, the price of an item, or the services/conveniences it enables, becomes lower, so consumers demand more
 - A little more (“rebound”)
 - More than the benefit (“backfire”)

Primary Aluminum Production (Q) and the Efficiency of Aluminum Smelting (e) (World)



From: Dahmus and Gutowski, 2010 (in prep)

Historical Efficiency and Consumption Trends

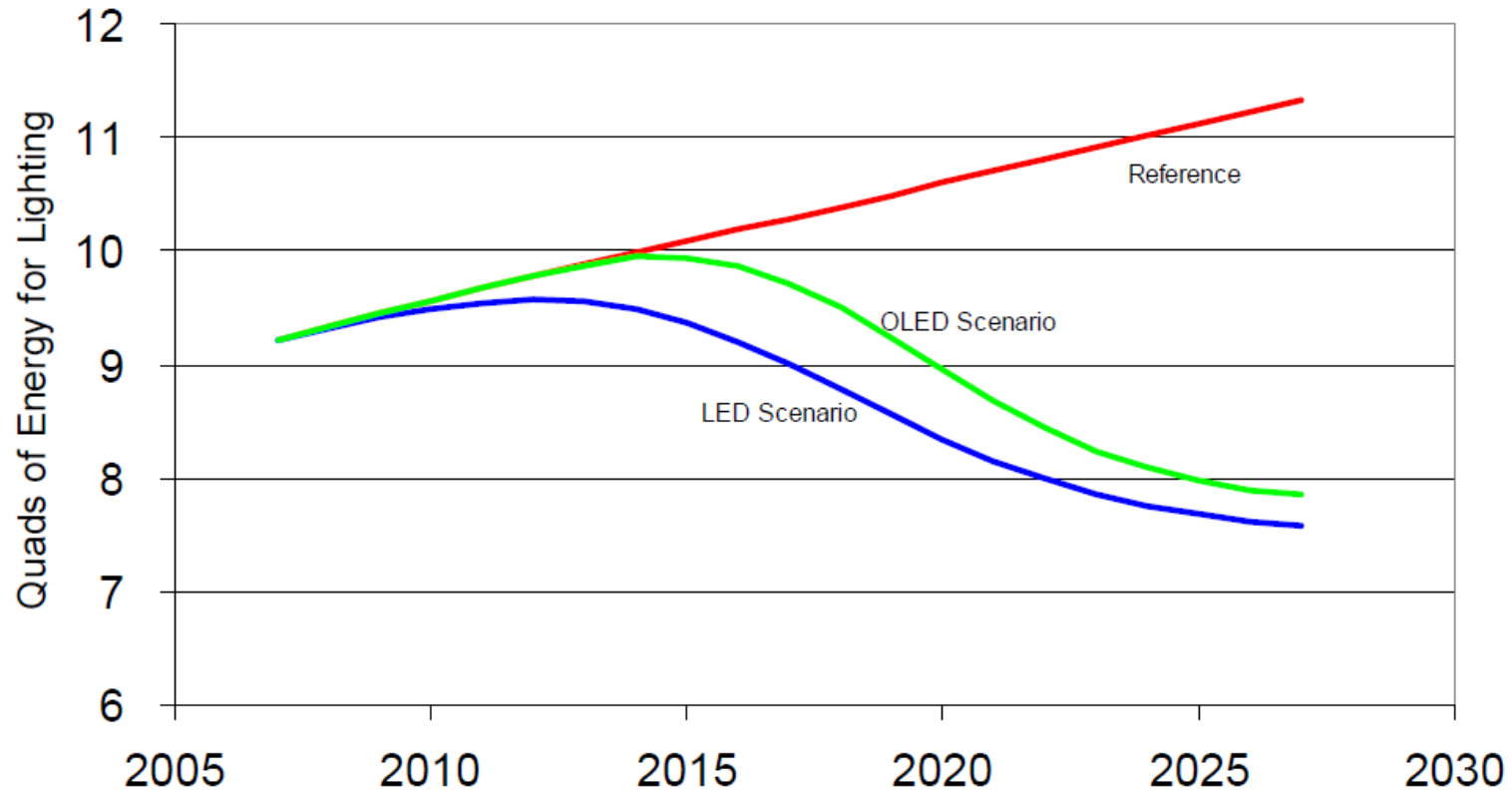
(Dahmus and Gutowski, JIE 2011)

