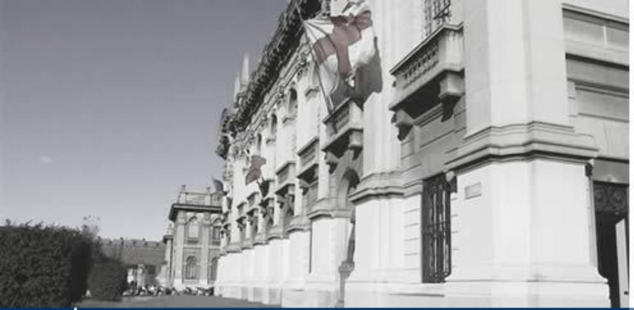


School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

A.A. 2019/2020

POLITECNICO DI MILANO

Course Highlights

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”
http://iscamap.chem.polimi.it/citterio/education/course-topics/ (English)
http://iscamap.chem.polimi.it/citterio/it/education/course-topics/ (Italiano)
e-mail: attilio.citterio@polimi.it

Course Organization - Aims

Lectures: Tuesday 12.15-15.15 (Room 3.1.6 ex. S.1.6)
Wednesday 13.15-16.15 (Room B.5.5 / LAB MA1)
Friday 13.15-16.15 (Room 9.0.3 / LAB MA1)
Lab. Mancinelli (Wednesday or Friday)
from 17/09/2019 to 20/12/2019 (lect.: 34(8) + 17(5)h, lab: 12h, Es: 16(8).

PowerPoint Notes in pdf (adobe acrobat) at:

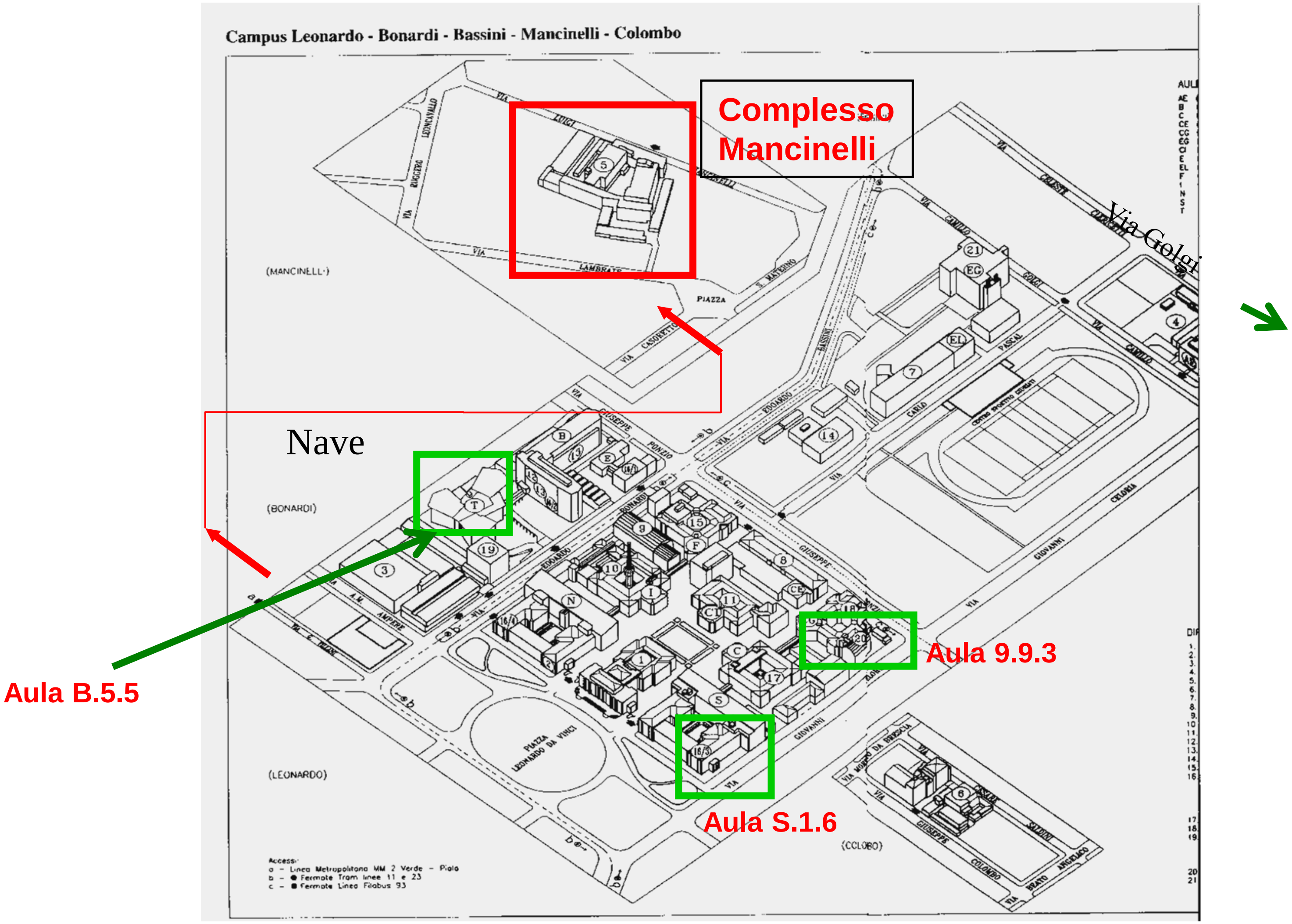
http://iscamap.chem.polimi.it/citterio/education/course-topics/ **(Green Chemistry)**

Requirements: at least 5 credits of General Chemistry (and 5 credits of Organic Chemistry).

Designed for:

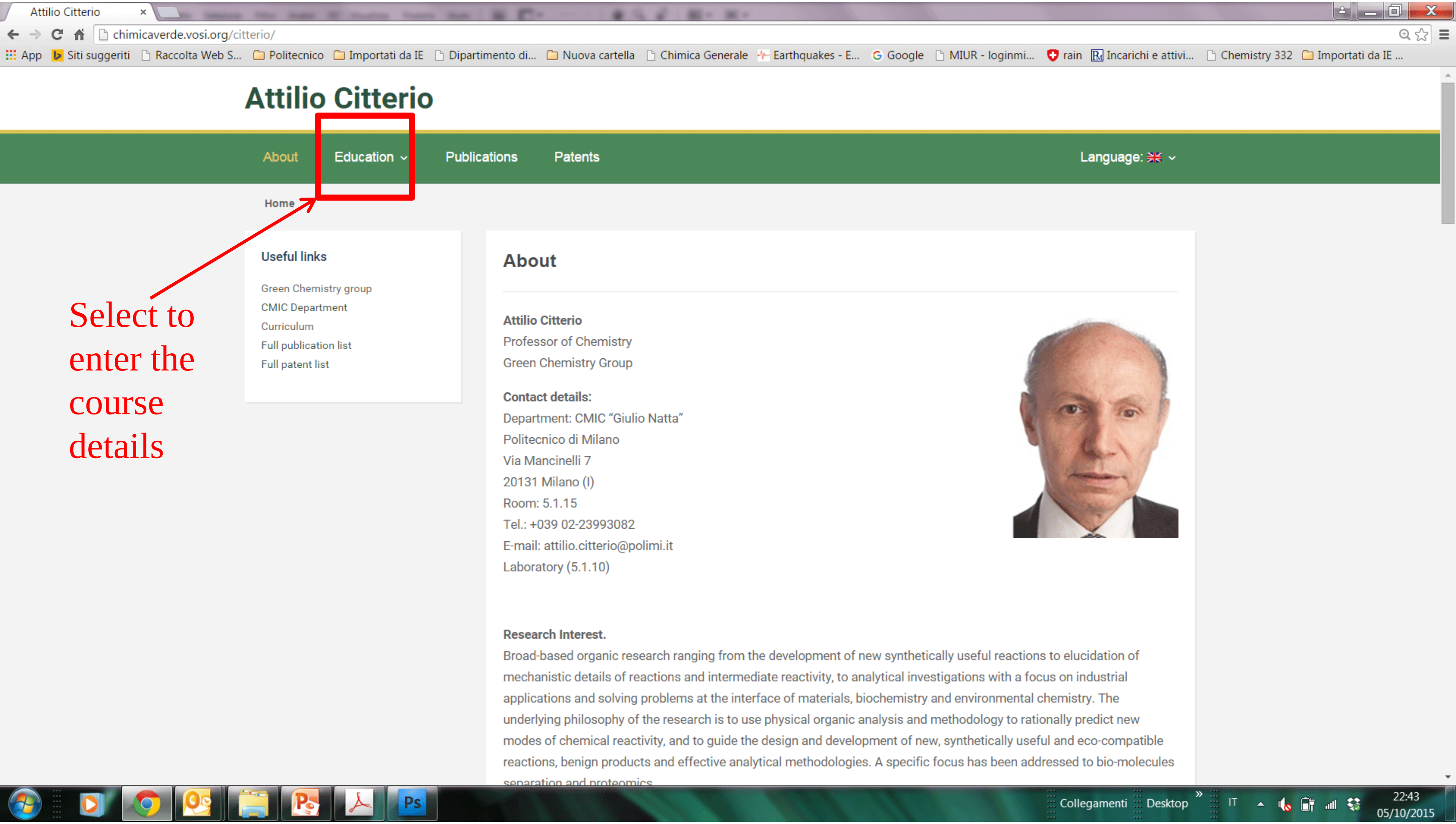
Chemical Engineers (5 credits), Safety Engineers (5 credits), Material Engineers (5 credits) and Environmental Engineers (8 credits) majors and minors, who are interested in the future of activities on our planet.

Classroom Location



Course Site:

http://iscamap.chem.polimi.it/citterio/education/



Attilio Citterio

Useful links

- Green Chemistry group
- CMIC Department
- Curriculum
- Full publication list
- Full patent list

About

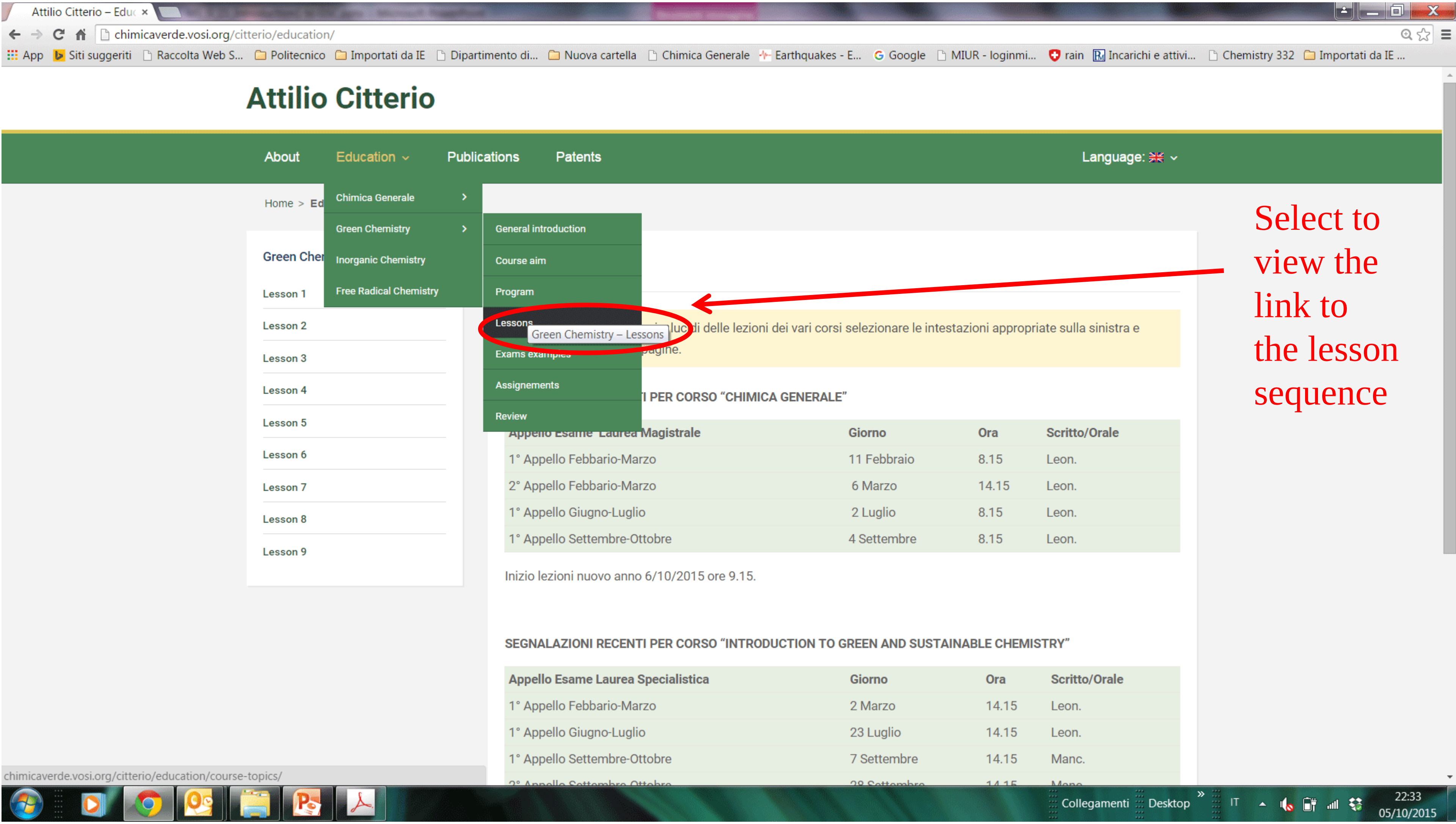
Attilio Citterio
Professor of Chemistry
Green Chemistry Group

Contact details:
Department: CMIC "Giulio Natta"
Politecnico di Milano
Via Mancinelli 7
20131 Milano (I)
Room: 5.1.15
Tel.: +039 02-23993082
E-mail: attilio.citterio@polimi.it
Laboratory (5.1.10)

Research Interest.
Broad-based organic research ranging from the development of new synthetically useful reactions to elucidation of mechanistic details of reactions and intermediate reactivity, to analytical investigations with a focus on industrial applications and solving problems at the interface of materials, biochemistry and environmental chemistry. The underlying philosophy of the research is to use physical organic analysis and methodology to rationally predict new modes of chemical reactivity, and to guide the design and development of new, synthetically useful and eco-compatible reactions, benign products and effective analytical methodologies. A specific focus has been addressed to bio-molecules separation and proteomics

Select to enter the course details

Course Site:
http://iscamap.chem.polimi.it/citterio/education/general-introduction/



…luc di delle lezioni dei vari corsi selezionare le intestazioni appropriate sulla sinistra e … pagine.

…I PER CORSO “CHIMICA GENERALE”

Appello Esame Laurea Magistrale	Giorno	Ora	Scritto/Orale
1° Appello Febbario-Marzo	11 Febbraio	8.15	Leon.
2° Appello Febbario-Marzo	6 Marzo	14.15	Leon.
1° Appello Giugno-Luglio	2 Luglio	8.15	Leon.
1° Appello Settembre-Ottobre	4 Settembre	8.15	Leon.

Inizio lezioni nuovo anno 6/10/2015 ore 9.15.

