Green Chemistry Education Webinar Series

Introduction to Green Engineering

July 29, 2014
Today’s Speakers

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Green Chemistry and Engineering: The How of Sustainability

Julie Beth Zimmerman, PhD
School of Engineering and Applied Science
School of Forestry and Environmental Studies
Yale University
Doing the right things wrong

- Can we appropriately and successfully address sustainability challenges if our designs are not in themselves sustainable?
Doing the right things wrong

Purifying water with acutely lethal substances
Doing the right things wrong

Precious, rare, toxic metals in photovoltaics
Doing the right things wrong

Agricultural crop efficiency from persistent pesticides
Doing the right things wrong

Energy saving compact fluorescent light bulbs reliant on toxic metals
How did we get there?

- Urgent and necessary challenges
- Noble goals
- Exciting science and technology
- Best of intentions
New Approach

- Innovation based
- Solutions oriented
- Advancing competitiveness
- Intrinsic versus circumstantial
- Systematic sustainability
Sustainability

“the design of human and industrial systems to ensure that mankind’s use of natural resources and cycles do not lead to diminished quality of life due either to losses in future economic opportunities or to adverse impacts on social conditions, human health, and the environment”

The necessary transformational change of engineering design
Impacts of Design Decisions

- For a typical product, 70% of the cost of development, manufacture and use is determined in its design phase.
- Analogous for environmental impacts.
Not just how you design but **what** you design

Schematic of potential benefits vs. investments

- **incremental**
- **re-engineer the system**
- **re-define the problem**

- Investments (i.e., time, money, resources, energy)
Leap frog or disruptive innovation
Sustainability

“Sustainability” without innovation is....unsustainable.

“Innovation” without sustainability is....unsustainable.
Biomimicry
How many chemical pigments are needed to produce this assortment of colors?

None! Color is produced through optical interference arising from the surface structure of the feathers.
Textiles...

How many pigments used here?
The textiles sector uses thousands of chemicals, many of them toxic.
Abalone Shell

- Twice as hard as high-tech ceramics.
- Behaves like metal under stress.
How Industry Makes Ceramics

- **BEAT...** clay to proper consistency.
- **BAKE...** at high temperatures (2000 - 3000 °F).
  - for prolonged periods (15 – 50 Hours).

(Ceramics Industry Major Contributor To Global Warming)
How do we make things?

“Heat, beat, and treat”
How nature makes things...

* Nature runs on sunlight
* Nature uses only the energy it needs
* Nature fits form to function
* Nature recycles everything
* Nature rewards cooperation
* Nature banks on diversity
* Nature demands local expertise
* Nature curbs excesses from within
* Nature taps the power of limits

- Janine Benyus, *Biomimicry*
Systems thinking
Principles of Green Engineering

1. **Green Chemistry**
3. Design for separation.
4. Maximize mass, energy, space, and time efficiency.
5. “Out-pulled” rather than “input-pushed”.
6. View complexity as an investment.
7. Durability rather than immortality.
9. Minimize material diversity.
10. Integrate local material and energy flows.
11. Design for commercial “afterlife”.
12. Renewable and readily available.

Anastas and Zimmerman, Environmental Science and Technology, March 1, 2003
View complexity as an investment

- Case for modular, standardized, platform-based, upgradable design
Integrate material and energy flows
Durability rather than immortality
Design for commercial “afterlife”

"When we reuse our products — much less recycle them — we keep our costs down significantly," says Rob Fischmann, head of worldwide recycling at Lexmark. "The second-time cost for these cartridges is essentially zero."
Renewable and readily available
CONCENTRATION OF HARDNESS AS CALCIUM CARBONATE IN MILLIGRAMS PER LITER

Figure 5.—Mean hardness as calcium carbonate at NASQAN stations during 1975 water year. Map at bottom is colored to show station data representing flow from the accounting unit.
Need rather than excess
Key concepts and relation to sustainable design

Fundamental concept: Technologies tend to evolve in similar ways towards “ideality”, where all of the benefits of a product can be achieved while the product itself ceases to exist physically.
How we typically waterproof surfaces
Lotus flower
Ideality, sustainability, & product design

Coffee decaffeination using methylene chloride

Coffee beans without caffeine

Coffee decaffeination using CO₂ (not a “solvent” by FDA)
Ideality, sustainability, & product design

The task is the cleaning of clothes; current product is detergent.
Ideation and Sustainability

The “ideal” solutions do represent leap-frog innovations

But.....
Corporate structural problems with ideality

- Leap-frog may not fit within portfolio – can a detergent company develop self-cleaning clothes?
- The will may be present, but the expertise may be lacking.
Leap-frog ideas can create structural problems
A necessary caveat: How do we know our frog is jumping in the right direction?

Some frogs are poisonous..

Sustainability is a process of continuous improvement, we can’t forget to check to make sure we’re actually improving.
Measurement Innovation

Everything that can be counted does not necessarily count; everything that counts cannot necessarily be counted.

- Albert Einstein
Principles of Green Engineering

1. Green chemistry.
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Anastas, PT and Zimmerman, JB (2003)
Environ. Sci. Tech., 37(5) 94A-101A.
Do Principles get us to the Destination?

