Digital Micro-Certification
"The Challenges of Sustainable Chemistry"

January – February 2024

Project Managers

- Gwenaëlle **BOUJARD** : gwenaelle.boujard@universite-paris-saclay.fr
- Rachel **MEALLET** : rachel.meallet@universite-paris-saclay.fr
- Laurent **SALMON** : laurent.salmon@universite-paris-saclay.fr

The main goal

"To introduce the basics of sustainable development (SD) to chemistry students (master's level) and provide them with ideas for reducing the environmental impact of their research (doctoral level)

Two levels of digital certification:

- Level 1 certification: SD basics in chemistry (Master – 10.5 h) ➝ 2023-2024
- Level 2 certification: chemistry research and SD (PhD – 10 h) ➝ 2024-2025
  - prerequisite: obtaining Level 1
  - enter the online training catalog with points recognition (ED)

Pedagogical content

Certification level 1 : SD basics in chemistry (Master 10.5 h) → 2023-2024

Module 1 : Introduction to SD in chemistry

Module 2.1 : Lifecycle analysis (ACV) – Ecodesign

Module 2.2 : Lifecycle analysis (ACV) – Principles and Methodology

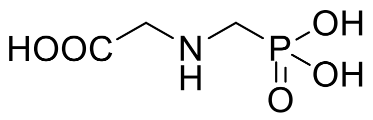
Module 3 : Chemical waste management and circular economy

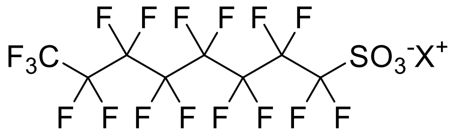
Module 4 : Renewable and bio-sourced chemistry

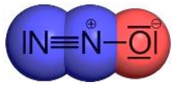
Module 5 : Environmental regulations and chemical standards

Module 6 : Environmental performance assessment in chemistry

L. SALMON (UPSay)
January 9, 2024 (Orsay)







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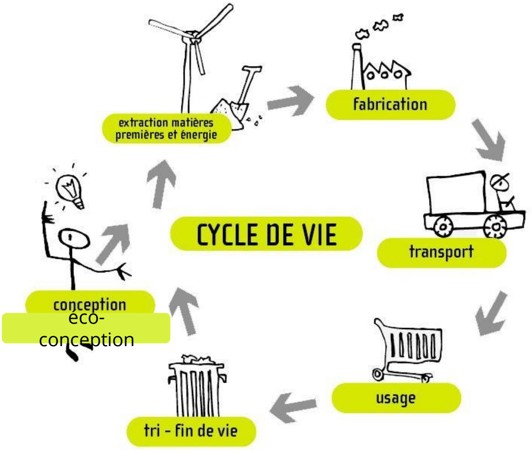
C. CANNIZZO (UEVE/CEA)
January 16, 2024 (Evry)



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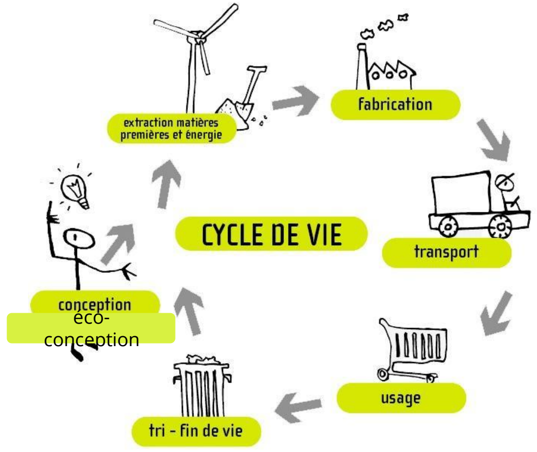
P. TARDIVEAU (UPSay)
January 23, 2024 (Versailles)



Pedagogical content

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S. HENRY-DAGUERRE
January 30, 2024 (Orsay)

SARPI VEOLIA

Pedagogical content

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M.-C. SCHERRMANN (UPSay)
February 6, 2024 (Evry)

Pedagogical content

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M. BOIVIN (UPSay)
February 13, 2024 (Versailles)

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M.-C. SCHERRMANN (UPSay)
February 20, 2024 (Orsay)

$$\text{PMI} = \frac{\text{total mass in a process or process step}}{\text{mass of product}}$$

- process mass intensity
- atom saving
- environmental factor
- carbon footprint
- etc

95% of chemistry students at UPSay have never had such a global vision of sustainable chemistry during their training

Module 1 – Introduction to sustainable development in chemistry

Basics in Biogeochemistry, Chemical Pollutants and Sustainable Development

Tuesday 9th, January 2024

Pr. Laurent SALMON

Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO)

Université Paris-Saclay, Orsay

laurent.salmon@universite-paris-saclay.fr
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Table of contents

1. The role of the chemical industry in France and in the world

a) The place of chemistry in our society

"99% of the objects that surround us have passed through the hands of a chemist at some point". *Stéphane Barbati, Univ. Aix-Marseille, 2011*

Upstream
Supplier sector (petroleum products, natural gas, agricultural products)

↓

Chemical industry →

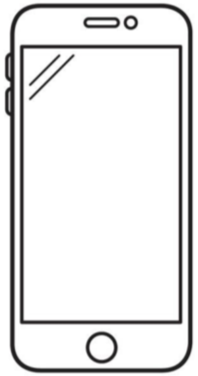
- Fuels
- Elastomers, plastics, textiles
- Soaps, detergents
- Fertilizers, pesticides
- Oils, fats
- Synthetic medicines
- Cosmetics, perfumes
- Sweeteners
- Dyes, inks
- Paints, varnishes
- Glues
- Explosives

↓

Downstream
All industrial sectors
Consumers

→

- Transport, energy
- Clothing
- Housing, building
- Agriculture, food
- Hygiene, health
- Culture, sports, leisure
- Communication, electronics



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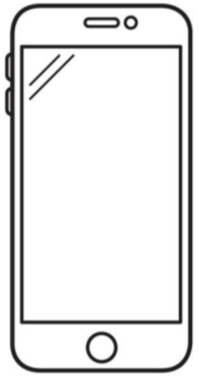


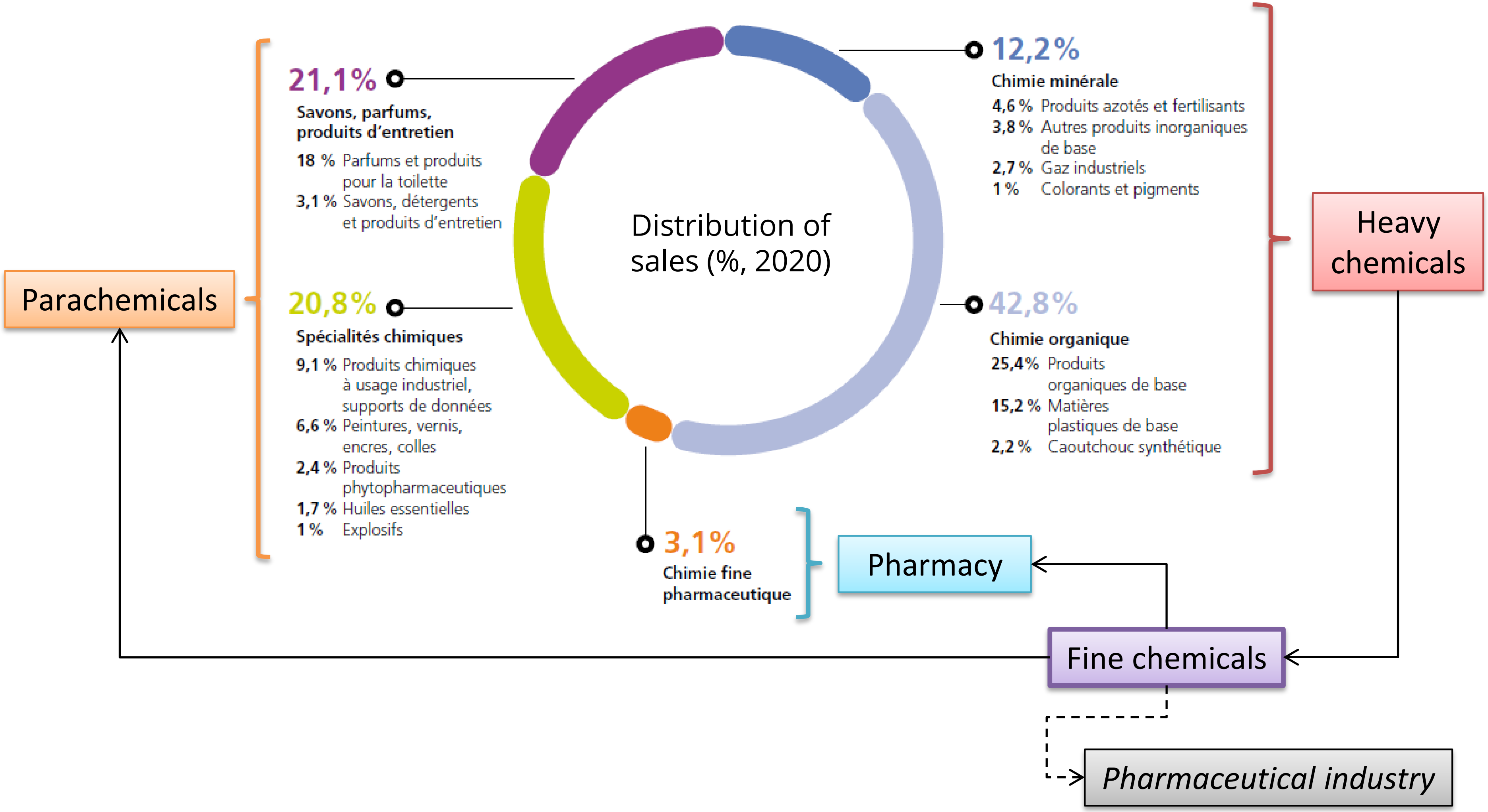
Chemistry is involved in life itself! →

- Muscular activity
- Nervous activity
- Digestion
- Breathing
- Reproduction
- Taste
- Smell...

Chemistry is involved in everyday life ←

- Transport, energy
- Clothing
- Housing, building
- Agriculture, food
- Hygiene, health
- Culture, sports, leisure
- Communication, electronics

b) Classification of chemical industry activities



c) The French chemical industry

- **7th in the world** (after USA, Japon, Germany, China, UK…)
- **2nd in Europe** (after Germany)
- **2nd largest industrial balance in France**:
  - 129 billions € in sales
  - trade balance: + 9,5 billions € (81,5 export – 72 import)
  - investments : 6,6 billions €
    - 60% : plant maintenance and regulations (HSE...)
    - 40% : business growth in France
  - R&D : 1,9 billions € (14 577 people in R&D, including 7 663 researchers)
- **1st industrial exporter in France** (*ahead of* automotive, electrical/electronic products, agri-food ind., aeronautics...)
- **4,000** companies, 94% of which are SMEs/VSEs
- **225,000** direct jobs and 700,000 indirect jobs
  - 70% technicians, managers, supervisors
  - 94% on permanent contracts

France Chimie 2022

d) Risks and the chemical industry's public image

- Despite all the *societal benefits* of the chemical industry, it suffers from a *poor public image,* which is partly justified:
  - health and pollution issues, chemical wastes management, toxicity…

Air pollution Toxicity Plastic pollution Chemical wastes Healthcare scandals

Water pollution Ecotoxicity GreenHousehold Gas Chemical weapons PFAS

Non-renewable resources Fertilizers Pesticides Synthetic drugs 'Eternal' pollutants

Soil pollution Accidents Explosions Endocrine disruptors Radioactive wastes

~~Chemistry is not the problem, it is the solution!~~

Chemistry is part of the problem, but it is also part of the solution to climate change and others environmental impacts (from World Economic Forum, Dec 6, 2021)

e) The chemical industry's efforts to protect the environment

« Commitment and Progress » program (France, 1990)

environmental protection and risk management

Total investments in 2020 : 3.2 billions €

The chemical industry reduces its environmental footprint:

- 61% GHG emissions since 1990
- 52% NOx emissions since 2005
- 33% particulate matter emissions since 2005
- 79% P emissions into water since 2005

France Chimie 2018

CCUS (Carbon Capture, Use and Storage): cf. Chapter « Energy production and consumption »

f) Challenges facing the chemical industry

- Although chemistry has reduced its impact on the environment in recent years, it needs to go further:
  - reduce consumption of energy and non-renewable (NR) raw materials
  - develop less stable and more specific molecules/materials
  - reduce waste production and move away from the linear economy

Green chemistry

H_2 production

Electrocatalysis

Ecodesign of chemicals

Safe products

Chemistry in water

Biotechnologies

Waste recycling

Click chemistry

CO_2 reduction

Catalysis at room temperature

Circular economy

Biodegradable chemicals and materials

Biobased raw materials

Solvent recycling

CCUS

Flow chemistry

Enzyme catalysis

Drug-specificity

Photocatalysis

Biofuels

Industrial ecology

We, *chemists,* with researchers of other disciplines, have the "cards in our hands" to develop *eco-responsible processes* and produce these *eco-compatible molecules/materials* in the near future

2. Basic elements of biogeochemistry and pollutant chemistry

universite PARIS-SACLAY | GRADUATE SCHOOL Chimie

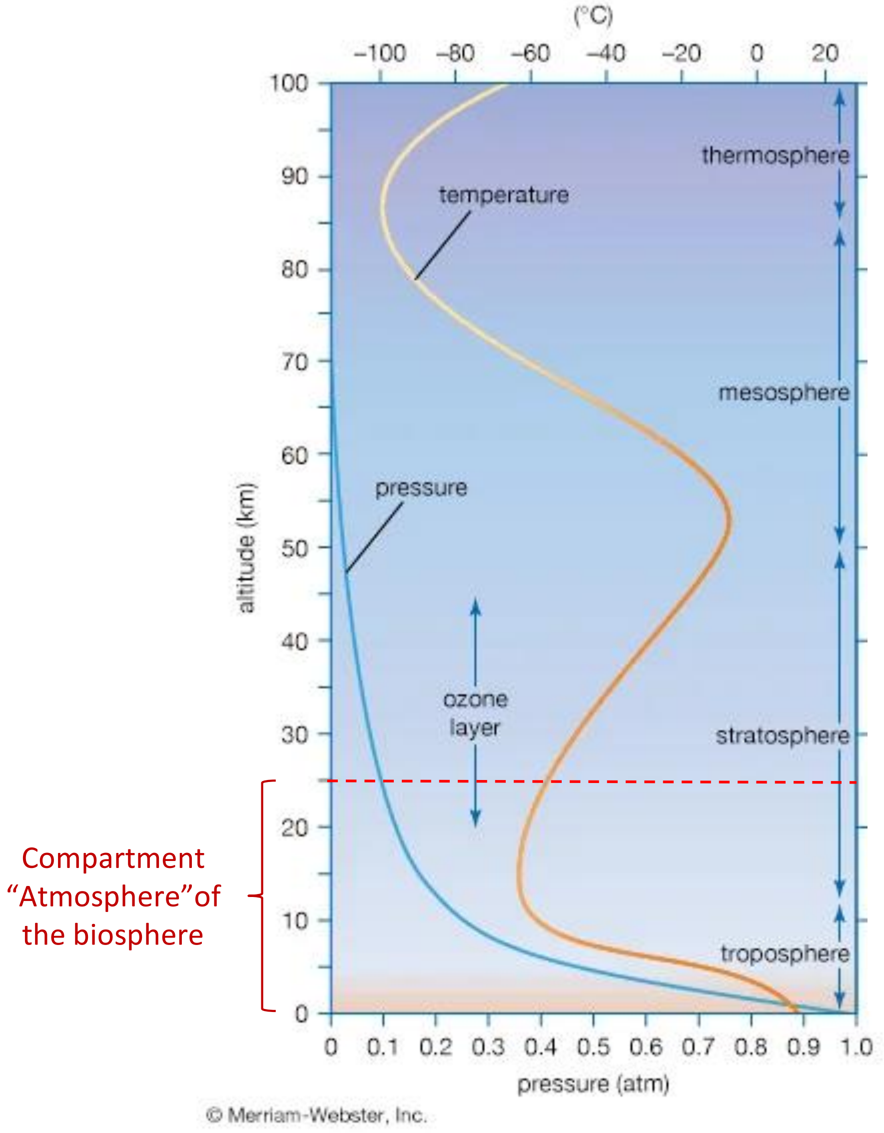
Biosphere

- all areas of the Earth inhabited by and including **living organisms** (3 main compartments) :

Atmosphere :
-**troposphere** : ~ 12 km altitude
-part of the **strastosphere** : up to 25 km altitude

Pedosphere (soil) :
-zone of crumbled rock where life is located
-some tens of meters deep and sediments

Hydrosphere :
-oceans and continental waters (lakes, wetlands...)
-10 km of depth



UNIVERSITE PARIS-SACLAY | GRADUATE SCHOOL Chimie

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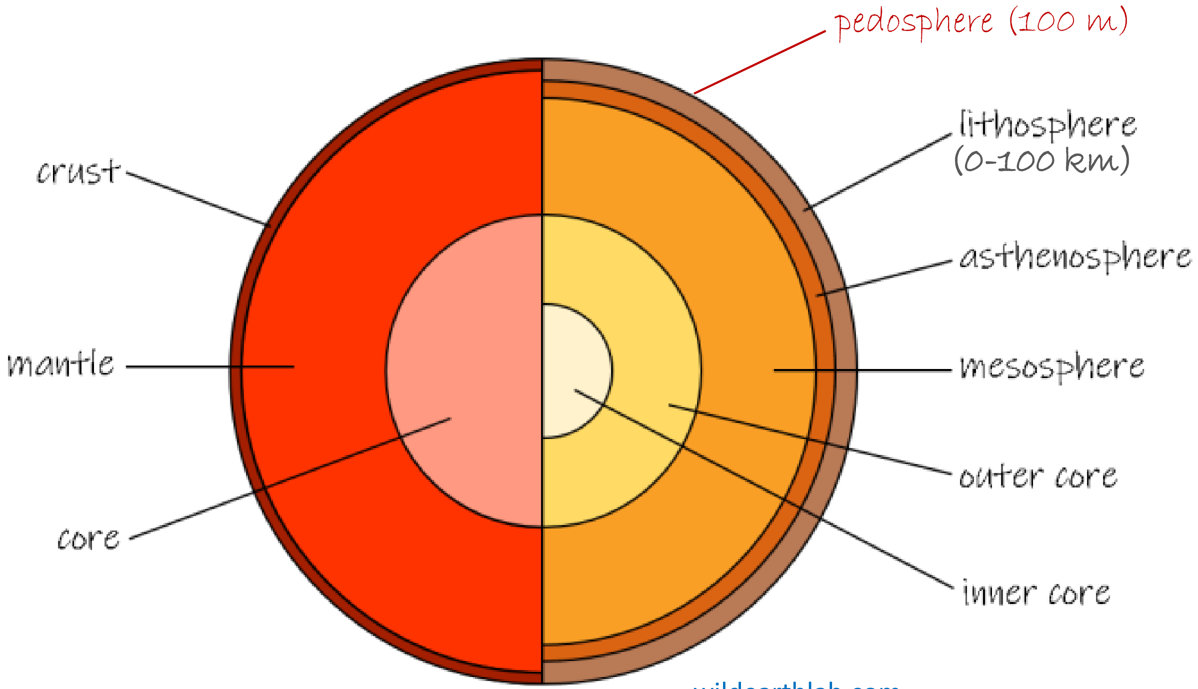

wildearthlab.com

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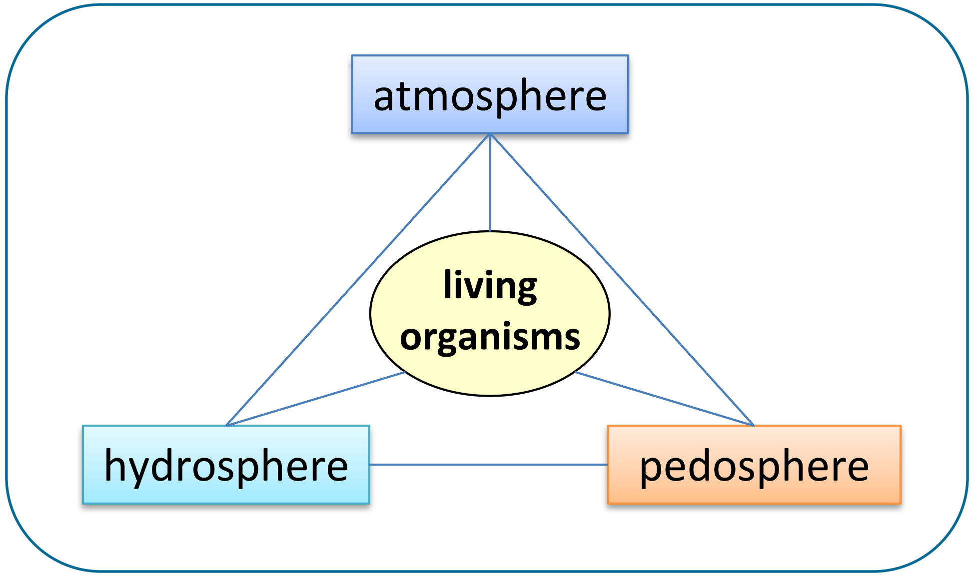


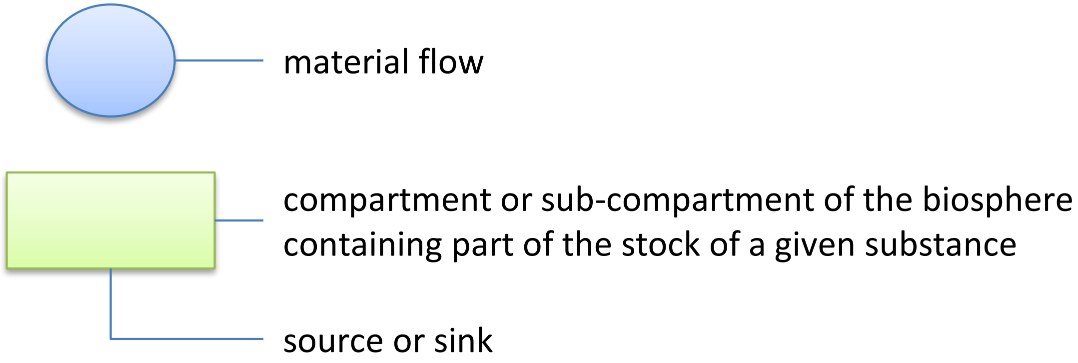
- **system** characterized by a state of **dynamic equilibrium** resulting from complex interactions between biological and physico-chemical processes

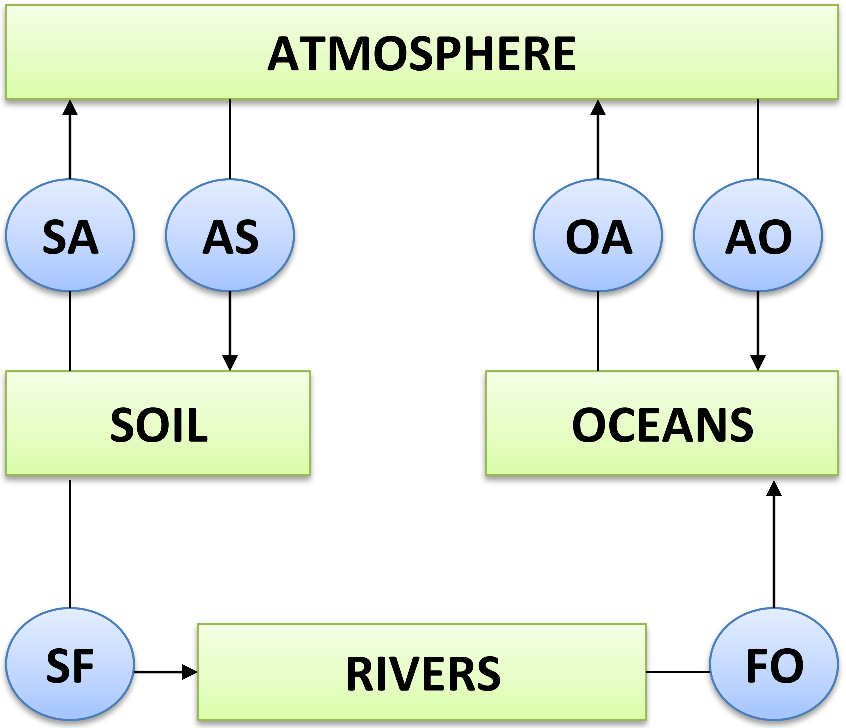
Biogeochemical cycles

- flow of matter between biosphere compartments

Biogeochemistry

- the science that studies the action of physicochemical and biological factors on biogenic and non-biogenic chemical substances as they circulate between the various compartments of the biosphere