Activity	Sector	Time Period	Avg Annual Efficiency Improvement (%)	Avg Annual Increase in Consumption (%)	Ratio: Consumption/ Efficiency
Pig Iron	Materials	1800-1990	1.4	4.1	3.0
Aluminum	Materials	1900-2005	1.2	9.8	7.9
N-Fertilizer	Food	1920-2000	1.0	8.8	8.9
Elec-Coal	Energy	1920-2007	1.3	5.7	4.5
Elec-Oil	Energy	1920-2007	1.5	6.2	4.2
Elec-Nat Gas	Energy	1920-2007	1.8	9.6	5.5
Freight Rail Travel	Transportation	1960-2006	2.0	2.5	1.2
Air Passenger Travel	Transportation	1960-2007	1.3	6.3	4.9
Motor Vehicle Travel	Transportation	1940-2006	0.3	3.8	11.0

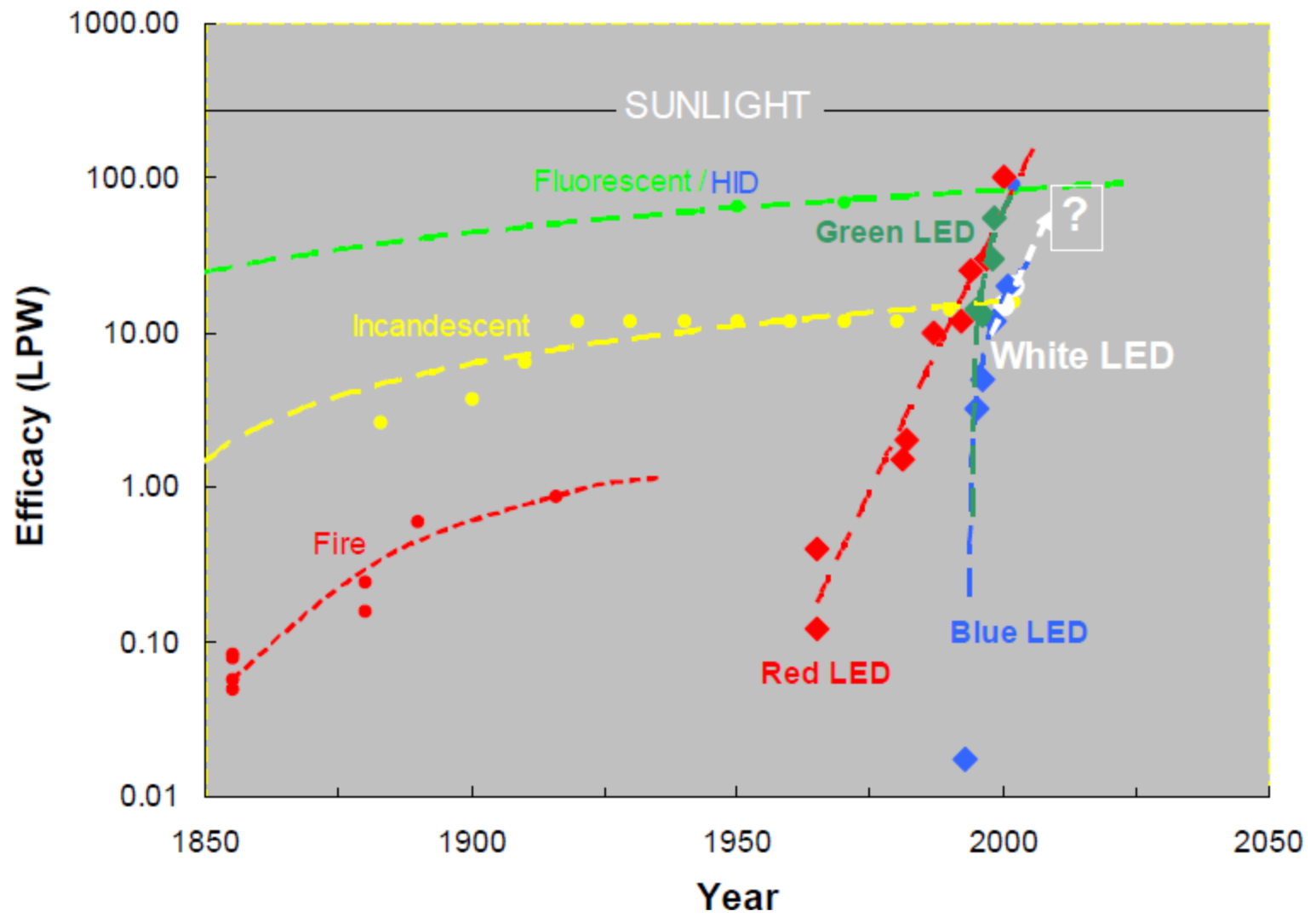
Example: Nano-Enabled Artificial Lighting