- **Design** principles
- Should produce superior products and projects
- Need to follow up with comprehensive assessment to ensure performance and guard against unintended effects
Life Cycle Assessment (LCA)

Focus Areas of Design Principles

Upstream technical systems performing causal activities
- Extraction Process
- Transport
- Refinement Process
- Transport

Technical system performing activities
- Manufacturing Process
- Transport

Downstream technical systems performing causal activities
- Use Process
- Transport
- Waste Treatment Process

Causal raw material extraction
Causal waste generation and emissions
Direct waste generation and emissions
Causal waste generation and emissions

Natural Environmental System

Used with permission. Copyright Raul Carlson and Ann-Christin Pålsson, CPM, Chalmers University of Technology, 1998
Overview

- Brief Description of LCA Methods

- Case Studies
  - Life cycle mercury emissions from CFLs
  - Use of nanomaterials in electronics

- Efforts to Integrate LCA and Green Chem/Engineering
Life Cycle Assessment (LCA) in Brief

A systems modeling tool for characterizing, locating and quantifying the environmental impacts of a product or service.

- Environmental impacts can occur at each life cycle stage and be non-intuitive.
- Need to consider all stages in order to inform design or policy decisions.
- Need to consider multiple environmental impacts, to ensure that we are not simply shifting burdens from one impact to another.
“Its advanced powertrain will deliver significant energy efficiency advantages and zero CO2 emissions without compromising driving enjoyment.”

- Ford, 1/8/11
Life Cycle Assessment Steps

Industrial Activity

Indirect (Background) Data Collected from Secondary Databases
(industrial production of materials and energy carriers)

Direct (Foreground) Data Collected from Primary Sources
(e.g., kWh electricity, liters water, kg finished materials)

Device Materials ➔ China Manufacturing ➔ Individual Packaging ➔ Use

transport / distribution

Assemble into a Life Cycle Inventory (LCI)
system-wide bill of resource use and emissions

Link to Life Cycle Impact Assessment (LCIA)
emission-fate-exposure-effect modeling of impacts
Linking Environmental Impacts to Damages

Midpoint categories (environmental problems)
- Photochemical oxidant formation
  - Human toxicity
  - Ozone depletion
  - Climate change
  - Acidification
  - Eutrophication
  - Ecotoxicity
  - Land use impacts
  - Species & organism dispersal
  - Abiotic resources depletion
  - Biotic resources depletion

Endpoint categories (environmental damages)
- Human Health
- Biotic & abiotic natural environment
- Biotic & abiotic natural resources
- Biotic & abiotic manmade resources

Source: Int J of LCA 9(6) 2004
Ex1 - Mercury Trade-Offs for CFLs

18SECONDS.ORG
CHANGE A BULB. CHANGE EVERYTHING.

United States

CFL LIGHTBULBS PURCHASED SINCE 1/1/07:
145,132,366

EQUIVALENCY:
DOLLARS SAVED: $4,285,091,159
CARS OFF THE ROAD: 1,029,592
POUNDS OF COAL SAVED: 15,108,686,214
POUNDS OF CO2 PREVENTED: 64,665,176,995

CHANGE A BULB, CHANGE EVERYTHING
It only takes 18 seconds to change a light. Save energy and cash now by switching to Energy Star CFL bulbs, available nearly everywhere light bulbs are sold.

HOW ENLIGHTENED IS YOUR AREA?

SELECT YOUR STATE OR FIND IT

The typical home has more than 40 sockets for light bulbs.
# Mercury Sources in US

The major sources of atmospheric mercury in the United States are:

<table>
<thead>
<tr>
<th>Source</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utility boilers</td>
<td>32.8%</td>
</tr>
<tr>
<td>MSW combustors</td>
<td>18.7%</td>
</tr>
<tr>
<td>Commercial/Ind boilers</td>
<td>17.9%</td>
</tr>
<tr>
<td>Medical waste incinerators</td>
<td>10.1%</td>
</tr>
<tr>
<td>Chlor-alkali</td>
<td>4.5%</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Fluorescent lamps</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

Total Emissions: 144 Mg/yr

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**Mercury Study Report to Congress**

Volume II: An Inventory of Anthropogenic Mercury Emissions in the United States
Indirect Mercury Emissions

Coal coming in

- Coal heat content
- Coal washing
- Coal Hg content

Electric Power Production

- Conversion efficiency
- Pollution control
- Volatilization fraction

Electricity mix

- Trans & dist losses
- Grid transfers

Electricity coming out

Reduced demand from lighting efficiency
US Results

Ex2- Carbon Nanotube Life Cycle

- Adapt consensus USEtox impact assessment model for SWNTs to include colloidal processes
- Only consider freshwater ecotoxicity
Differential CNT Toxicity

- Metallic or semiconducting depending on chirality and number – this also helps determine toxicity
- Large variation among CNT types in parameters that affect fate, transport, and toxicity

Purification and treatment
Aspect ratio
Residual metal content

Chirality

Functionalization
Worst Case Scenario
100% release; All CNTs stable in water column

Realistic Scenario
Modeled concentrations based on fate and transport parameter estimates

Gottschalk et al. (2009). Env. Sci. Technol. 43, 9216-9222
CNT Ecotoxicity Production vs Releases

SAN FRANCISCO — I.B.M. scientists are reporting progress in a chip-making technology that is likely to ensure that the basic digital switch at the heart of modern microchips will continue to shrink for more than a decade.

The advance, first described in the journal Nature Nanotechnology on Sunday, is based on carbon nanotubes — exotic molecules that have long held out promise as an alternative to silicon from which to create the tiny logic gates now used by the billions to create microprocessors and memory chips.