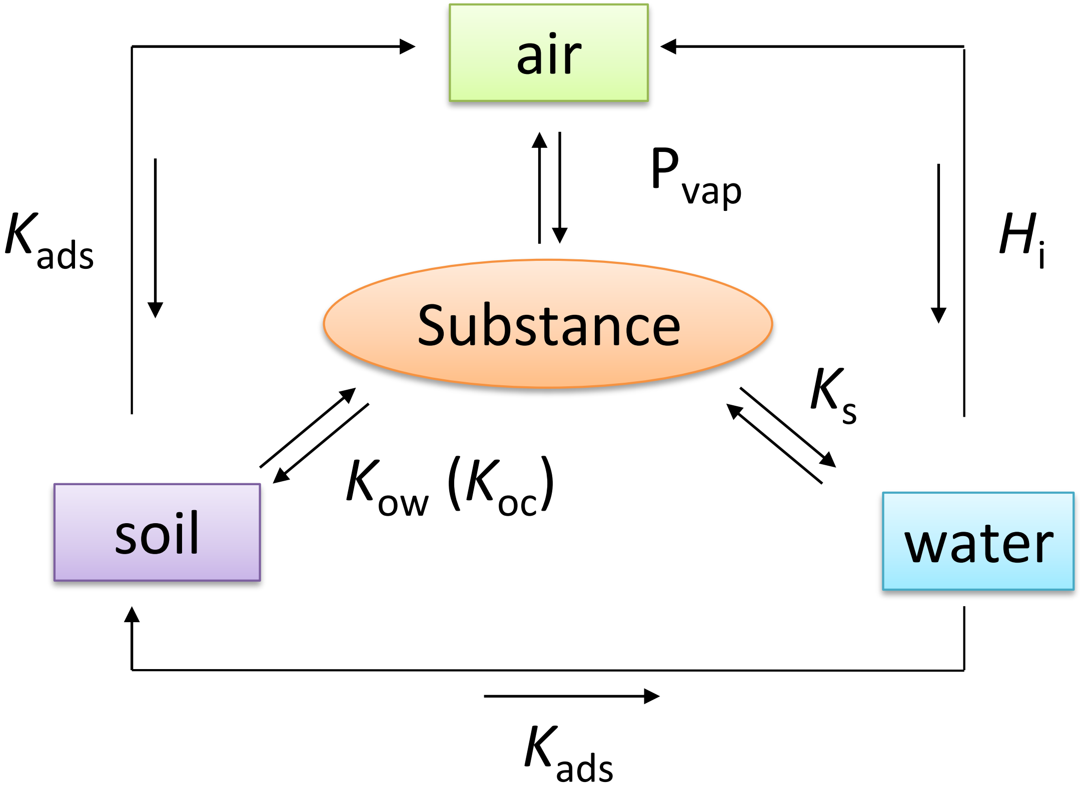


Simple model of a biogeochemical cycle

Distribution of a substance in the biosphere

- The *distribution* of a substance in the compartments of the biosphere depends on its *physico-chemical properties*
    - Phase change temperatures
    - Equilibrium constants

1. **Vapor pressure (P_{vap}):**
   pressure of the saturated gas phase above the liquid or solid phase
2. **Solubility in water (hydrophilicity): K_s**
   solubility constant
3. **Solubility in fat (lipophilicity): K_{ow}**
   distribution coefficient [octanol/water]
4. **Adsorption on organic matter: K_{oc}**
   distribution coefficient [$C_{organic}$/water]
5. **Adsorption on solid surface: K_{ads}**
6. **Solubility of gas in water: H_i**
   Henry's constant



All these constants depend on pressure and temperature

- The *physico-chemical properties* of a substance depends on:
    - *the external environment*
    - *its **structure**!*

⇨ Structure-activity relationships (SAR)

Critical Reviews in Environmental Science and Technology, 45:1277–1377, 2015
Published with license by Taylor & Francis
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DOI: 10.1080/10643389.2014.955627

Prediction of the Fate of Organic Compounds in the Environment From Their Molecular Properties: A Review

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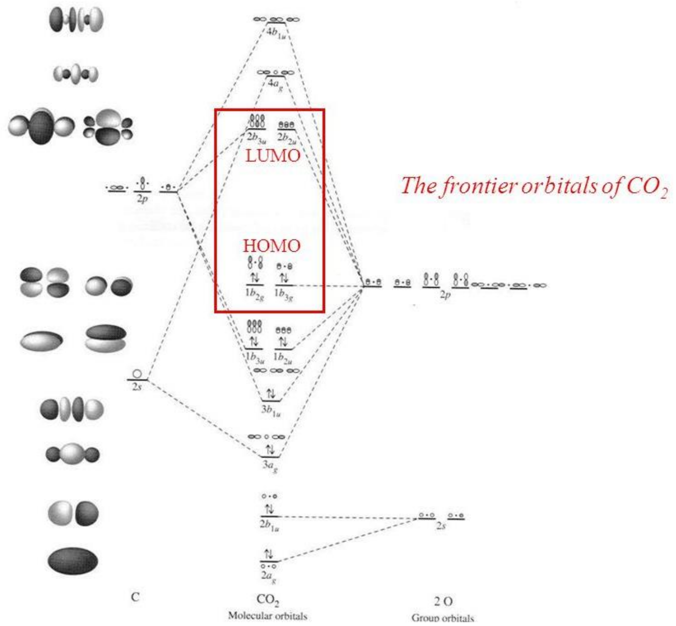
[4]*Université de Toulouse – INPT, Ecole d'Ingénieurs de Purpan – UPS, IRSAMC, Laboratoire de Chimie et Physique Quantiques – CNRS, UMR 5626, Toulouse, France*
[5]*INRA, UMR 1221 LISAH (Laboratoire d'étude des Interactions Sol - Agrosystème – Hydrosystème), Montpellier, France*
[6]*INRA, UMR 1347 Agroécologie, Dijon, France*
[7]*IRSTEA, UR MALY, Villeurbanne, France*

A comprehensive review of quantitative structure-activity relationships (QSAR) allowing the prediction of the fate of organic compounds in the environment from their molecular properties was done. The considered processes were water dissolution, dissociation, volatilization, retention on soils and sediments (mainly adsorption and desorption), degradation (biotic and abiotic), and absorption by plants. A total of 790 equations involving 686 structural molecular descriptors are reported to estimate 90 environmental parameters related to these processes. A significant number of equations was found for dissociation process (pK_a), water dissolution or hydrophobic behavior (especially through the K_{OW} parameter), adsorption to soils and biodegradation. A lack of QSAR was observed to estimate desorption or potential of transfer to water. Among the 686 molecular descriptors, five were found to be dominant in the 790 collected equations and the most generic ones: four quantum-chemical descriptors, the energy of the highest occupied molecular orbital (E_{HOMO}) and the energy of the lowest unoccupied molecular orbital (E_{LUMO}), polarizability (α) and dipole moment (μ), and one constitutional descriptor, the molecular weight. Keeping in mind that the combination of descriptors belonging to different categories (constitutional, topological, quantum-chemical) led to improve QSAR performances, these descriptors should be considered for the development of new QSAR, for further predictions of environmental parameters. This review also allows finding of the relevant QSAR equations to predict the fate of a wide diversity of compounds in the environment.



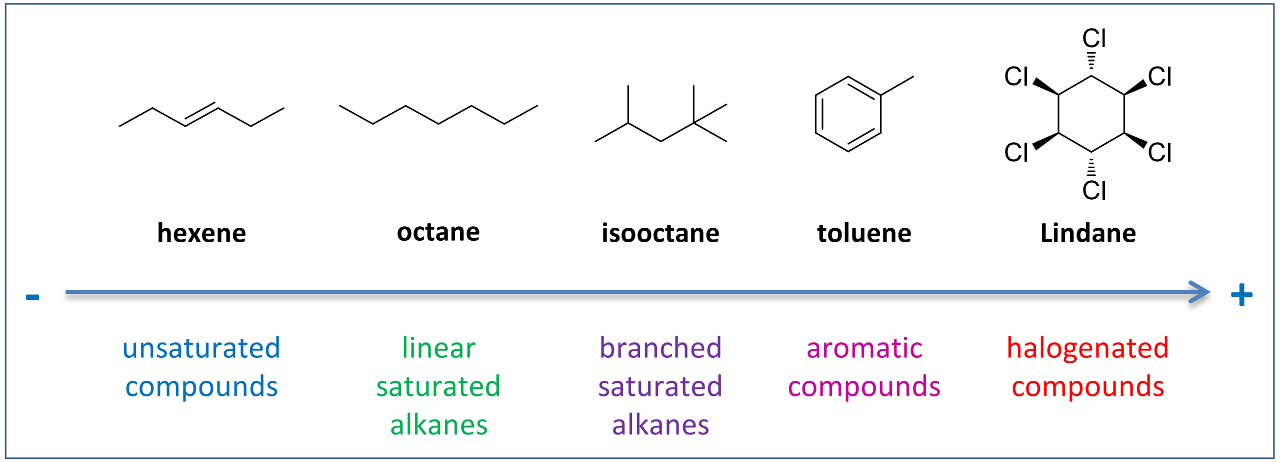
Biodegradability and persistence of chemicals

⇨ Structure-activity relationships (SAR)

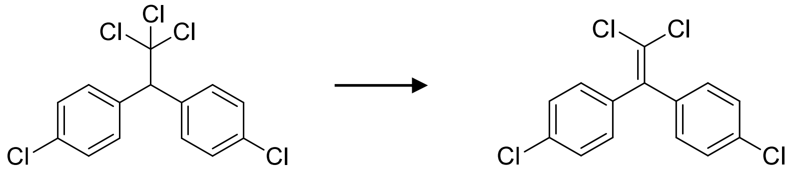
- Biodegradability: a substance is said to be *biodegradable* if, under the action of *living organisms* (bacteria, fungi, algae...), it can decompose into various elements that have *no harmful effect* on the natural environment.

Final biodegradability (OCDE) : > 60% in 28 days

- Persistence: the ability of substances to persist in the environment without alteration by physical, chemical or biological processes.
  - inorganic substances are in principle persistent
  - organic compounds may be non-persistent, slightly persistent or very persistent (cf. POP = persistent organic pollutants)



Comparative persistence of some organic compounds



Dichloro**D**iphényl**T**richloroéthane
DDT

Dichloro**D**iphényldichloro**E**thylène
DDE

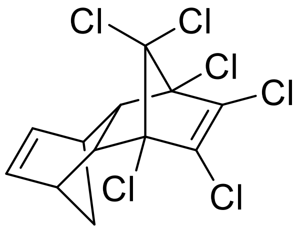
- *Metabolites* of some persistent chemicals may be persistent themselves.

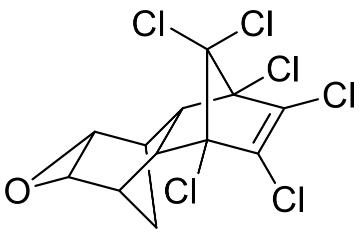
Persistent Organic Pollutants (POP)

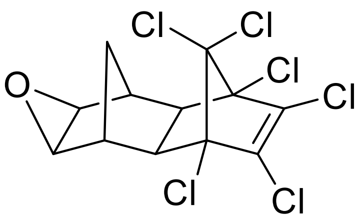
- *Chemicals* that:
  - accumulate in living organisms,
  - are persistent in the environment,
  - are toxic,
  - can be mobile over long distances.

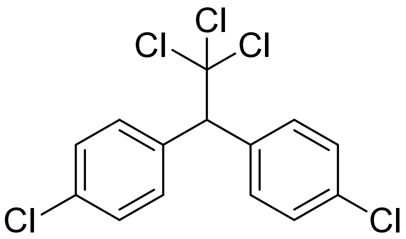
Stockholm Convention on persistent organic pollutants (POPs)
(2001)

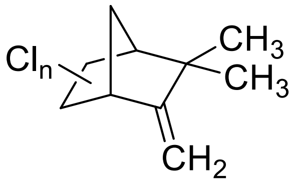
UNITED NATIONS ECONOMIC COMMISSION FOR EUROPE
Aarhus Protocol on POP
(1998)

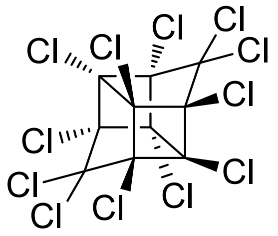

Aldrine
insecticide

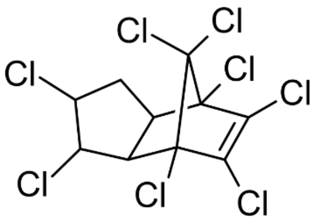

Dieldrine
insecticide

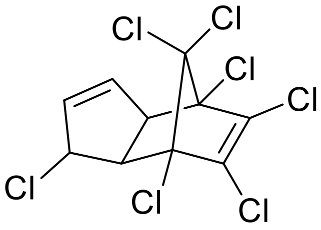

Endrine
insecticide

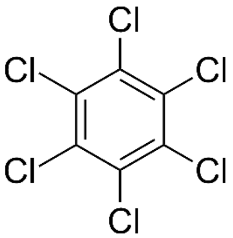

DDT
insecticide

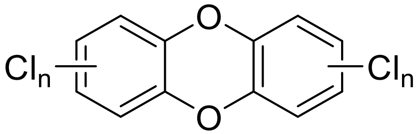

Toxaphene
insecticide

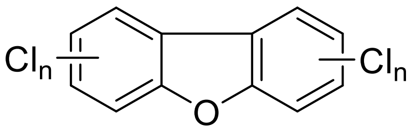

Mirex
insecticide

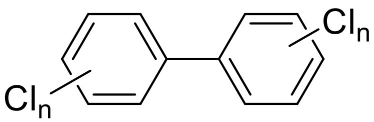

Chlordane
insecticide


Heptachlore
insecticide


Hexachlorobenzene
fungicide


PCDD (dioxines)
incineration residues...


PCDF (furanes)
incineration residues...


PCB
plastic additives...

"The Dirty Dozen" (Stockholm Convention/Aarhus Protocol, 2003-2004)

Persistent Organic Pollutants (POP)

Stockholm Convention on persistent organic pollutants (POPs)
(2001)

UNITED NATIONS ECONOMIC COMMISSION FOR EUROPE
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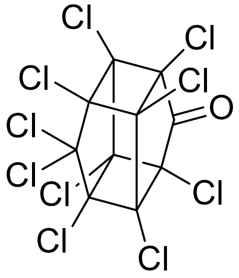
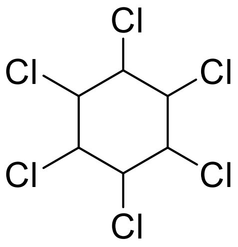
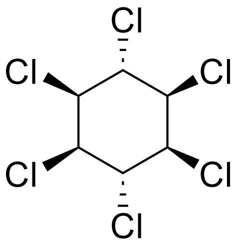


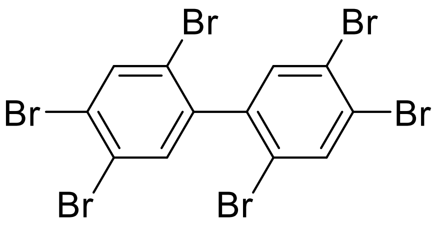
Chlordecone
insecticide



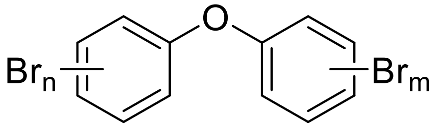
HCH (α,β,γ…)
insecticides



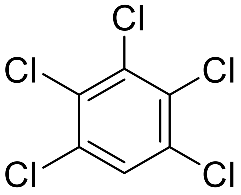
γ-HCH (Lindane)
insecticide



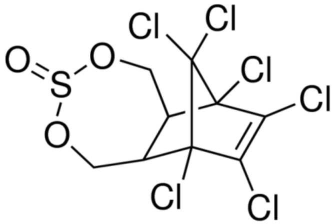
hexabromobiphenyls
flame retardant



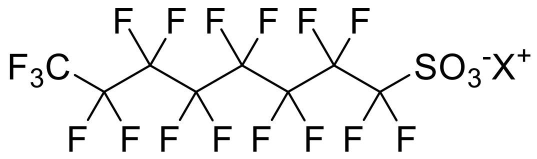
Polybrominated diphenyl ethers (PBDE) *flame retardant*



Pentachlorobenzene
fungicide



Endosulfane
insecticide



Cf. Dupont de Nemours (Teflon, « Dark Waters »)

Perfluorooctane sulfonic acid (PFOS)
Cf PFAS

Stockholm convention/Aarhus Protocol (2009/2011)

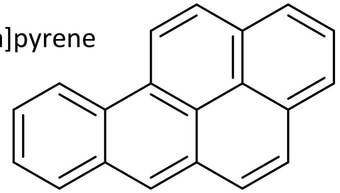
Persistent Organic Pollutants (POP)

- *Chemicals* that:
  - **accumulate** in living organisms,
  - are **persistent** in the environment,
  - are **toxic**,
  - can be **mobile** over long distances.

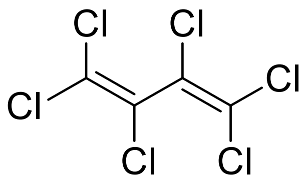
Stockholm Convention on persistent organic pollutants (POPs)
(2001)

UNITED NATIONS ECONOMIC COMMISSION FOR EUROPE
Aarhus Protocol on POP
(1998)

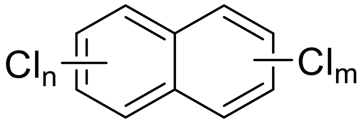
Ex: benzo[a]pyrene



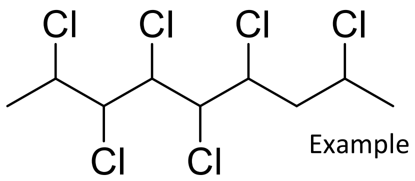
Polycyclic Aromatic Hydrocarbons PAH (**HAP**)
by-products of incomplete combustion



Hexachlorobutadiene
industrial chemical

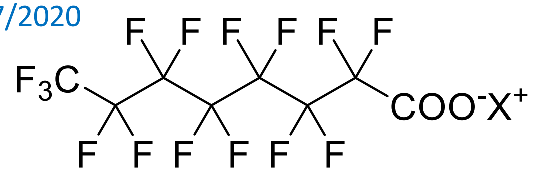


Polychlorinated naphtalenes
additives, insulating agent



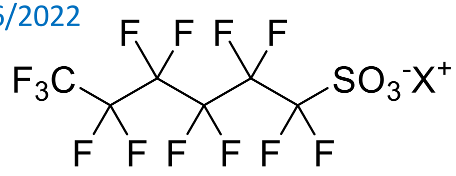
Short-chain chlorinated paraffines (SCCP/**PCCC**)
metalworking fluids

07/2020



Perfluorooctanesulfonic acid (PFOA)
PFAS : non-stick coatings (frying pans...), µ-wave packaging

06/2022



Perfluorohexanesulfonic acid (PFHxS)
PFAS : technical clothing additives, foams, packaging...

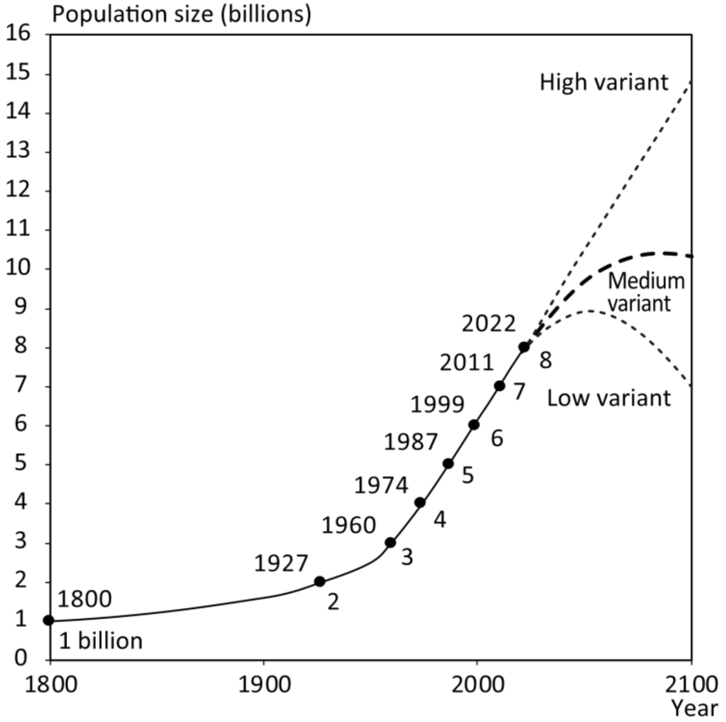
Other per/poly-fluoroalkylated substances (PFAS)
→ evaluation in progress (INERIS, ANSES, ECHA...)

Aarhus Protocol (2012-2022)

Human impact on the environment

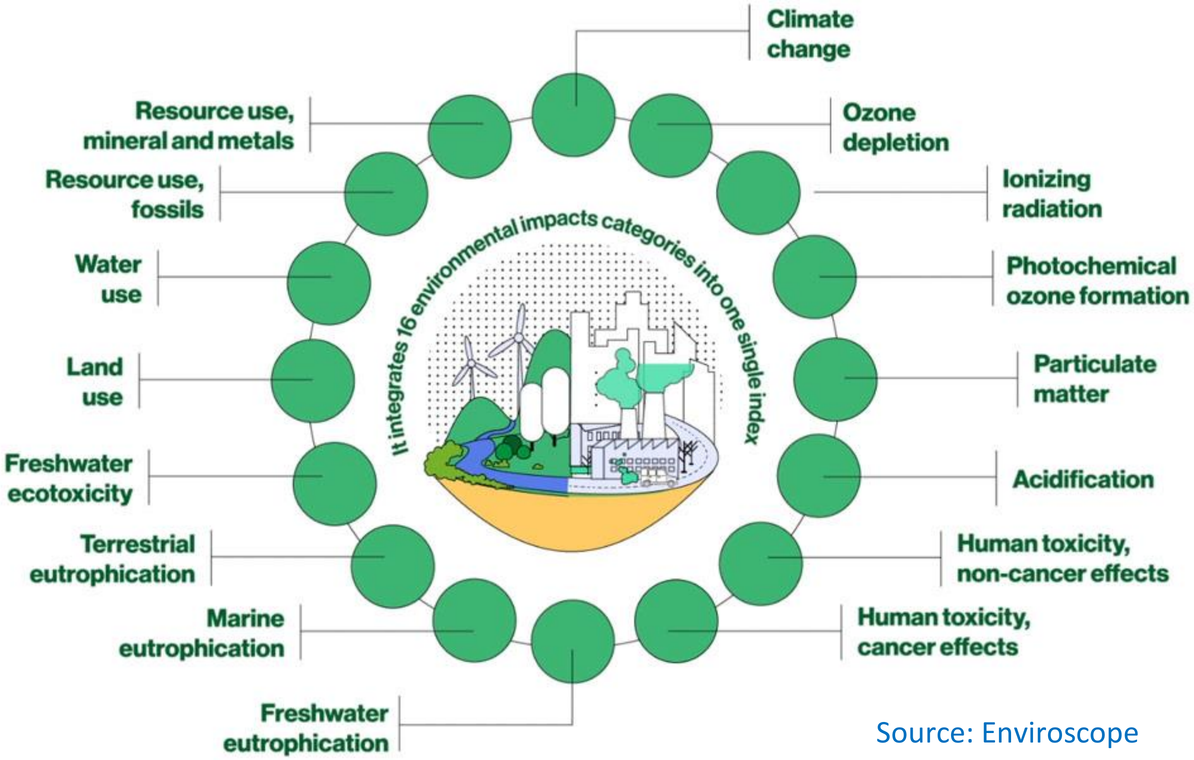
Man has become the *determining factor* in the biosphere. He is transforming the environment through the development of:

- energy production and consumption,
- industrialization (1850),
- agriculture (food needs),
- infrastructures (roads, housing…).



World population growth since 1800 and projections to 2100
Gilles Pison, Population & Sociétés, no. 604, INED, October 2022. Source : United Nations.