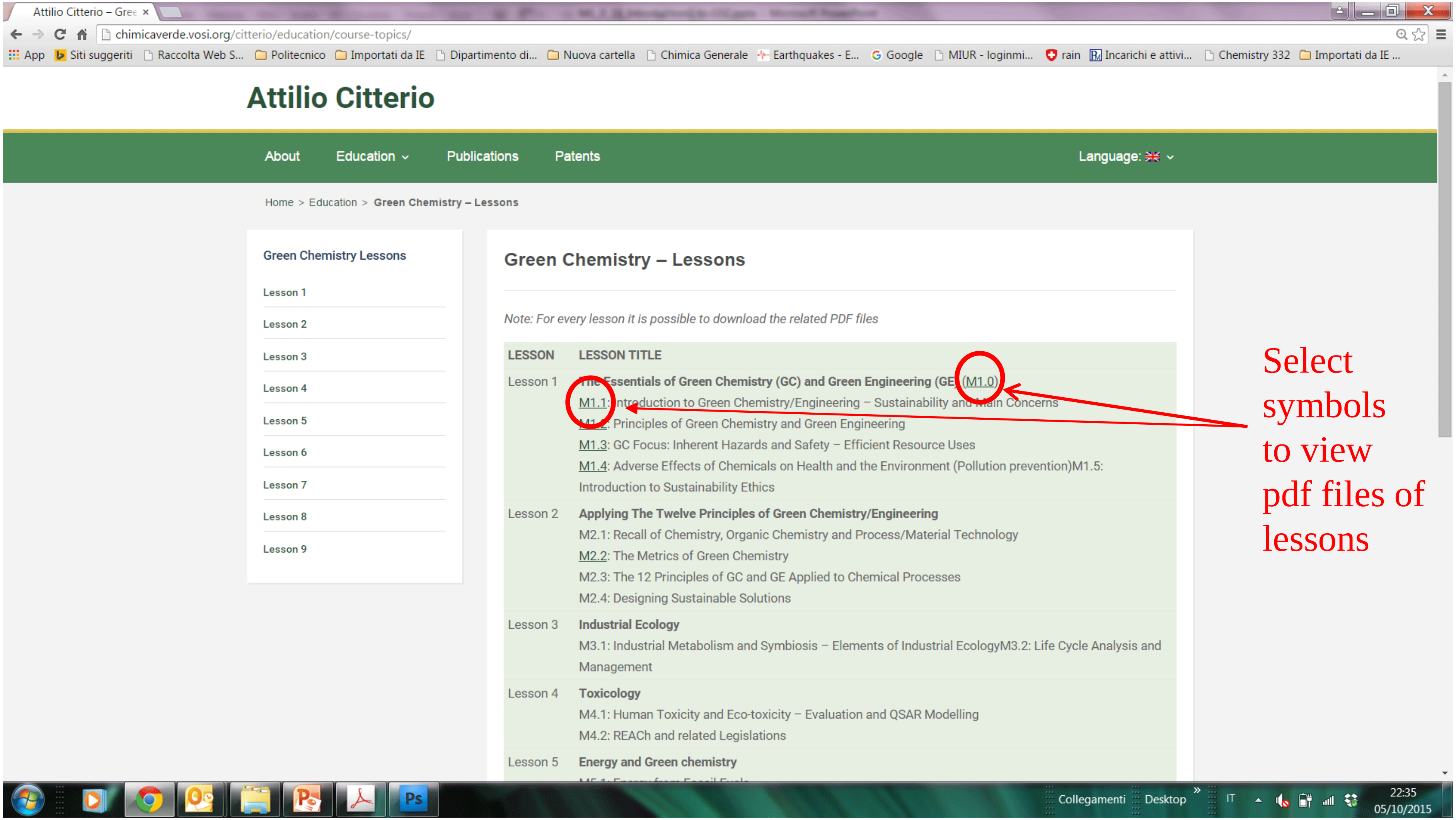
SEGNALAZIONI RECENTI PER CORSO “INTRODUCTION TO GREEN AND SUSTAINABLE CHEMISTRY”

Appello Esame Laurea Specialistica	Giorno	Ora	Scritto/Orale
1° Appello Febbario-Marzo	2 Marzo	14.15	Leon.
1° Appello Giugno-Luglio	23 Luglio	14.15	Leon.
1° Appello Settembre-Ottobre	7 Settembre	14.15	Manc.
2° Appello Settembre-Ottobre	28 Settembre	14.15	Manc.

Select to view the link to the lesson sequence

Course Page with pdf file:

http://iscamap.chem.polimi.it/citterio/education/course-topics/



Attilio Citterio

Home > Education > **Green Chemistry – Lessons**

Green Chemistry Lessons

- Lesson 1
- Lesson 2
- Lesson 3
- Lesson 4
- Lesson 5
- Lesson 6
- Lesson 7
- Lesson 8
- Lesson 9

Green Chemistry – Lessons

Note: For every lesson it is possible to download the related PDF files

LESSON	LESSON TITLE
Lesson 1	**The Essentials of Green Chemistry (GC) and Green Engineering (GE)** (M1.0) M1.1: Introduction to Green Chemistry/Engineering – Sustainability and Main Concerns M1.2: Principles of Green Chemistry and Green Engineering M1.3: GC Focus: Inherent Hazards and Safety – Efficient Resource Uses M1.4: Adverse Effects of Chemicals on Health and the Environment (Pollution prevention)M1.5: Introduction to Sustainability Ethics
Lesson 2	**Applying The Twelve Principles of Green Chemistry/Engineering** M2.1: Recall of Chemistry, Organic Chemistry and Process/Material Technology M2.2: The Metrics of Green Chemistry M2.3: The 12 Principles of GC and GE Applied to Chemical Processes M2.4: Designing Sustainable Solutions
Lesson 3	**Industrial Ecology** M3.1: Industrial Metabolism and Symbiosis – Elements of Industrial EcologyM3.2: Life Cycle Analysis and Management
Lesson 4	**Toxicology** M4.1: Human Toxicity and Eco-toxicity – Evaluation and QSAR Modelling M4.2: REACh and related Legislations
Lesson 5	**Energy and Green chemistry**

Select symbols to view pdf files of lessons

Summary of Subjects Addressed

L1 – The Essentials of Green Chemistry (GC) and Green Engineering (GE) – Sustainability

L2 – Applying the twelve Principles of Green Chemistry and Green Engineering

L3 – Industrial Ecology

L4 – Toxicology

L5 – Raw Organic Materials from Biomasses

L6 – Bioprocesses and Biotechnology

L7 – Energy and Green Chemistry

L8 – Chemical Process Optimization and Intensification

L9 – Intrinsic Safety

L10 – Bookcase of Green Chemistry Problems (Process Selection through green metrics - Recycling of materials, Substitution of VOC and Solvents, Bioprocesses)

Sustainable Development

Sustainability is a crucial part of present and future technology, but the term is ambiguous. *Main definition:*

'… Development that meets the needs of the present generation, without compromising the ability of future generations to meet their own needs.'

Brundtland Commission, UN Earth Summit 1992
Rio de Janeiro, Brazil

Some declinations:

- Materials from the earths crust (e.g. heavy metals) must not be systematically increased in nature
- Persistent substances produced by society (DDT, CFC's) must not be systematically increased
- The physical basis for earth's productive natural cycles must not be systematically deteriorated
- There must be fair and efficient use of resources with respect to meet the human needs

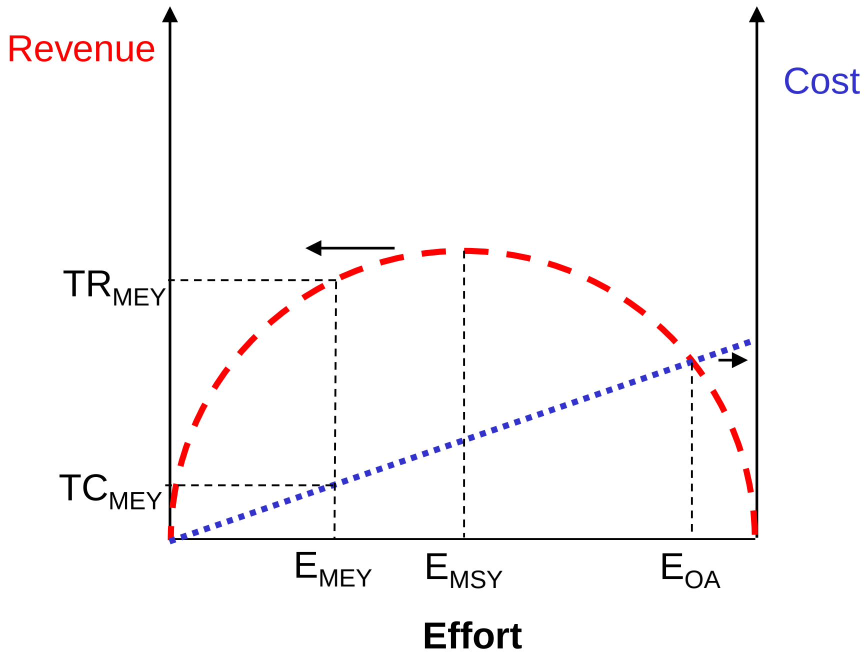
The Natural Step (Sweden)

Concerns for Common Resources

The common (global) resources are object of attention in the industrial ecology and in sustainable engineering because the limited availability of these resources can adversely influence the progresses due to modern technology.

Example: the relationship among fishing effort, cost, and revenue.

- TR = total revenue
- E = level of fishing effort
- MEY = max. economic yield
- MSY = max. sustainable yield
- OA = open access



“The Question of the Commons” B.J. McCay and J.A. Acheson Eds. Tucson , 311-326, 1987

Use of Energy and Materials under Socio-Ecological Regimes in World History

	per capita annual use	
	Energy	Material
Basic human metabolism (biomass intake by nutrition)	3,5 *GJ*	1 *t*
Hunter-gatherers (uncontrolled solar energy use)	10-20 *GJ*	2-3 *t*
Agrarian societies (controlled solar energy use)	60-80 *GJ*	4-5 *t*
Industrial/Technological society (fossil energy use)	250 *GJ*	20-22 *t*

Quantifying Sustainability

Realistic and defensible goals for sustainability and their implementation will not be easily establish in practice, but the principles by which one could proceed are reasonably straightforward. They are:

- Establish the limiting rate of use of the environmental, economic, or equity component
- Allocate the allowable limit by some appropriate method to those which are influenced by that limit.
- Compare the current situation with the permitted allocation
- Consider potential corrective actions.

In a number of cases it will be necessary to select a time horizon over which sustainability must be evaluated. Generally a 50 year (i.e. roughly two human generations) is considered as a reasonable period for assessment.

Linking Industrial Ecology Activity to Sustainability

Many of the sustainable dialogs involve environmental perturbations and it is useful to consider how such issues might be prioritized. From recent analyses a reasonable exposition of Grand Objectives is the following:

➊ - Ω_1 : Preserve the existence of human species

➋ - Ω_2 : Preserve the capacity for sustainable development and the stability of human systems

➌ - Ω_3 : Preserve the diversity of life

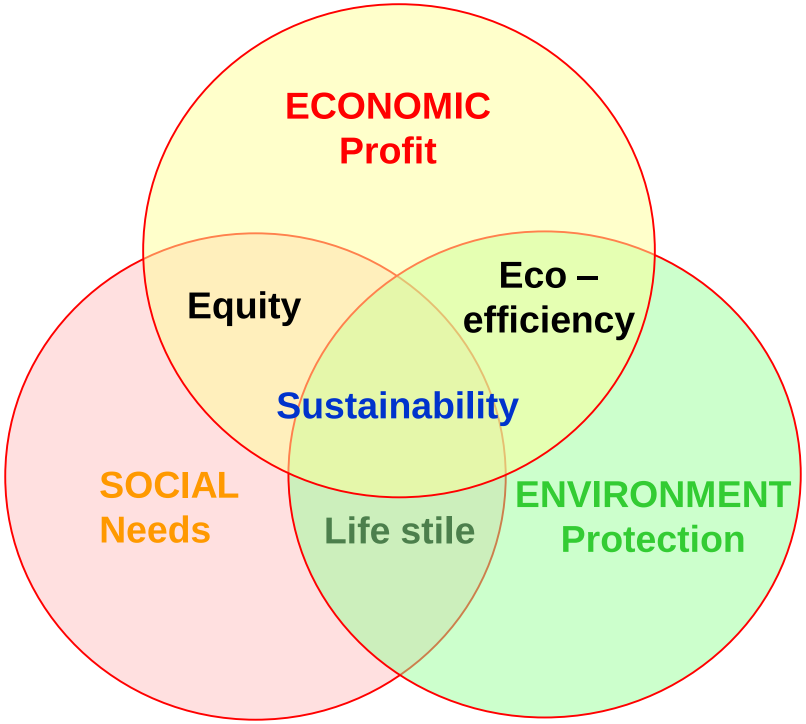
➍ - Ω_4 : Preserve the aesthetic richness of the planet.

If it is granted that these objectives are universal, there are certain basic societal requirements that must be satisfied if the objectives are to be met. In the case of Ω_1 these are the minimization of environmental toxicity and the provision of basic needs, For Ω_2 the requirements are a dependable energy supply and availability of suitable material resources. For Ω_3 to maintain a suitable amount of natural areas and biological diversity. For Ω_4 to control waste of various kinds, and, in general, degradation of the visible world.

Sustainable Development = Balance between Three Primary Pillars

The three pillars of sustainability:

- Needs of society **(the social objective)**;
- Efficient use of scarce resources **(the economical objective)**;
- Need to reduce the burden on eco-system to maintain the natural bases for life **(the environmental objective)**.



In the business community, sustainability is coined in **“the triple bottom line”**

Contributes of Chemistry to Sustainable Development

Chemistry could contribute at three levels to sustainable development:

1. Provision of chemical products that establish and ensure social and economic wealth.
2. Conservation of resources by development of:
   a. More effective chemical processes
   b. Renewable energy sources
   c. Chemical products that enhance significantly the effectiveness of production processes and products in other areas,
   d. Products that allow the consumer to use resources more effectively,
   e. Design products that fits into a recycling concept, and
   f. Products that base on renewable resources and biological cycles.
3. Management of resources, substances and materials in a safe and in an environmentally benign manner.

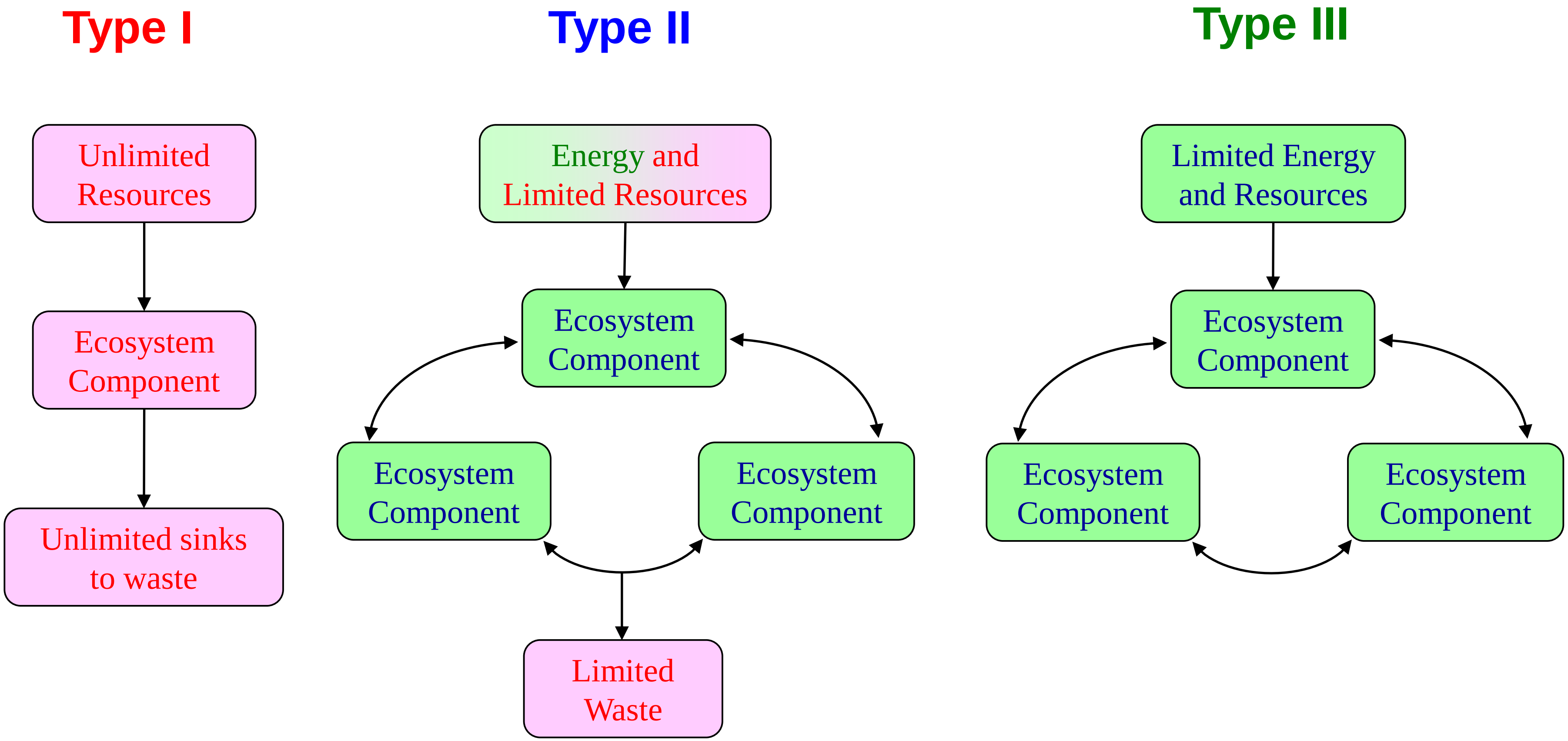
Adapted from M. S. Reisch, *Chem. Eng. News* 79(36), 17 (2001).

New Sensitivity

It is Essential that Chemists, Engineers and Public Managers Should Place a Major Focus on the Environmental Consequences of Chemical Products and the Processes by which these Products are Made.