- No realistic substitutions
- Lighting is undergoing a “nano-enabled” evolution to SSL
- SSL: About 10 times as efficient as incandescent, 2 times fluorescent
- Last 30 times as long as incandescent, 3 times as long as CFLs
- So, we’ll use less energy and generate fewer energy-related emissions, right?

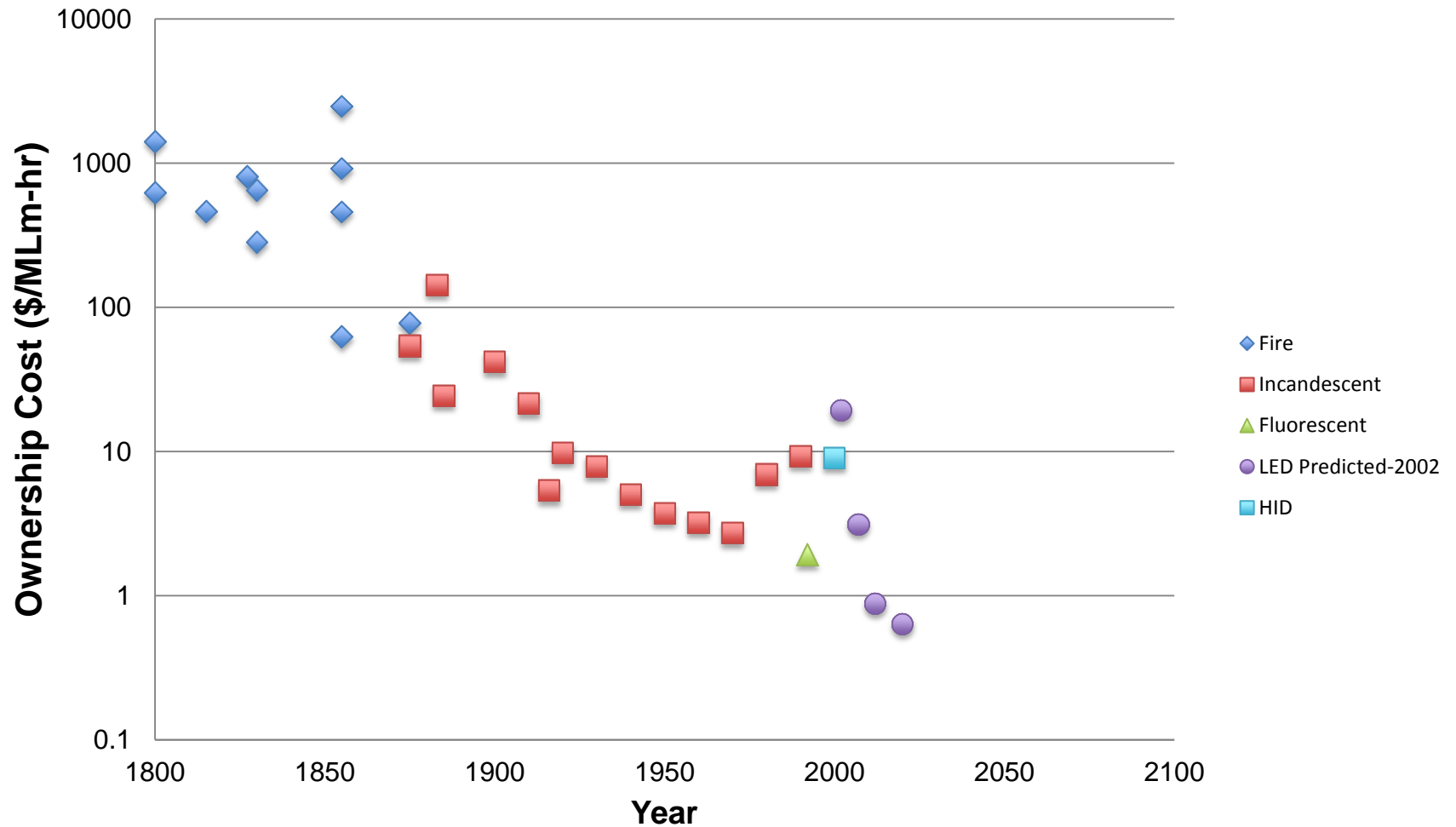
Projections for Energy Consumption for Lighting Through 2027 (US)