The I.B.M. scientists at the T.J. Watson Research Center in Yorktown Heights, N.Y., have been able to pattern an array of carbon nanotubes on the surface of a silicon wafer and use them to build hybrid chips with more than 10,000 working transistors.
Life Cycle of Nano-enabled Products

Should a new GE principle be no nano?

A

- Global Warming
- Acidification
- Carcinogenics
- Non carcinogenics
- Respiratory effects
- Eutrophication
- Ozone Depletion
- Ecotoxicity
- Smog Formation

Si wafer production
W sputter plasma etch
remaining processes

Cr-Au e-beam evaporation

B

- Impact categories

Au mining/refining
electricity
chemicals
remaining processes

Global Warming
Acidification
Carcinogenics
Non carcinogenics
Respiratory effects
Eutrophication
Ozone Depletion
Ecotoxicity
Smog Formation

CNT synthesis is insignificant: <0.000000000000001% of impacts

Integration of Green Chem/Eng + LCA

We’re getting closer...
Green Chemistry Limitations

- GC Principles guard against use of toxic inputs, but the field does not have a consensus quantitative method for evaluating upstream inherent risk.

- *iSustain* metrics for green chemistry principles

\[
I = \frac{\sum_i (MatImpact_i)(wt\% \ RawMat_i)(100 - Rec\%_i)}{\sum_i (wt\% \ RawMat_i)(100 - Rec\%_i)} \\
\text{scaled 1-100 on safety, health effects, environment, regulatory status}
\]

- Only considers ‘first tier’ inputs, doesn’t consider multiple intermediate steps and complexities.
Green Chemistry and LCA

- *Life cycle assessment and green chemistry: the yin and yang of industrial ecology*
  - Anastas and Lankey

- *Life-Cycle Approaches for Assessing Green Chemistry Technologies*
  - Lankey and Anastas

- LCA identifies hotspots and GC used to inform design...
Life Cycle Assessment Limitations

characterization factors have units of impact/kg emitted...

zero emissions means zero impacts
Polycarbonate is contaminated with Cl
Requires stoichiometric quantities of phosgene
Phosgene is highly toxic and corrosive
To calculate the LCI of a product system generating a given reference flow, we first calculate the activity vector, which represents all outputs of the product system, including all intermediate flows

$$\vec{q} = A \times \vec{\gamma} \Rightarrow \vec{\gamma} = A^{-1} \times \vec{q}$$

and multiply the vector of activity levels with the matrix of elementary flows

$$\vec{e} = B \times \vec{\gamma}$$

Impacts are calculated with the inventory vector and characterization factors:

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} \\ c_{21} & c_{22} & c_{23} & c_{24} \\ c_{31} & c_{32} & c_{33} & c_{34} \end{pmatrix} \begin{pmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \end{pmatrix} = \begin{pmatrix} i_1 = \sum_{m=1}^{4} c_{1m} \cdot e_m \\ i_2 = \sum_{m=1}^{4} c_{2m} \cdot e_m \\ i_3 = \sum_{m=1}^{4} c_{3m} \cdot e_m \end{pmatrix}$$
Now calculate impacts based on use of all intermediate flows, rather than emissions

\[ i^* = \sum_{k} c_k \cdot \gamma_k \]

This represents life cycle inherent hazard or toxicity, NOT based on projected emissions.
Conclusions

- Life cycle modeling is a useful complement to Green Engineering design principles

- Indirect impacts or benefits may outweigh direct effects, so be careful for unintended trade-offs

- New tools and metrics are being introduced regularly to support Green Engineering practices
GC3 Webinar on Green Engineering

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Thanks!
GC3 Webinar on Green Engineering

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Green Engineering Case Studies: Methods and Applications

- Economic Assessment
  - Materials Recovery Facility for Computer Displays (CRTs)
  - Cell Phone Disassembly

- Toxicity Potential and Chemical Hazard Assessment
  - Utility Meter Products
  - Thin Film Photovoltaics (CIGS)

- Hazardous Waste, Resource Depletion and Toxicity Potentials
  - Light Emitting Diodes (LEDs)
  - Artificial Lighting (LEDs, CFLs, Incandescent)
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Materials flow for end-of-life electronics

- Obsolete electronics
  - Collection and separation
    - MRF
  - Donation
- Reuse
- Smelter
- CRT Mfg.
- Plastics Mfg.
- Chemical recycling
- Refurbished
- Metal
- Mixed Plastic
- Glass
- Separated Plastics
- Mixed Plastic
- Waste landfills
- Incineration

Mfg.: Manufacturing
MRF: materials recovery facility

Cathode Ray Tube (CRT) recycling

**Glass-to-Glass recycling**
- Closed loop recycling
- Conventional process
  - Separate case and metal part
  - Depressurize the tube, grind to cullet
  - Mixed output
- Saw cutting process
  - Cut with saw
  - Intact panel and funnel glass
  - Separate panel and funnel glass

**Glass-to-Lead (Pb) recycling**
- Open loop recycling
- Pb in the CRTs
- Crush and remove foreign materials
- Pb smelter

---

CRTs after depressurized

Exporting harm, 2002

Saw cut CRT: funnel, panel.

Deer2, 2003

Secondary copper (Cu) recycling

- **Blast Furnace**
  - Electronic scrap: 5 ~ 40 % Cu
  - Reduction: \( \text{Fe} + \text{Cu}_2\text{O} \rightarrow \text{FeO} + 2\text{Cu} \)
  - Black Copper: 70 ~ 85%Cu

- **Converter**
  - Oxidation: \( 4\text{Cu} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{O} \)
  - Blister Copper: ~95% Cu, oxide form.