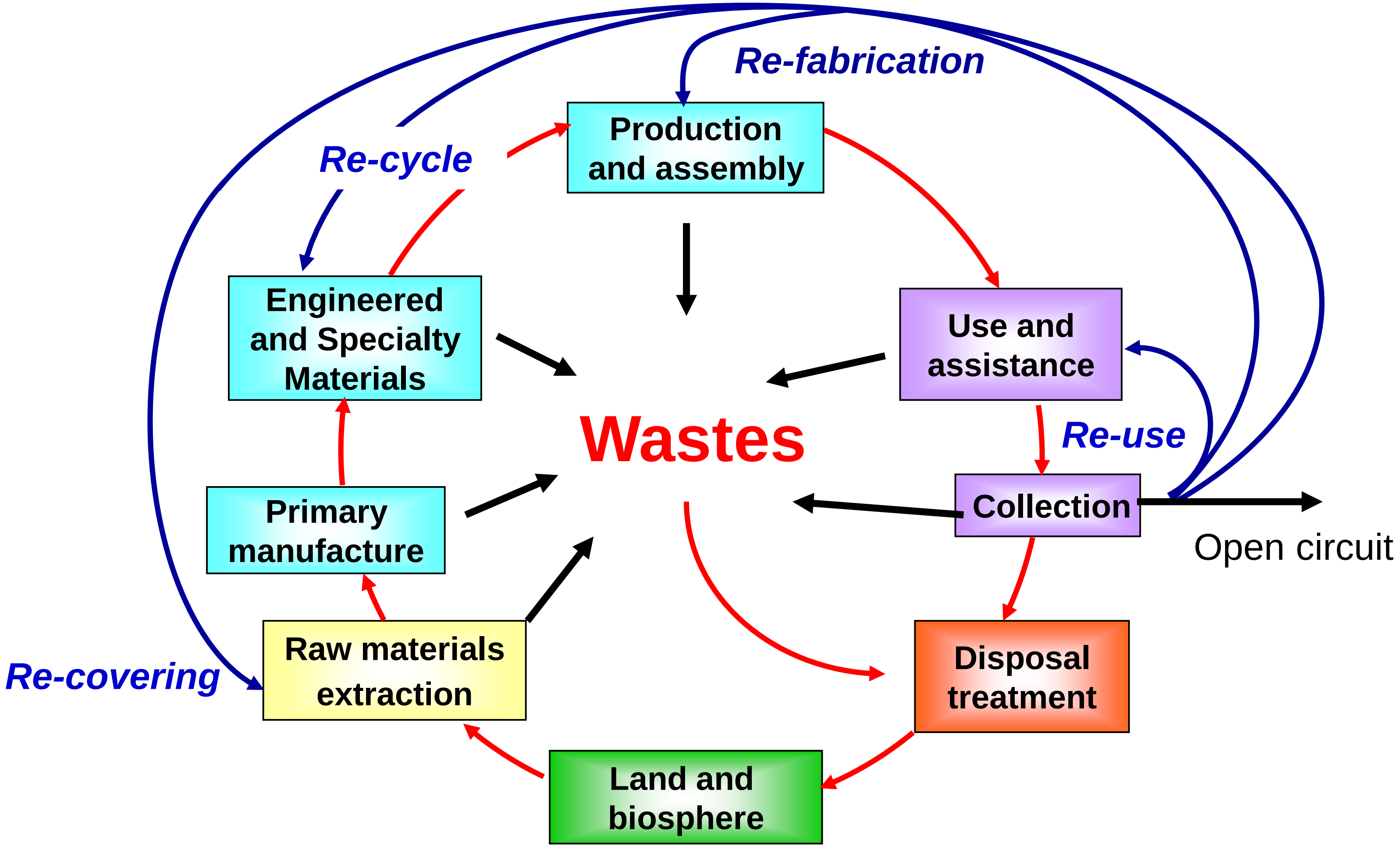
We must consider our chemical ecological footprint

Industrial Ecology (Type of Industrial Regimes)



ATOMS in Wastes are the same than in Raw Materials!!!

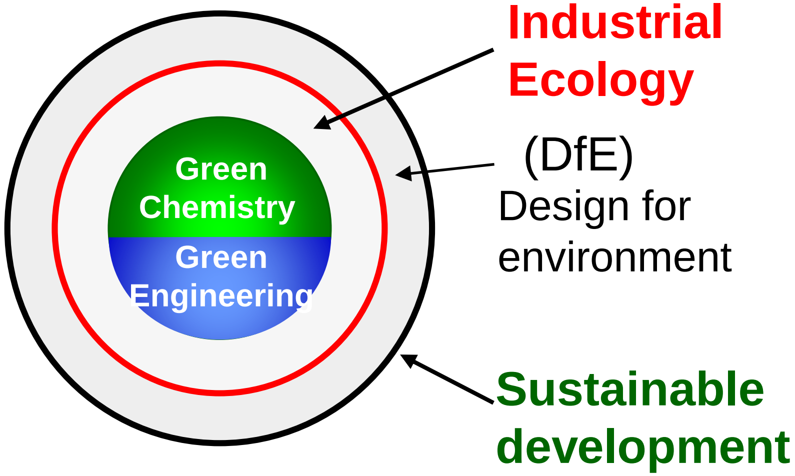
Industrial Production Processes – Circular Economy
(Life Cycle of Products Include Re-activities)



Industrial Ecology - Chemistry for Sustainability - Intrinsic Safety – Green Engineering

Industrial Ecology =
science of sustainability with emphasis on careful use and reuse of resources

Green Chemistry (for Sustainability) =
chemical transformation science with low environmental impact and attention to resources and energy efficient use



Green Chemistry

Green Engineering

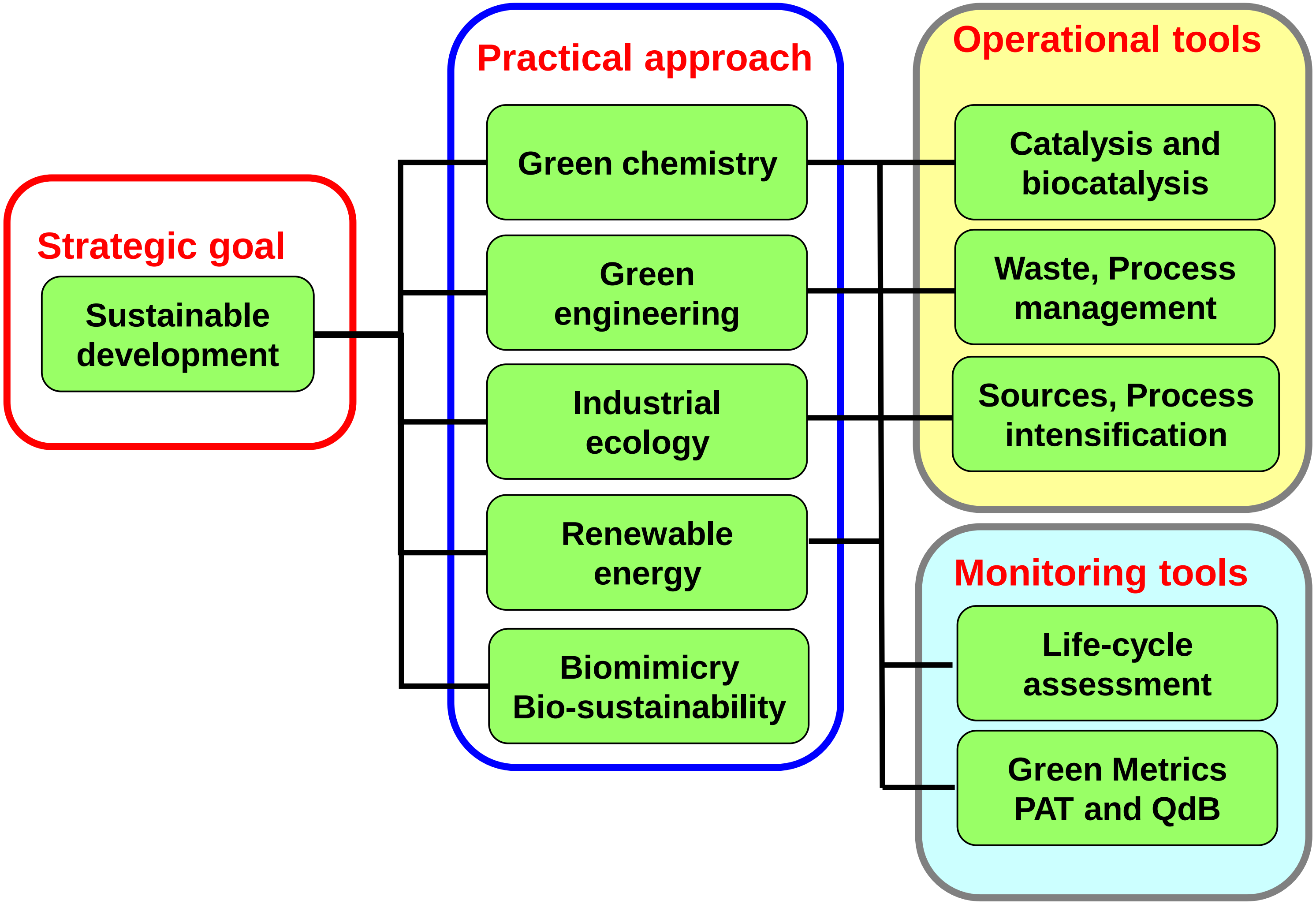
Industrial Ecology

(DfE)
Design for environment

Sustainable development

Intrinsic Safety and Green Engineering (for sustainability) =
Science and technology devoted to reduction / elimination of concerns associated to materials used and processing, with permanent and inseparable insertion into industrial processes.

Route to Sustainable Development



Strategic goal

Sustainable development

Practical approach

Green chemistry

Green engineering

Industrial ecology

Renewable energy

Biomimicry
Bio-sustainability

Operational tools

Catalysis and biocatalysis

Waste, Process management

Sources, Process intensification

Monitoring tools

Life-cycle assessment

Green Metrics
PAT and QdB

GREEN CHEMISTRY FOR SUSTAINABILITY

DEFINITION (“U.S.”)

*Green Chemistry is the use of a group of principles able to reduce or eliminate the use and generation of hazardous substances in the design, manufacture and application of chemical products**.

CHEMISTRY for SUSTAINABILITY DEALS WITH:

- Minimize Waste, Energy and Resource Use
- Utilize Catalysts instead of Reagents
- Utilize Non-Toxic Reagents and Intermediates
- Utilize Renewable Resources
- Recycle of Products and Materials
- Improvement of Atom Efficiency and E Factor
- Use of Systems without Solvents or with Recyclable Environmentally Benign Solvents, ….. etc.

** Green Chemistry Theory & Practice, P T Anastas & J C Warner, Oxford University Press 1998*

Green Engineering - Goals of Principles

- Provide a framework
  - Applicable
  - Effective
  - Appropriate

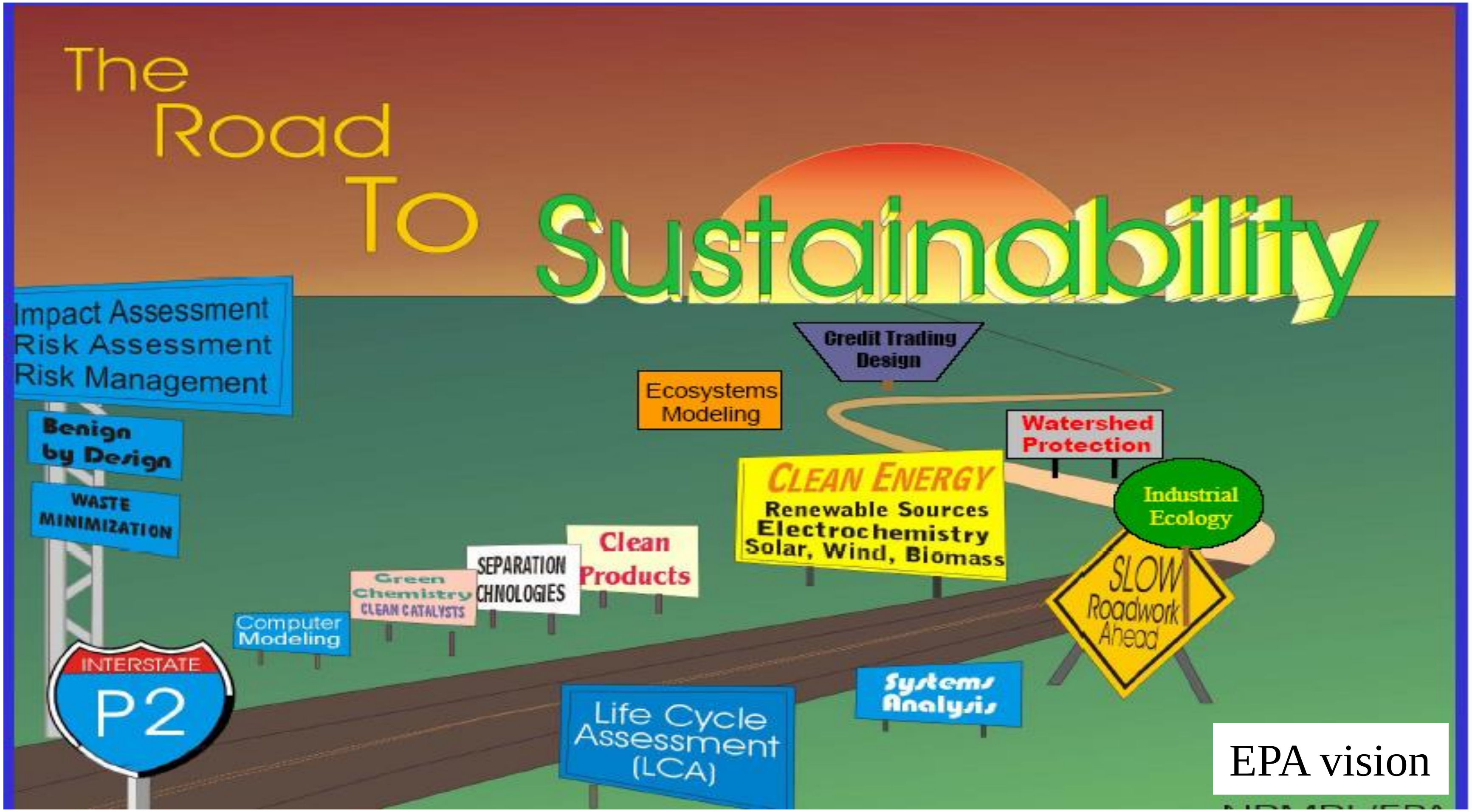
- Apply across disciplines
  - Chemical, Civil, Environmental, Mechanical, Systems…

- Apply across scales of design
  - Molecular architecture to construct chemical compounds
  - Product architecture to create an useful product (i.e. computer)
  - Urban architecture to build a city

What is “Green”?

