

Introduction to Green Chemistry

Environmental Protection Agency (EPA)

<http://www.epa.gov/epahome/aboutepa.htm>

– History

In July of 1970, the White House and Congress worked together to establish the EPA in response to the growing public demand for cleaner water, air and land. Prior to the establishment of the EPA, the federal government was not structured to make a coordinated attack on the pollutants that harm human health and degrade the environment. The EPA was assigned the daunting task of repairing the damage already done to the natural environment and to establish new criteria to guide Americans in making a cleaner environment a reality.

– Mission

EPA leads the nation's environmental science, research, education and assessment efforts. The mission of the Environmental Protection Agency is to protect human health and the environment. Since 1970, EPA has been working for a cleaner, healthier environment for the American people.

- 1970 Clean Air Act. Regulates air emissions.
- 1972 National Environmental Policy Act. Requires in part that EPA review environmental impact statements of proposed major federal projects (e.g. highways, buildings, airports, parks and military complexes).
- 1972 Clean Water Act. Establishes the sewage treatment construction grants program and a regulatory and enforcement program for discharges of pollutants into U.S. waters.
- 1972 Federal Insecticide, Fungicide & Rodenticide Act. Governs distribution, sale and use of pesticide products. All pesticides must be registered (licensed) by EPA.
- 1972 Ocean Dumping Act. Regulates the intentional disposal of materials into ocean waters.
- 1974 Safe Drinking Water Act. Establishes primary drinking water standards.
- 1976 Toxic Substances Control Act. Requires the testing, regulating, and screening of all chemical produced or imported in the U.S.
- 1976 Resource Conservation & Recovery Act. Regulates solid and hazardous waste from “cradle to grave.”
- 1976 Environmental Research & Development Demonstration Act. Authorizes all EPA research programs.
- 1980 Comprehensive Environmental Response, Compensation & Liability Act, better known as Superfund. Provides for a federal “superfund” to clean up abandoned hazardous waste sites, accidental spills and other emergency releases of pollutants in the environment.
- Emergency Planning & Community Right-to-Know Act. Requires that industries report toxic releases and encourages
- 1990 Pollution Prevention Act. Seeks to prevent pollution by encouraging companies to reduce the generation of pollutants through cost-effective changes in production, operation, and raw material use.

CHEM 483:

Introduction to Green Chemistry



All of the listed acts, except:

- *1990 Pollution Prevention Act. Seeks to prevent pollution by encouraging companies to reduce the generation of pollutants through cost-effective changes in production, operation, and raw material use.*

deals with pollution after it occurs

The others focus on the treatment or abatement of pollution “command and control.” In some instances, Congress passed these laws which placed limits on pollution and timetables with little regard to *science/technology* or economic cost.

CHEM 483:

Introduction to Green Chemistry



Hence, these earlier acts are geared to improve our environment by controlling our exposure to hazardous substances.

e.g., part of the *Emergency Planning and Community Right to Know Act* is the *Toxic Release Inventory*.



requires companies to report the use and/or release of certain hazardous chemicals.

Consider what was done in 1997:

- Industry report ~24 billion pounds of hazardous chemicals were treated, recycled, used for energy production, disposed of or release to the environment.
- Covered only 650 of the 75K chemicals in use in the USA today.
- Only companies manufacturing or processing over 25,000 lbs or use more than 10,000 lbs of a listed substance are required to report.

Long way to go using this approach!

CHEM 483:

Introduction to Green Chemistry



Since the EPA is responsible for implementing and enforcing these laws, industry views the EPA as an adversary, i.e., views environmental regulations with disdain and as an economic hardship.

With passage of the **1990 Pollution Prevention Act** a new paradigm has emerged at the EPA.

- Focuses on pollution prevention instead of treatment and remediation.
- Partners with industry to develop more flexible and cost effective methods of preventing pollution at the source.

Hence, in 1991 green chemistry became a formal focus of the EPA.

CHEM 483:

Introduction to Green Chemistry



Green Chemistry or *Environmentally Benign Chemistry* is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

Taken from Paul T. Anastas and John C. Warner, *Green Chemistry Theory and Practice*, Oxford Univ. Press, New York, 1998.

Therefore, instead of limiting *Risk* by controlling *Exposure* to hazardous chemicals, green chemistry attempts to reduce or eliminate the *Hazard* thus negating need to control *Exposure*.