Associated environmental impacts (cf. LCA/ACV):



Source: Enviroscope

⇨ The main causes of chemical pollution:

- Energy production and consumption
- Industrial activities
- Agricultural activities

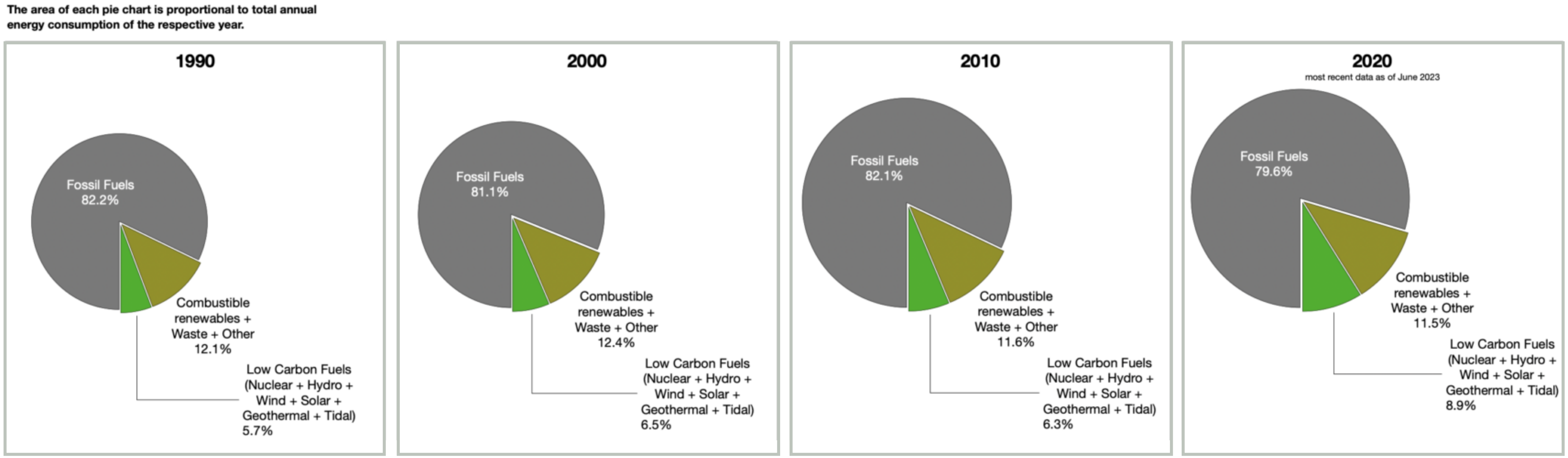
3. Main sources of chemical pollution

I. Energy production:
   - carbon cycle, greenhouse effect, fossil fuels, alternatives)

II. Industrial activities:
   - synthetic materials, halogenated derivatives, metallurgy, sulfur and TME cycles

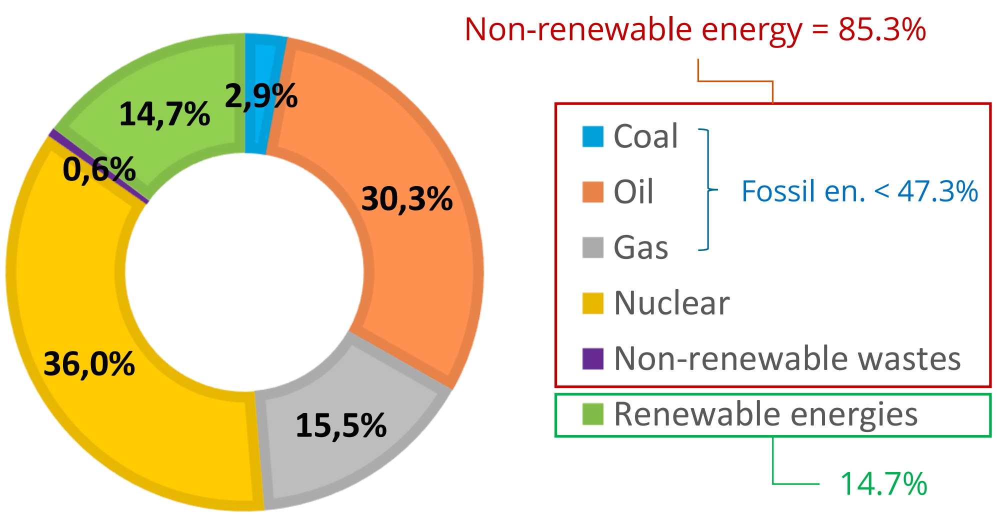
III. Agricultural activities:
   - fertilizers, pesticides, nitrogen and phosphorus cycles

I. First cause of pollution: energy production and consumption



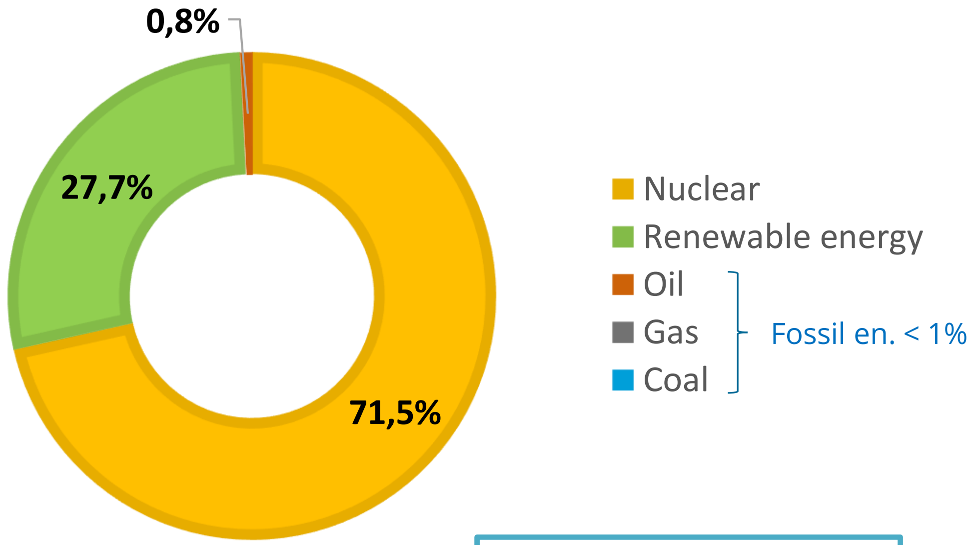
Source : EIA 2022

a. Primary energy consumption and production in France (2022)



2008 : total = 3152 TWh
2014 : total = 2977 TWh
2022 : total = 2482 TWh

Consumption



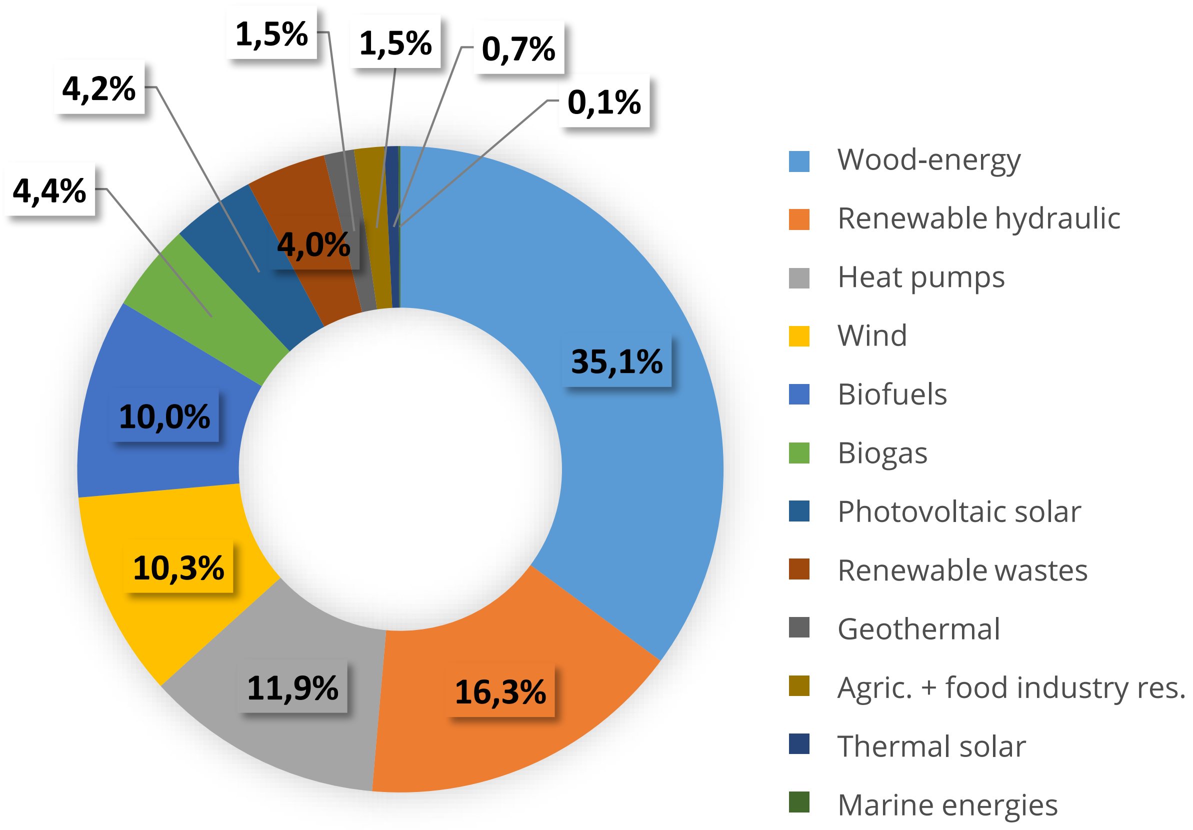
2008 : total = 1593 TWh
2016 : total = 1547 TWh
2017 : total = 1535 TWh
2022 : total = 1249 TWh

Production *(50% of energy needs)*

Source : SDES

Primary energy: whose source is available in nature without transformation
Renewable energy: regeneration ≥ consumption: wind, solar, photovoltaic, geothermal, wood, renewable hydraulics, heat pumps, biofuels...

b. Renewable primary energy production in France (2021)



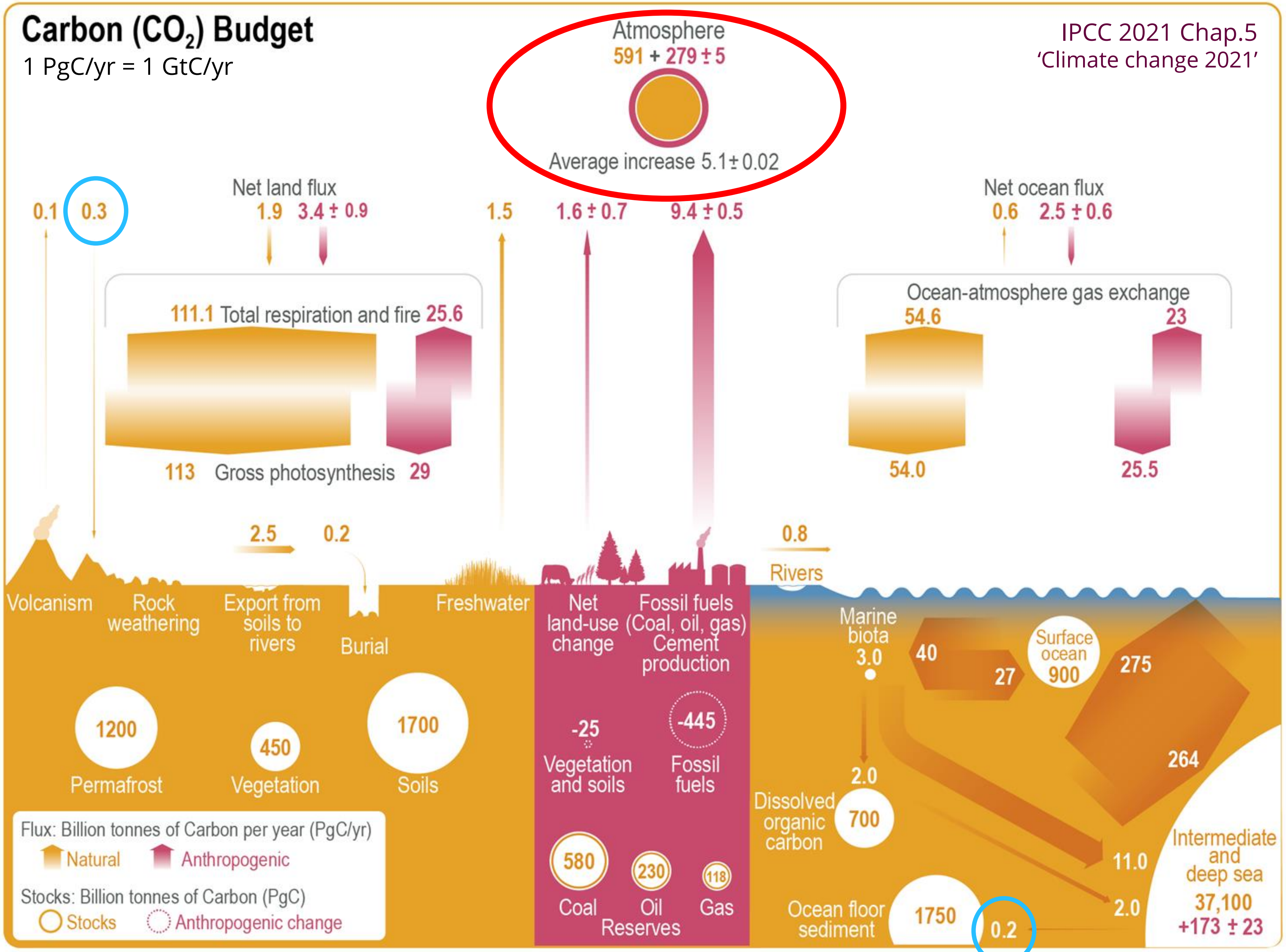
2021 : total = 345 TWh

(22.7% of total PE production in 2021)

Source : SDES

Primary energy: whose source is available in nature without transformation
Renewable energy: regeneration ≥ consumption: wind, solar, photovoltaic, geothermal, wood, renewable hydraulics, heat pumps, biofuels...

c. The carbon cycle



c. The carbon cycle

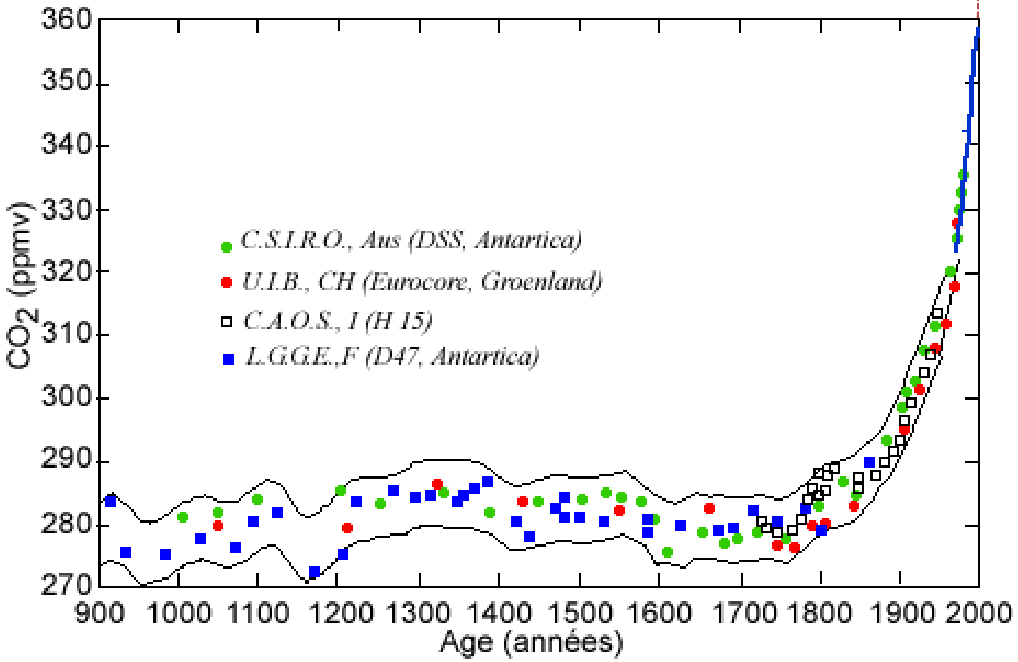
The emission of fossil carbon (long cycle) into the atmosphere (short cycle) is an irreversible process on a human scale…

…unless we can capture and store this carbon permanently at a GtC/yr scale in the near future (cf. CCUS)!

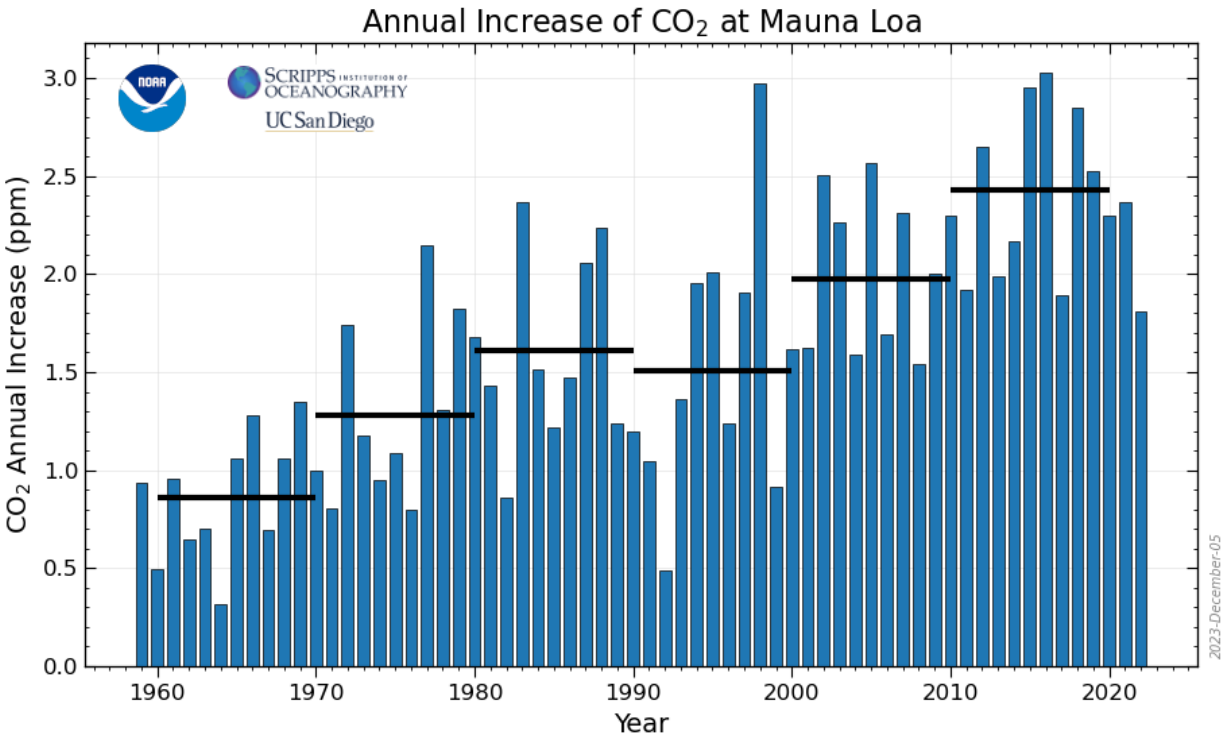
c. The carbon cycle

Variation in atmospheric CO_2 content

◆ **2023** : 420.5 ppm (+ 2 to 3 ppm/yr)
(Mauna Loa, annual mean, Nov. 2023)

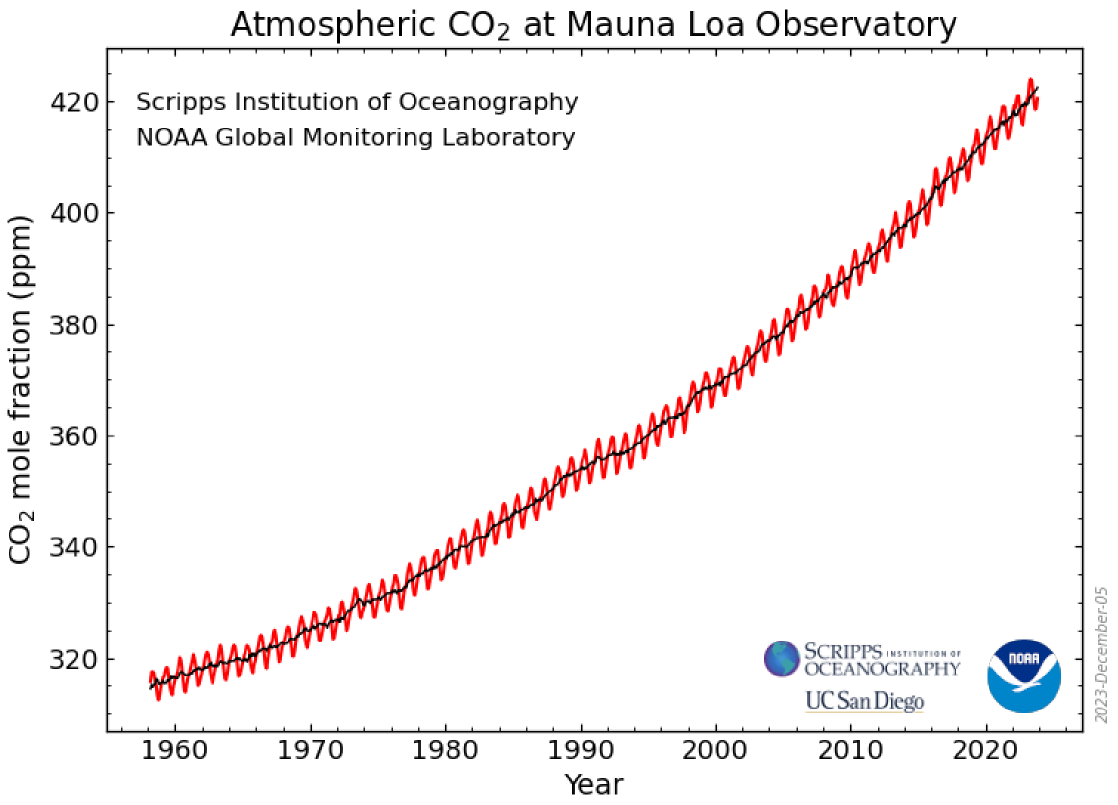


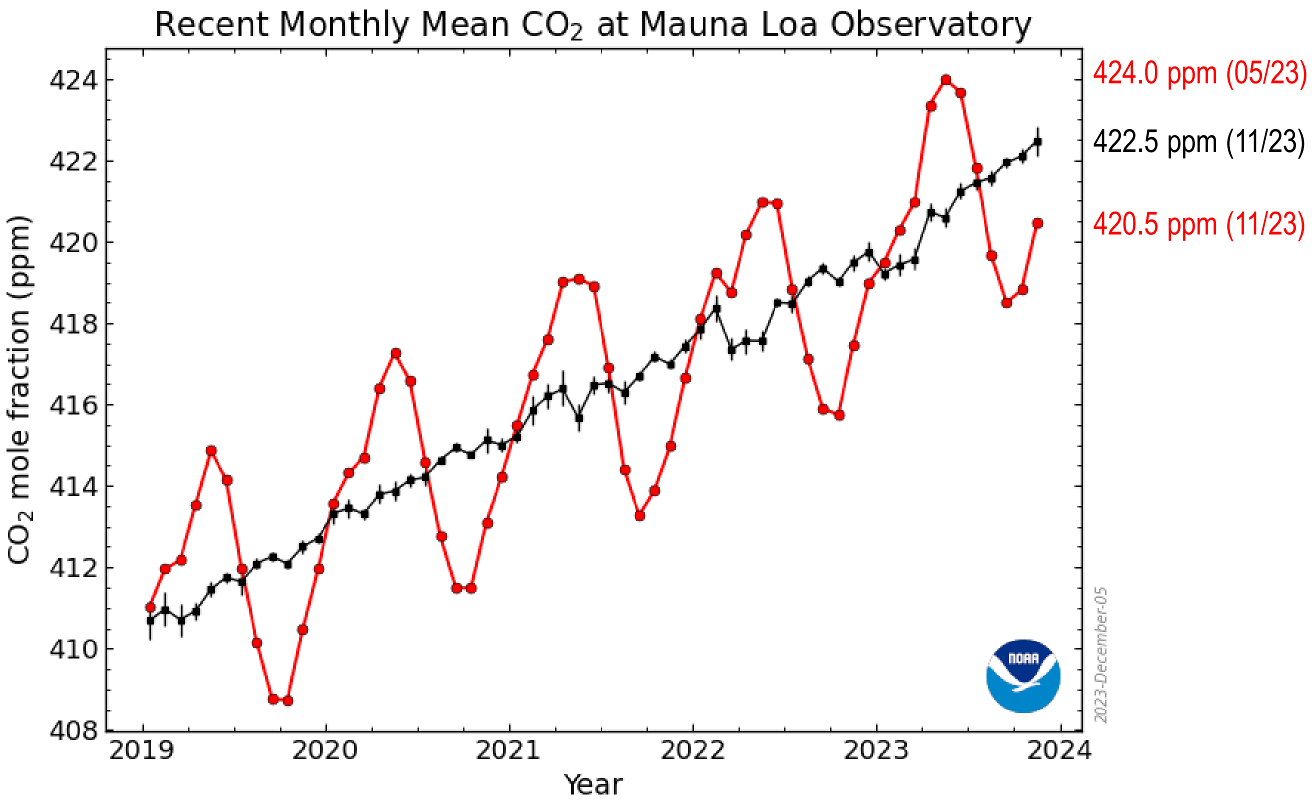
Compilation d'aprés J.M. Barnola et J. Chappelaz (LGGE), figure extraite et modifiée à partir du site http://www.balzan.it/english/pb2001/lorius/sintesi.htm



c. The carbon cycle

Variation in atmospheric CO_2 content





UNIVERSITE PARIS-SACLAY GRADUATE SCHOOL Chimie

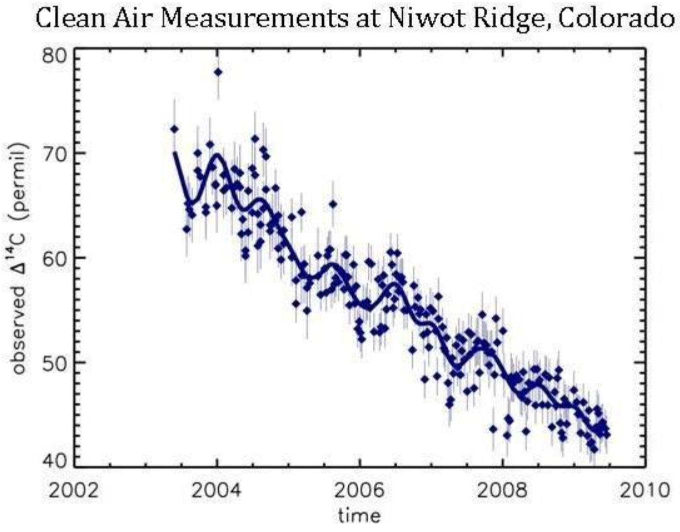
c. The carbon cycle

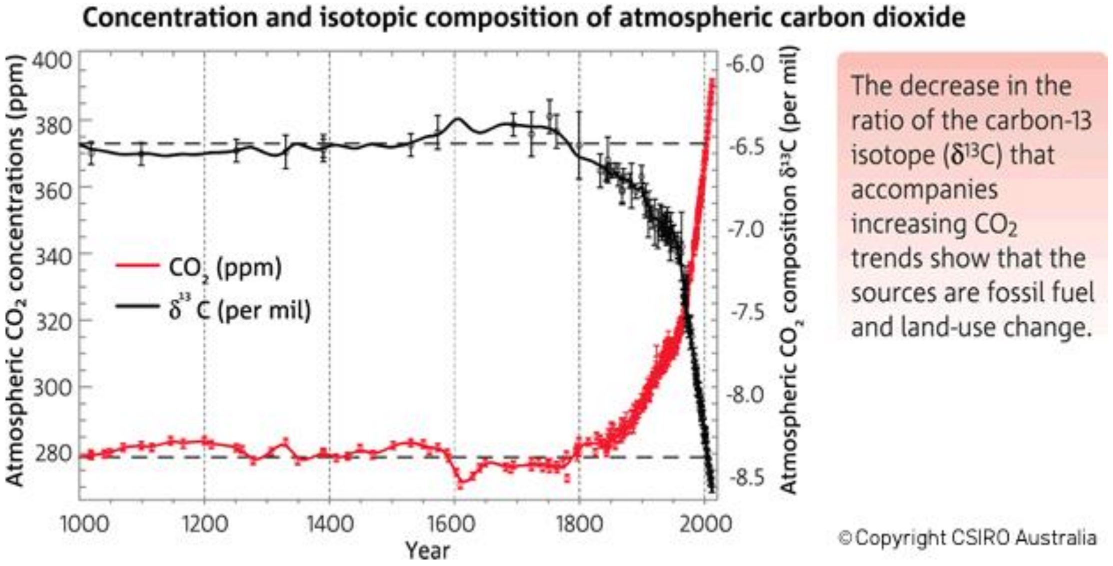
Yes, the increase in CO_2 in the air is the result of human activity!