✓Sustainable

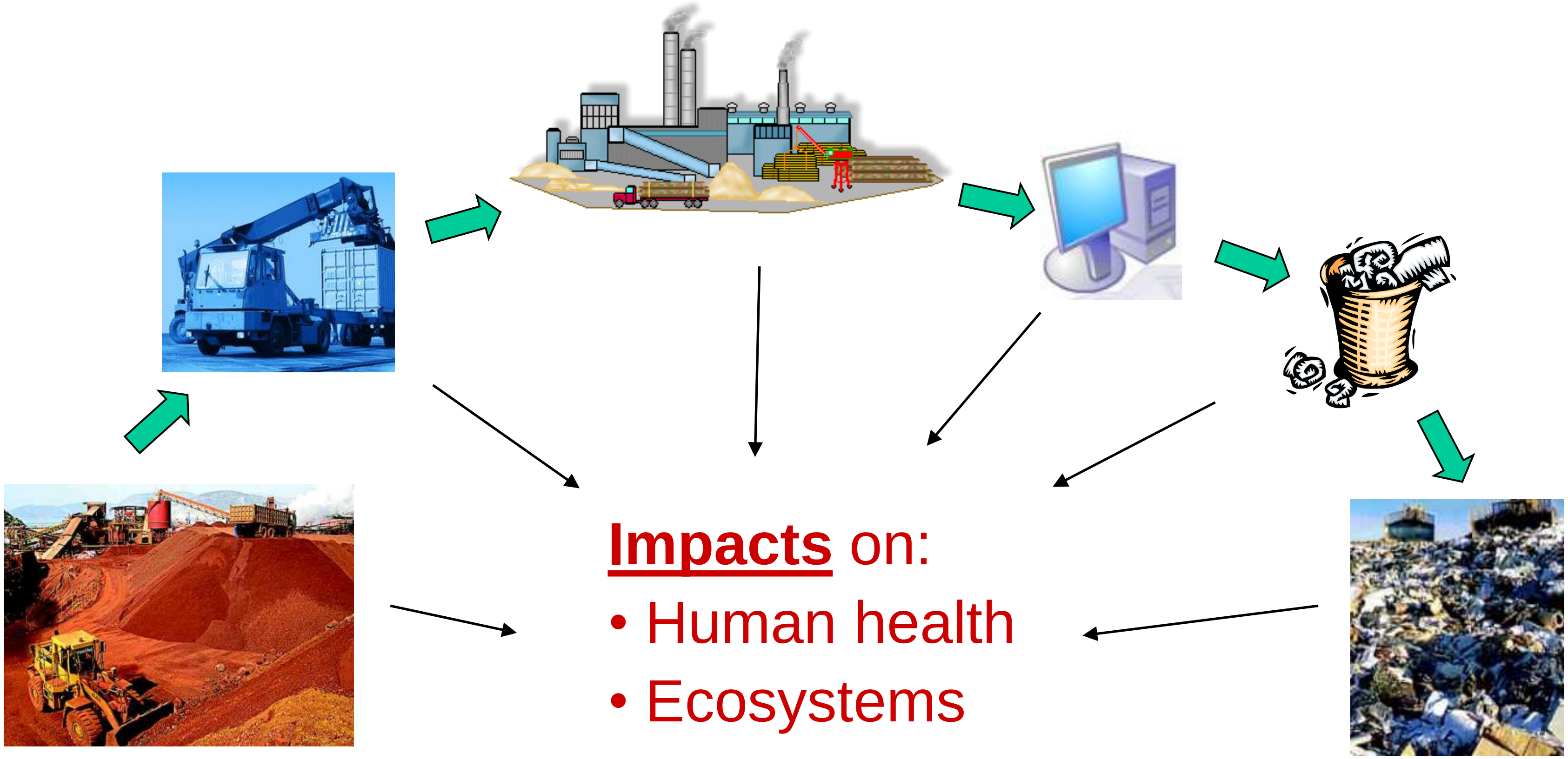
✓ Kinder and gentler to people and the planet



EPA vision

Life Cycle Analysis

”From cradle to grave”



Impacts on:

- Human health
- Ecosystems
- Resources

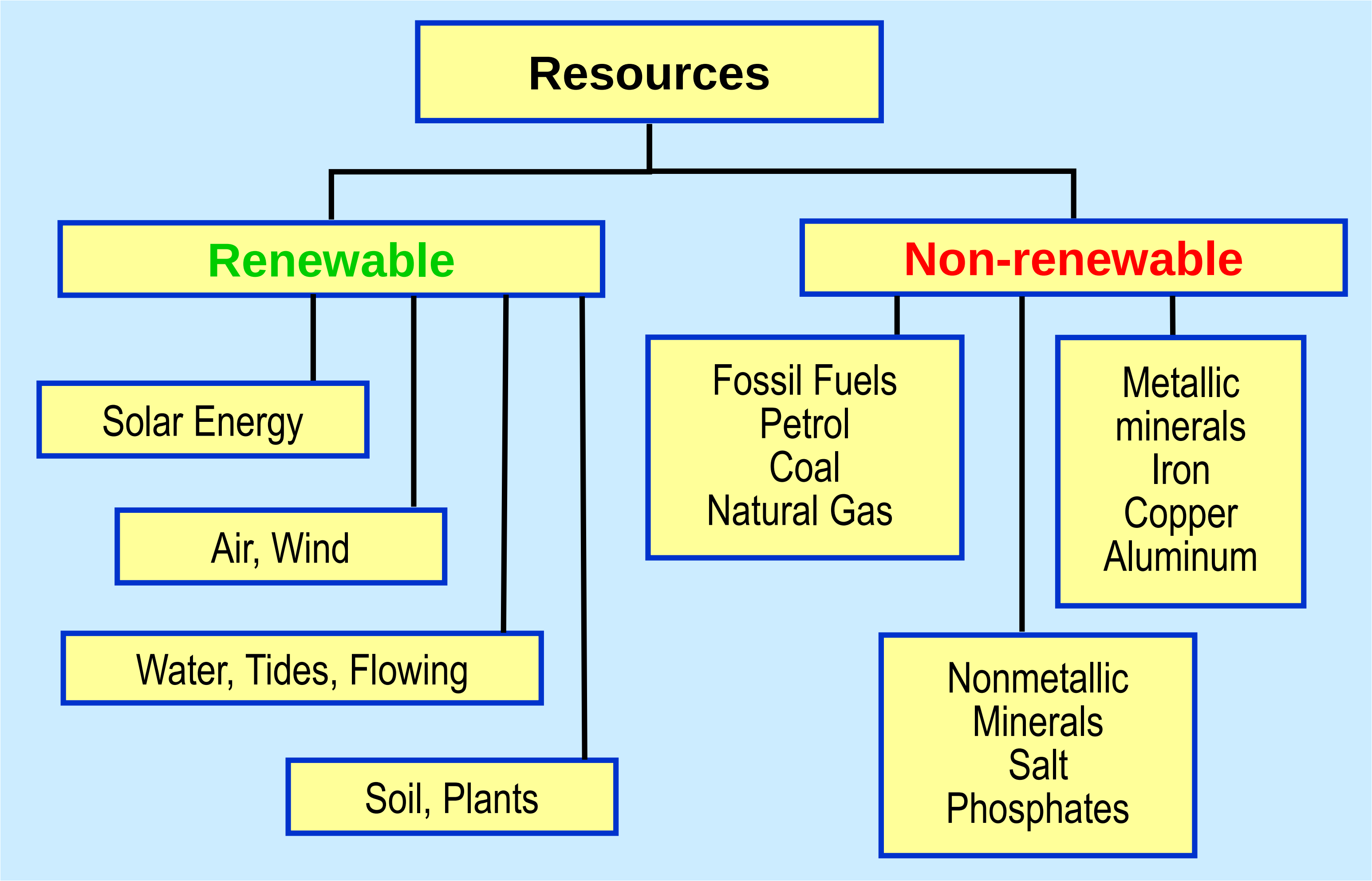
Life Cycle Thinking

Life Cycle Thinking

Sustainability Decision Support

The process of taking into account in decision making, as far as possible, all resources consumption, environmental, health, social, and economic implications that are associated with the life cycle of a product (good or service), considering, for instance the extraction of resources, production, use, transport, recycling, and waste disposal. This process helps to avoid the "shifting of burdens", i.e. of impacts or resource consumption, among life cycle stages, geographic areas, and environmental and human health problem fields such as Climate Change, Summer Smog, Acid Rain, etc.

Resource = Matter Obtained from Environment (living or not) to Meet Human Needs



Resources

Renewable

Solar Energy

Air, Wind

Water, Tides, Flowing

Soil, Plants

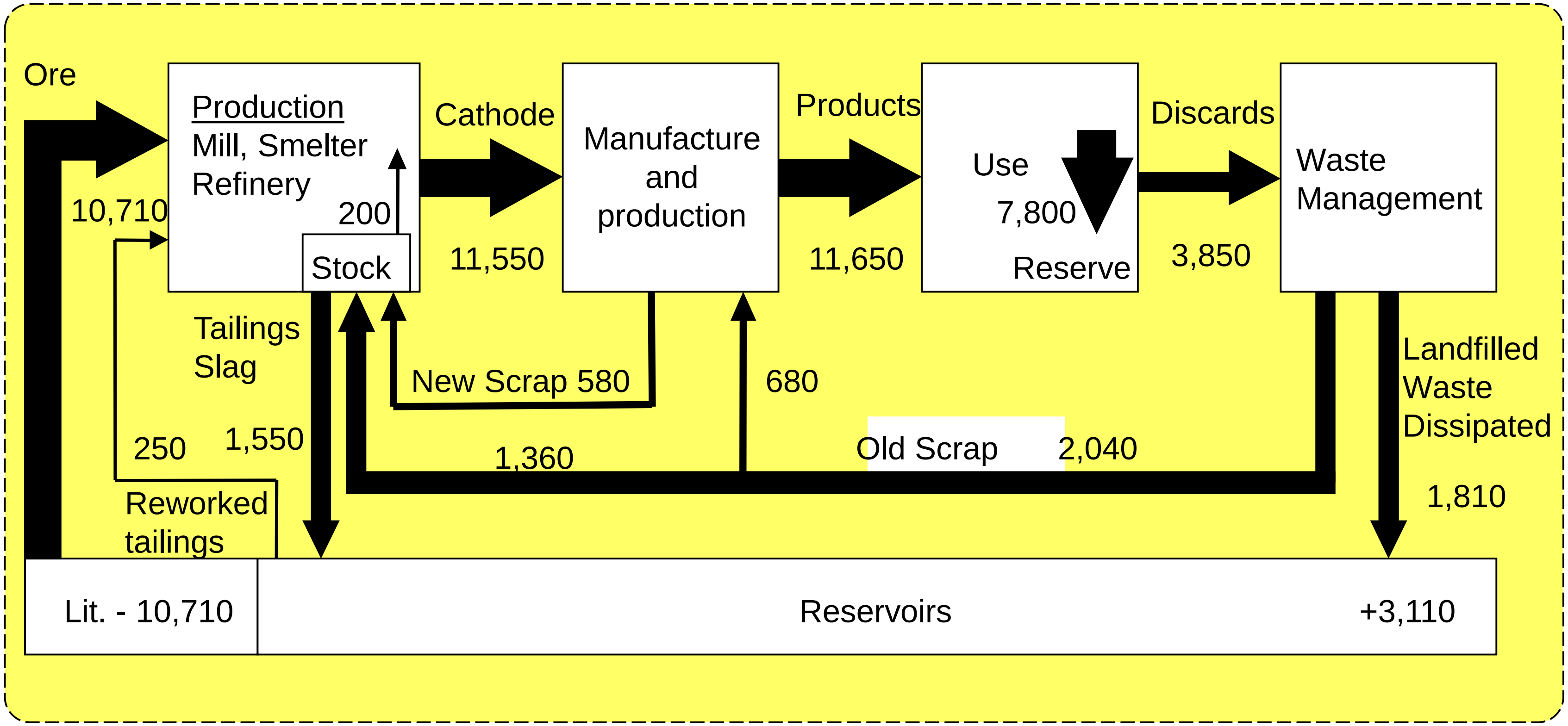
Non-renewable

Fossil Fuels
Petrol
Coal
Natural Gas

Metallic minerals
Iron
Copper
Aluminum

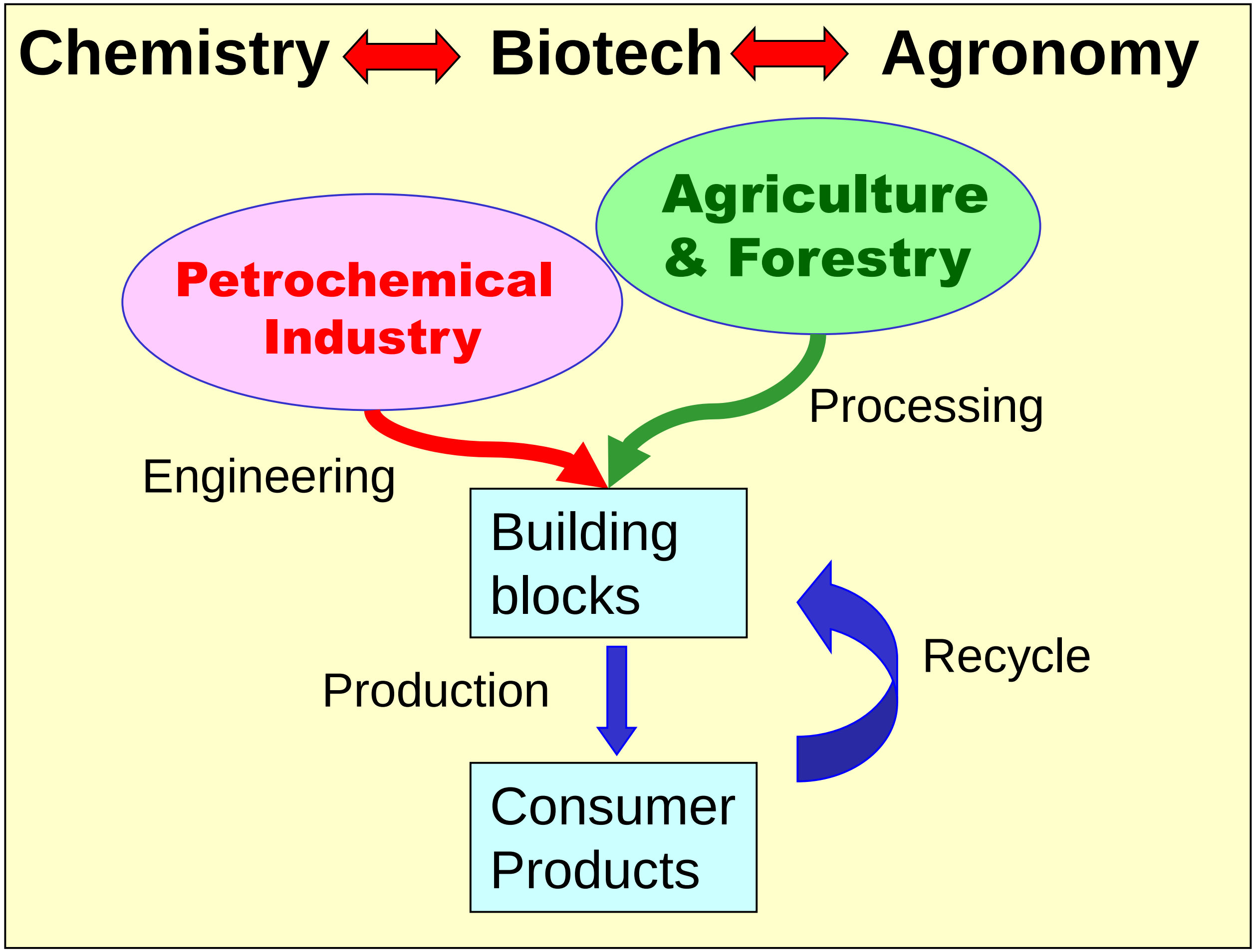
Nonmetallic Minerals
Salt
Phosphates

Substance or Material Flow Analysis:
The Global Copper Cycle, 1990-2000 (kt)



System Boundary (Closed System): "STAF World"