- **Anode Furnace**
  - Reduce Cu (reductant: plastics, wood)
  - Cu cast into Anode: ~ 98.5% Cu

- **Refining Electrolysis**
  - Dissolved in \( \text{H}_2\text{SO}_4 \) electrolyte
  - Pure Cu deposited on cathode: 99.99%
  - Precious metals recovered as anode slimes

Precious metals recovery

- Silver, gold, platinum, palladium
- By-products of copper smelter
- Anode slime from copper electrolysis process.

Flow of cost and revenue in a MRF

Material Recovery Facility (MRF)

Resale system/component

Materials recovery

Fee from customers

Fixed costs

Variable costs

Equipment cost

Building cost

Labor cost

Energy cost

Materials cost

Transportation cost

Cost analysis (1)

Annual operating cost for an e-waste MRF.

Cost element

<table>
<thead>
<tr>
<th>Cost element</th>
<th>Cost (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labor</td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td></td>
</tr>
<tr>
<td>Transportation</td>
<td></td>
</tr>
<tr>
<td>Equipment</td>
<td></td>
</tr>
<tr>
<td>Building</td>
<td></td>
</tr>
</tbody>
</table>

Unit operation

<table>
<thead>
<tr>
<th>Unit operation</th>
<th>Cost (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collection</td>
<td></td>
</tr>
<tr>
<td>Sorting</td>
<td></td>
</tr>
<tr>
<td>Testing</td>
<td></td>
</tr>
<tr>
<td>Dismantling</td>
<td></td>
</tr>
<tr>
<td>Size reduction</td>
<td></td>
</tr>
<tr>
<td>Separation</td>
<td></td>
</tr>
<tr>
<td>Landfill</td>
<td></td>
</tr>
<tr>
<td>CRT recycling</td>
<td></td>
</tr>
<tr>
<td>Sales</td>
<td></td>
</tr>
<tr>
<td>Customer rebate</td>
<td></td>
</tr>
</tbody>
</table>

CRT: 75 wt%, CPU: 25 wt%. Treatment amount: 2,500 ton/year.

Revenue analysis (1)

Distribution of revenue by revenue source

Metals recovery 28%
Plastics recovery 7%
Resale systems/components 5%

Fee charged to customers 60%

CRT: 75 wt%, CPU: 25 wt%, Total treatment: 2,500 ton/year.

Green Engineering Case Studies: Methods and Applications

- **Economic Assessment**
  - Materials Recovery Facility for Computer Displays (CRTs)
  - Cell Phone Disassembly

- **Toxicity Potential and Chemical Hazard Assessment**
  - Utility Meter Products
  - Thin Film Photovoltaics (CIGS)

- **Hazardous Waste, Resource Depletion and Toxicity Potentials**
  - Light Emitting Diodes (LEDs)
  - Artificial Lighting (LEDs, CFLs, Incandescent)
Characteristics of the product system for a cell phone

Hierarchical “bill of materials” based structure of a cellular phone

- **I=0**: Cell phone
  - **I=1 (n=5)**: Battery, Charger, Main PCB, Display module, Camera module, Enclosure/mechanical
    - **I=3 (n=55)**: User interface, Baseband, RF/IF, Memory, Mechanical, Power amplifier
      - **I=4 (n=100)**: IC, Discrete semiconductor, Optical semiconductor, Passive, Battery
        - **I=5 (n=222)**: Diode, Transistor
        - **I=6 (n=614)**: Resistor, Capacitor, Magnetic

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Reducing toxicity potential in RIO Tronics electronic utility meter products

(a) PulsePoint - for domestic gas meters
(b) RegistRead – for dial indexes on both gas and electric meters
(c) RotaRead - for rotary gas meters
(d) Remote Consumption Display (RCD) – display unit connectable to other meter sensors
Product bill-of-materials

- Bill of materials information provided by RIO Tronics
- Component compositions are quantified based on information provided by component manufacturers/suppliers and also estimated through dimensional specifications (e.g., printed wiring board components).
- Composition uncertainty is introduced due to reliability of data

Lam, Lim, Ogunseitan, Shapiro, Saphores, Brock, Schoenung, *IEAM, Volume 9, Number 2, pp. 319-328*
Fraunhofer IZM Toxic Potential Indicator (TPI)

Takes into account three main toxicity inputs based on European Union (EU) regulations:

1) Occupational exposure limits based on maximum workplace concentration (MAK) or EU carcinogenic classification;
2) Water hazard classification (WGK); and
3) Risk phrases (R-phrases)

Outputs a TPI score for materials from zero to 100.
Two component TPI scoring methods

1) Sum-weighted Component TPI method – weights TPI scores by mass of materials in components

\[ TPI_{\text{sum}}_k = \sum \text{mass}_{j,k} \ast TPI_{j,k} \]

2) Max Component TPI method – assigns max TPI score to component based on highest impact material

\[ TPI_{\text{max}}_k = \max(TPI_{\text{all_materials},k}) \]

where \( j \) represents material and \( k \) represents component.
Summary Results for Both Component TPI Scoring Methods (e.g., PulsePoint)