- fossil fuels (8.5 GtC/yr)
- Land use (1,5 GtC/yr)
- cement (1 GtC/yr)

$$\partial^{13}C = \left[\frac{\left(\frac{[^{13}C]}{[^{12}C]}\right)_{ech}}{\left(\frac{[^{13}C]}{[^{12}C]}\right)_{std}} - 1 \right] \times 1000$$

CO_2 source	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)
Fossil fuels	-1000	-28
Biomass	+45	-26
Hydrosphere	+45	-10
Atmosphere	+45	-8





GreenHouse Gases (GHG)

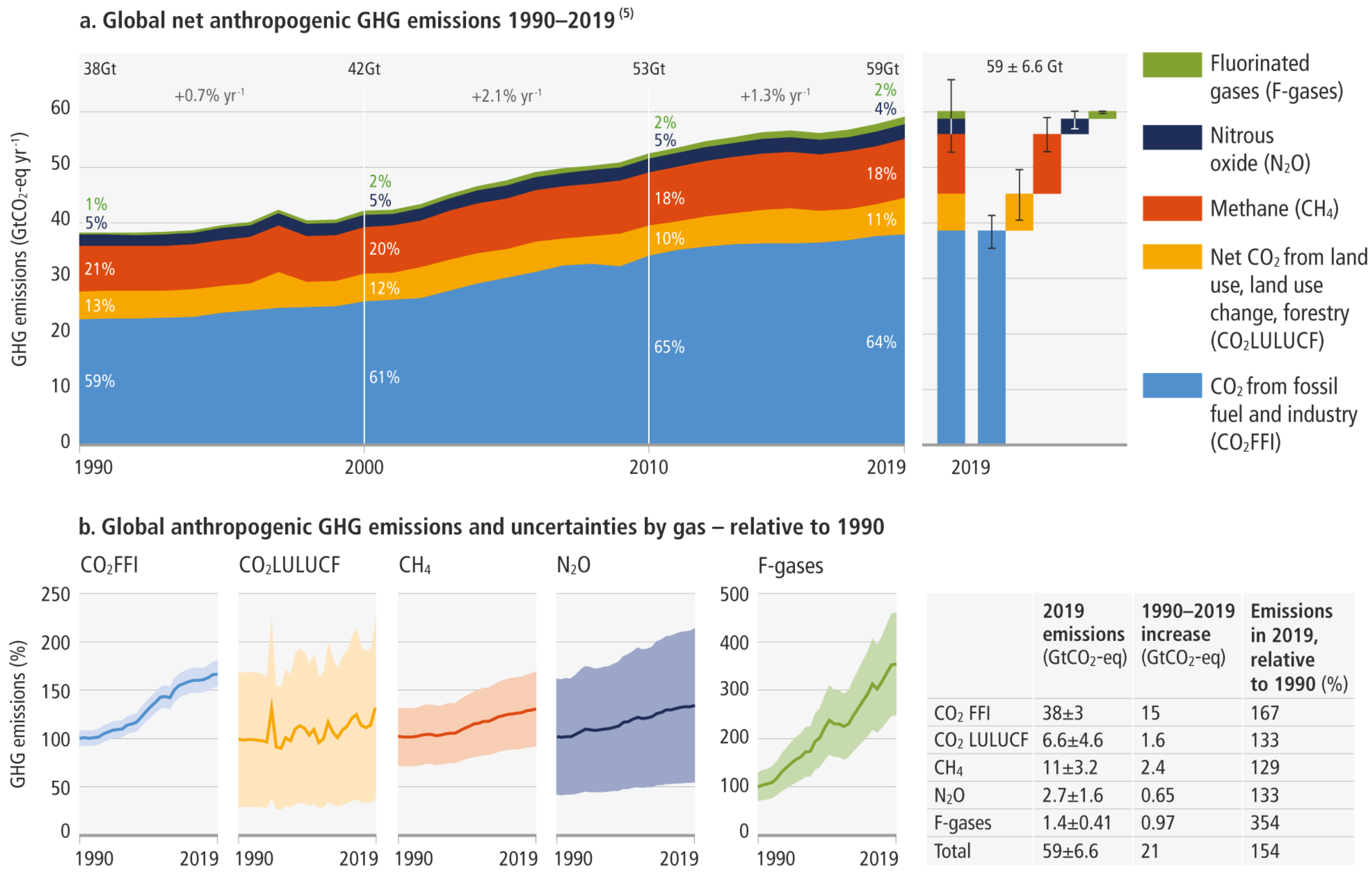
c. The carbon cycle

Gas (not including H_2O)	Atm. content (2018)	ΔF (GWP/PRG @ 100 years)*
CO_2	409 ppm	1
CH_4	1,86 ppm	30
N_2O	331 ppb	265
O_3 tropospheric	50 ppb	-
R11 (CCl_3F)	232 ppt	5,160
R12 (CCl_2F_2)	522 ppt	10,300
SF_6	11 ppt	22,800

* GWP : Global Warming Potential
PRG : Potentiel de Réchauffement Global

Bold: highly stable

Global net anthropogenic emissions have continued to rise across all major groups of greenhouse gases.



	2019 emissions (GtCO2-eq)	1990–2019 increase (GtCO2-eq)	Emissions in 2019, relative to 1990 (%)
CO_2 FFI	38±3	15	167
CO_2 LULUCF	6.6±4.6	1.6	133
CH_4	11±3.2	2.4	129
N_2O	2.7±1.6	0.65	133
F-gases	1.4±0.41	0.97	354
Total	59±6.6	21	154

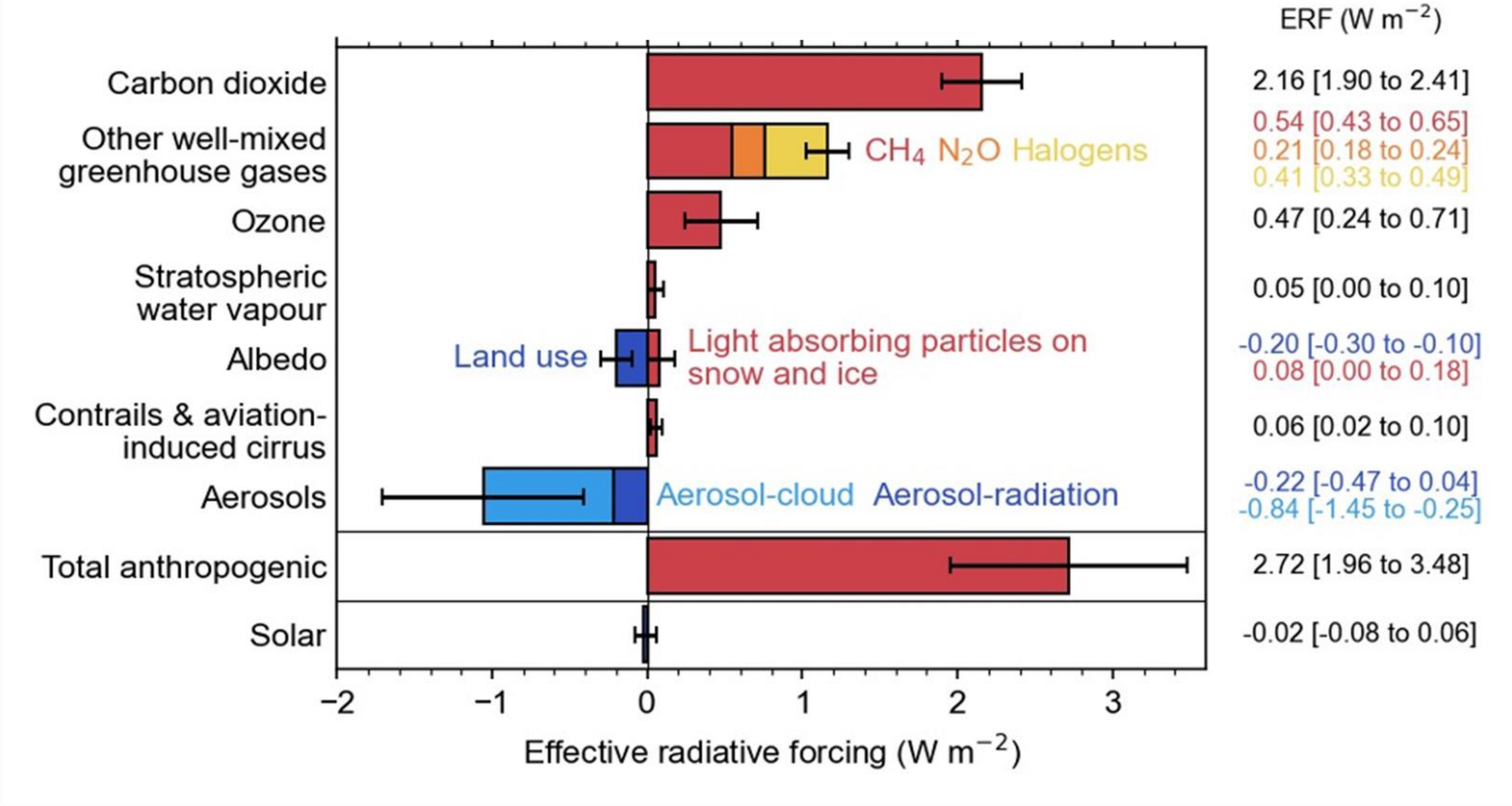
The solid line indicates central estimate of emissions trends. The shaded area indicates the uncertainty range.

IPCC AR6 WGIII

GreenHouse Gases (GHG)

c. The carbon cycle

Change in effective radiative forcing from 1750 to 2019

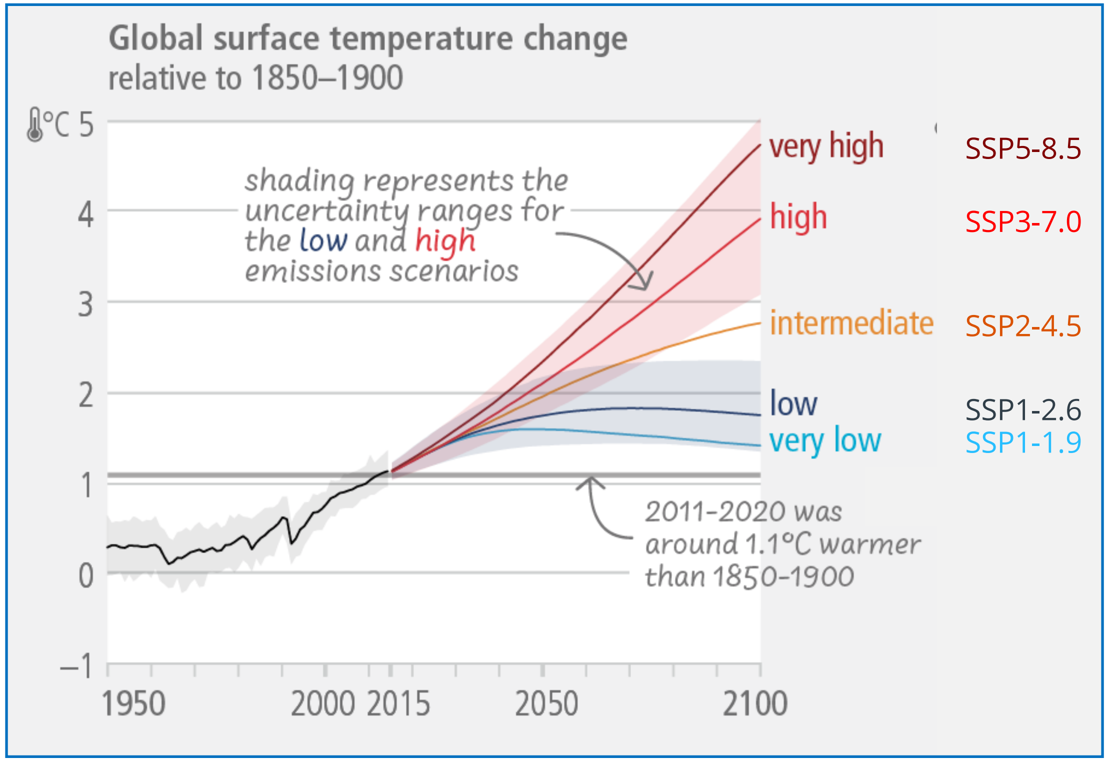


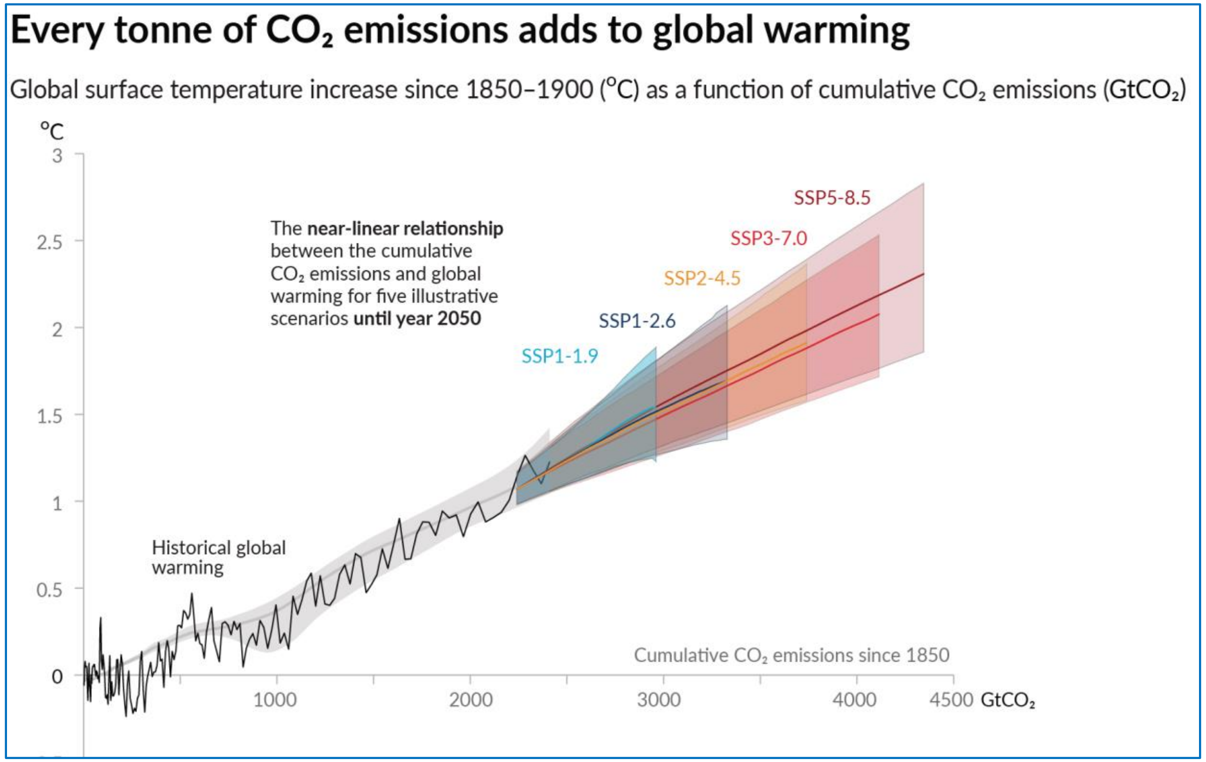
IPCC AR6 WGIII

IPCC emissions scenarios

https://www.ipcc.ch/report/ar6/syr/figures

c. The carbon cycle



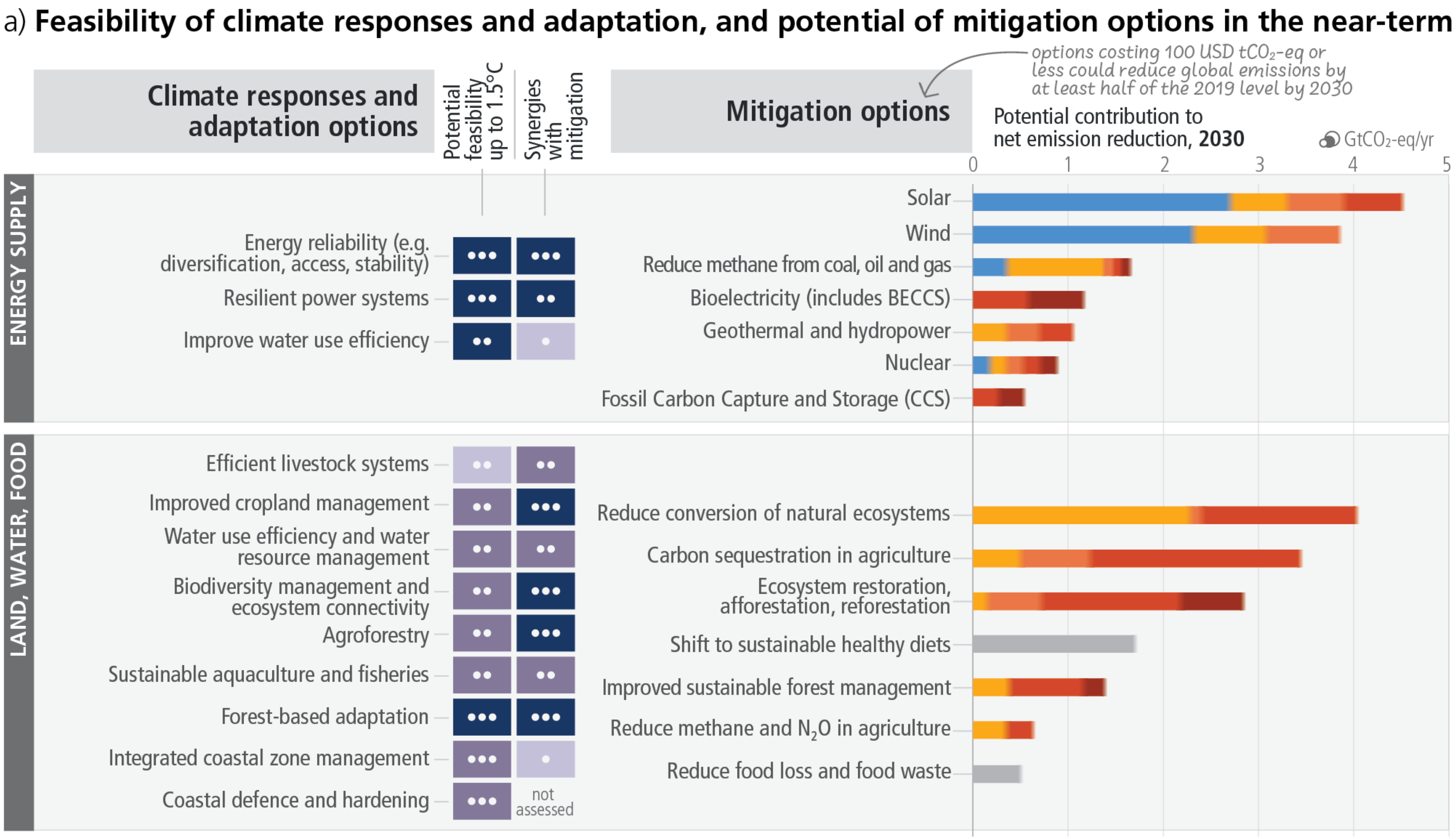


SSPx-y: Shared Socio-economic Pathway x; y = radiative forcing (W/m²)

c. The carbon cycle

IPCC emissions scenarios

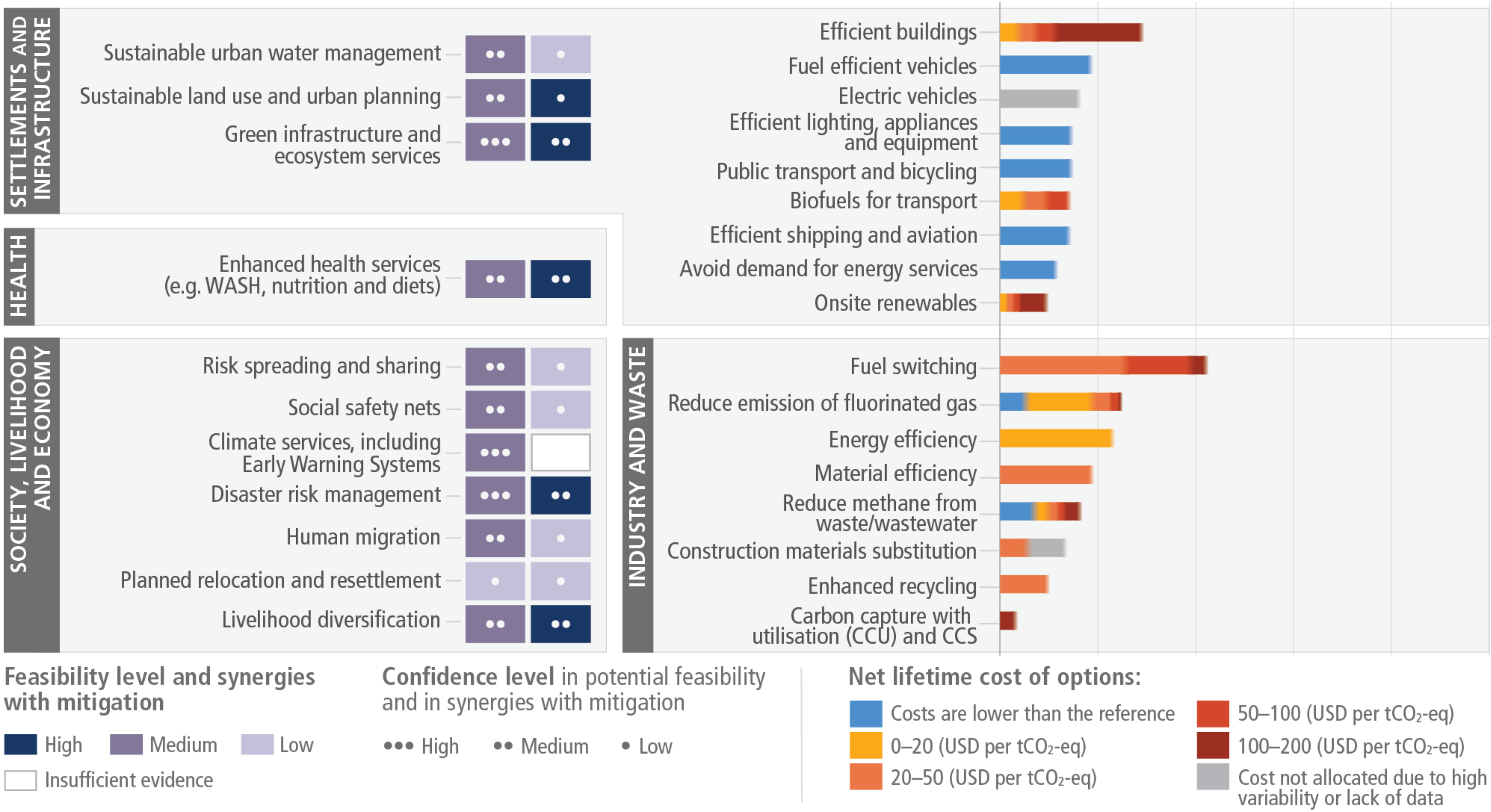
https://www.ipcc.ch/report/ar6/syr/figures