Renewable Sources of Organic-Bio Chemicals



Chemistry ⟷ Biotech ⟷ Agronomy

Petrochemical Industry

Agriculture & Forestry

Processing

Engineering

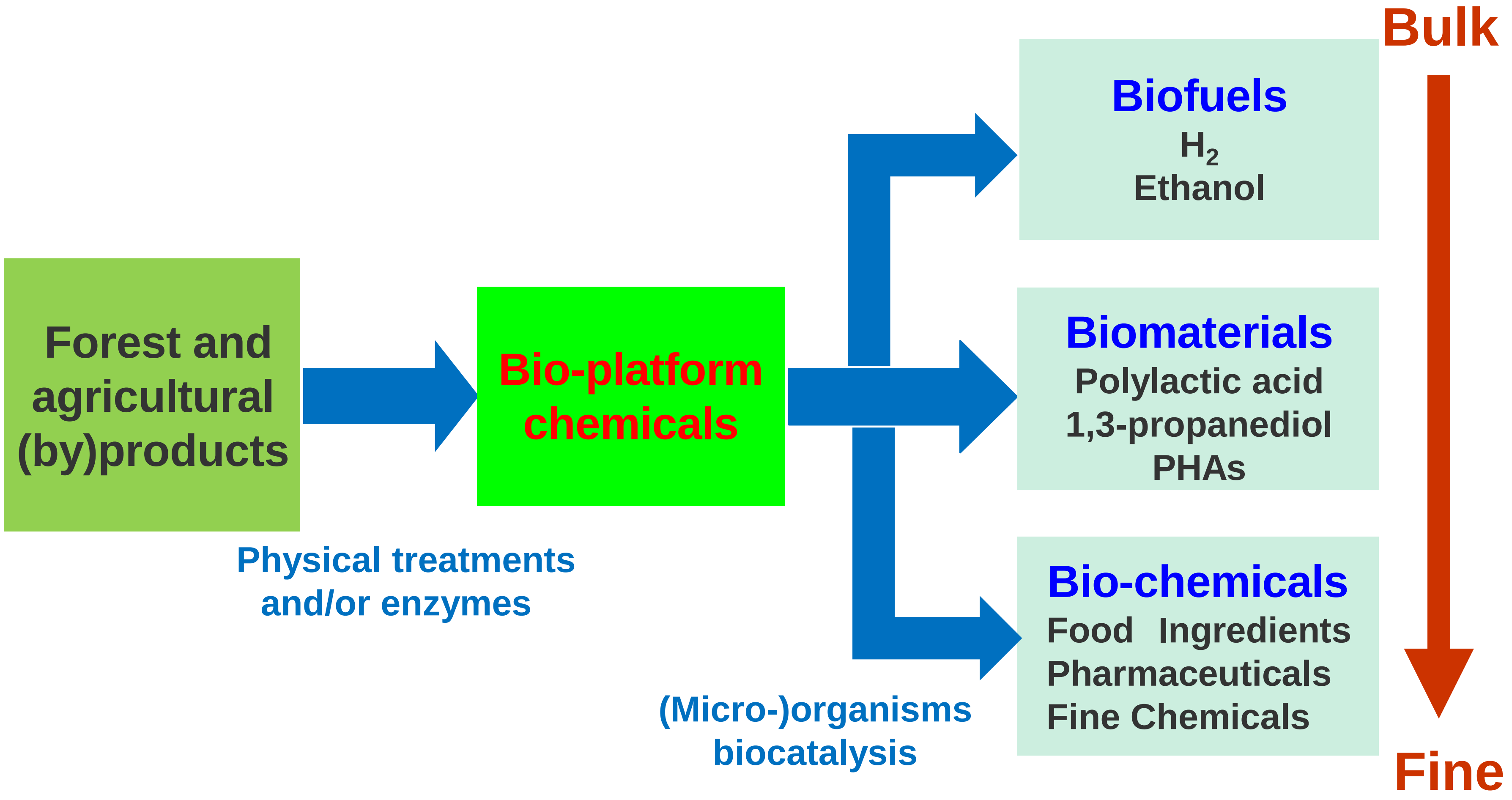
Building blocks

Production

Consumer Products

Recycle

Industrial Biotechnology (IB) Value Chain



Forest and agricultural (by)products

Physical treatments and/or enzymes

Bio-platform chemicals

(Micro-)organisms biocatalysis

Biofuels
H_2
Ethanol

Biomaterials
Polylactic acid
1,3-propanediol
PHAs

Bio-chemicals
Food Ingredients
Pharmaceuticals
Fine Chemicals

Bulk

Fine

Source: DSM (2004): *Industrial (White) Biotechnology*

Energy Sources

The main part of the energy used by society is obtained from several sources, some primary, other derived from these:

Primary Sources:

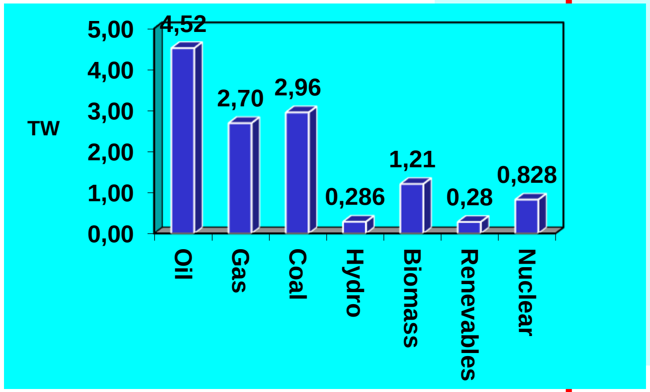
- Solar Energy
- Lunar Energy
- Geo Energy
  - Geothermal
  - Nuclear

Derived Sources:

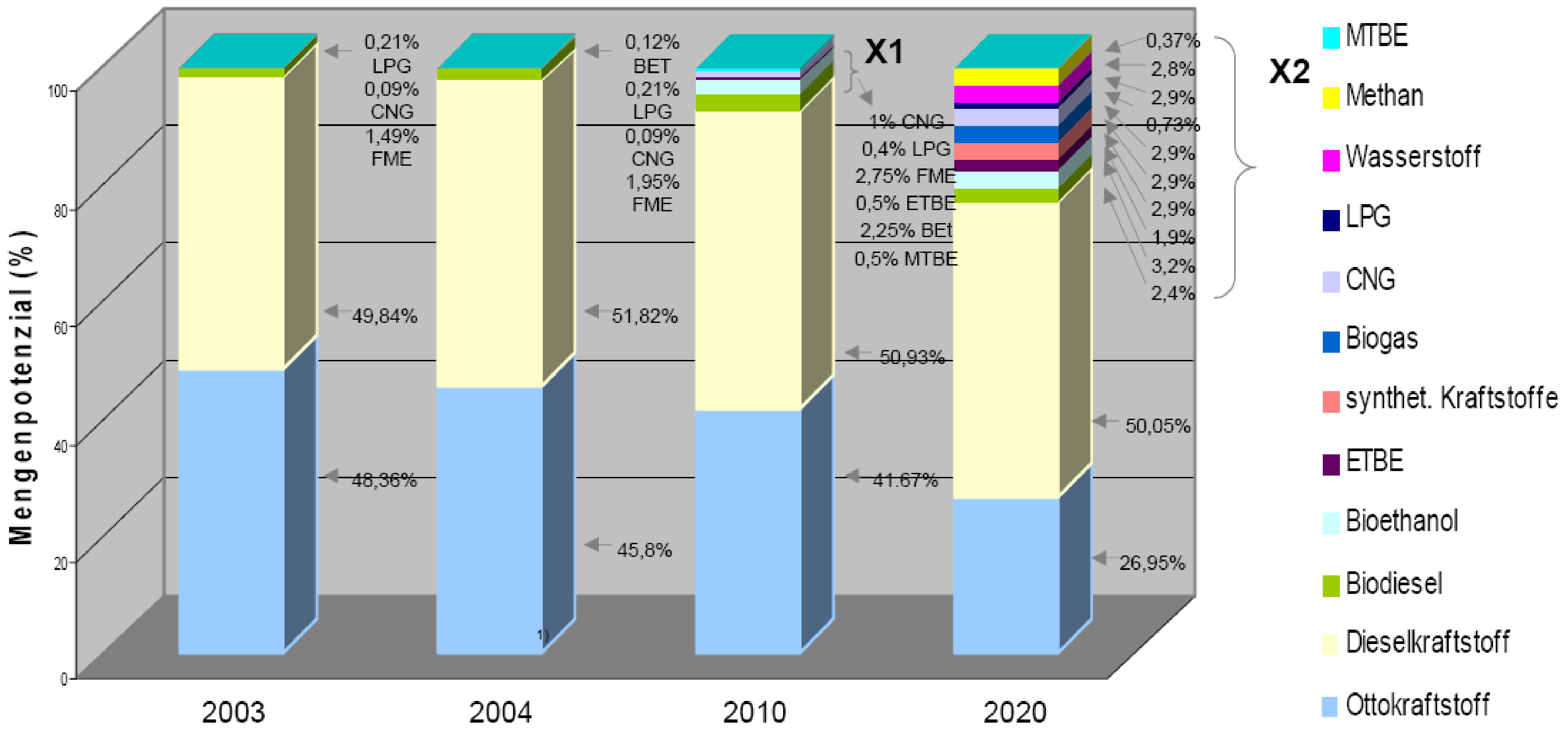
- **First order**
  - Fossil fuels
  - Biomass
  - Flowing water
  - Tides
  - Wind
  - Waves
- **Second order**
  - Electricity
  - Animal
  - Human

Distribution of average values of energy use (in TW)

Total: 13.0 ,
U.S.A.: 3.3 ,
Italy : 0.25
(*TW = Terawatt*)

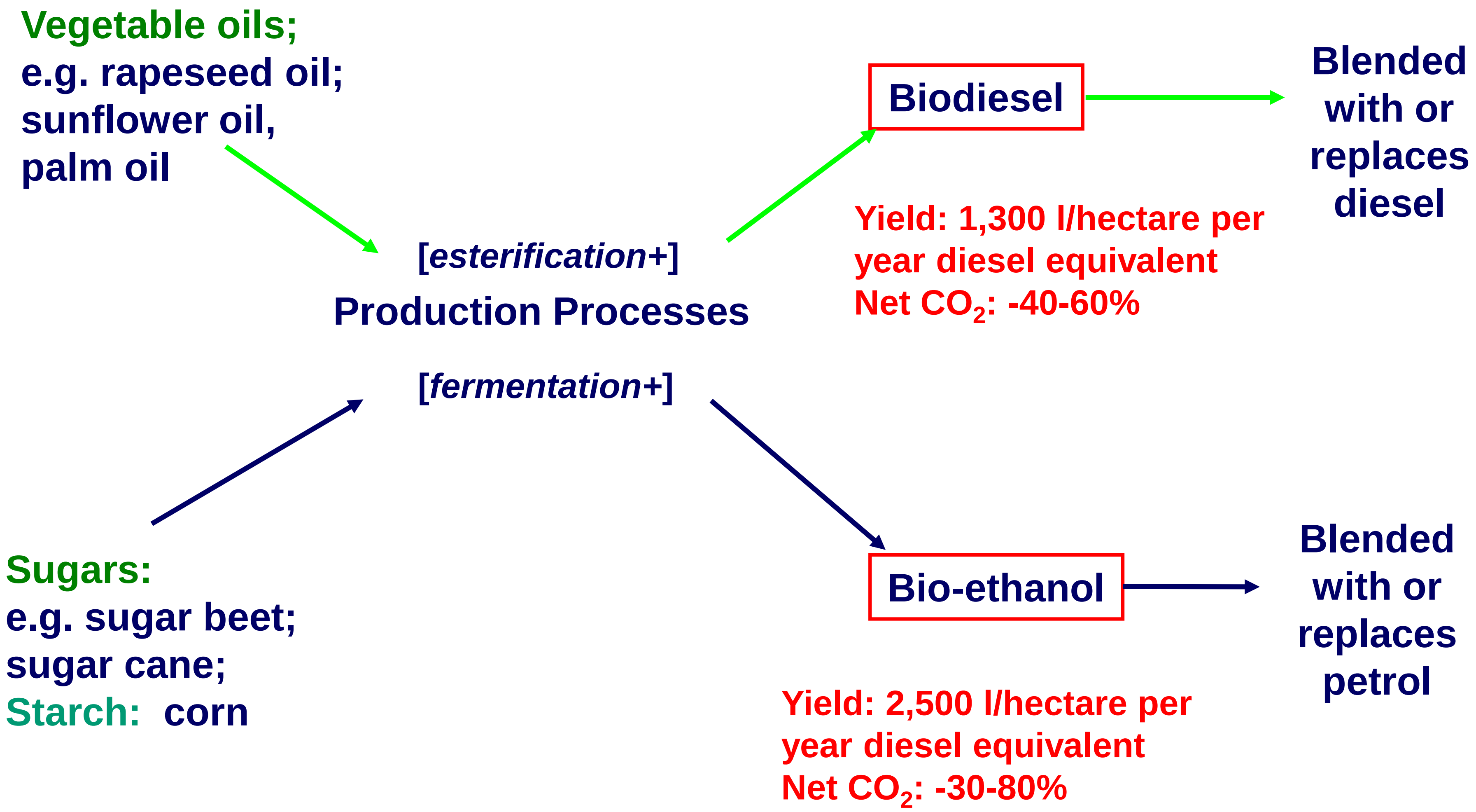


Relative Potential of Fuel Market (German Evaluation)



X_1 : According to report there is a theoretical potential for biofuels of up to 9%.
X_2 : According to report there is a theoretical potential for biofuels of up to 1/3 of the present fuels market.

First Generation Biofuels



Vegetable oils;
e.g. rapeseed oil;
sunflower oil,
palm oil

[*esterification*+]

Production Processes

[*fermentation*+]

Sugars:
e.g. sugar beet;
sugar cane;
Starch: corn

Biodiesel

Blended with or replaces diesel

Yield: 1,300 l/hectare per year diesel equivalent
Net CO_2: -40-60%

Bio-ethanol

Blended with or replaces petrol

Yield: 2,500 l/hectare per year diesel equivalent
Net CO_2: -30-80%

Alternative Heating (old and new)

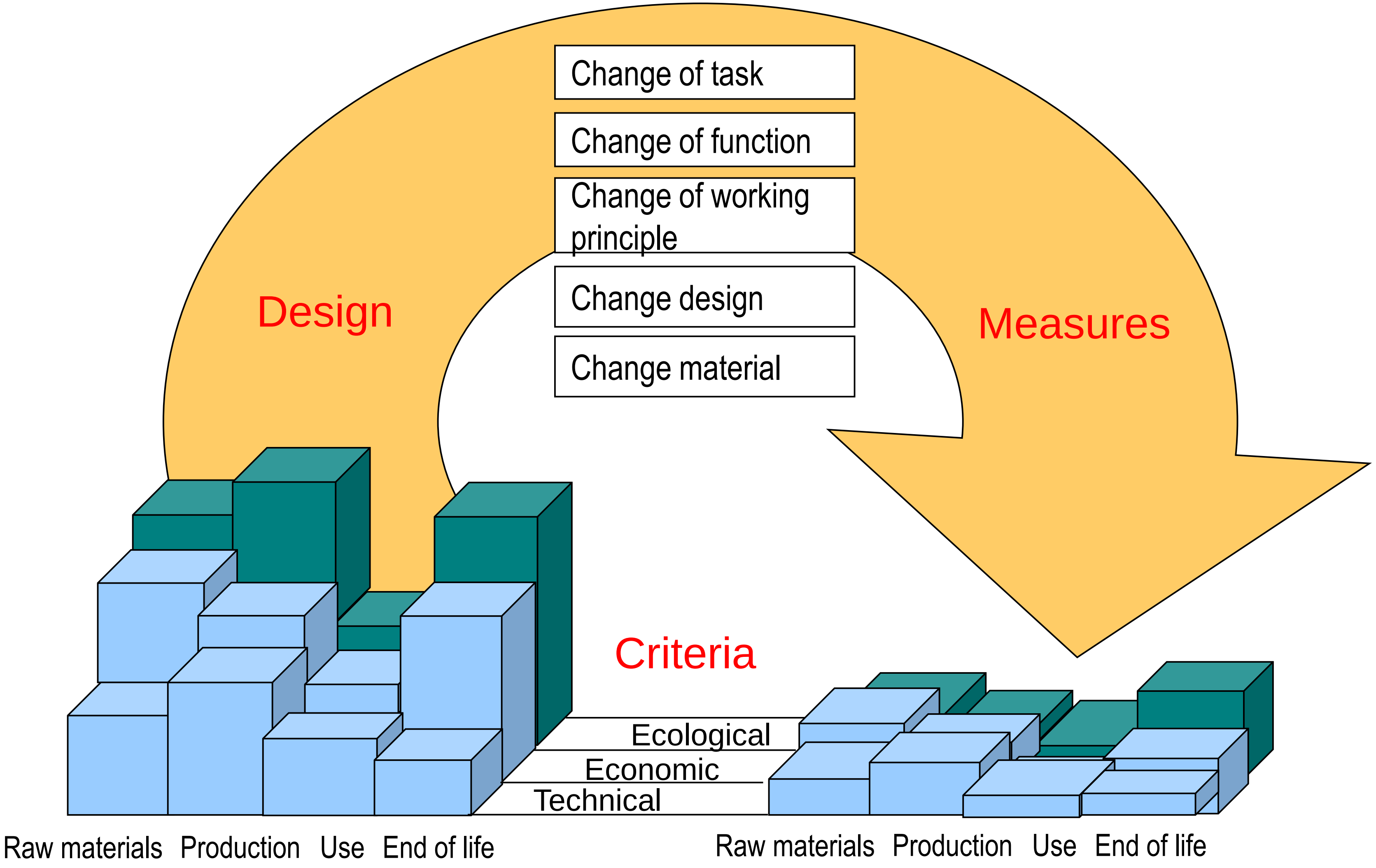

Microwave


oil bath


heating mantel


Bunsen

Design for Environment (DfE): Integrated Product Development



Change of task

Change of function

Change of working principle

Change design

Change material

Design

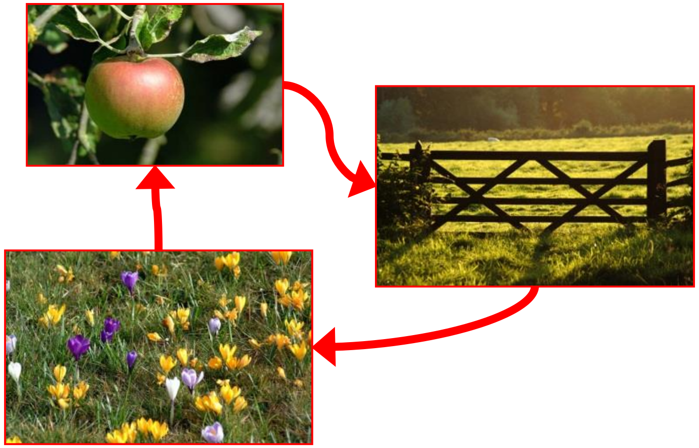
Measures

Criteria

Natural and Industrial Ecosystems and DFE: Industrial Metabolism

The analogy of industrial systems to natural systems:

- both have cycles of energy and nutrients/materials.
- strategies of nature to meet sustainability:
    - recycling/decomposing
    - renewing
    - conservation and population control
    - toxins stay in place
    - multiple function of one organism



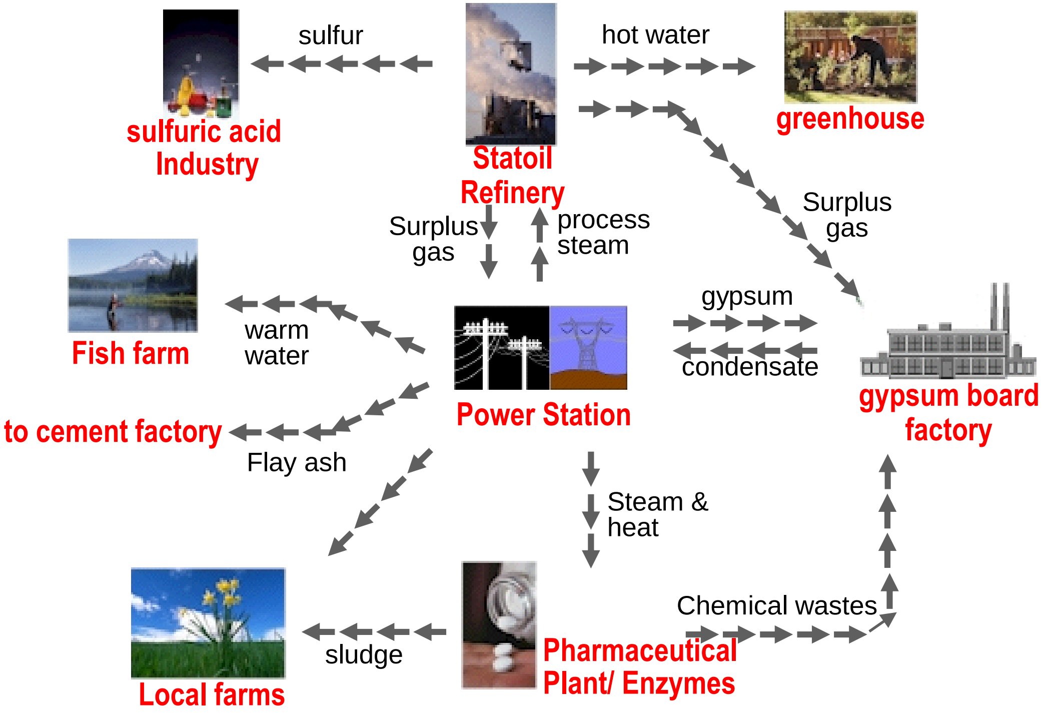
Industrial Ecology - Applications.

Eco-Industrial Parks: Industrial Symbiosis

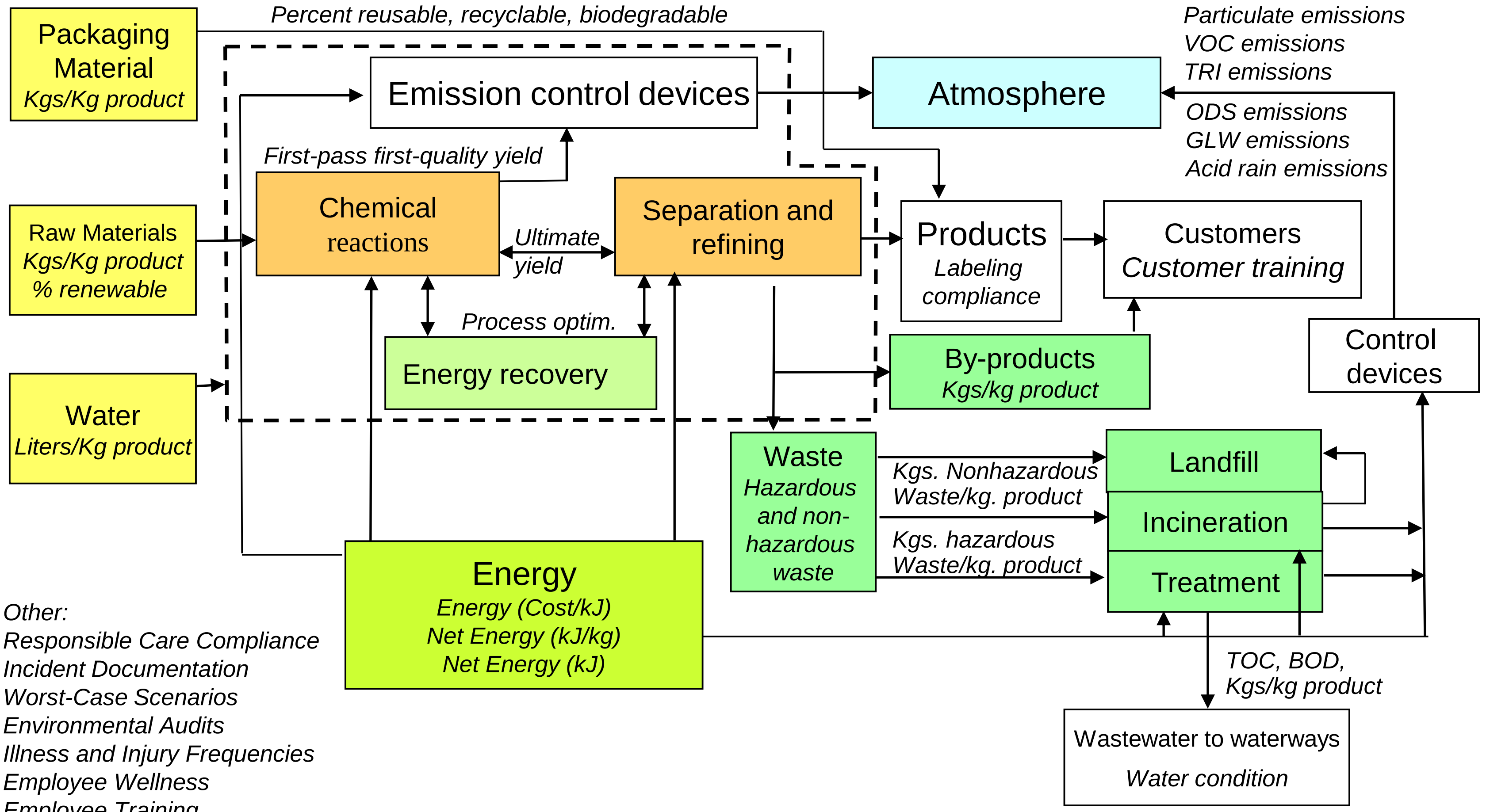
Well- known example of the Kalundborg park

The Kalundborg park involves 5 players:

- “Asnæs” power station, coal-fired
- “Statoil” refinery
- Gyproc, a plasterboard factory
- Novo Nordisk, a biotech firm
- City water and Heat supply



Processes: Tools Used in Chemical Production



Other:
Responsible Care Compliance
Incident Documentation
Worst-Case Scenarios
Environmental Audits
Illness and Injury Frequencies
Employee Wellness
Employee Training

NOTE: VOC = volatile organic compound, TRI = toxic release inventory, ODS = ozone depleting substances, RLW = River/Lakes waste, TOC = total organic carbon, BOD = biological oxygen demand.

Process Selection:
Propylene Oxide – Alternative Synthetic Routes

$$CH_3CH{=}CH_2 + HOCl \rightarrow CH_3CH(OH)CH_2Cl$$

$$CH_3CH(OH)CH_2Cl + Ca(OH)_2 \rightarrow PO + CaCl_2 + H_2O$$

$$CH_3CH(CH_3)CH_3 + O_2 \rightarrow (CH_3)_3COOH$$

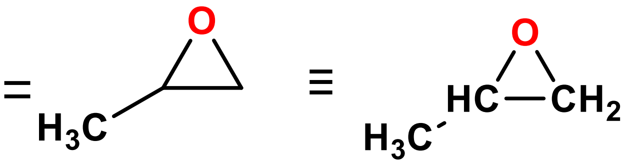
$$(CH_3)_3COOH + CH_3CH{=}CH_2 \rightarrow PO + TBA$$

$$C_2H_5C_6H_5 + O_2 \rightarrow C_6H_5CH(OOH)CH_3\ (ROOH)$$

$$R\text{-}OOH + CH_3CH{=}CH_2 \rightarrow PO + Styrene + H_2O$$

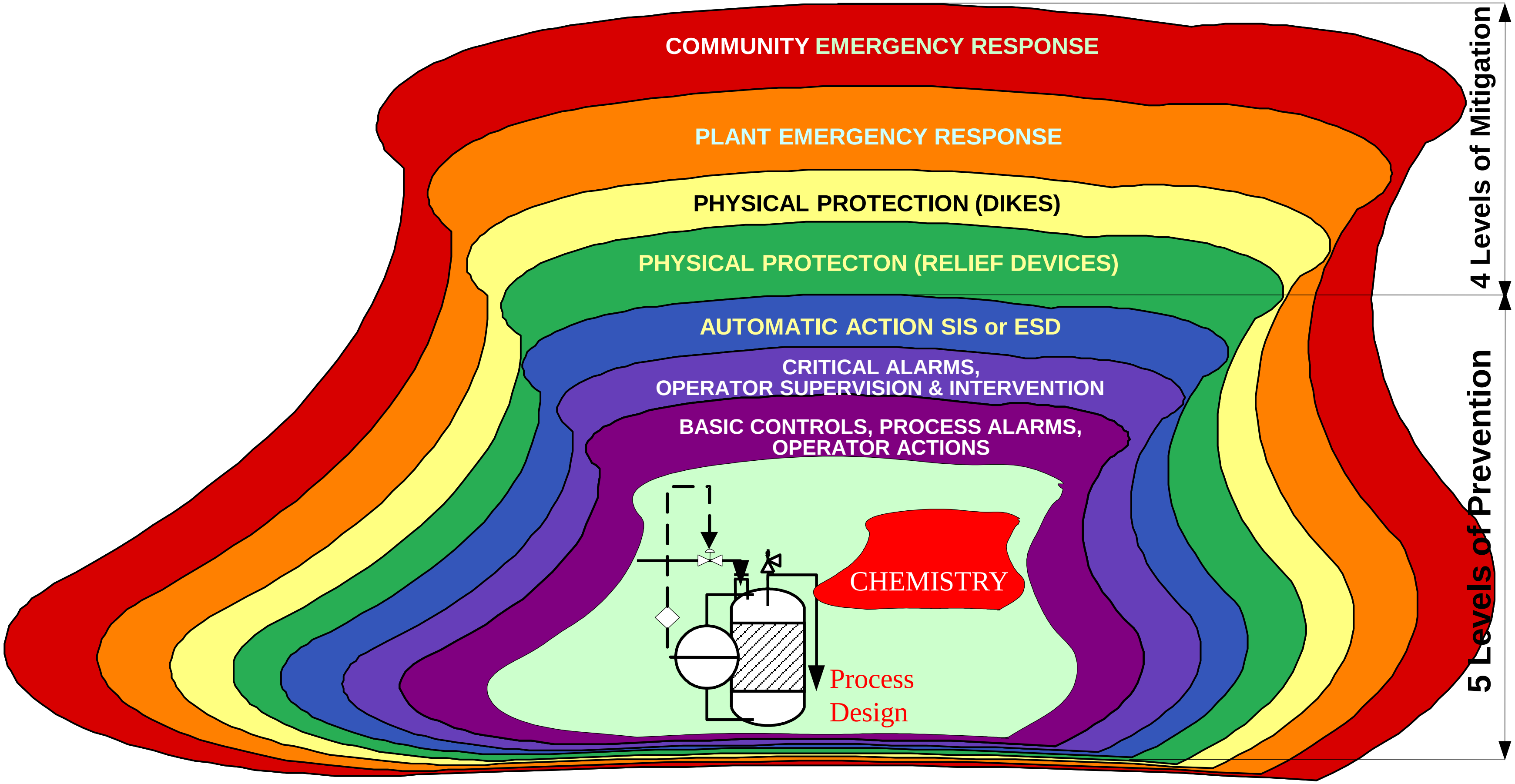
$$CH_3CH{=}CH_2 + H_2O_2 \xrightarrow[\text{silicalite}]{\text{Ti}} PO + H_2O \quad \text{cost??}$$

PO =



- Chlorohydrin route
  - Stoichiometric amount of waste salt
- ARCO route
  - Good if MTBE can be used through *tert*-butanol
- POSM route
  - Increasing recognized, but styrene as co-product
- **Direct oxidation**
  - Not yet available but studied by several companies.

Prevention/Mitigation:
Layers of Protection for a Chemical Plant



COMMUNITY EMERGENCY RESPONSE

PLANT EMERGENCY RESPONSE

PHYSICAL PROTECTION (DIKES)

PHYSICAL PROTECTON (RELIEF DEVICES)

AUTOMATIC ACTION SIS or ESD

CRITICAL ALARMS,
OPERATOR SUPERVISION & INTERVENTION

BASIC CONTROLS, PROCESS ALARMS,
OPERATOR ACTIONS

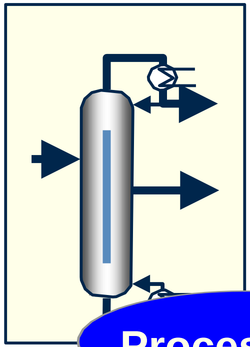
CHEMISTRY

Process
Design

4 Levels of Mitigation

5 Levels of Prevention

Reaction and Process Design: Enabling Innovation in Chemistry


Processing

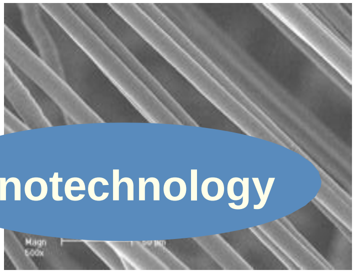

Product Design

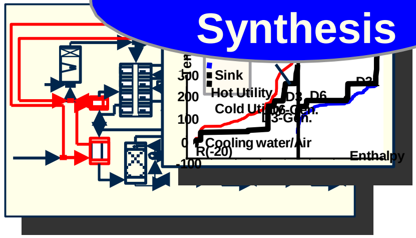

Synthesis


Bioprocessing


Catalysis

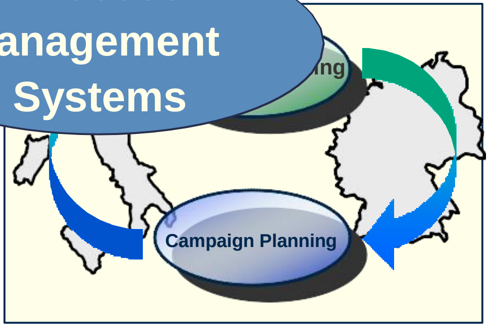
- Flexibility
- Cost efficiency
- Less waste