Risk = function (hazard, exposure)

* Don't use or produce hazardous substances, the risk is zero.

CHEM 483:

Introduction to Green Chemistry



Green Chemistry has received much recognition in the area of research and development in both industry and academia.

e.g.,

- the journal *Green Chemistry* was first published by RSC in 1999.
- Presidential Green Chemistry Challenge Awards were established in 1995 by Clinton Administration.
- ACS established Green Chemistry Institute.

see individual websites for details

CHEM 483:

Introduction to Green Chemistry



The **Presidential Green Chemistry Challenge Awards** recognize outstanding achievements in green chemistry/technology. Only chemistry award given out at the presidential level.

Criteria include:

- Greener reaction conditions for an old synthesis .
- A greener synthesis for an old chemical.
- The synthesis of a new compound that is less toxic but has the same desirable properties as an existing compound.

CHEM 483:

Introduction to Green Chemistry



Presidential Green Chemistry Challenge

1998: Professor Barry M. Trost, Stanford University

The Development of the Concept of Atom Economy

Innovation and Benefits: Professor Trost developed the concept of atom economy: chemical reactions that do not waste atoms. Professor Trost's concept of atom economy includes reducing the use of nonrenewable resources, minimizing the amount of waste, and reducing the number of steps used to synthesize chemicals. Atom economy is one of the fundamental cornerstones of green chemistry. This concept is widely used by those who are working to improve the efficiency of chemical reactions.

1997: Professor Joseph M. DeSimone, Univ. of NC & NC State Univ.

Design and Application of Surfactants for Carbon Dioxide

Innovation and Benefits: Professor DeSimone developed new detergents that allow carbon dioxide (CO₂), a nontoxic gas, to be used as a solvent in many industrial applications. Using CO₂ as a solvent allows manufacturers to replace traditional, often hazardous chemical solvents and processes, conserve energy, and reduce worker exposure to hazardous substances.

1996: Professor Mark Holtzapple, Texas A&M University

Conversion of Waste Biomass to Animal Feed, Chemicals, and Fuels

Innovation and Benefits: Professor Holtzapple developed a family of technologies that convert waste biomass, such as sewage sludge and agricultural wastes, into animal feed products, industrial chemicals, or fuels, depending on the technology used. Because these technologies convert waste biomass into useful products, other types of basic resources, such as petroleum, can be conserved. Also, the technologies can reduce the amount of biomass waste going to landfills or incinerators.

CHEM 483:

Introduction to Green Chemistry



The Twelve Principles of Green Chemistry:

Anastas and Warner have developed the Twelve Principles of Green Chemistry to aid one in assessing how green a chemical, a reaction or a process is.

1. It is better to **prevent waste** than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to **maximize the incorporation of all materials** used in the process into the final product.
3. Wherever practicable, **synthetic methodologies** should be designed to use and generate substances that **possess little or no toxicity** to human health and the environment.
4. Chemical products should be designed to **preserve efficacy of function while reducing toxicity**.
5. The use of **auxiliary substances** (e.g. solvents, separation agents, etc.) **should be made unnecessary whenever possible** and, innocuous when used.
6. **Energy requirements** should be recognized for their environmental and economic impacts and **should be minimized**. Synthetic methods should be conducted at ambient temperature and pressure.

CHEM 483:

Introduction to Green Chemistry



7. A raw material **feedstock should be renewable** rather than depleting whenever technically and economically practical.

8. **Unnecessary derivatization** (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be **avoided** whenever possible.

9. **Catalytic reagents** (as selective as possible) **are superior** to stoichiometric reagents.

10. Chemical **products should be designed** so that at the end of their function they **do not persist** in the environment and **break down into innocuous degradation products**.

11. Analytical methodologies need to be further developed to allow for **real-time in-process monitoring and control** prior to the formation of hazardous substances.

12. Substances and the **form of a substance** used in a chemical process **should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires**.

CHEM 483:

Introduction to Green Chemistry



The Twelve Principles of Green Engineering:

Anastas, P.T., and Zimmerman, J.B., "Design through the Twelve Principles of Green Engineering", *Env. Sci. and Tech.*, 37, 5, 94A-101A, 2003.

1. **Inherent Rather Than Circumstantial**

Designers need to strive to ensure that all materials and energy inputs and outputs are as inherently nonhazardous as possible.

2. **Prevention Instead of Treatment**

It is better to prevent waste than to treat or clean up waste after it is formed.