<table>
<thead>
<tr>
<th>PulsePoint Component Rank</th>
<th>Sum-weighted method (baseline)</th>
<th>Sum-weighted method (sensitivity analysis)</th>
<th>Max method (baseline)</th>
<th>Max method (sensitivity analysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bracket</td>
<td>Bracket</td>
<td>Grommet</td>
<td>Grommet</td>
</tr>
<tr>
<td>2</td>
<td>Cable wire</td>
<td>Cable wire</td>
<td>Bracket</td>
<td>Bracket</td>
</tr>
<tr>
<td>3</td>
<td>Grommet</td>
<td>Magnets</td>
<td>Spring clip</td>
<td>Spring clip</td>
</tr>
<tr>
<td>4</td>
<td>Magnet base-B</td>
<td>Grommet</td>
<td>Printed wiring board</td>
<td>Printed wiring board</td>
</tr>
<tr>
<td>5</td>
<td>Spring clip</td>
<td>Magnet base-B</td>
<td>Resistor</td>
<td>Resistor</td>
</tr>
</tbody>
</table>
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Overview of CIGS Technology

CIGS is one of the most promising thin-film PV technologies
CIGS = CuInGaS/Se

http://solarcellcentral.com/solar_page.html
Module Layer

- Encapsulant
- Top Conducting Oxide (N-Type Window)
- Buffer Layer
- CIGS (P-Type Absorber)
- Metal Back Electrode
- Substrate

Layer Options

- EVA
- EMA
- Polyurethanes
- Silicones
- Zn$^{2+}$ Oxide
- Boron
- Aluminum
- Gallium
- Cd based
- Zn based
- In based
- Cu(In,Ga)Se$_2$
- Cu(In,Ga)(S,Se)$_2$
- CuInS$_2$
- Mo
- Solid: SLS Glass
- Flexible: Metal or Polymer

*EVA: Ethylene Vinyl Acetate, EMA: Ethylene Methacrylic Acid  *SLS: Soda Lime Glass

CIGS Production
P-Type Absorber

Cu(In,Ga)Se$_2$
Cu(In,Ga)(S,Se)$_2$
CuInS$_2$

Industrial Methods
Co-evaporation
Sulfurization/Selenization

Laboratory Methods
Ink Printing
Electrodeposition
Chemical Vapor Deposition

## CHA Tools: TPI and Green Screen for Safer Chemicals

<table>
<thead>
<tr>
<th>Priority Human Health Effects (PE)</th>
<th>Human Health Effects (HH)</th>
<th>Ecotoxicity (Eco)</th>
<th>Environmental Fate (EF)</th>
<th>Physical Hazards (Phy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carcinogenicity (C)</td>
<td>Acute Toxicity (AT)</td>
<td>Acute Aquatic Toxicity (AA)</td>
<td>Persistence (P)</td>
<td>Explosivity (E)</td>
</tr>
<tr>
<td>Mutagenicity (M)</td>
<td>Irritation and Corrosion (IC)</td>
<td>Chronic Aquatic Toxicity (CA)</td>
<td>Bioaccumulation (B)</td>
<td>Flammability (F)</td>
</tr>
<tr>
<td>Reproductive (R)</td>
<td>Skin/Eye Sensitization (S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Developmental (D)</td>
<td>Immune System effects (IS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endocrine Disruption (ED)</td>
<td>Systemic Organ Toxicity (SOT)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Neurological (N)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Utilizes 17 hazard traits from United Nations Globally Harmonized System (GHS)

*CHA: Chemical Hazard Assessment*

When all hazard traits are accounted for use iterative scheme to determine final hazard benchmark.

**Benchmark 1:** Chemical of High Concern

**Benchmark 2:** Use but Search for Safer Substitutes

**Benchmark 3:** Use but Still Opportunity for Improvement

**Benchmark 4:** Safer Chemical

Must pass all benchmark criteria before considered for next level.

---

Substance Level CHA Example: Green Screen of CdS

<table>
<thead>
<tr>
<th>CAS #/Material</th>
<th>PE</th>
<th>HH</th>
<th>Eco</th>
<th>EF</th>
<th>Phy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1306-23-6/CdS</td>
<td>C</td>
<td>M</td>
<td>R</td>
<td>D</td>
<td>ED</td>
</tr>
</tbody>
</table>

Use GHS and other national and international standardized hazard classification systems to determine relative hazard of each trait.

## Substance Level CHA Example: Green Screen of CdS

<table>
<thead>
<tr>
<th>CAS #/Material</th>
<th>PE</th>
<th>HH</th>
<th>Eco</th>
<th>EF</th>
<th>Phy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1306-23-6/CdS</td>
<td>1A</td>
<td>3</td>
<td>2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>--</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Use GHS and other national and international standardized hazard classification systems to determine relative hazard of each trait

*ND: Not Detectable or No Data

Substance Level CHA Example: Green Screen of CdS

<table>
<thead>
<tr>
<th>CAS #/Material</th>
<th>PE</th>
<th>HH</th>
<th>Eco</th>
<th>EF</th>
<th>Phy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1306-23-6/CdS</td>
<td>1A</td>
<td>3</td>
<td>2</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