c. The carbon cycle

IPCC emissions scenarios

https://www.ipcc.ch/report/ar6/syr/figures

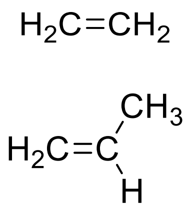


d. Natural Gas

The "cleanest" of fossil fuels – VOC (volatile organic compounds)/COV

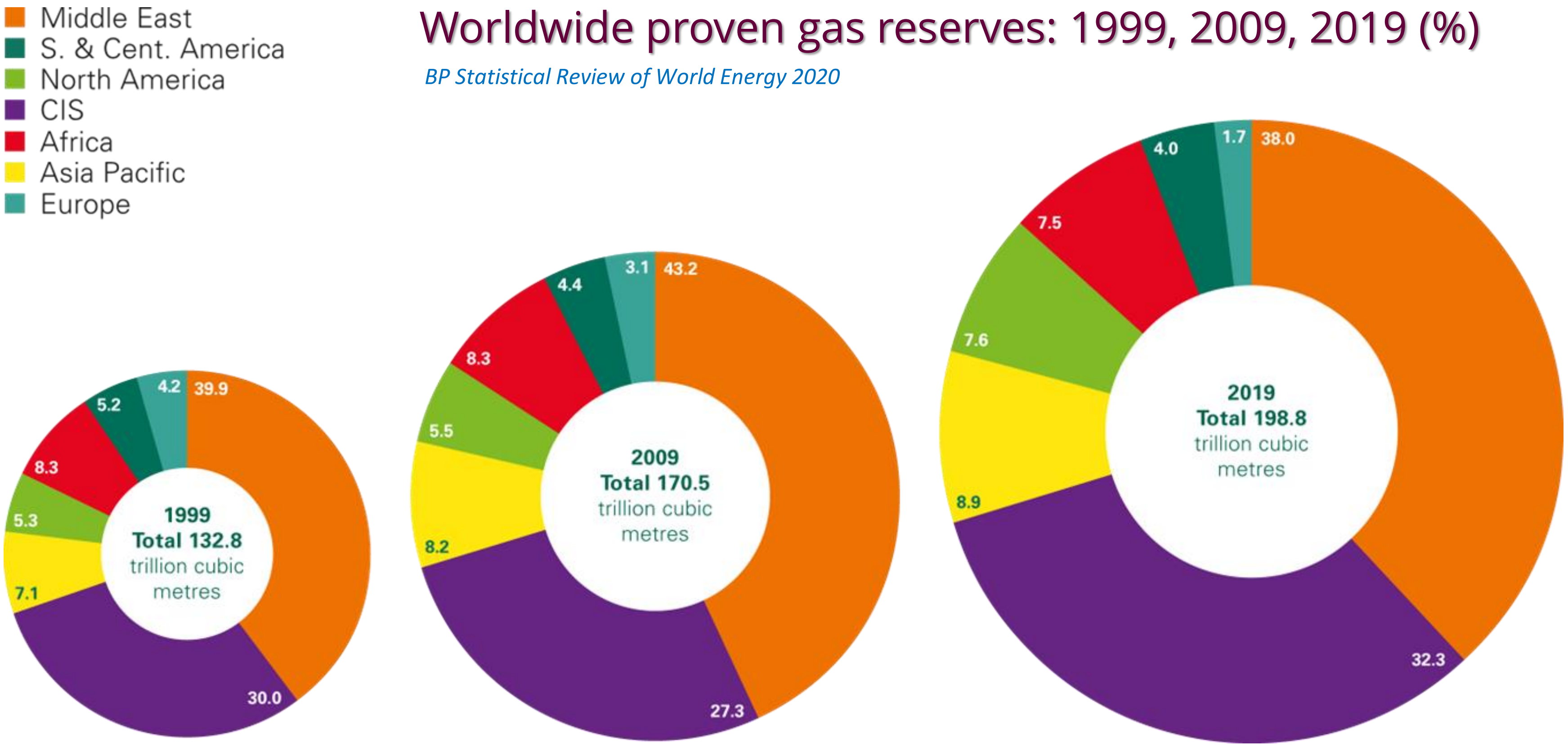
Components	%
CH_4	90
C_2H_6	5
C_3H_8	1
C_4H_{10}	0,2
N_2	2,2
CO_2	1,4

cracking



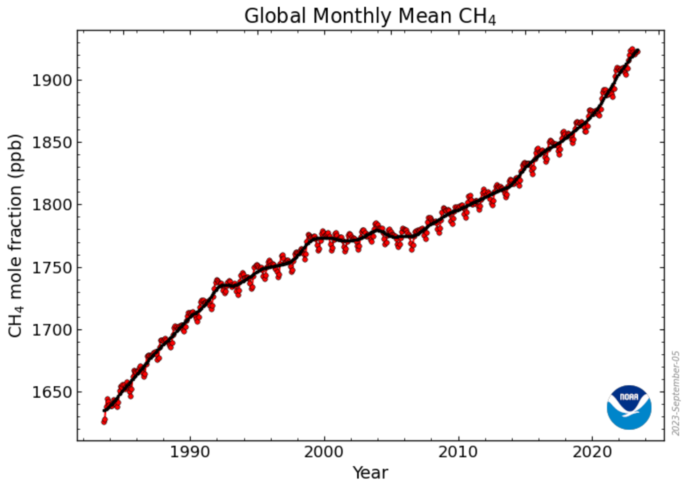
Worldwide proven gas reserves: 1999, 2009, 2019 (%)

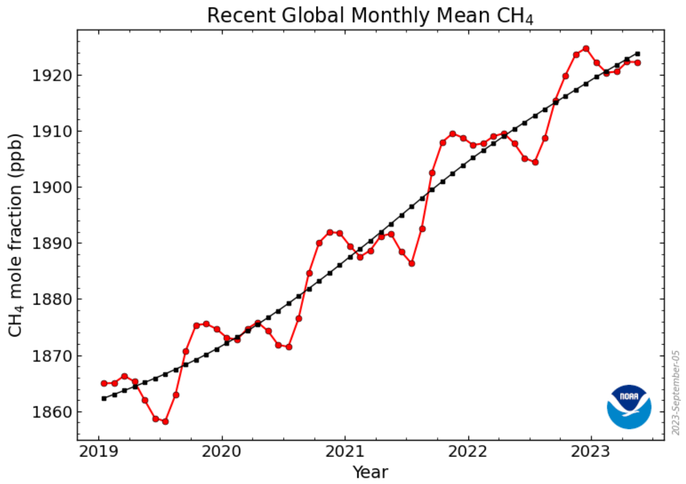
BP Statistical Review of World Energy 2020

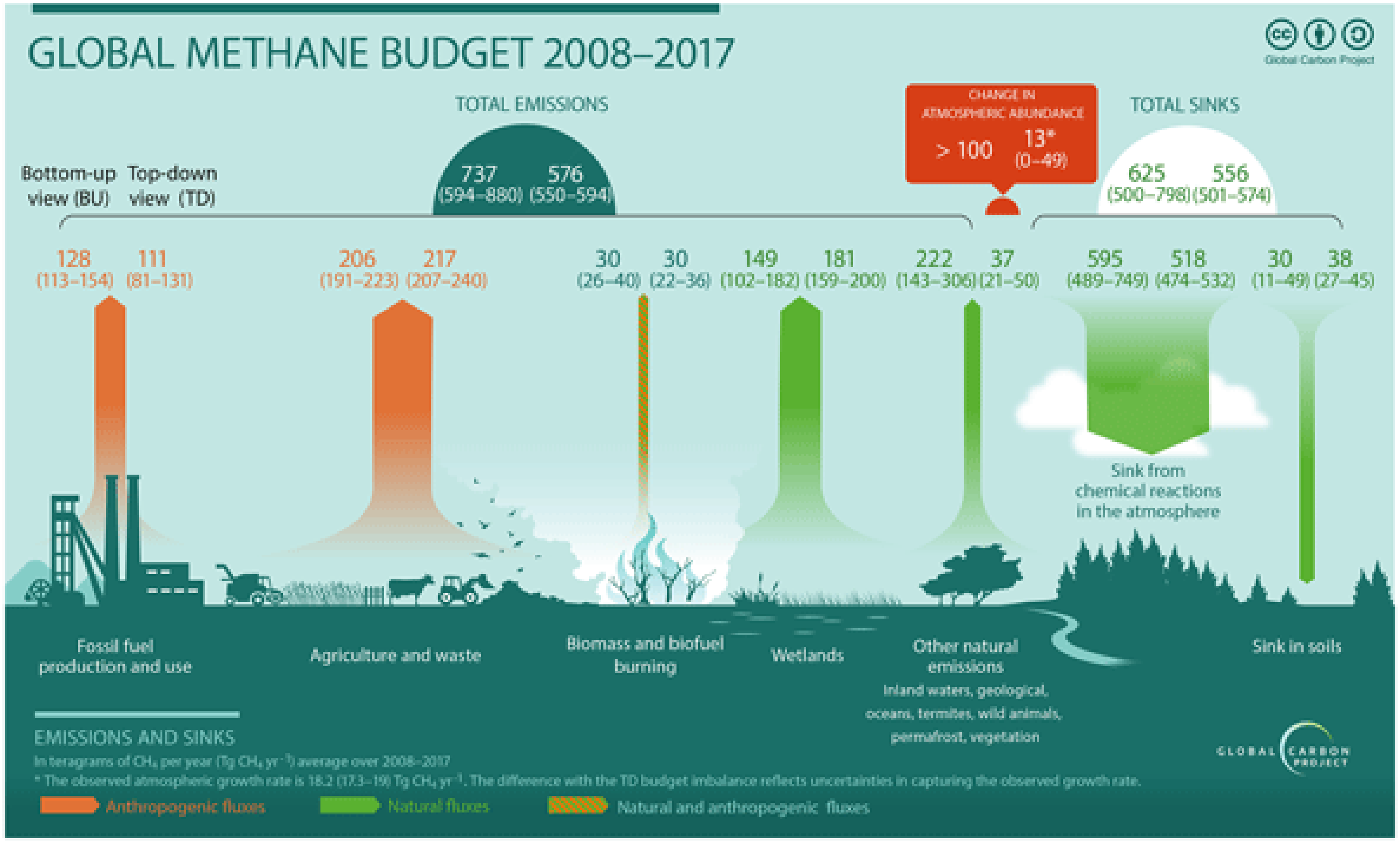


World consumption (2022) = 4,037 Gm^3 ➡ 50 yr… at least!

d. Natural Gas



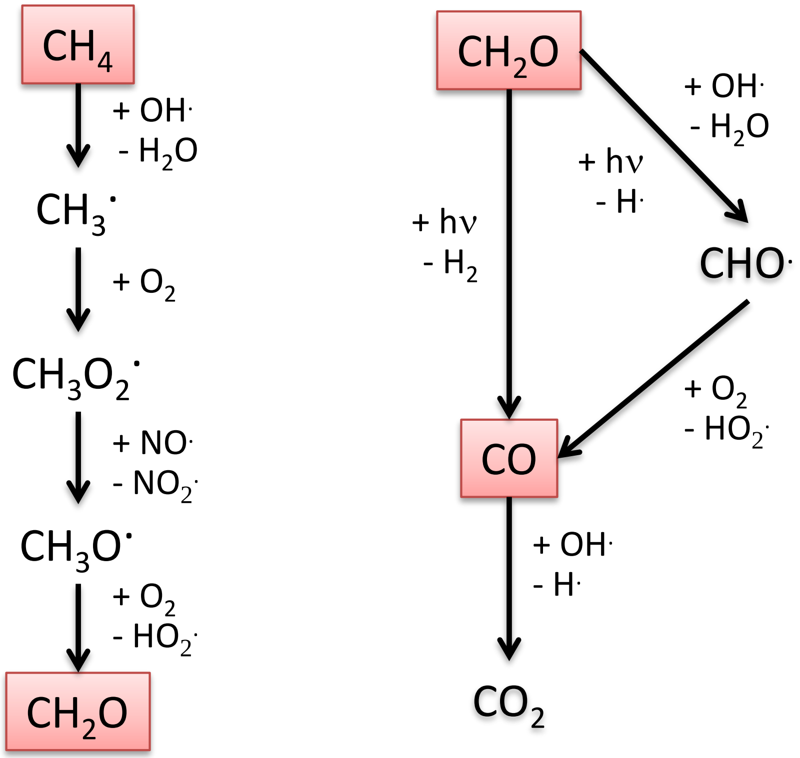




Anthropogenic sources of methane: 1-coal mines, natural gas, oil industry, 2-livestock (rumination/excrements), 3-domestic waste landfills/waste treatment, 4-biomass combustion, 5-rice plants, 6-biofuels.

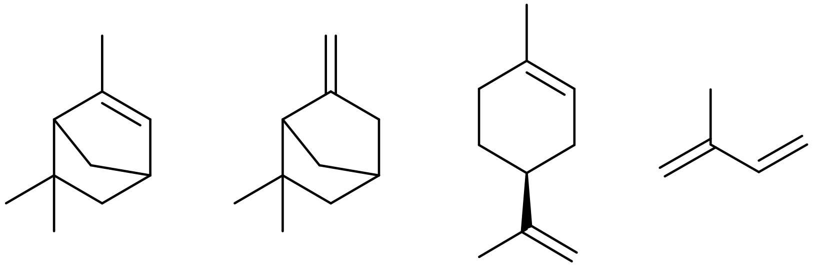
d. Natural Gas

Methane decomposition in the troposphere



Other VOCs: non-methane hydrocarbons (NMHC)

Source	Amount (Tg/yr)
Arbres (isoprene, terpenes)	600… 1200
Venicules	30… 50
Solvants	10… 20



α-Pinene β-Pinene Limonene Isoprene

e. Coal

The dirtiest and most inconvenient fuel!

- Devastating and dangerous **extraction**
- Difficult and expensive to **transport**
- Average **sulfur content** = 0.4 to 2%
- Combustion efficiency: depends on **coal quality**
- Coal combustion releases CO_2 and **CO (toxic)**
- Coal contains **nitrogenous** impurities (nitrates, nitrites, ammoniac)

Coal quality	C	H	O	N	Heat capacity (MJ/kg)
Wood*	50	6	43	1	11.7
Peat	59	6	33	2	12.5
Lignite	69	5	25	1	25
Hard coal	88	5	5-15	1	35
Anthracite	95	2-3	2-3	traces	37

$$\text{Sulfides } (FeS_2) \xrightarrow[\Delta]{O_2} SO_2 \xrightarrow{1/2\ O_2} SO_3 \xrightarrow{H_2O} H_2SO_4$$

H_2SO_4: Sulfuric acid, acid rain

$$\text{Nitrogenous cpd} \xrightarrow[\Delta]{O_2} NO^{\cdot} \xrightarrow[\Delta]{O_2} NO_2^{\cdot} \xrightarrow{H_2O} HNO_3$$

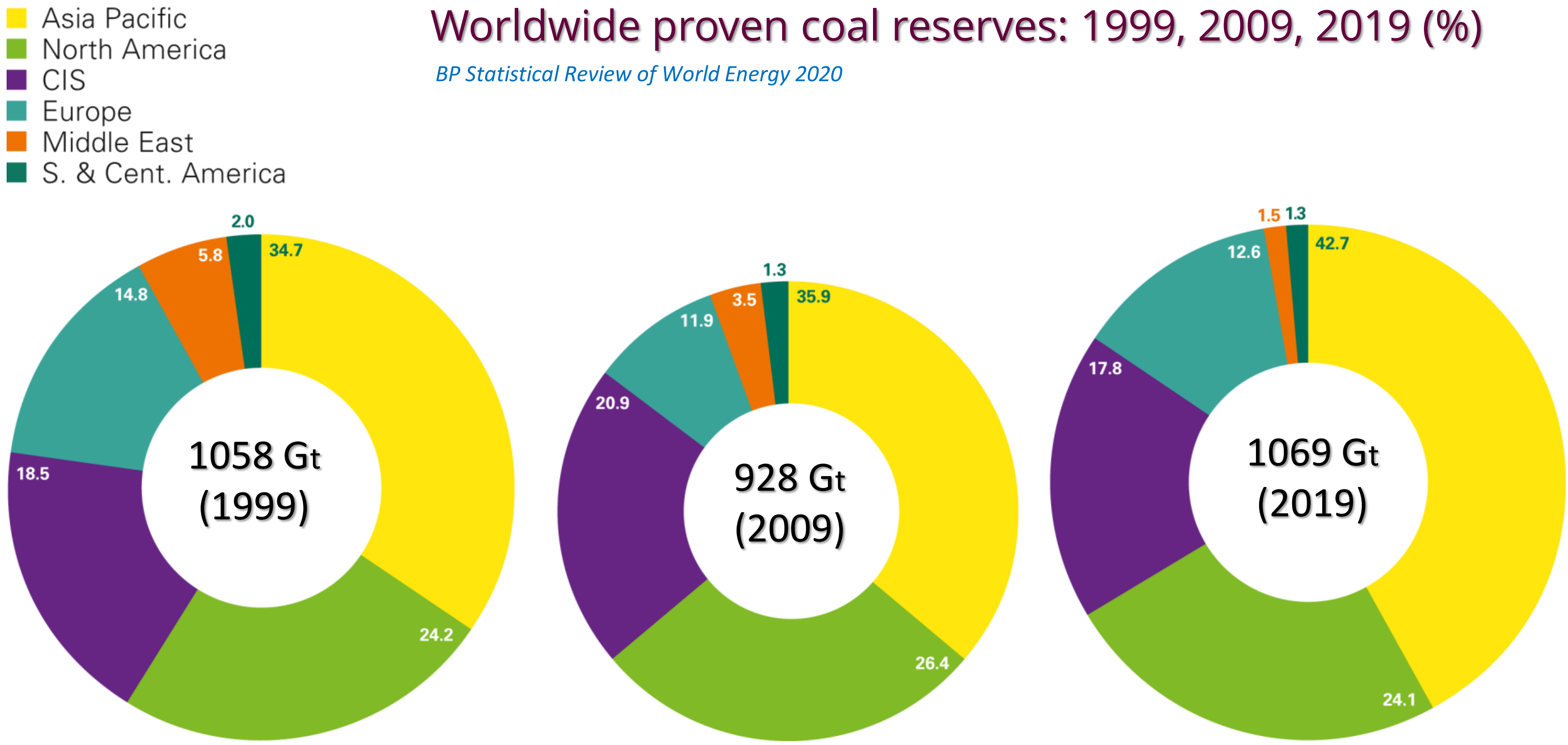
$NO^{\cdot}$: toxic; $NO_2^{\cdot}$: toxic; HNO_3: Nitric acid, acid rain

Coal combustion releases SO_2 and NO_x

e. Coal

Worldwide proven coal reserves: 1999, 2009, 2019 (%)

BP Statistical Review of World Energy 2020

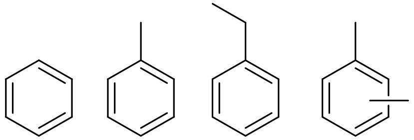


World consumption (2019) = 5.5 Gt ➡ 200 yr…

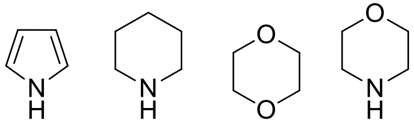
f. Oil

“Liquid fuels”

- Mixture of **hydrocarbons** (HC):
  - aliphatic HC
  - aromatic HC (BTEX)
  - heterocyclic HC
  - organic impurities
  - mineral impurities (including heavy metals)



Benzene, toluene, ethylbenzene, xylenes



Pyrrole, piperidine, dioxane, morpholine

- Uses (France, 2019)
  - petrochemicals: **18%**
  - energy production : **82%**
  - Various fuels (oil refineries: distillation, cracking, reforming)

Fraction	Molecule size	Use
Gas	C_1-C_4	Gas engine
Gasoline	C_5-C_{12}	Gasoline engine
Kerosene	C_{12}-C_{16}	Plane engine
Diesel	C_{16}-C_{18}	Diesel engine
Lubricant	C_{18}-C_{20}	lubricating oils
Wax	C_{20}-C_{40}	Candles, wax paper
Asphalt	> C_{40}	Asphalt, tar

Environmental impacts

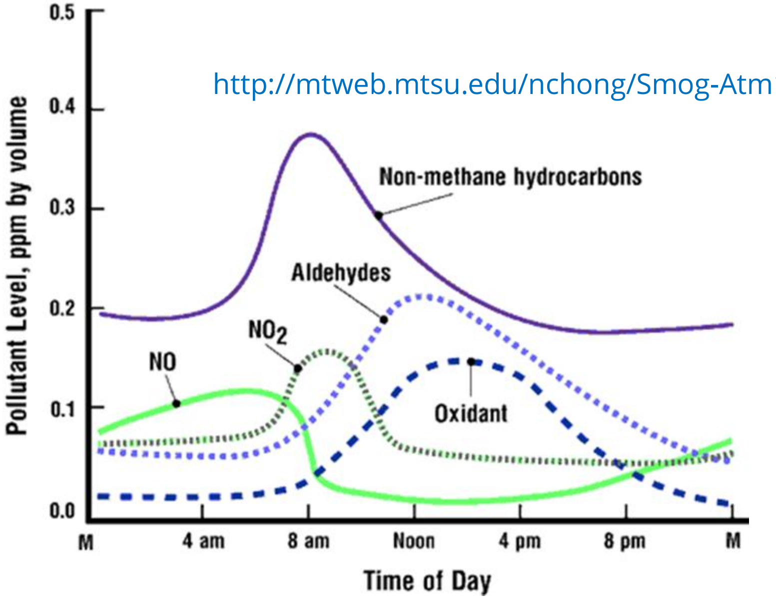
f. Oil

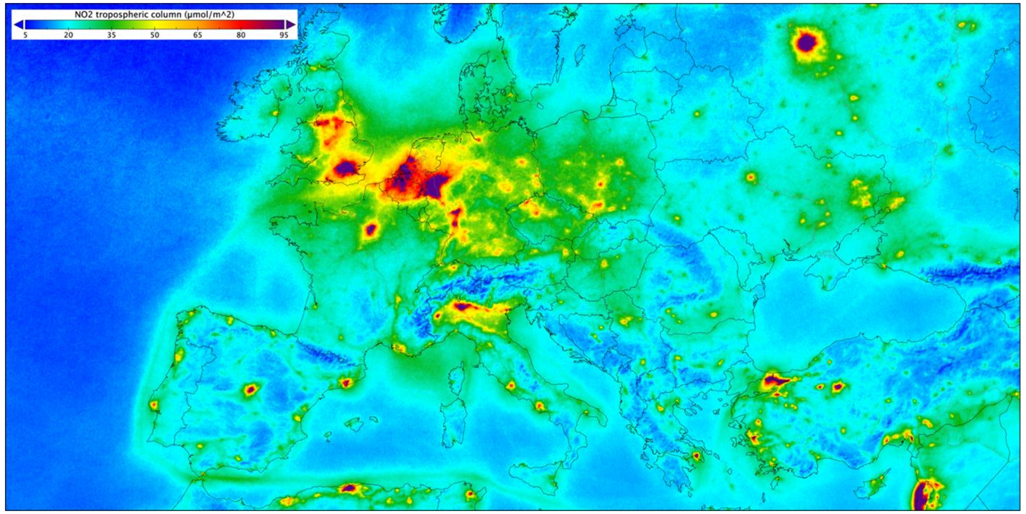
- **extraction** (soil and marine pollution, CH_4 release)
- **transport** (oil spills, deballasting)
- **air pollution** due to internal combustion engine use:
  - improved octane rating: **$Pb(Et)_4$** → BTEX (CMR)
  - particulate matter (PMx), **HAP** (diesel)
  - exhaust gases : unburned **HC**, CO, **NO_x**

catalytic converters → $CO_2 + H_2O + N_2$

parasitic reaction: $2\ NO + CO \rightarrow \mathbf{N_2O} + CO_2$

http://mtweb.mtsu.edu/nchong/Smog-Atm1.htm





Overall NO_2 pollution (Europe, 2019) ***esa*** *– space in images*

1. automobile traffic ($HC + NO^{\cdot} + \varepsilon NO_2^{\cdot}$)
2. sunrise (λ < 420 nm):