“Energy Savings Potential of Solid State Lighting in General Illumination Applications”, Navigant Consulting, Washington DC (2006)



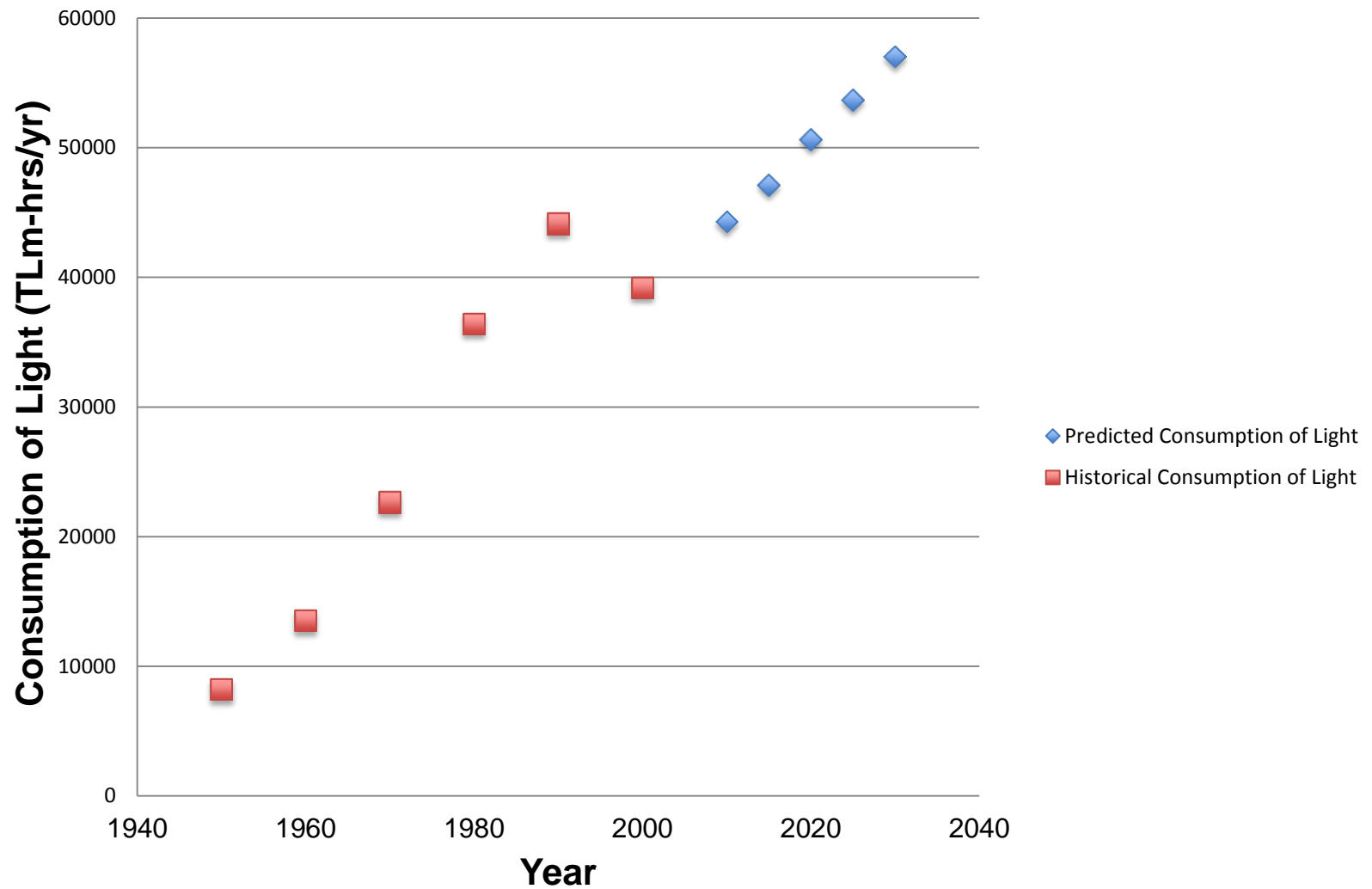
Total Cost of Ownership for Artificial Lighting, 1800-2010