High Hazard in Priority Health Effects

Medium Hazard in Priority Health Effects and High Hazard in Human Health Effects

Very High Health Toxicity

CdS = Benchmark 1: Chemical of Concern

*CHA: Comparative Hazard Assessment

### Process Level CHA Example: CIGS Deposition

<table>
<thead>
<tr>
<th>CIGS Deposition Process</th>
<th>GS-Based Benchmark frequency</th>
<th>TPI score frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>low    mid  high  very high</td>
</tr>
<tr>
<td><strong>Type of Processing</strong></td>
<td><strong>Specific Deposition Method</strong></td>
<td>4  3  2  1</td>
</tr>
<tr>
<td><strong>Industrial Process</strong></td>
<td>Coevaporation</td>
<td>0  1  4  0</td>
</tr>
<tr>
<td><strong>Ink Printing</strong></td>
<td>Spray Pyrolysis of CuInS$_2$</td>
<td>0  0  2  1</td>
</tr>
<tr>
<td><strong>Electrodeposition</strong></td>
<td>Kapmann Method</td>
<td>1  1  4  2</td>
</tr>
<tr>
<td><strong>Industrial Process</strong></td>
<td>Sulfurization/ Selenization</td>
<td>1  1  4  1</td>
</tr>
<tr>
<td><strong>Chemical Vapor Deposition</strong></td>
<td>AP-MOCVD</td>
<td>0  0  6  1</td>
</tr>
<tr>
<td><strong>Electrodeposition</strong></td>
<td>Kapmann Method with Ammonia</td>
<td>1  1  4  3</td>
</tr>
</tbody>
</table>

**Hazard**

Low  →  High  →  Low  →  High

Green Engineering Case Studies: Methods and Applications

- Economic Assessment
  - Materials Recovery Facility for Computer Displays (CRTs)
  - Cell Phone Disassembly

- Toxicity Potential and Chemical Hazard Assessment
  - Utility Meter Products
  - Thin Film Photovoltaics (CIGS)

- Hazardous Waste, Resource Depletion and Toxicity Potentials
  - Light Emitting Diodes (LEDs)
  - Artificial Lighting (LEDs, CFLs, Incandescent)
3. Materials and Methods
3.1. Materials

○ Small LEDs

<table>
<thead>
<tr>
<th>Sample Name (color/intensity)</th>
<th>Red /Low</th>
<th>Red /High</th>
<th>Yellow /Low</th>
<th>Yellow /High</th>
<th>Green /Low</th>
<th>Green /High</th>
<th>Blue /Low</th>
<th>Blue /High</th>
<th>White</th>
</tr>
</thead>
<tbody>
<tr>
<td>LED Color</td>
<td>Red</td>
<td>Red</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Green</td>
<td>Green</td>
<td>Blue</td>
<td>Blue</td>
<td>White</td>
</tr>
<tr>
<td>Luminous Intensity (mcd)</td>
<td>150</td>
<td>6000</td>
<td>50</td>
<td>9750</td>
<td>50</td>
<td>5000</td>
<td>400</td>
<td>900</td>
<td>10000</td>
</tr>
<tr>
<td>Average Weight (g)</td>
<td>0.3098</td>
<td>0.2792</td>
<td>0.3130</td>
<td>0.2822</td>
<td>0.3114</td>
<td>0.2984</td>
<td>0.2982</td>
<td>0.3001</td>
<td>0.3068</td>
</tr>
</tbody>
</table>

Figure

3. Materials and Methods
3.1. Materials

○ Bulbs

<table>
<thead>
<tr>
<th></th>
<th>Incandescent Bulb</th>
<th>CFL Bulb</th>
<th>LED Bulb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wattage (W)</td>
<td>60</td>
<td>13</td>
<td>7.3</td>
</tr>
<tr>
<td>Luminous Intensity (lumens)</td>
<td>860</td>
<td>800</td>
<td>280</td>
</tr>
<tr>
<td>CRI (Color Rendering Index)</td>
<td>100</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Color Temperature</td>
<td>3000*</td>
<td>2700</td>
<td>3000-3500</td>
</tr>
<tr>
<td>Lifetime (hours)</td>
<td>1000</td>
<td>10,000</td>
<td>50,000</td>
</tr>
<tr>
<td>Working Voltage (V)</td>
<td>120</td>
<td>120</td>
<td>85-265</td>
</tr>
<tr>
<td>Weight (g)</td>
<td>26</td>
<td>58</td>
<td>172</td>
</tr>
</tbody>
</table>
## 4. Results and Discussion

### 4.1. Leachability Test: Small LEDs

TCLP results for U.S. EPA hazardous waste regulation

<table>
<thead>
<tr>
<th>Substance</th>
<th>TCLP Threshold</th>
<th>LED (color/intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Red /Low</td>
</tr>
<tr>
<td>Aluminum</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Antimony</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Arsenic</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Barium</td>
<td>100.0</td>
<td>-</td>
</tr>
<tr>
<td>Cerium</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Chromium</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Copper</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Gallium</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Gold</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Indium</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Iron</td>
<td>N/A</td>
<td>-332.5</td>
</tr>
<tr>
<td><strong>Lead</strong></td>
<td>5.0</td>
<td><strong>186</strong></td>
</tr>
<tr>
<td>Mercury</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Nickel</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Silver</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Tungsten</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Yttrium</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Zinc</td>
<td>N/A</td>
<td>-</td>
</tr>
</tbody>
</table>