$HC + NO^{\cdot} + O_2 \rightarrow COV + PAN + NO_2^{\cdot}$

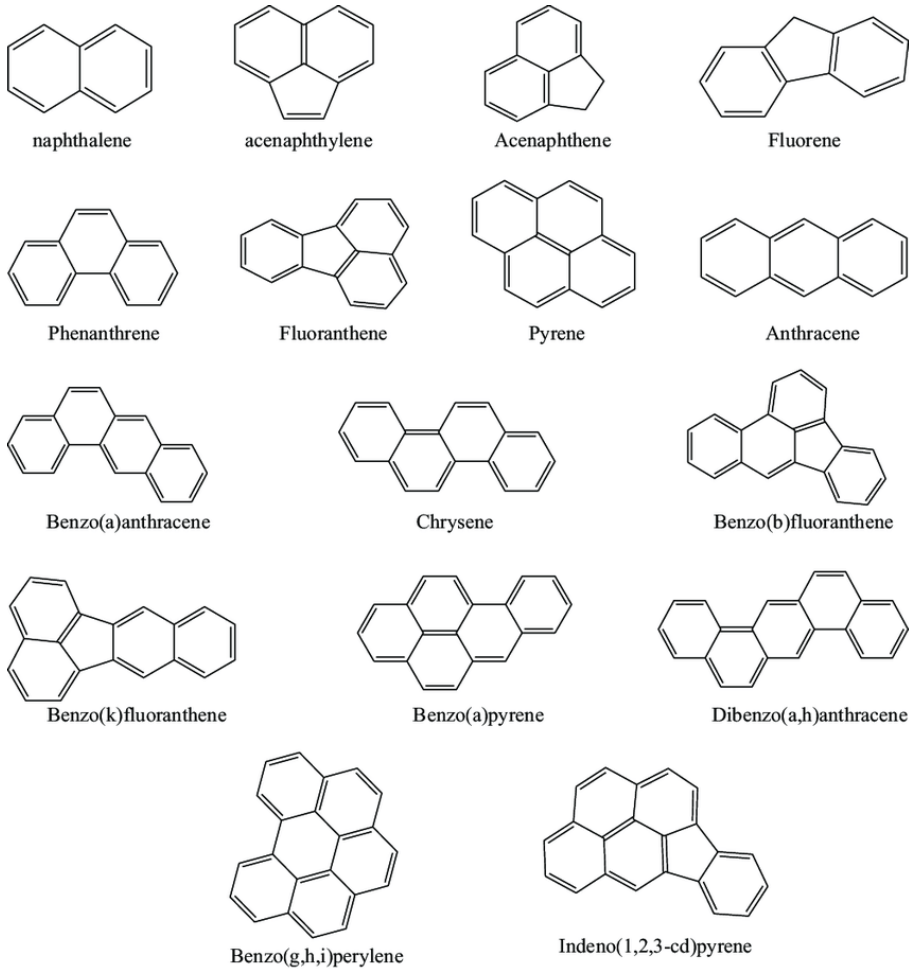
$NO_2^{\cdot} \rightarrow \mathbf{O} + NO^{\cdot}$

$O + O_2 \rightarrow \mathbf{O_3}$ (*tropospheric ozone peak*)

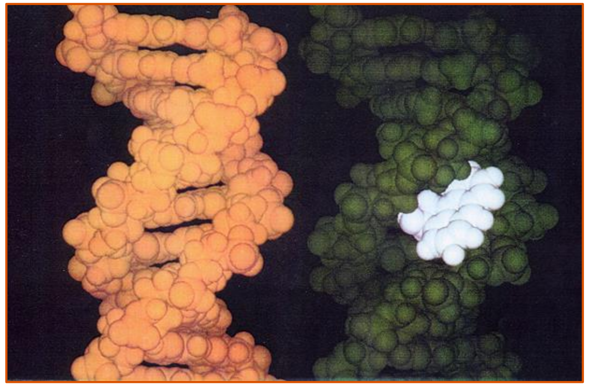
f. Oil

Environmental impacts

Polycyclic Aromatic Hydrocarbons (**PAH**/HAP)



- Pyrolysis or incomplete combustion of organic matter:
  - incineration of agricultural waste
  - combustion of wood, coal, household waste (incinerators...)
  - diesel engines
  - cigarette combustion, food cooking
- Characteristics:
  - in + or - complex mixtures
  - hundreds of PAHs and PAH derivatives exist
  - biodegraded (slowly) in surface soil layers
  - in water, most PAHs are adsorbed to sediments
- Toxicity (poorly understood/mixtures):
  - systemic effects (hepatic, hematological, immunological, atherosclerosis, etc)
  - CMR effects

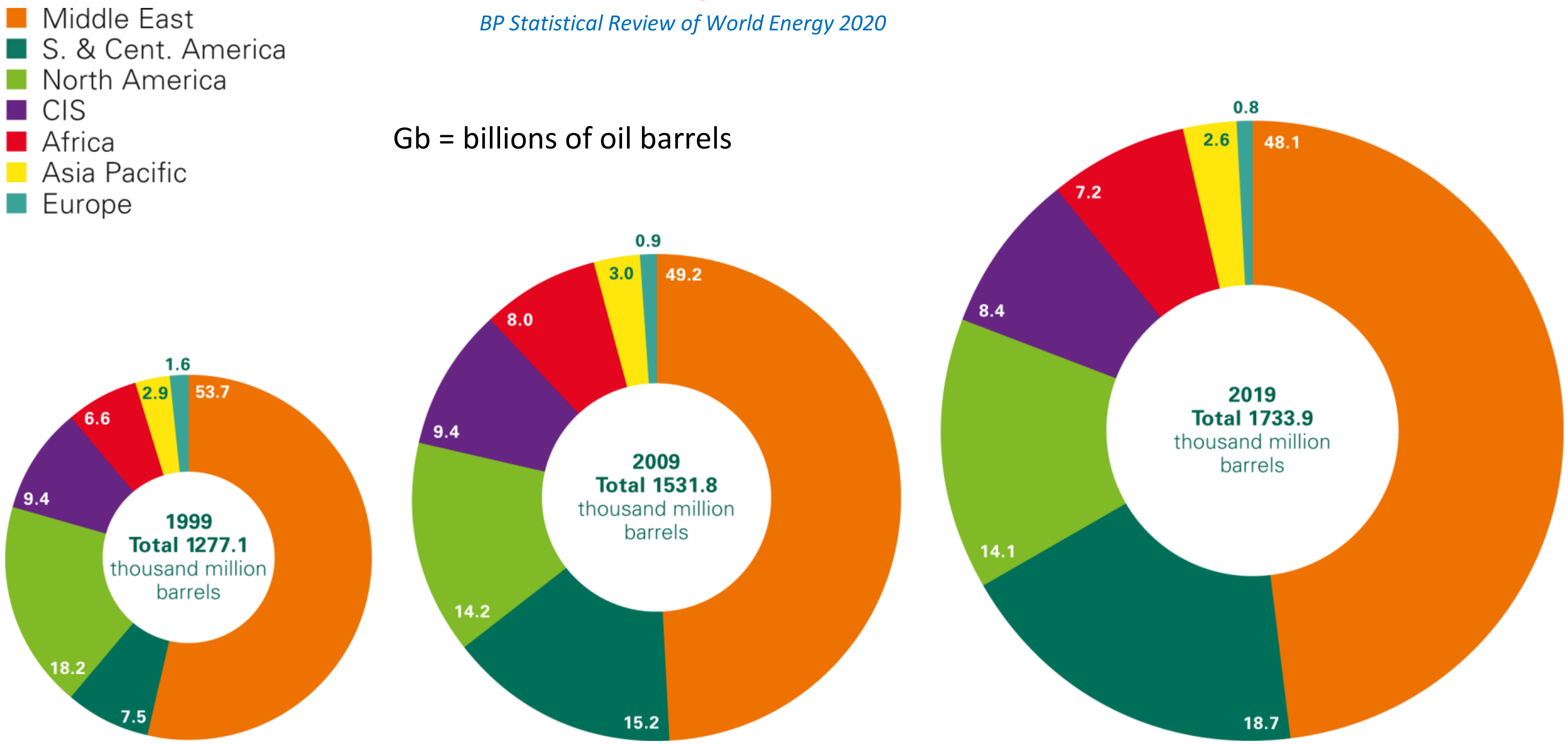


f. Oil

Worldwide proven oil reserves: 1999, 2009, 2019 (%)

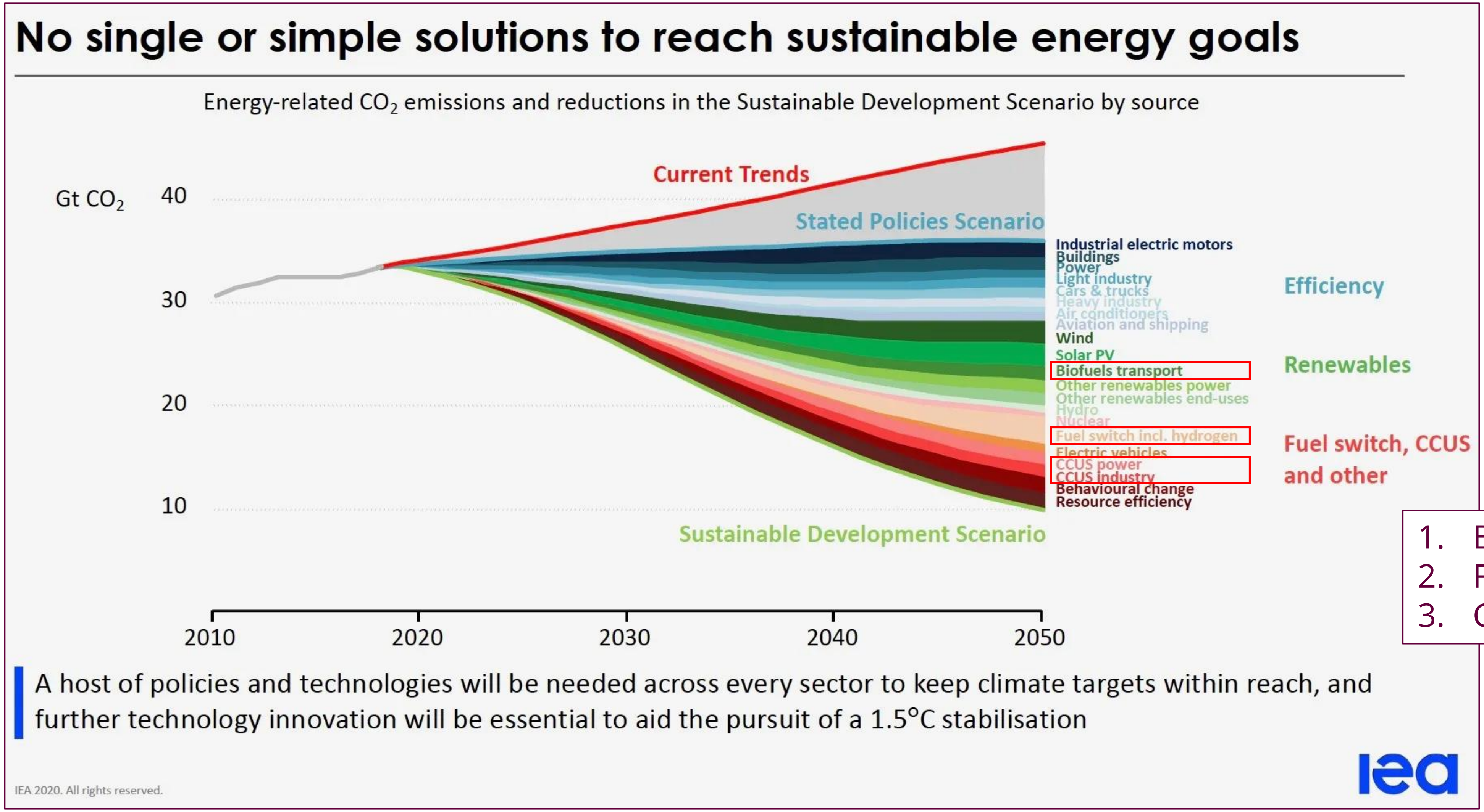
BP Statistical Review of World Energy 2020

Gb = billions of oil barrels



World consumption (2021) = 35.4 Gb/yr (180,000 L/s!) → **50 yr… at least!**

g. Potential alternatives

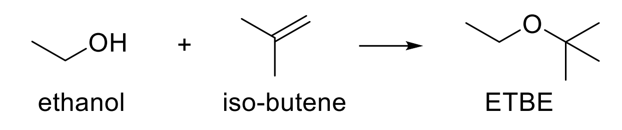


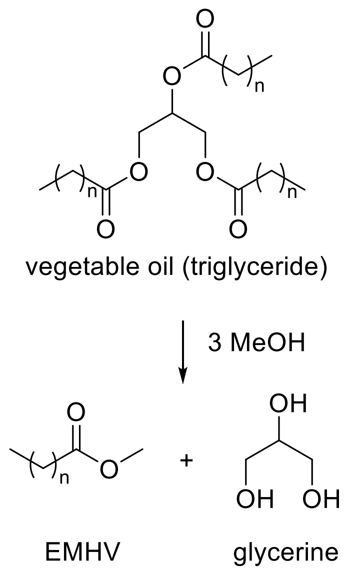
1. Biofuels
2. Fuel cells (H_2)
3. CCUS

g. Potential alternatives

1. Biofuels

- 1st generation biofuels (3 types) :
  - biodiesel
    - oilseed crops (colza, tournesol, soja) → **HVP** (pure plant oil) and **EMHV** (vegetable oil methyl ester)
  - bioethanol
    - fermentation of sugar beet, sugar cane or wheat/corn → **ethanol** and **ETBE** (ethyl tert-butylether)
  - biomethane
    - from biogas



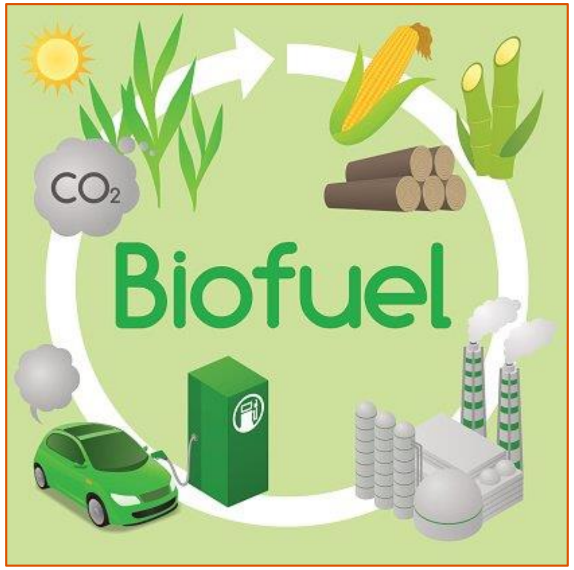


➡ Not a convincing LCA at all!

- 2nd generation biofuels
  - use of agricultural (straw) or forestry **residues**
  - use of dedicated **non-food crops** (coppice)

- 3rd generation biofuels
  - use of sugar- or fatty acid-rich microalgae

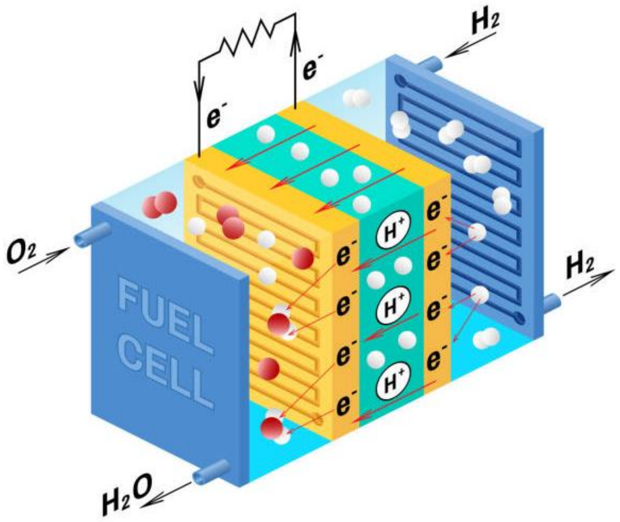
- 4th generation biofuels
  - synthetic biology of cyanobacteria and algae



➡ C from biomass : GWP ~ 0

2. Fuel cells (hydrogene)

g. Potential alternatives



- Advantages:
  - no pollutant emissions
- Disavantages:
  - high cost
  - large storage volume
  - flammability of dihydrogen

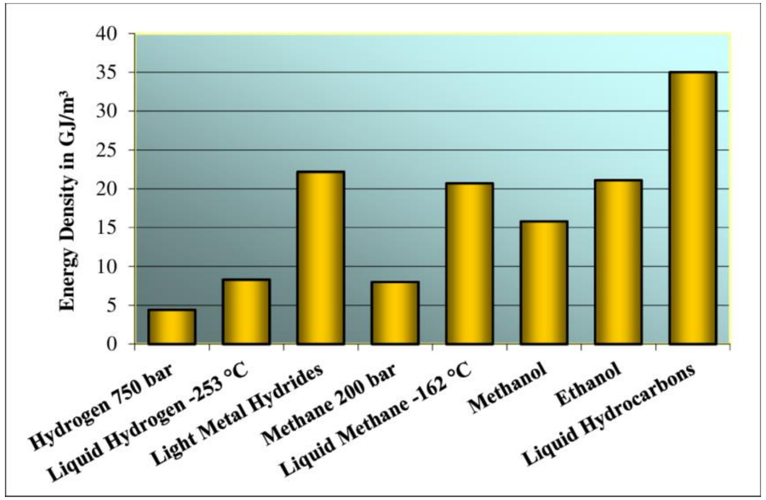
Non-renewable : > 99% !

H_2 production (2021, EIA)

48% : natural gas steam reforming
28% : hydrocarbons reforming
23% : coal gasification
0,04% : water electrolysis
< 1% : biomethane reforming!

Renewable : < 1% !

Volumetric energy density of various fuels



The many colours of hydrogen

	Colour	Fuel	Process	Products
	Brown/Black	Coal	Steam reforming or gasification	$H_2 + CO_2$ (released)
	White	N/A	Naturally occurring	H_2
	Grey	Natural Gas	Steam reforming	$H_2 + CO_2$ (released)
	Blue	Natural Gas	Steam reforming	$H_2 + CO_2$ (% captured and stored)
	Turquoise	Natural Gas	Pyrolysis	H_2 + C (solid)
	Red	Nuclear Power	Catalytic splitting	$H_2 + O_2$
	Purple/Pink	Nuclear Power	Electrolysis	$H_2 + O_2$
	Yellow	Solar Power	Electrolysis	$H_2 + O_2$
	Green	Renewable Electricity	Electrolysis	$H_2 + O_2$

3. CCUS

Carbon Capture, Utilisation, and Storage

g. Potential alternatives

Industrial CO_2 sequestration involves 3 stages:

- CO_2 capture at the main industrial emission sources (power plants, cement works, refineries, steelworks...)
- CO_2 transport by pipeline or ship (supercritic CO_2)
- CO_2 storage in a confined environment

3. CCUS

Carbon Capture, Utilisation, and Storage

g. Potential alternatives

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- CO_2 capture at the main industrial emission sources (power plants, cement works, refineries, steelworks...)
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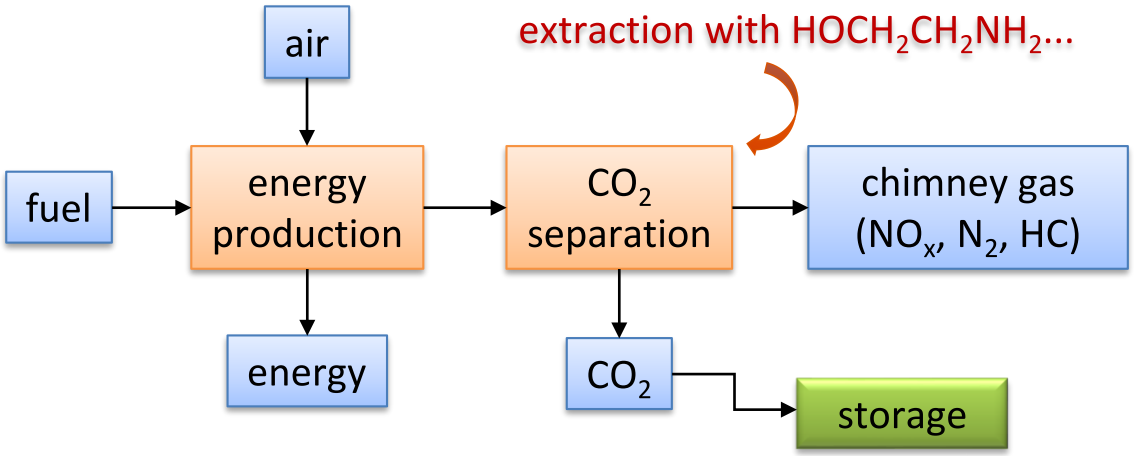
- CO_2 storage in a confined environment

1- post-combustion (for older plants)



g. Potential alternatives

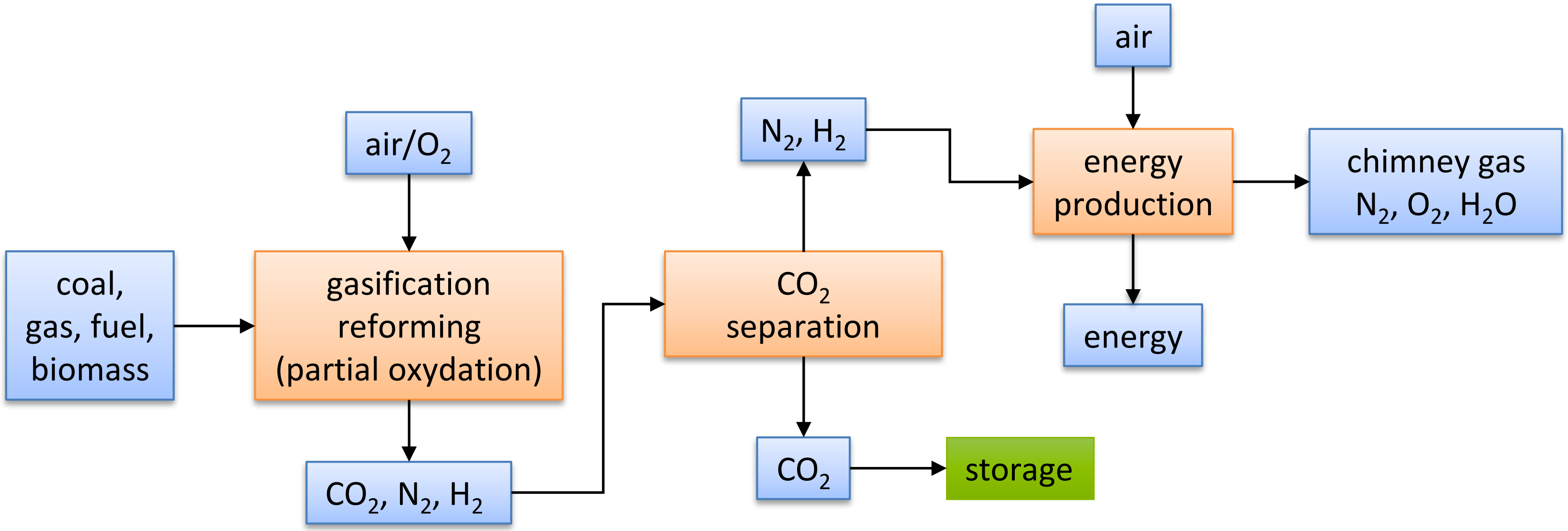
3. CCUS

Carbon Capture, Utilisation, and Storage

Industrial CO_2 sequestration involves 3 stages:

- CO_2 capture at the main industrial emission sources (power plants, cement works, refineries, steelworks...)
- CO_2 transport by pipeline or ship (supercritic CO_2)
- CO_2 storage in a confined environment

2- pre-combustion (for new plants)



3. CCUS

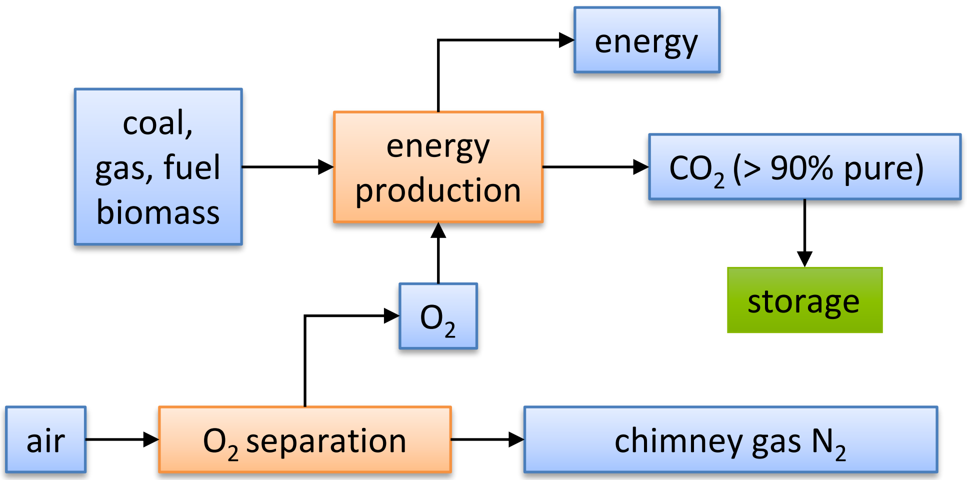
Carbon Capture, Utilisation, and Storage

g. Potential alternatives

Industrial CO_2 sequestration involves 3 stages:

- CO_2 capture at the main industrial emission sources (power plants, cement works, refineries, steelworks...)
- CO_2 transport by pipeline or ship (supercritic CO_2)
- CO_2 storage in a confined environment

3- oxy-combustion (for new plants)



g. Potential alternatives

3. CCUS

Carbon Capture, Utilisation, and Storage

Industrial CO_2 sequestration involves 3 stages:

- CO_2 capture at the main industrial emission sources (power plants, cement works, refineries, steelworks...)
- CO_2 transport by pipeline or ship (supercritic CO_2)
- CO_2 storage in a confined environment

The separated CO_2 is compressed and therefore liquefied to facilitate transport (expensive in energy!)