Data for Fire and Incandescence modified from W.D. Nordhaus,
In T.F. Breshnahan and R.J. Gordon, Eds., The Economics of
New Goods (U of Chicago Press, 1997) pp. 29-70.
Data for SSL-LEDS taken from 2002 U.S. SSL Roadmap.

Expressed in 2010 dollar amounts

Past and Predicted Consumption of Light



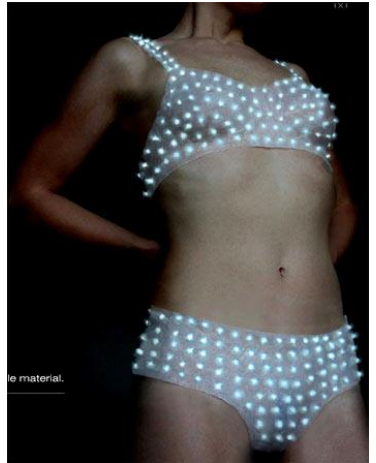
Source for predicted consumption: Energy Savings Potential of Solid-State Lighting in General Illumination Applications 2010 to 2030 Navigant Consulting, 2010

Summary trends

YEAR	Real Price of Fuel	Efficiency of Lighting	Real Price of Light	Consumption of Light	Energy for Light	Energy/ Person for Light	% of Total Energy Devoted to Light
1800	1	1	1	1	1	1	1
1900	0.27	14.5	.024	220	8.97	2.45	~1
2000	0.18	700	0.0003	34,000	72.92	11.63	10

xlighbox.en.alibaba.com







Costs and Benefits

- (1) Each of these applications, viewed by itself, is more efficient than what it replaced.
- (2) Many, maybe all, of these applications help us to be safer, healthier, happier, more productive, and “greener”
- (3) But viewed collectively, will our energy and material consumption continue to increase?

Nano may make us “greener”, but will it make us more sustainable?

Combining physical and social science...

J Y Tsao, H D Saunders, J R Creighton, M E Coltrin and J A Simmons (2010) "Solid-state lighting: an energy-economics Perspective", *J. Phys. D: Appl. Phys.* 43 (2010) 354001

There is a *massive* potential for growth in the consumption of light if new lighting technologies are developed with higher luminous efficacies and lower cost.

This increased consumption may increase both human productivity but also the consumption of energy associated with that productivity.

Is the increase in human productivity and quality of life due to an increase in consumption of light worth the increased potential for exposure and use of energy?

In conclusion... there is a need to work both
sides of the equation

“Greener” product chains—lower embodied energy, fewer toxic materials, lower waste production, less exposure, greater eco-efficiency

Better understanding of the social contexts in which nano-enabled products are used— the need to address the complex factors emergent across the complete product chain that contribute to resource consumption, while recognizing benefits to society