- "N/A" : Not Applicable, "-" : Not Detected
4. Results and Discussion

4.1. Leachability Test: **Small LEDs**

○ TTLC results for State of California hazardous waste regulation

<table>
<thead>
<tr>
<th>Substance</th>
<th>TTLC Threshold</th>
<th>Red/Low</th>
<th>Red/High</th>
<th>Yellow/Low</th>
<th>Yellow/High</th>
<th>Green/Low</th>
<th>Green/High</th>
<th>Blue/Low</th>
<th>Blue/High</th>
<th>White</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>N/A</td>
<td>97.0</td>
<td>158.0</td>
<td>104.0</td>
<td>156.0</td>
<td>79.6</td>
<td>156.0</td>
<td>153.0</td>
<td>73.4</td>
<td>84.5</td>
</tr>
<tr>
<td>Antimony</td>
<td>500</td>
<td>15.4</td>
<td>2.0</td>
<td>2.8</td>
<td>1.9</td>
<td>3.6</td>
<td>2.5</td>
<td>1.3</td>
<td>1.5</td>
<td>25.9</td>
</tr>
<tr>
<td>Arsenic</td>
<td>500</td>
<td>11.8</td>
<td>111.0</td>
<td>8.0</td>
<td>84.6</td>
<td>7.8</td>
<td>15.2</td>
<td>5.7</td>
<td>5.4</td>
<td>-</td>
</tr>
<tr>
<td>Barium</td>
<td>10000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cerium</td>
<td>N/A</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chromium</td>
<td>500(VI);2500(III)</td>
<td>138.0</td>
<td>28.6</td>
<td>32.7</td>
<td>27.9</td>
<td>84.1</td>
<td>49.3</td>
<td>50.9</td>
<td>30.3</td>
<td>65.9</td>
</tr>
<tr>
<td>Copper</td>
<td>2500</td>
<td>87.0</td>
<td>3818.0</td>
<td>956.0</td>
<td>2948.0</td>
<td>1697.0</td>
<td>3702.0</td>
<td>3892.0</td>
<td>2153.0</td>
<td>31.8</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>N/A</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gallium</td>
<td>N/A</td>
<td>135.6</td>
<td>95.0</td>
<td>63.8</td>
<td>79.1</td>
<td>75.6</td>
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<td>2.1</td>
<td>1.5</td>
<td>3.8</td>
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<tr>
<td>Gold</td>
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<td>39.8</td>
<td>45.8</td>
<td>30.5</td>
<td>30.1</td>
<td>40.2</td>
<td>176.3</td>
<td>32.5</td>
<td>118.6</td>
<td>115.9</td>
</tr>
<tr>
<td>Indium</td>
<td>N/A</td>
<td>3.4</td>
<td>1.7</td>
<td>2.5</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Iron</td>
<td>N/A</td>
<td>285558.2</td>
<td>363890.8</td>
<td>300905.6</td>
<td>398630.4</td>
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<td>395652.2</td>
<td>339234.5</td>
<td>256499.3</td>
<td>311303.6</td>
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<tr>
<td>Lead</td>
<td>1000</td>
<td>8103.0</td>
<td>8.9</td>
<td>7.7</td>
<td>-</td>
<td>5.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mercury</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<tr>
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<td>2000</td>
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<td>2054.0</td>
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<td>1564.0</td>
<td>1741.0</td>
<td>4083.0</td>
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<td>114.2</td>
<td>-</td>
<td>58.4</td>
<td>-</td>
<td>78.5</td>
<td>91.8</td>
<td>79.1</td>
<td>84.3</td>
<td>110.8</td>
</tr>
<tr>
<td>Silver</td>
<td>500</td>
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<td>409.0</td>
<td>248.0</td>
<td>336.0</td>
<td>270.0</td>
<td>306.0</td>
<td>418.0</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Zinc</td>
<td>5000</td>
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<td>66.2</td>
<td>36.5</td>
<td>63.6</td>
<td>41.8</td>
<td>62.5</td>
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<td>36.7</td>
<td>49.2</td>
</tr>
</tbody>
</table>

- "N/A" : Not Applicable, "-" : Not Detected
4. Results and Discussion
4.1. Leachability Test: Bulbs

○ TCLP results for U.S. EPA hazardous waste regulation

<table>
<thead>
<tr>
<th>Substance</th>
<th>TCLP Threshold</th>
<th>Incandescent Bulb</th>
<th>CFL Bulb</th>
<th>LED Bulb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ground to less than 2 mm</td>
</tr>
<tr>
<td>Aluminum</td>
<td>N/A</td>
<td>13.3</td>
<td>39.8</td>
<td>59.8</td>
</tr>
<tr>
<td>Antimony</td>
<td>N/A</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Arsenic</td>
<td>5</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Barium</td>
<td>100</td>
<td>0.3</td>
<td>2.4</td>
<td>3.3</td>
</tr>
<tr>
<td>Cerium</td>
<td>N/A</td>
<td>47.9</td>
<td>7.6</td>
<td>19.6</td>
</tr>
<tr>
<td>Chromium</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Copper</td>
<td>N/A</td>
<td>ND</td>
<td>4.3</td>
<td>3.1</td>
</tr>
<tr>
<td>Gadolinium</td>
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<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Gallium</td>
<td>N/A</td>
<td>3.6</td>
<td>0.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Gold</td>
<td>N/A</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Indium</td>
<td>N/A</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Iron</td>
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<td>967</td>
<td>1180</td>
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<td>Lead</td>
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<td>0.1</td>
<td>132</td>
<td>44.4</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Nickel</td>
<td>N/A</td>
<td>14.1</td>
<td>7.3</td>
<td>17.0</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>N/A</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Silver</td>
<td>5</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Tungsten</td>
<td>N/A</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Yttrium</td>
<td>N/A</td>
<td>7.1</td>
<td>64.9</td>
<td>26.3</td>
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<tr>
<td>Zinc</td>
<td>N/A</td>
<td>0.9</td>
<td>16.0</td>
<td>175</td>
</tr>
</tbody>
</table>