Nanotechnology

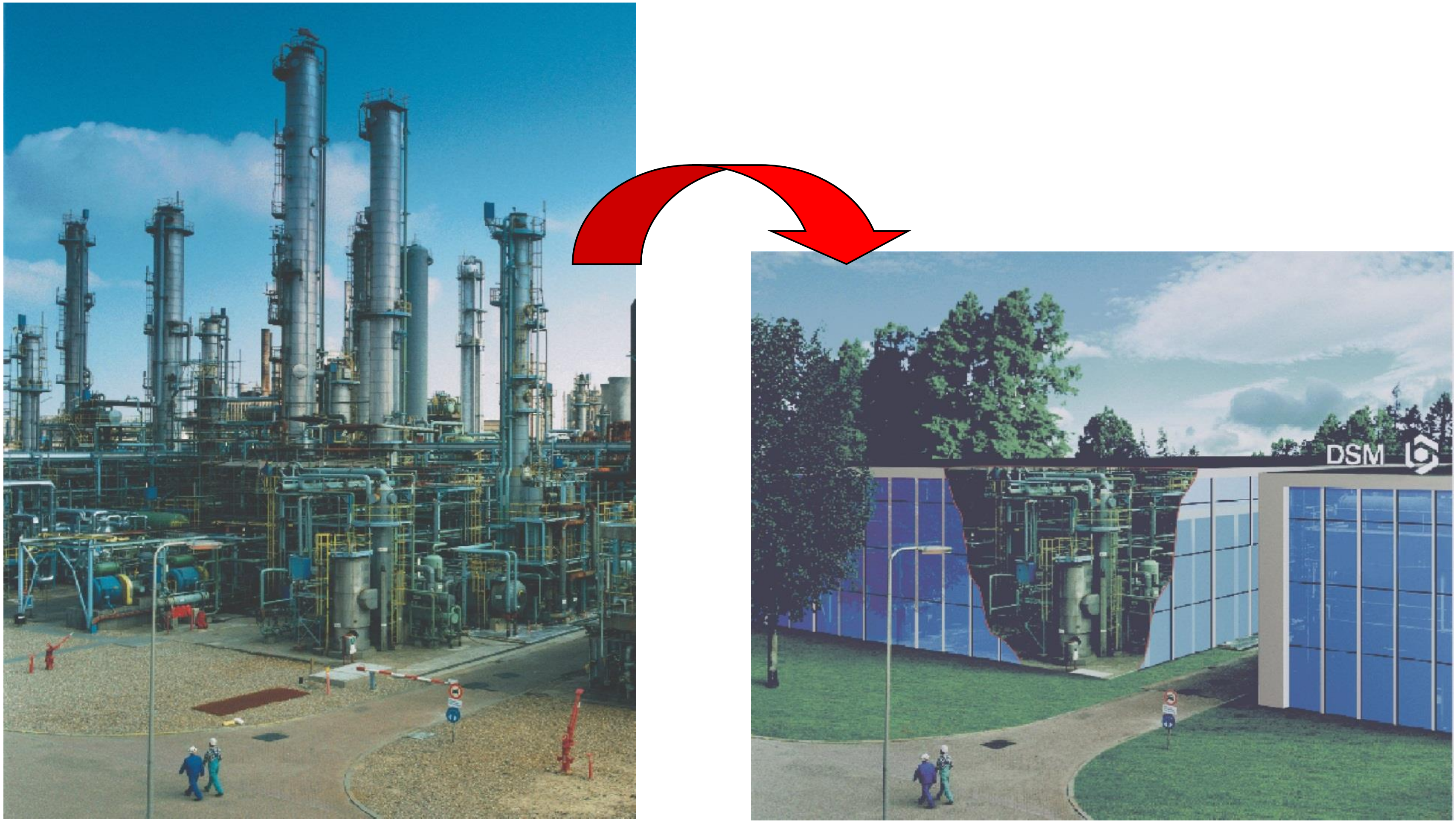

Process Synthesis


In silico-Technology

Expert System


Process Management Systems

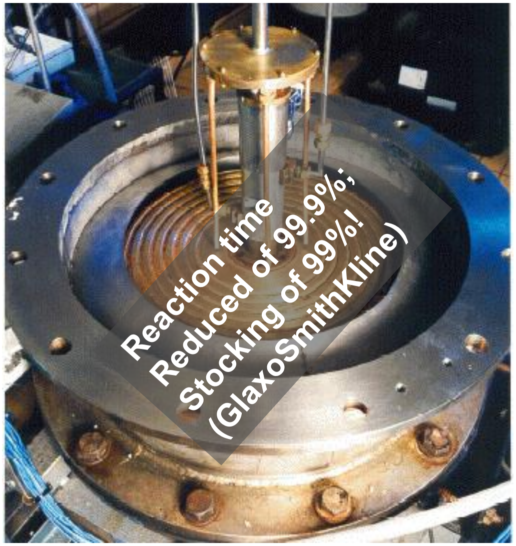
Chemical Industry Aims on Sustainability



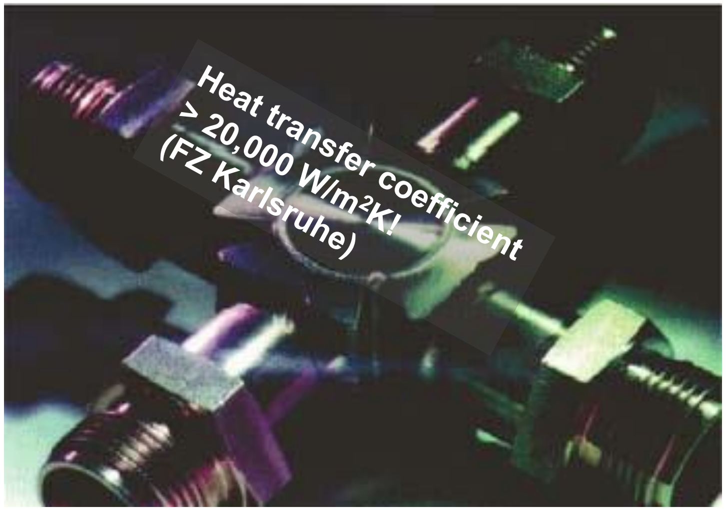
Where we are...

...and where we want to be

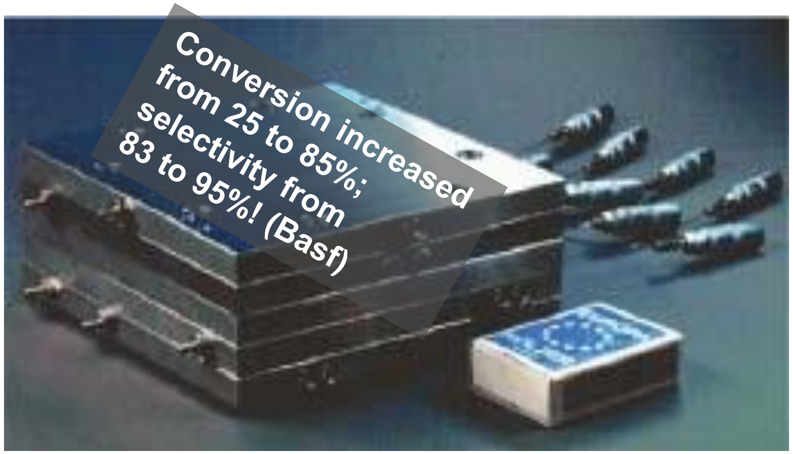
Process Intensification:
Some Examples of intensified Equipment



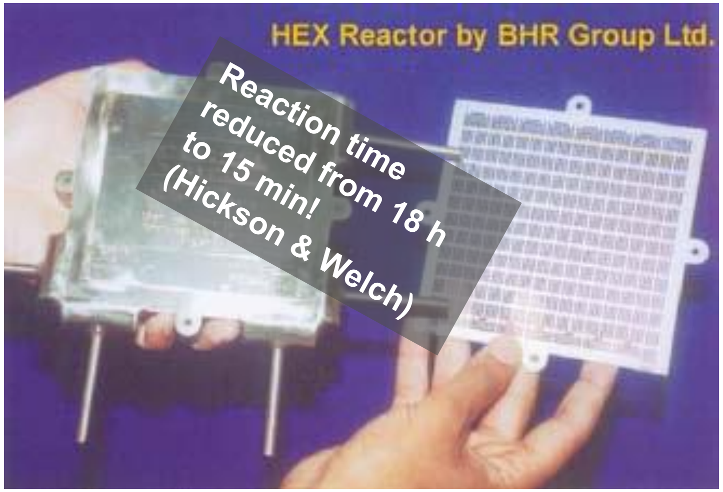
Reaction time
Reduced of 99.9%;
Stocking of 99%!
(GlaxoSmithKline)



Heat transfer coefficient
> 20,000 W/m^{2}K!
(FZ Karlsruhe)

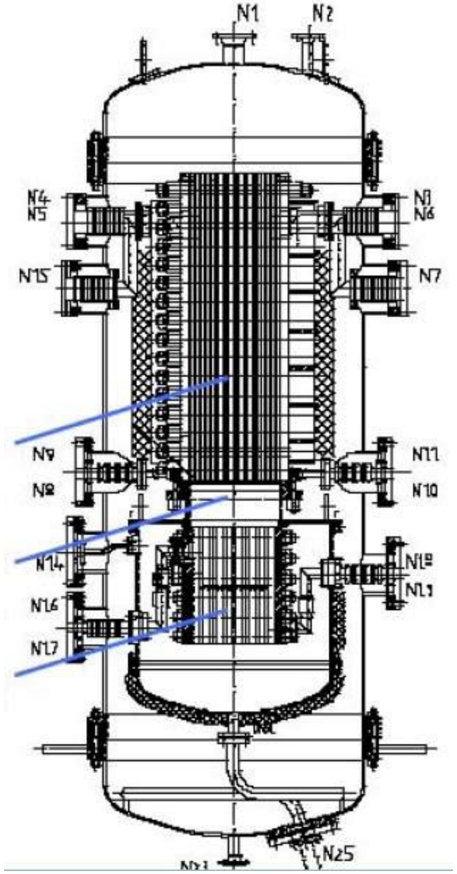


Conversion increased
from 25 to 85%;
selectivity from
83 to 95%! (Basf)



Reaction time
reduced from 18 h
to 15 min!
(Hickson & Welch)

Process Intensification: Micro-structured Epoxidation Reactor

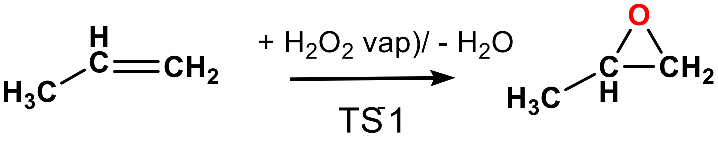


Reaction
(micro-structured)

Mixing
(micro-structured)

H_2O_2 evaporation
(micro-structured)

Model Synthesis:



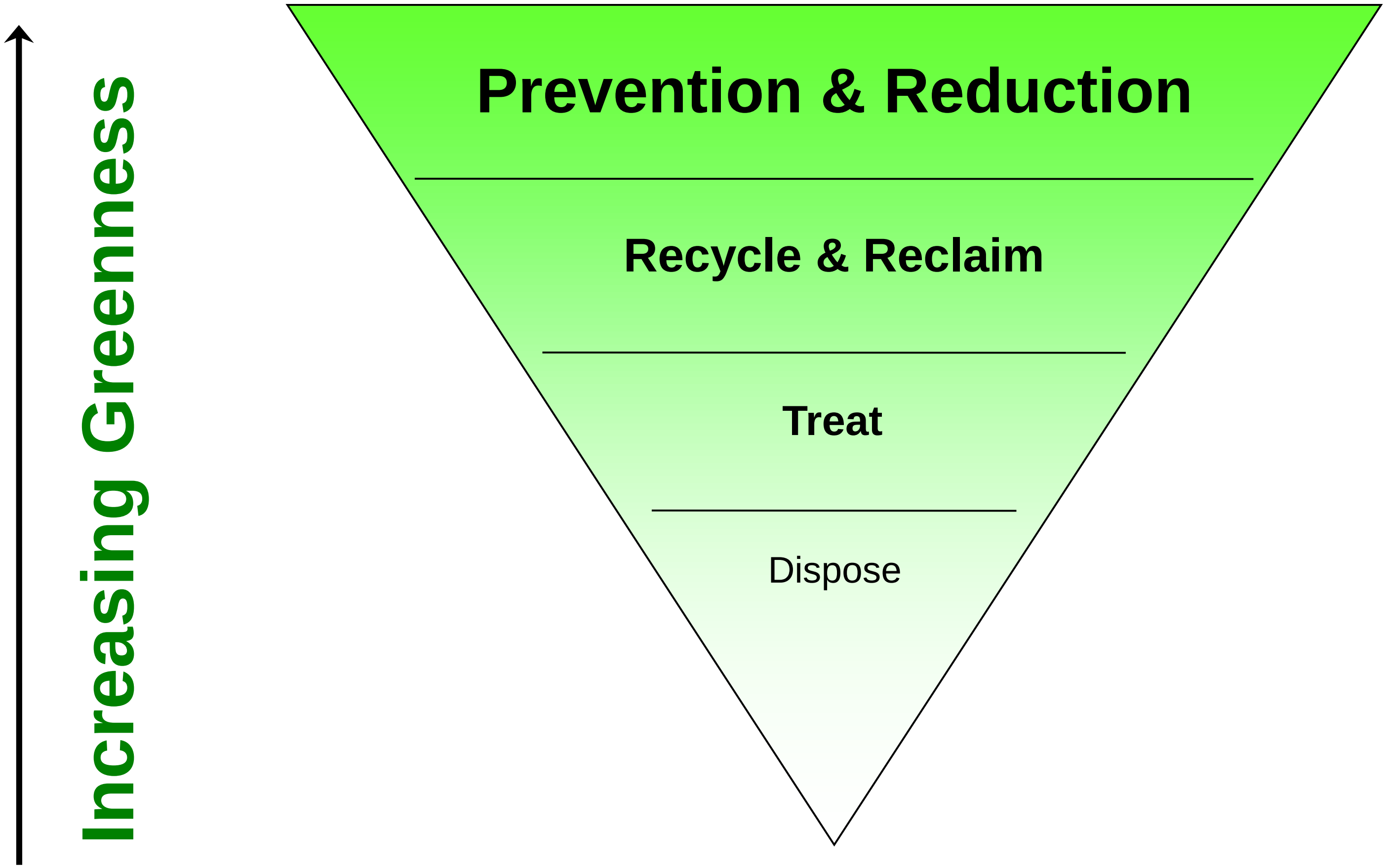
> 95%

Features:

- Modular (unit operations, capacity)
- Multi-purpose (catalyst and reaction)
- Reaction under pressure
- Reactions in the explosive regime

http://www.thyssenkrupp-industrial-solutions.com/fileadmin/documents/brochures/uhde_brochures_pdf_en_10000032.pdf

Pollution Prevention Hierarchy

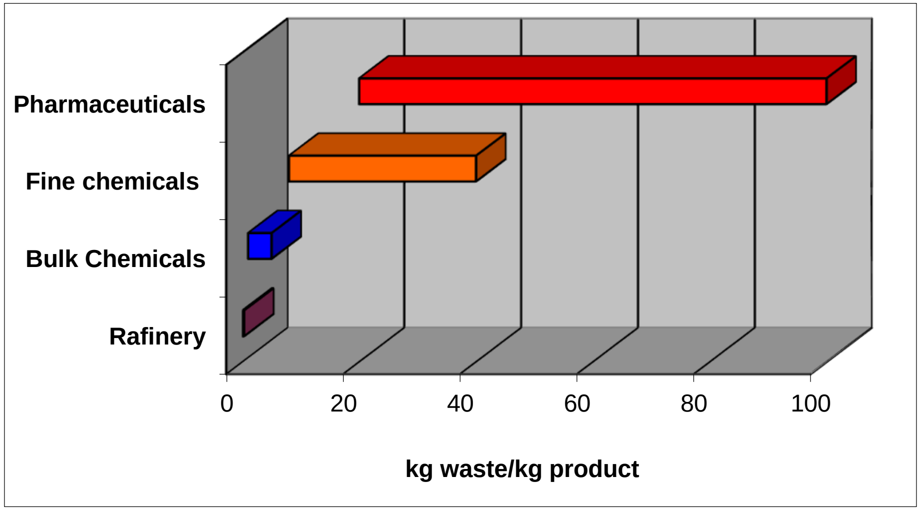


Wastes and Chemical Industry

Can be quantified according to industry:

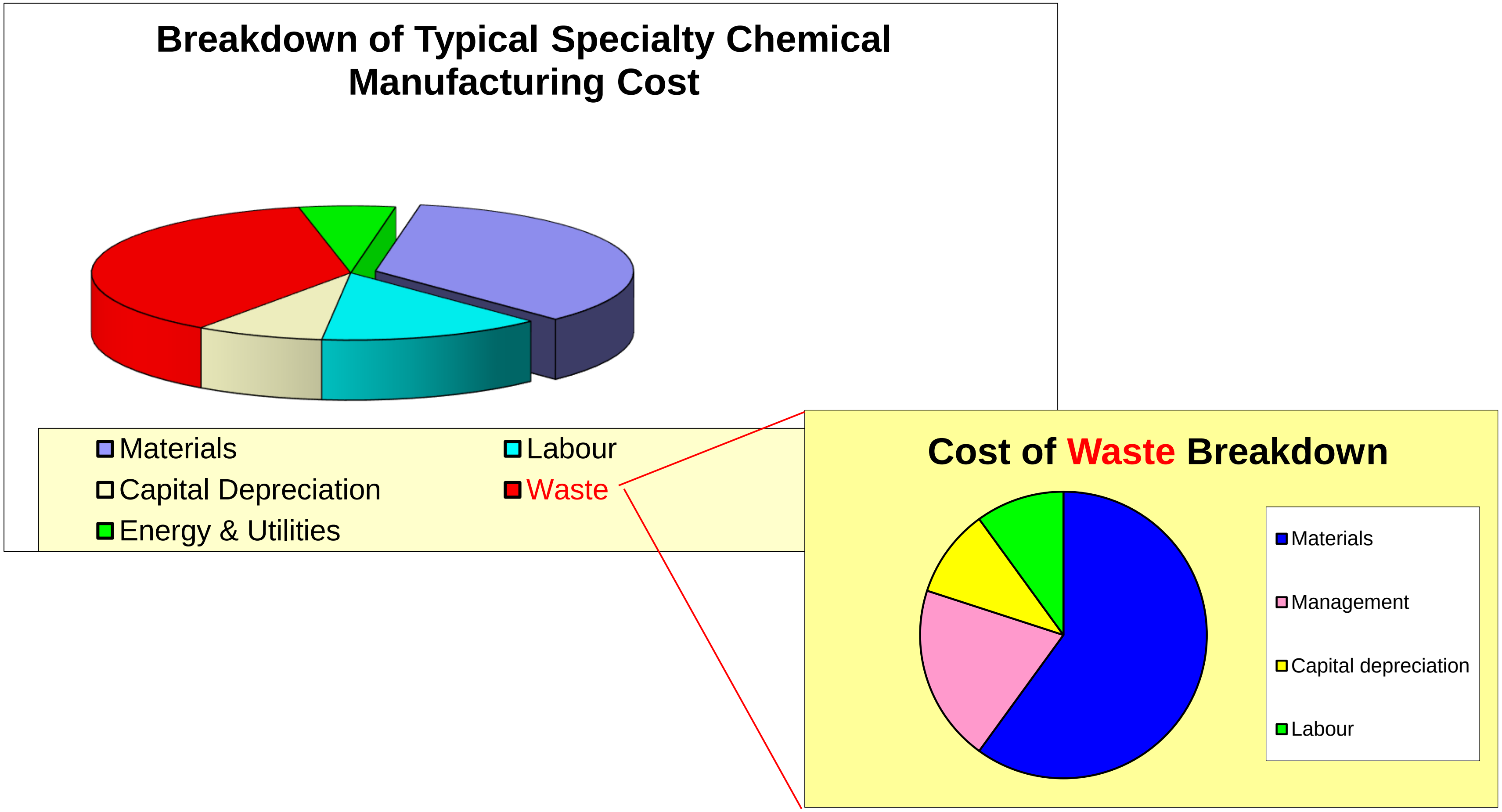
Industry Segment	Ton/year	Ratio Kg Byproducts/Kg Product
Oil refining	10^6 - 10^8	<0.1
Bulk chemicals	10^4 - 10^6	1 – 5
Fine Chemical	10^2 - 10^4	5 – 50
Pharmaceuticals	10 - 10^3	25 - 100+

- Areas traditionally thought of as being dirty (oil refining & bulk chemical production) are relatively clean - they need to be so because margins per Kg are low.
- Newer industries with higher profit margins and employing more complex chemistry produce relatively much more waste.

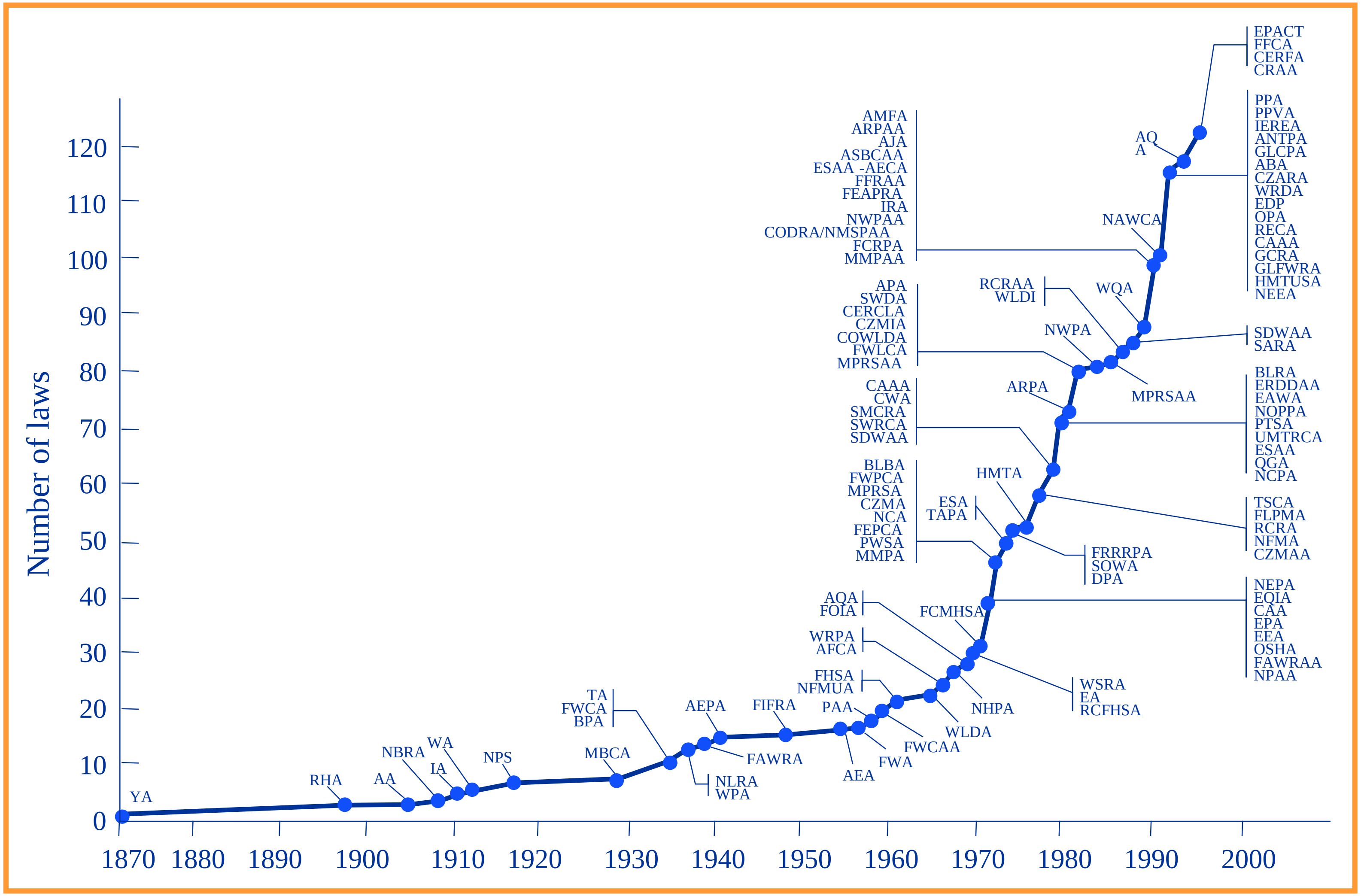


R A Sheldon *J. Chem. Tech. Biotech*. 1997, 68, 381

Waste in the Specialty Chemicals Industry



Cumulative Growth in Environmental Regulations



Estimated Numbers of Chemicals (EPA estimates, 2010)

Number of Chemicals:	28,000,000	
Chemicals in Commerce:	10,000,000	
Industrial Chemicals:	240,000	(millions of products)
New Chemicals:	3-4,000	/year (1,000 in US)
Pesticides:	800	(21,000 products)
Food Additives:	9,500	
Cosmetic Ingredients:	8,500	(50,000 products)
Medicines to humans:	3,500	

- By limiting the synthesis strictly to combinations of 30 atoms of just C, N, O, or S, **more than 10^{60} structures are possible !**
- Expanding the allowable elements to other heteroatoms (e.g., P and halogens), the limits to the numbers of possible structures defies imagination. Also known as “chemical space”

Chemical Risk and Law

All of these acts, with few exceptions, deal with pollution after it is formed. These laws are in general focused on the treatment or abatement of pollution and have become know as "command and control" laws. In many instances these laws place limits on pollution and timetables for compliance, with little regard to whether the science/technology could attain these goals and with little regard to the economic costs of these laws.

Risk associated with a toxic chemical is a function of Hazard and Exposure. The "end of the pipe" laws attempt to control Risk by dealing with the prevention of the Exposure to toxic hazardous chemicals. Of course all to often prevention of Exposure has failed.

$$\text{Risk} = f(\text{Hazard}, \xcancel{\text{Exposure}})$$

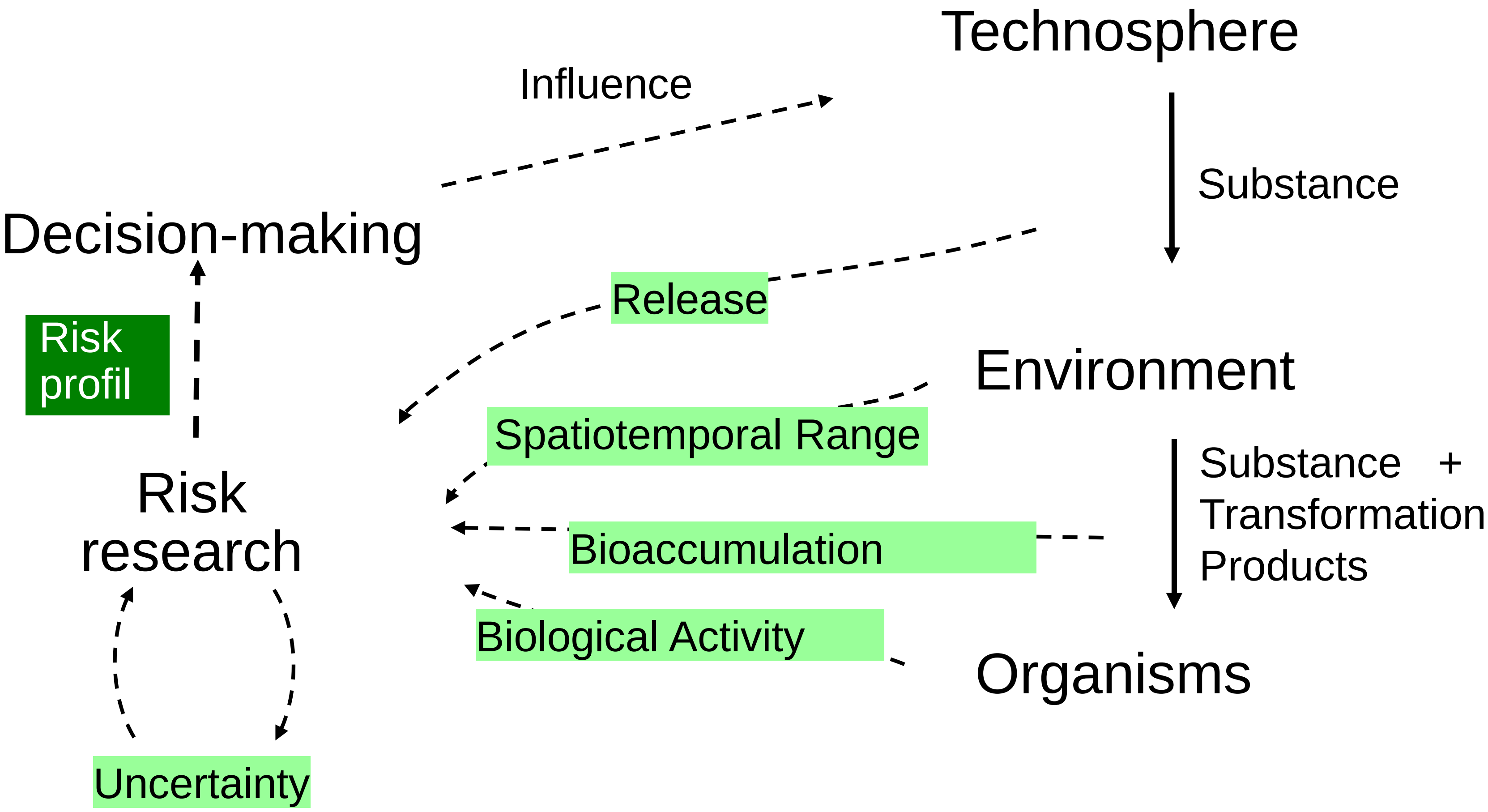
Focus on Hazard Elimination!

- Green Chemistry, instead of limiting Risk by controlling our Exposure to hazardous chemicals, attempts to reduce and preferentially eliminate the Hazard thus negating the necessity to control Exposure. The bottom line is, if we don't use or produce hazardous substances, then the Risk is zero, and we don't have to worry about the treatment of hazardous substances or limiting our exposure to them.
- Green chemistry has gained a strong foothold in the areas of research and development in both industry and academia. Several conferences and meetings are held each year with green chemistry/technology as their focus.

$$\mathbf{Risk = f(\xcancel{Hazard}, Exposure)}$$

Control the hazard, no need to worry about the exposure!

Risk Management Cycle and Eco-toxicological Information on Chemical Products



Technosphere

Influence

Substance

Decision-making

Release

Risk profil

Environment

Spatiotemporal Range

Substance + Transformation Products

Risk research

Bioaccumulation

Biological Activity

Organisms

Uncertainty

International Treaties

Great Lakes Water Quality Agreement

- Agreement between the U.S. and Canada
- Created an international joint commission to draft regulations and make recommendations on all actions affecting the Great Lakes, their tributaries, and adjacent riparian areas

COP21 (Paris 2015)

- At the Paris climate conference (COP21) in December 2015, 195 countries adopted the first-ever universal, legally binding global climate deal (to well below 2°C).

International Treaties: The Montreal Protocol

Addresses ozone depletion

- 1987 Protocol Requirements:
  - 50% reduction in the 1986 CFC productions levels by 1999
  - Freeze on the 1986 halons production and consumption levels
- London Amendment of 1990:
  - Phase out CFCs entirely by 2000
- Amendments of 1992:
  - Accelerated timetable for reducing ozone depleting substances
- Implementation in the U.S. through Title VI of the Clean Air Act Amendments of 1990:
  - Production of all Class I substances (CFCs, halons, carbon tetrachloride, and methyl chloroform) phased out by 2000
  - Production of Class II substances (HCFCs) phased out by 2030

International Treaties: The Kyoto Protocol and Paris Agreement

- Kyoto protocol (1998) addresses greenhouse gas emissions, signed by various nations (not by U.S., China)
- If ratified, a nation would have to:
  - Reduce greenhouse gas emissions (CO_2, NO_x, and CH_4) 7% below 1990 levels
  - Reduce HCFC, CFC, and HFC 7% below 1995 levels over the period from 2008 to 2012
  - The Protocol also contains provisions whereby credits for greenhouse gas emissions can be earned by carbon reducing activities, e.g. reforestation.
- Paris Agreement (2015) aims to strengthen the global response to the threat of climate change, in the context of sustainable development and efforts to eradicate poverty.

European REACh Legislation

The green chemistry is driven by an European legislation context increasingly restrictive in terms of protection of human health and environment …

✓ **Regulations to reduce the toxicity of chemical substances**

REACh 2006: Regulation on **R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emicals. It entered into force on 1st June 2007 and from 2008 registration is required. Terminato nel 2018.

Following the REACh system, the companies manufacturing or importing more than *one tonne* of a chemical substance per year, are required to gather information on substance properties, provide an analysis of risk associated to the substance use, and to Register in a central database at the European AGENCY dedicated to this subject: the European Chemicals Agency (ECHA English).
SITE: http ://echa.europa.eu/home_en.asp

1999/13/CE : diminution des émissions de Composés Organiques Volatils
1999/45/CE : directive sur les produits dangereux
2004/42/CE : directives limitant l'usage des solvants dans les peintures

Environmental Compliance and PP: International Organization for Standards

- International Organization for Standards (ISO) is a private sector non-governmental organization founded in Switzerland in 1947.
- Promotes international harmonization and development of manufacturing, product, and communications standards.
- **ISO 14000** series – environmental management standards:
  - Voluntary
  - Standards and guidance documents on environmental management, eco-labeling, auditing, life-cycle assessment, and environmental performance evaluation.
  - Calls for environmental policies that represent a commitment to environmental compliance and pollution prevention
  - Aims to promote effective environmental management systems in organizations. The standards seek to provide cost-effective tools that make use of best practices for organizing and applying information about environmental management.

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- Girard, J.E., *Principles of Environmental Chemistry*; Jones and Bartlett: Sudbury, MA, 2005

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Books on Green Chemistry

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http://www.rsc.org/science/esef.html

http://www.gscn.net/indexE.html

http://www.epa.gov/greenchemistry/index.html

http://web.chem.monash.edu.au/GreenChem/

http://eco-web.com/

Presidential Green Chemistry Challenge Awards -Winners and nominations: http://www.epa.gov/greenchemistry/

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