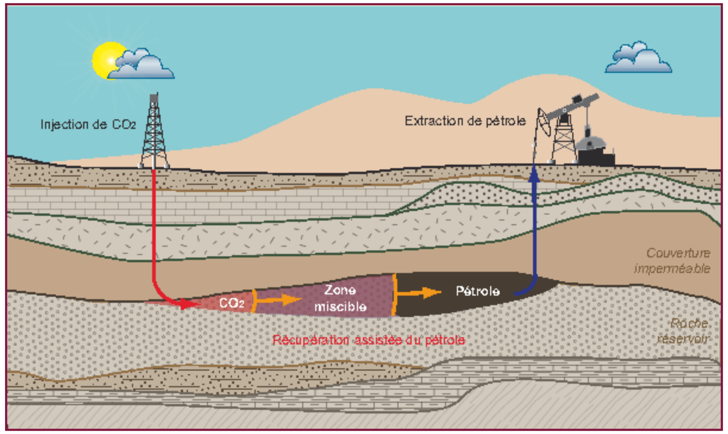
g. Potential alternatives

3. CCUS

Carbon Capture, Utilisation, and Storage

Industrial CO_2 sequestration involves 3 stages:

- CO_2 capture at the main industrial emission sources (power plants, cement works, refineries, steelworks...)
- CO_2 transport by pipeline or ship (supercritic CO_2)
- CO_2 storage in a confined environment
    - deep saline aquifers (largest storage capacities)
    - old oil and gas fields (improved oilfield productivity)
    - deep, unmineable coal seams (exploitation of natural gas trapped in these structures)



Many research programs funded mainly by oil companies

Questions under study:

- Is it economically feasible to bear the cost of CO_2 capture and storage (which consumes 10-20% of fuel)?
- What about natural resource management?
- Is geological storage of CO_2 sustainable over thousands years?
- future uses: CO_2 reduction (to CH_3OH...)?

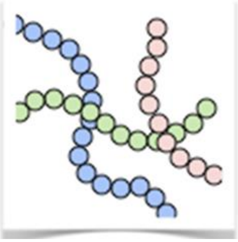
II. Second cause of pollution: industrial activities

1. Synthetic materials
2. Halogenated derivatives
3. Metallurgy

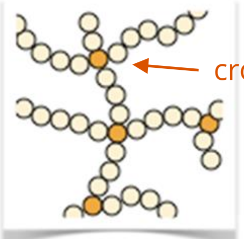
Rubber and elastomers – **Plastics** – Synthetic textiles

1. Synthetic materials

- 2 types of plastic:
  - **thermoplastic** = linear polymer that melts gradually and can be reformed (e.g. polyethylene) → <u>recyclable</u>
  - **thermosetting plastic** = three-dimensional network polymer or thermoset that can no longer be softened (e.g. bakelite) → <u>non-recyclable</u>

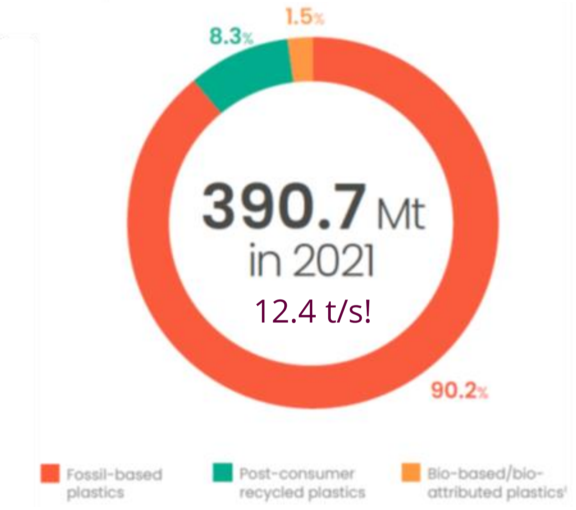


Mechanical conversion (reversible)



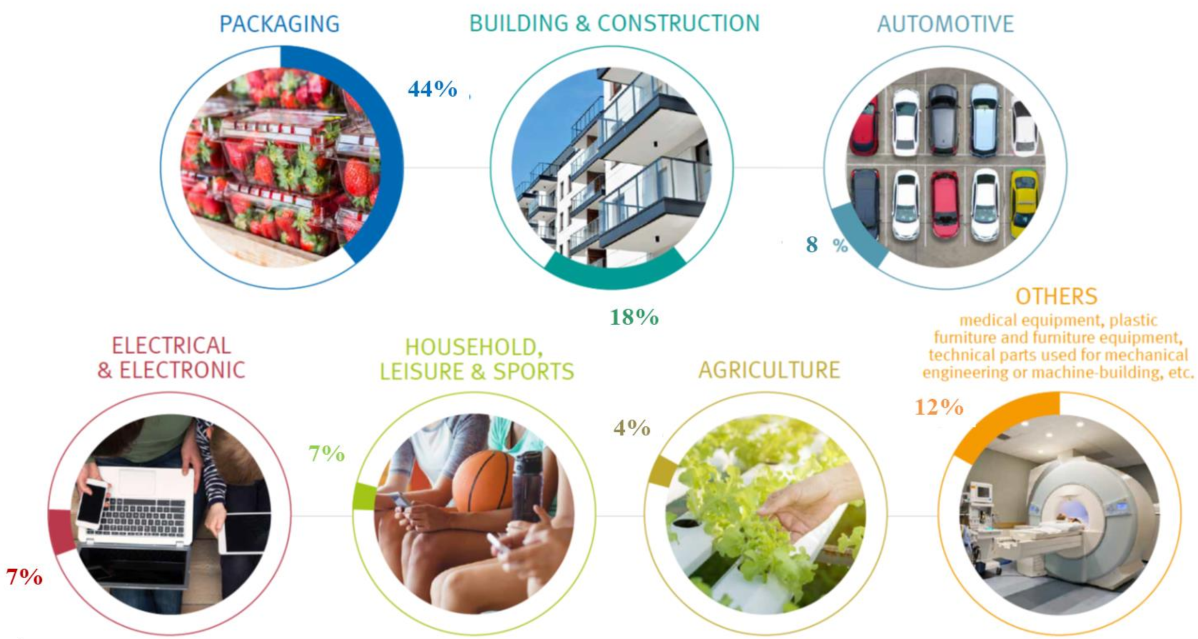
Chemical conversion (irreversible)

- World production (2021)



PlasticEurope Market Research Group

Total converter demand = 57,2 Mt (Europe, 2021)

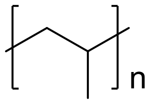


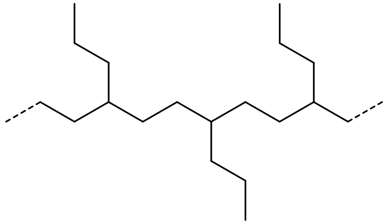
1. Synthetic materials

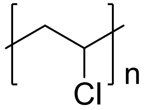
Rubber and elastomers – **Plastics** – Synthetic textiles

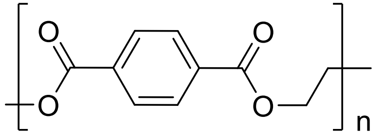
- Plastic demand by polymer types (2017)

ABS : acrylonitrile butadiene styrene
EPS : expandable polystyrene
LLD : linear low density
MD : medium density
PBT : polybutylene terephtalate
PC : polycarbonate
PMMA : polymethyl methacrylate

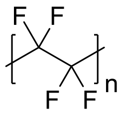


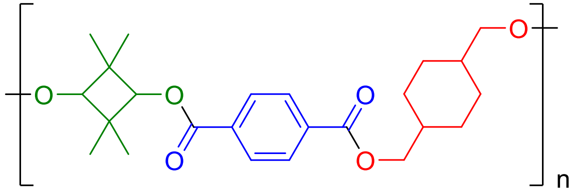


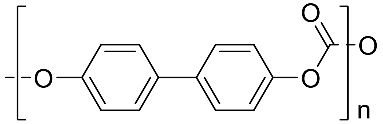


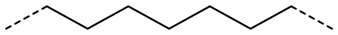


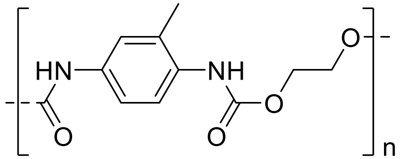
PlasticEurope Market Research Group

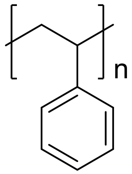










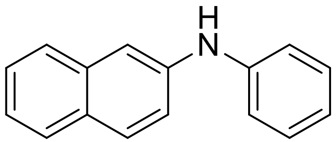


Rubber and elastomers – **Plastics** – Synthetic textiles

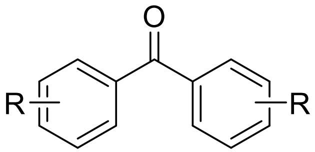
1. Synthetic materials

- **Plastic additives:**

  Not only does the synthesis of plastics involve the use of toxic or CMR substrates (**BPA**, **HCHO**, **phenol**, **phosgene**, **ethylene glycol**...) or catalysts (CrO_3...), but plastics also contain numerous additives.

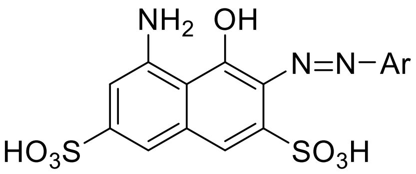


N-phényl-β-naphtylamine



diphénylketone derivatives

stabilizing agents (antioxydant and anti-UV agents, heat stabilizers)

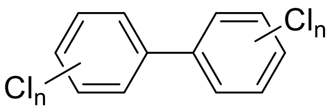


"azo" compounds

dyes

-air
-surfactants, soaps
-CFCs prohibited

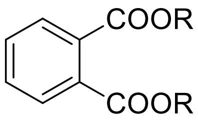
foaming agents



PCB

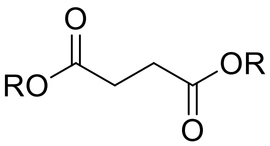
polychlorinated biphenyls

-toxic, POP
-209 different PCBs!
-manufacture/use banned in France since 1987



R = Bu : DBP
R = $CH_2CH_2OCH_3$: DMEP
R = $CH_2CH(Et)Bu$: DOP

Phtalates
-less toxic, but less efficient



Succinates
-biosourced

plasticizing agents

universite PARIS-SACLAY | GRADUATE SCHOOL Chimie

Rubber and elastomers – **Plastics** – Synthetic textiles

1. Synthetic materials

- Main drawbacks of plastics:
  - Macro/micro/nano-plastic waste (non-biodegradable)
  - Combustion: release CO_2, HCl...
  - Flammable materials (except those containing halogens...)
  - Inocuity (release of toxic monomers, additives...)

➡ contamination of the entire food chain

Ingestion of 5 g/person/week!

Most Plastic Products Release Estrogenic Chemicals: A Potential Health Problem that Can Be Solved

Chun Z. Yang,[1] Stuart I. Yaniger,[2] V. Craig Jordan,[3] Daniel J. Klein,[2] and George D. Bittner[1,2,4]

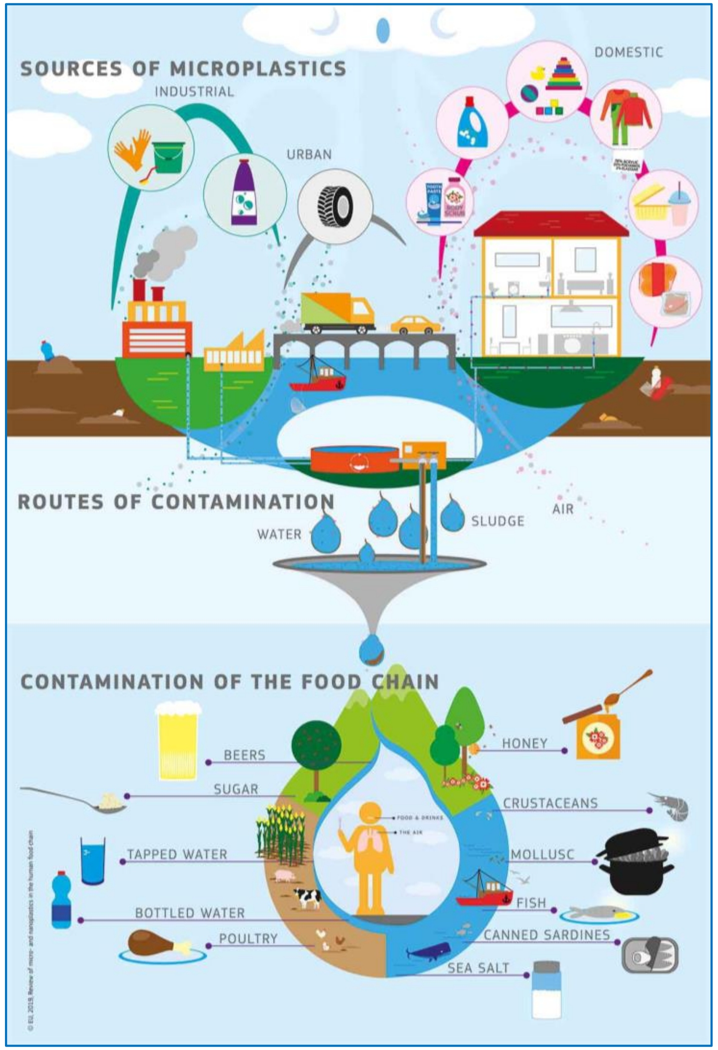
[1]CertiChem Inc., Austin, Texas, USA; [2]PlastiPure Inc., Austin, Texas, USA; [3]Lombardi Comprehensive Cancer Center, Georgetown University Medical Center, Washington, DC, USA; [4]Neurobiology Section, School of Biology, University of Texas, Austin, Texas, USA

RESULTS: Almost all commercially available plastic products we sampled—independent of the type of resin, product, or retail source—leached chemicals having reliably detectable EA, including those advertised as BPA free. In some cases, BPA-free products released chemicals having more EA than did BPA-containing products.

CONCLUSIONS: Many plastic products are mischaracterized as being EA free if extracted with only one solvent and not exposed to common-use stresses. However, we can identify existing compounds, or have developed, monomers, additives, or processing agents that have no detectable EA and have similar costs. Hence, our data suggest that EA-free plastic products exposed to common-use stresses and extracted by saline and ethanol solvents could be cost-effectively made on a commercial scale and thereby eliminate a potential health risk posed by most currently available plastic products that leach chemicals having EA into food products.

EA : estrogenic activity – BPA : bisphenol A

Environmental Health Perspectives **2011**, *119*, 989



Food Additives and Contaminants **2019**, *36*, 639

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  - Flammable materials (except those containing halogens...)
  - Inocuity (release of toxic monomers, additives...)

Ingestion of 5 g/person/week!

Rapid single-particle chemical imaging of nanoplastics by SRS microscopy

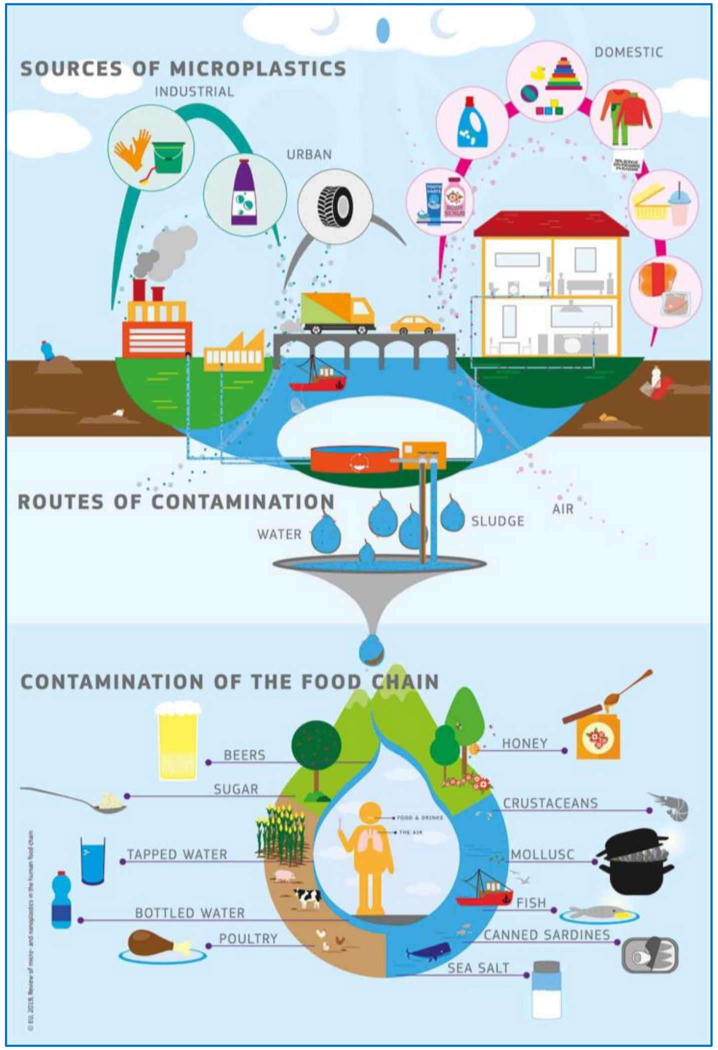
Naixin Qian[a], Xin Gao[a], Xiaoqi Lang[a], Huiping Deng[b], Teodora Maria Bratu[b], Qixuan Chen[c], Phoebe Stapleton[d], Beizhan Yan[b,1], and Wei Min[a,e,1]

Edited by Eric O. Potma, University of California, Irvine, CA; received January 11, 2023; accepted October 24, 2023 by Editorial Board Member Shaul Mukamel

Plastics are now omnipresent in our daily lives. The existence of microplastics (1 µm to 5 mm in length) and possibly even nanoplastics (<1 µm) has recently raised health concerns. In particular, nanoplastics are believed to be more toxic since their smaller size renders them much more amenable, compared to microplastics, to enter the human body. However, detecting nanoplastics imposes tremendous analytical challenges on both the nano-level sensitivity and the plastic-identifying specificity, leading to a knowledge gap in this mysterious nanoworld surrounding us. To address these challenges, we developed a hyperspectral stimulated Raman scattering (SRS) imaging platform with an automated plastic identification algorithm that allows micro-nano plastic analysis at the single-particle level with high chemical specificity and throughput. We first validated the sensitivity enhancement of the narrow band of SRS to enable high-speed single nanoplastic detection below 100 nm. We then devised a data-driven spectral matching algorithm to address spectral identification challenges imposed by sensitive narrow-band hyperspectral imaging and achieve robust determination of common plastic polymers.

240,000 particles/L of bottled water!

Proc. Natl. Acad. Sci. **2024**, *121*, e2300582121



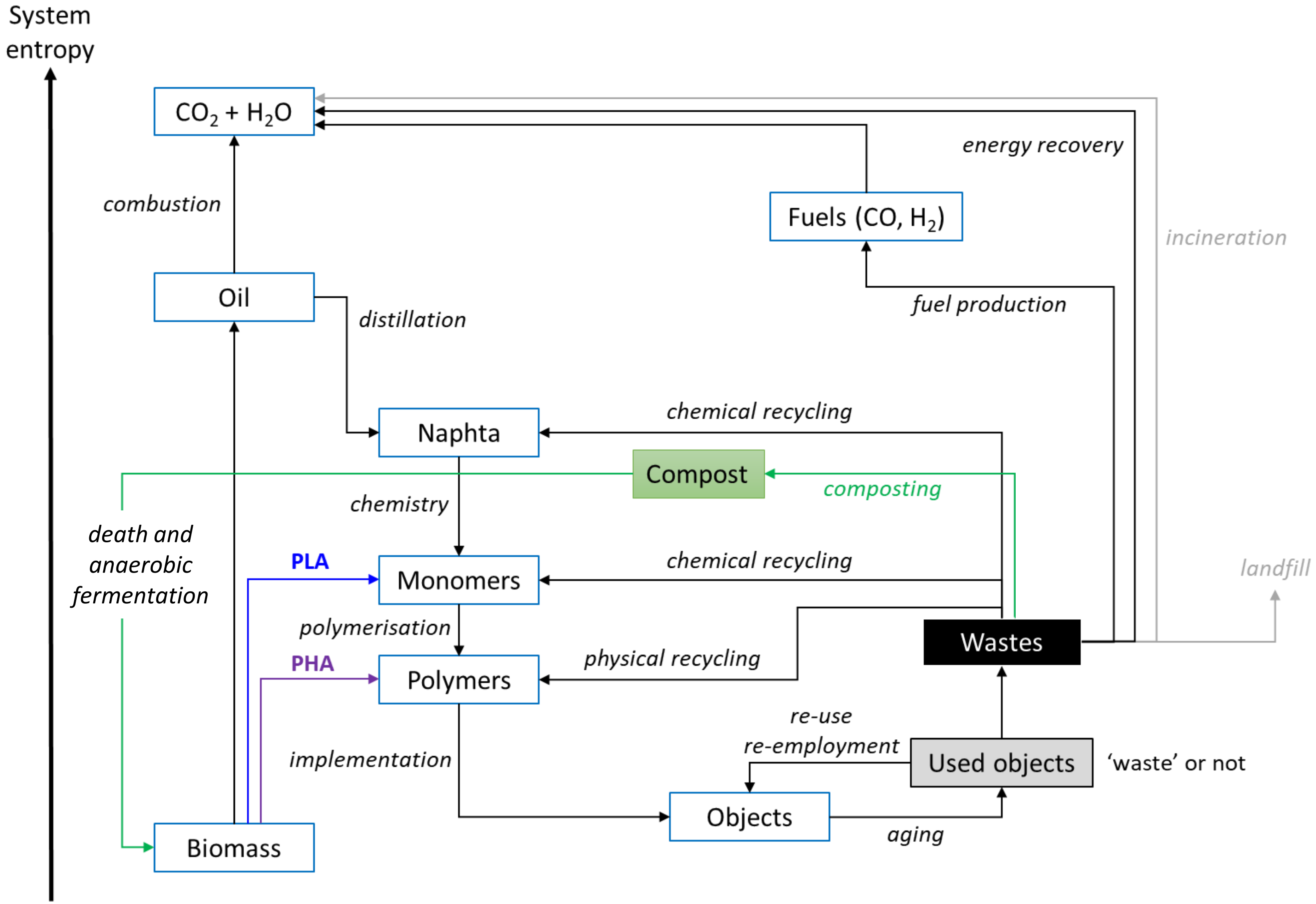
Food Additives and Contaminants **2019**, *36*, 639

Rubber and elastomers – **Plastics** – Synthetic textiles

1. Synthetic materials

- Plastics recycling:

Entropic aspects of the life cycle of conventional plastics (very brief, purely qualitative diagram, based on Duval, 2004)



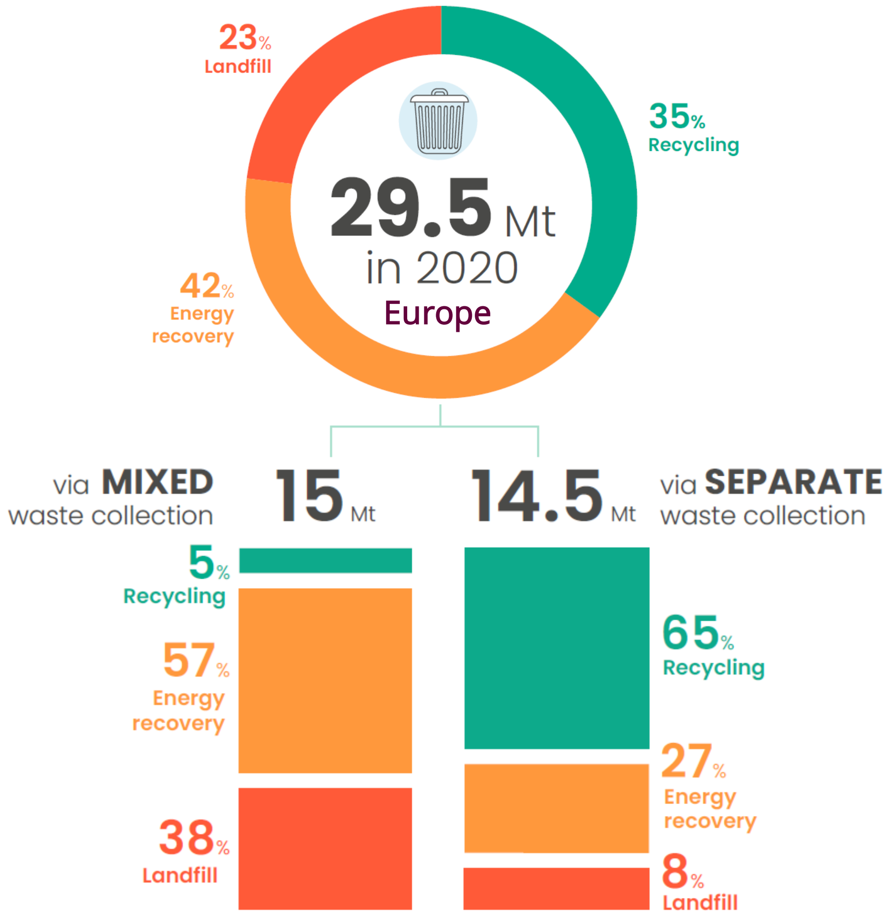
PLA: polylactic acid
PHA: polyhydroxyalcanoate
} bio-plastics

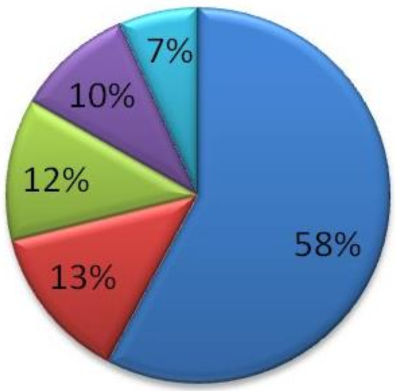
LCA not totally convincing!