-"N/A" : Not Applicable, "-" : Not Detected
4. Results and Discussion
4.1. Leachability Test: Bulbs

○ TTLC results for State of California hazardous waste regulation

<table>
<thead>
<tr>
<th>Substance</th>
<th>TTLC Threshold</th>
<th>Incandescent Bulb</th>
<th>CFL Bulb</th>
<th>LED Bulb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>N/A</td>
<td>40,100</td>
<td>31,700</td>
<td>947,000</td>
</tr>
<tr>
<td>Antimony</td>
<td>500</td>
<td>ND</td>
<td>117</td>
<td>123</td>
</tr>
<tr>
<td>Arsenic</td>
<td>500</td>
<td>ND</td>
<td>2.6</td>
<td>ND</td>
</tr>
<tr>
<td>Barium</td>
<td>10000</td>
<td>4.1</td>
<td>17.8</td>
<td>364</td>
</tr>
<tr>
<td>Cerium</td>
<td>N/A</td>
<td>9.4</td>
<td>9.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Chromium</td>
<td>500 (VI); 2500 (III)</td>
<td>5.8</td>
<td>1.1</td>
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</tr>
<tr>
<td>Copper</td>
<td>2500</td>
<td>942</td>
<td>111,000</td>
<td>31,600</td>
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<td>Gadolinium</td>
<td>N/A</td>
<td>ND</td>
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<td>0.1</td>
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<td>Gallium</td>
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<td>7.9</td>
<td>6.0</td>
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<tr>
<td>Gold</td>
<td>N/A</td>
<td>ND</td>
<td>ND</td>
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</tr>
<tr>
<td>Indium</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
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<td>Iron</td>
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<td>12,800</td>
<td>12,300</td>
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<tr>
<td>Lead</td>
<td>1000</td>
<td>6.9</td>
<td>3860</td>
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<td>Mercury</td>
<td>20</td>
<td>0.1</td>
<td>18.3</td>
<td>0.4</td>
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<td>Nickel</td>
<td>2000</td>
<td>188</td>
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<td>151</td>
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<td>Phosphorus</td>
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<td>127</td>
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<tr>
<td>Silver</td>
<td>500</td>
<td>16.2</td>
<td>12.2</td>
<td>159</td>
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<td>Tungsten</td>
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<td>1.4</td>
<td>1.2</td>
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<tr>
<td>Yttrium</td>
<td>N/A</td>
<td>0.6</td>
<td>2540</td>
<td>1.7</td>
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<td>Zinc</td>
<td>5000</td>
<td>320</td>
<td>34,500</td>
<td>4540</td>
</tr>
</tbody>
</table>

-"N/A" : Not Applicable, “ND” : Not Detected

Lim, Kang, Ogunseitan and Schoenung, *Environmental Science & Technology* 2013, 47, 1040-1047
4. Results and Discussion
4.3. Toxicity Potential: Bulbs

○ Comparison of the incandescent, CFL, and LED bulbs taking into account design lifetimes (1000, 10,000, 50,000 hr, respectively).

<table>
<thead>
<tr>
<th>Environmental Impact Assessment Category and Method</th>
<th>Incandescent Bulb</th>
<th>CFL Bulb</th>
<th>LED Bulb</th>
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<tbody>
<tr>
<td>Resource Depletion Potential</td>
<td>CML 2001</td>
<td>1</td>
<td>3</td>
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<tr>
<td></td>
<td>EPS 2000</td>
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<td>5</td>
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<td>Hazard-based Toxicity Potential</td>
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<td>PEL-TWA</td>
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<td>REL-TWA</td>
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<td>8</td>
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<td></td>
<td>TPI</td>
<td>1</td>
<td>16</td>
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<tr>
<td>Life Cycle Impact (USEtox™)-based Toxicity Potential</td>
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<td>22</td>
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<tr>
<td></td>
<td>Rural Air</td>
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<td>22</td>
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<td></td>
<td>Freshwater</td>
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<td>25</td>
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<tr>
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<td>Sea Water</td>
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<td>22</td>
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<td>Natural Soil</td>
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<td>26</td>
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<td>Agricultural Soil</td>
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<td>22</td>
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<tr>
<td>Eco-toxicity Potential</td>
<td>Urban Air</td>
<td>1</td>
<td>22</td>
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<tr>
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<td>Rural Air</td>
<td>1</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Freshwater</td>
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</tr>
<tr>
<td></td>
<td>Agricultural Soil</td>
<td>1</td>
<td>22</td>
</tr>
</tbody>
</table>

- The CFL and LED bulbs have higher resource depletion and toxicity potentials.
- The CFL bulb exhibits higher toxicity potentials than the LED bulb.
- The lower potentials of LED bulb are mainly due to the longer life of LED bulb.
Concluding Remarks

– The environmental and human health impacts of engineered products can be reduced through the application of green engineering principles.

– Various methods can be implemented to guide greener design, including economic impact assessment; life cycle assessment; hazardous waste, resource depletion and toxicity potential; and chemical hazard assessment.

– Implementation of these methods early in the design phase maximizes the potential benefit to society while also maximizing engineering functionality.
Thanks for joining us!

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