3. **Design for Separation**

Separation and purification operations should be designed to minimize energy consumption and materials use.

4. **Maximize Efficiency**

Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.

5. **Output-Pulled Versus Input-Pushed**

Products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials.

The Twelve Principles of Green Engineering:

6. **Conserve Complexity**

Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.

7. **Durability Rather Than Immortality**

Targeted durability, not immortality, should be a design goal.

8. **Meet Need, Minimize Excess**

Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw.

9. **Minimize Material Diversity**

Material diversity in multicomponent products should be minimized to promote disassembly and value retention.

10. **Integrate Material and Energy Flows**

Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows.

11. **Design for Commercial "Afterlife"**

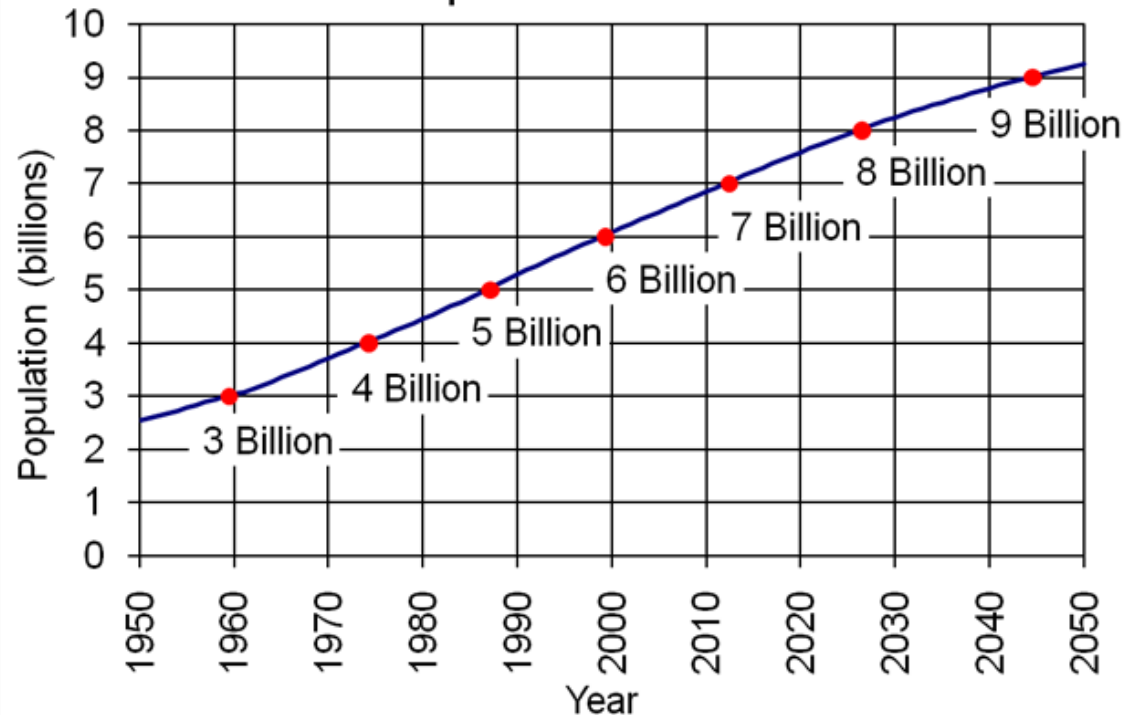
Products, processes, and systems should be designed for performance in a commercial "afterlife."

12. **Renewable Rather Than Depleting**

Material and energy inputs should be renewable rather than depleting.

World Population 1950-2050

World Population: 1950-2050



Source: U.S. Census Bureau, International Data Base, December 2010 Update.

Rank	Country or Area	Population
1	China	1,330,141,295
2	India	1,173,108,018
3	United States	310,232,863
4	Indonesia	242,968,342
5	Brazil	201,103,330
6	Pakistan	184,404,791
7	Bangladesh	156,118,464
8	Nigeria	152,217,341
9	Russia	139,390,205
10	Japan	126,804,433

Difference between “Renewable” and “Sustainable”

For example, consider producing ethanol from corn.

- Renewable because you can do it more than once.

However, not sustainable if it requires

- fossil fuel input for traction, irrigation, fertilizer.
- Petroleum based insecticides and pesticides.
- depletes topsoil.

Possible on a very small scale (family garden).

World population.

Today:

6,897,078,213

Midyear 2050:

9,256,342,700