Rubber and elastomers – **Plastics** – Synthetic textiles

1. Synthetic materials

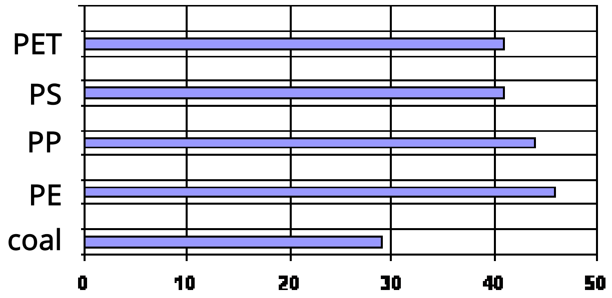
- Plastics recycling (only thermoplastic polymers are recyclable):





- PE (waste containers, drainage pipes, bags…)
- PP (packaging, bottles, automotive sector…)
- PS (hangers, flower pots, yoghurt pots)
- PET (fleece, carpets, tennis balls…)
- PVC (swimming pool linings, shoe soles, coated fabrics…)

Energy recovery (GJ/ton)

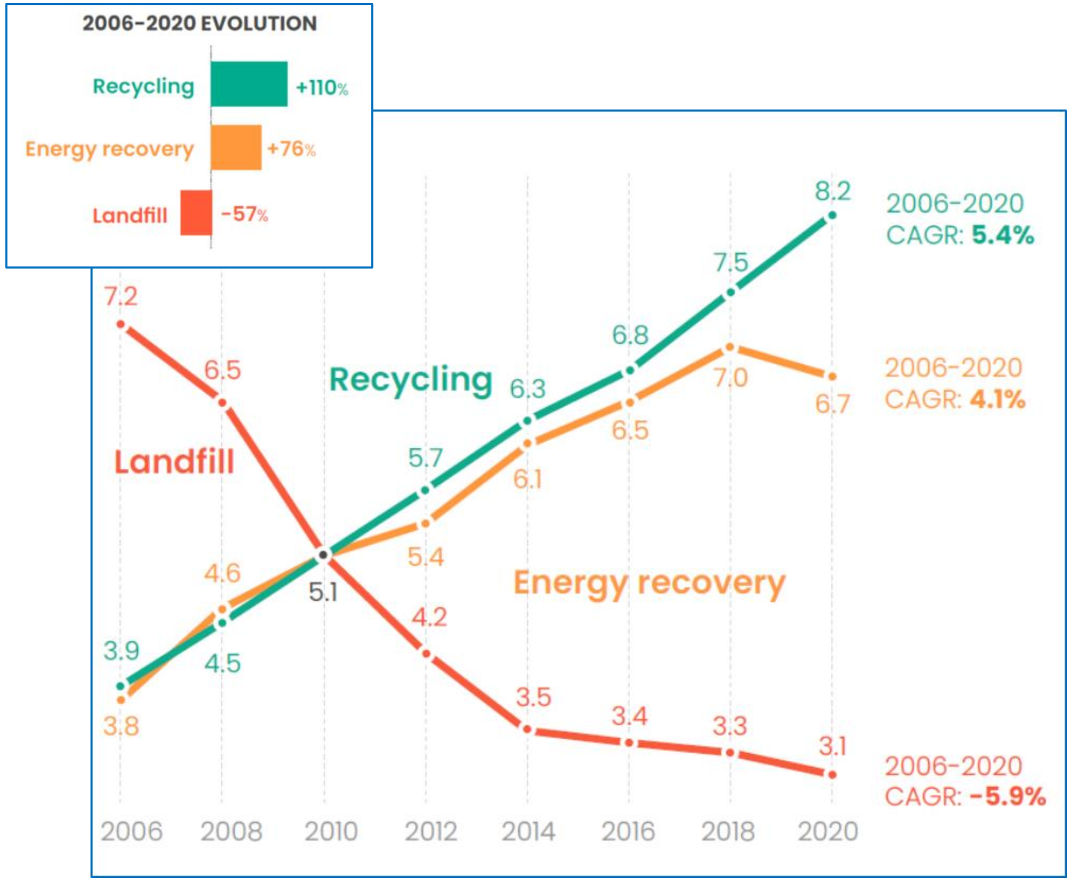


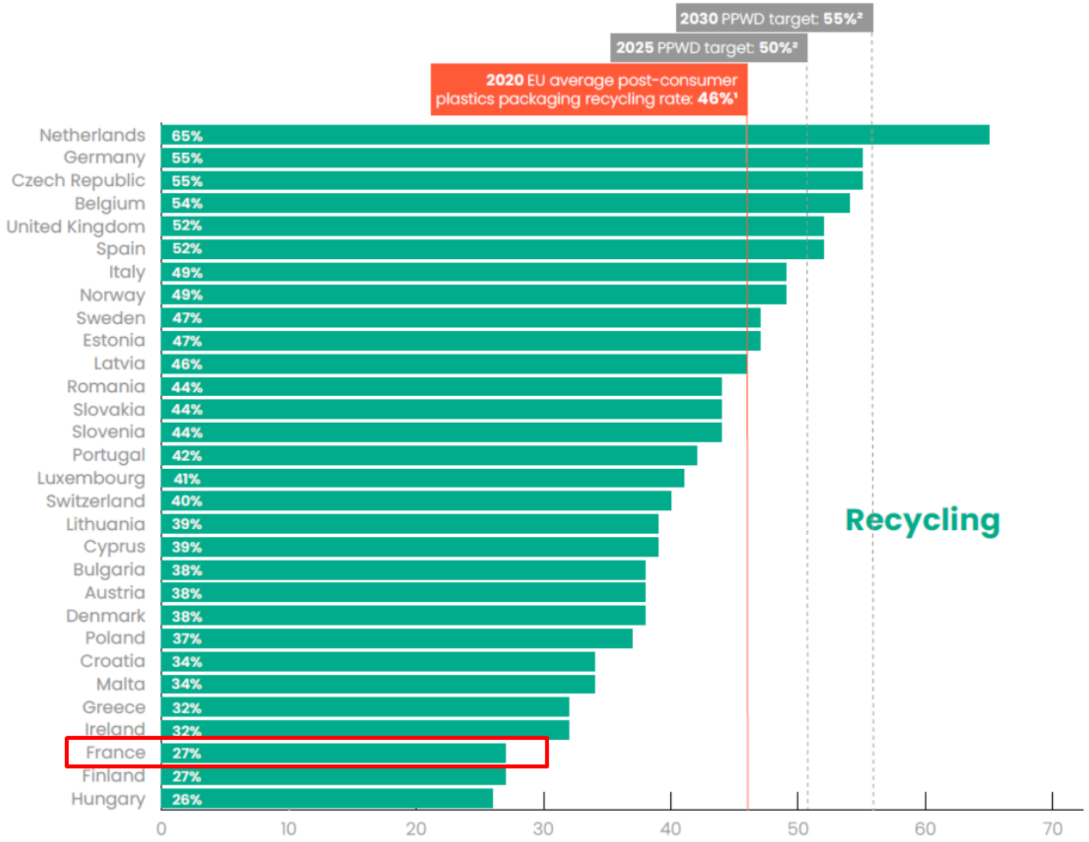
High calorific value: suitable for incineration

Rubber and elastomers – **Plastics** – Synthetic textiles

1. Synthetic materials

- Plastics recycling (only thermoplastic polymers are recyclable):



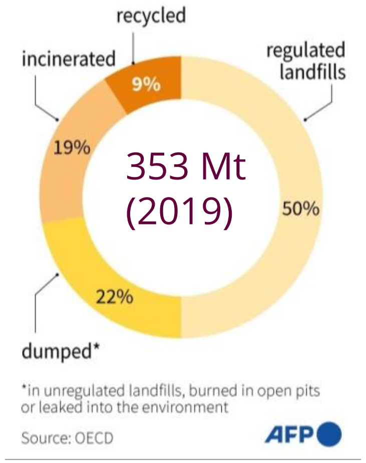


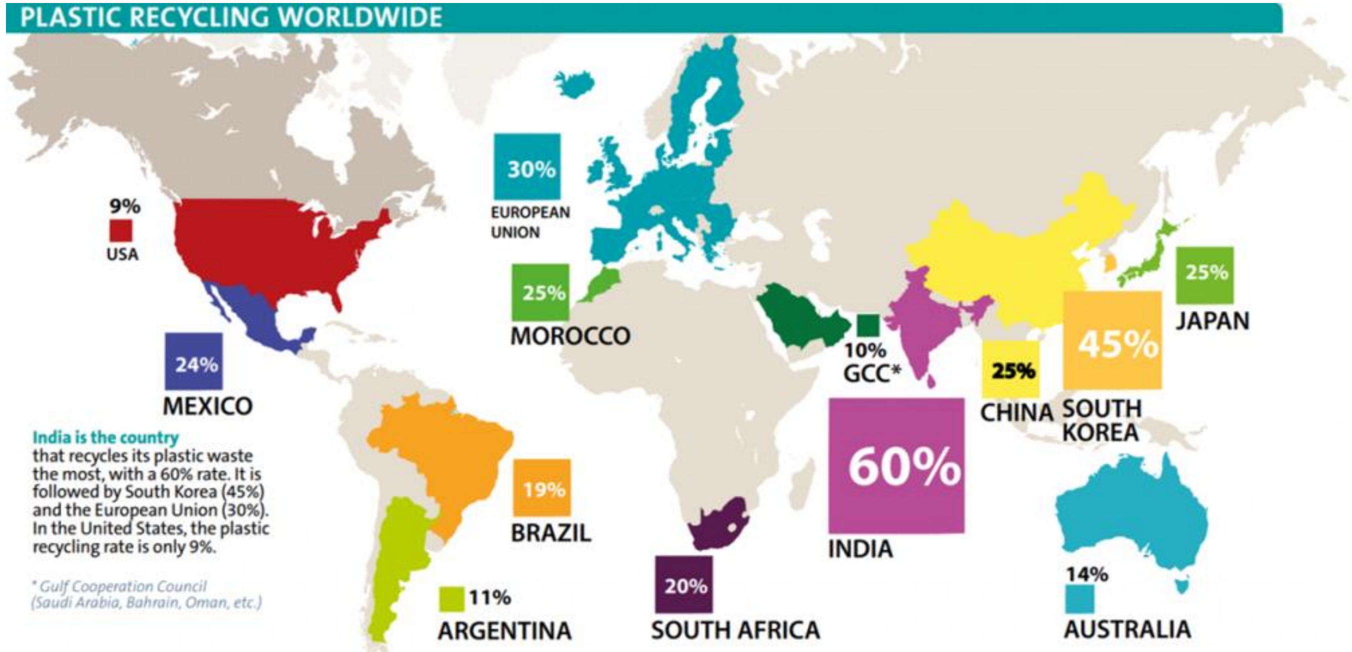
Source : PlasticEurope Market Research Group 2022

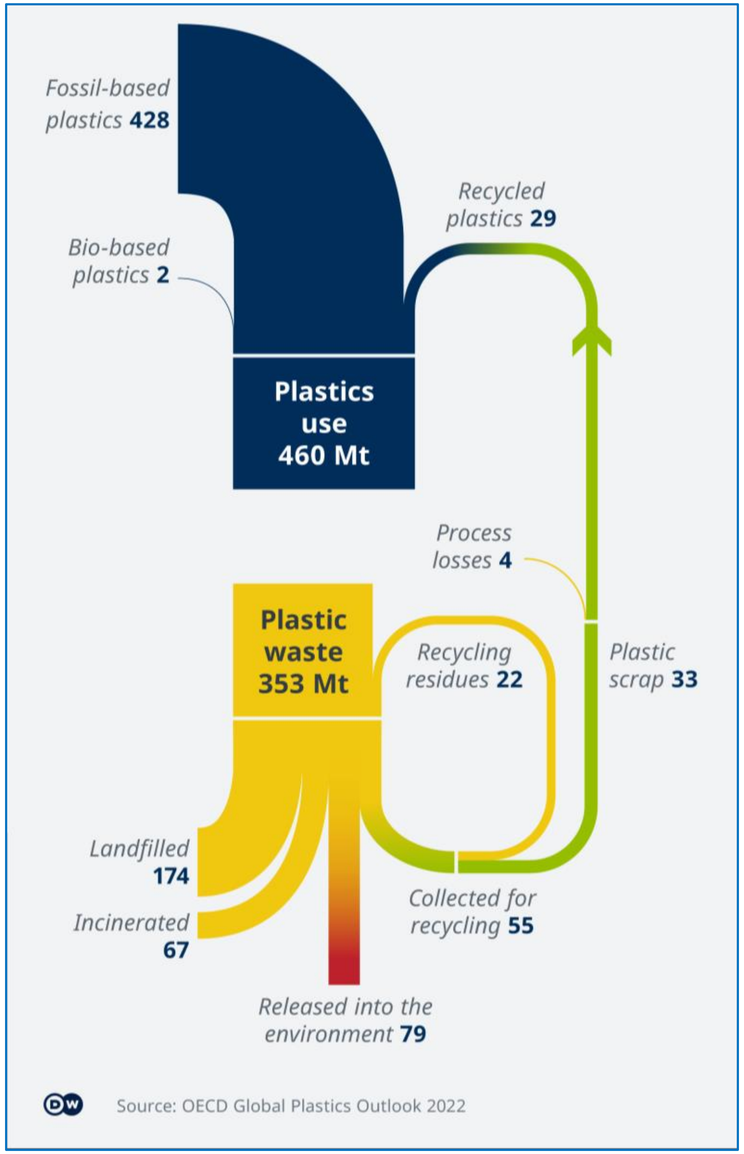
1. Synthetic materials

- Plastics recycling (worldwide, 2019):

o Recycling : 9%
o Energy recovery : 19%
o Landfill : 50%
o Released into the environment : **22%** (79 Mt!)







Presentation

2. Halogenated derivatives

❖ Inorganic chlorine compounds (industry)

- Na^+Cl^-, Cl_2, HCl, ClO^-, ClO_2^-, ClO_3^-, ClO_4^-

❖ Chlorinated Volatile Organic Compounds (VOC)

- vinyl chloride
- methyl chloride CH_3Cl
- chlorinated solvents :
  - dichloromethane CH_2Cl_2 (DCM)
  - chloroforme $CHCl_3$
  - carbon tetrachloride CCl_4 (TCM)
  - perchlorethylene $Cl_2C=CCl_2$ (PCE)
  - 1,1,1-trichloroethane $Cl_3C\text{-}CH_3$ (1,1,1-T)
  - trichlorethylene $Cl_2C=CHCl$ (TCE)
- Chlorofluorocarbons (CFC) and derivatives

possible human carcinogen (IARC C2B)

probable human carcinogen (IARC C2A)

known human carcinogen (IARC C1)

❖ Persistent Organic Pollutants (POPs)

- organochlorinated pesticides
- halogenated PAH
- PCB, furanes, dioxines
- PFAS

> ➢ Chlorinated derivatives are generally lipophilic and therefore bioaccumulative.
> ➢ Chlorinated VOCs can (depending on their physico-chemical properties) have an impact on the greenhouse effect or ozone depletion.

→
- Disturbance of the C cycle
- Disturbance of the O_2 cycle

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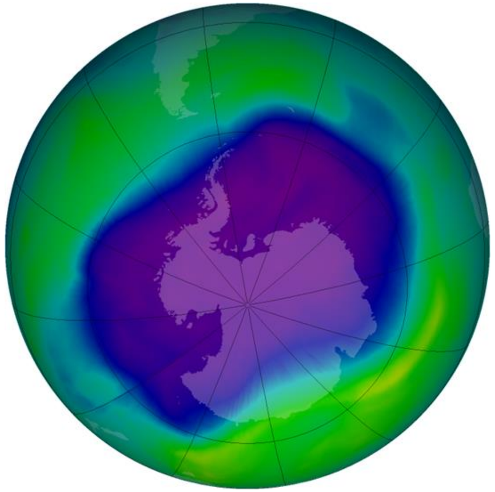
Ozone O_3

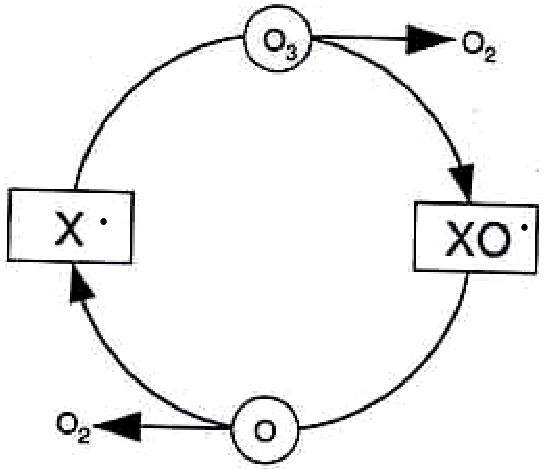
2. Halogenated derivatives

- stratospheric (≠ tropospheric) ozone:
    - maximum abundance is at an altitude of ~ 30 km
    - the ozone layer filters UV at λ < 310 nm
    - O_2/O_3 equilibrium at ~ 30 km, but global ozone levels fell by 4% between 1980 and 2000

$$3\,O_2 \underset{\lambda < 1180\text{ nm}}{\overset{\lambda < 242\text{ nm}}{\rightleftarrows}} 2\,O_3$$



- degradation of stratospheric ozone:
    - reactive species : $X^{\cdot}$ ($HO^{\cdot}$, $Cl^{\cdot}$, $NO^{\cdot}$)
    - act as a *catalyst* for ozone degradation



$$O_3 \xrightarrow{\lambda < 1180\text{ nm}} O_2 + O$$

$$X^{\cdot} + O_3 \rightarrow XO^{\cdot} + O_2$$

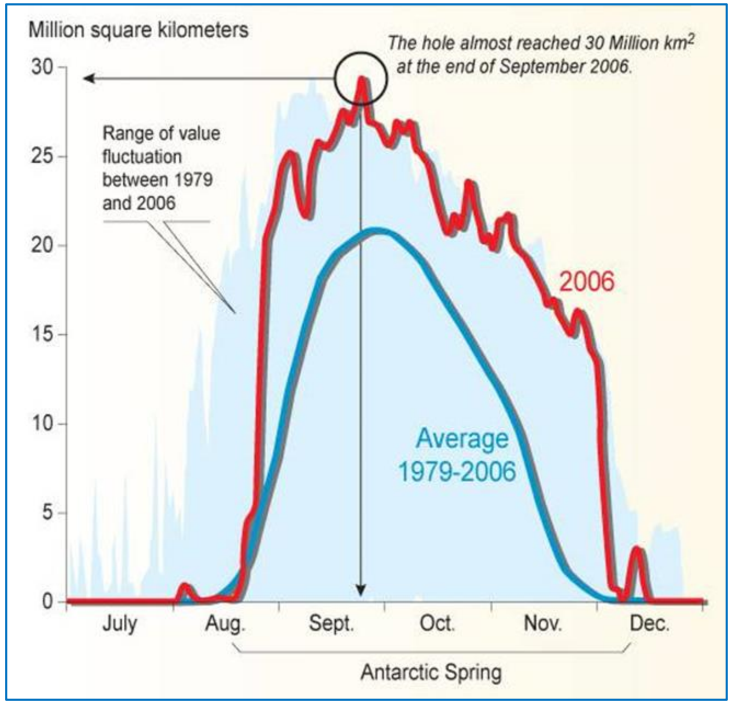
$$XO^{\cdot} + O \rightarrow X^{\cdot} + O_2$$

$$O_3 + O \rightarrow 2\,O_2$$

$$2\,O_3 \rightarrow 3\,O_2$$

Nobel price in Chemistry 1995

Paul J. Crutzen
Mario J. Molina
F. Sherwood Rowland



Ozone O_3

2. Halogenated derivatives

- **HO_x**: $HO^\cdot/HO_2^\cdot$ (hydroxyle/perhydroxyle radicals)

λ < 1180 nm

$$O_3 \rightarrow O_2 + O$$
$$HO^\cdot + O_3 \rightarrow HO_2^\cdot + O_2$$
$$HO_2^\cdot + O \rightarrow HO^\cdot + O_2$$
$$2\,O_3 \rightarrow 3\,O_2$$

$HO_2^\cdot$ can also degrade ozone: $HO_2^\cdot + O_3 \rightarrow HO^\cdot + 2\,O_2$

- **$NO_x^\cdot$**: $NO^\cdot/NO_2^\cdot$ (come from the oxidation of atmospheric nitrogen)

But today it is mainly N_2O !

λ < 1180 nm

$$O_3 \rightarrow O_2 + O$$
$$NO^\cdot + O_3 \rightarrow NO_2^\cdot + O_2$$
$$NO_2^\cdot + O \rightarrow NO^\cdot + O_2$$
$$2\,O_3 \rightarrow 3\,O_2$$

Nitrous Oxide (N2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century
A. R. Ravishankara, *et al.*
Science **326**, 123 (2009);
DOI: 10.1126/science.1176985

Not covered by the Montreal Protocol...

- **$ClO_x^\cdot$**: $Cl^\cdot/ClO^\cdot$

λ < 1180 nm

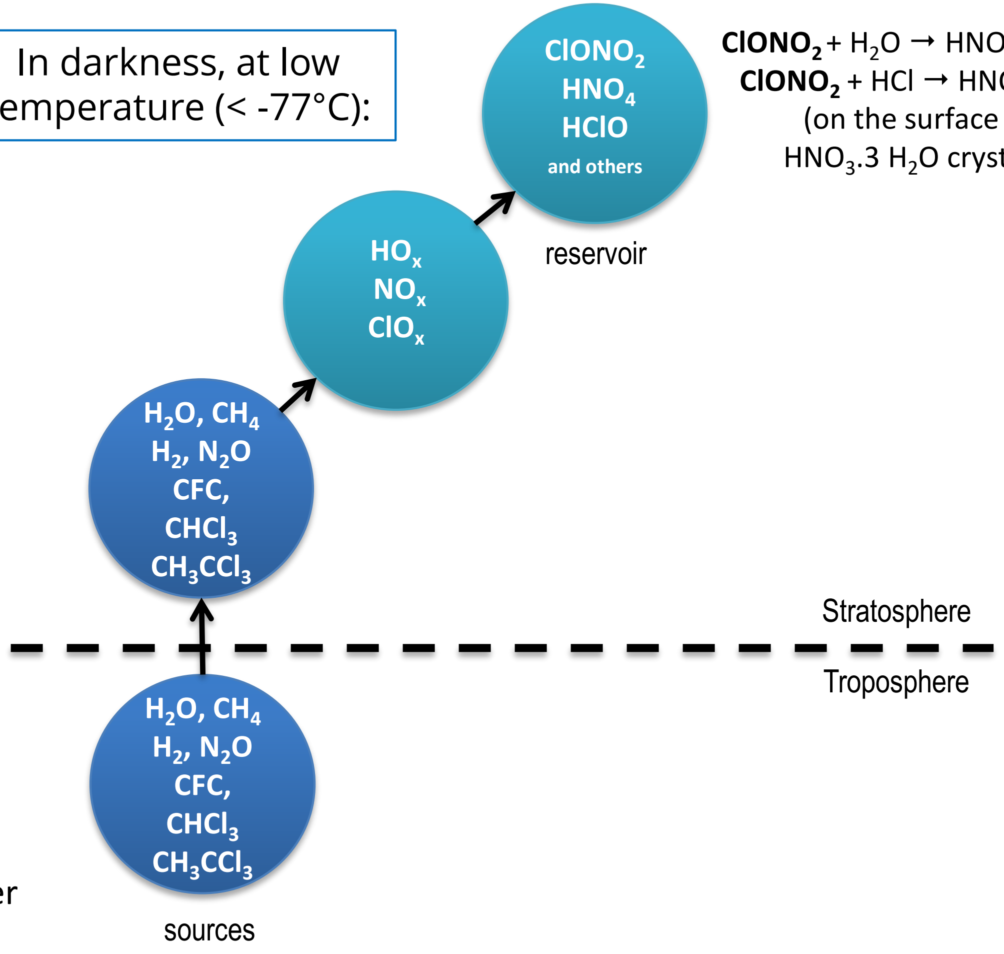
$$O_3 \rightarrow O_2 + O$$
$$Cl^\cdot + O_3 \rightarrow ClO^\cdot + O_2$$
$$ClO^\cdot + O \rightarrow Cl^\cdot + O_2$$
$$2\,O_3 \rightarrow 3\,O_2$$

- The sources of $Cl^\cdot$ are:

-aerosols (NaCl crystals): minor effect
-CH_3Cl from the slow combustion of organic matter or produced by certain algae
-CFCs: highly stable, easily reaching the stratosphere

- Bromine reacts in the same way.

In darkness, at low temperature (< -77°C):



$$\mathbf{ClONO_2} + H_2O \rightarrow HNO_3 + \mathbf{HOCl}$$
$$\mathbf{ClONO_2} + HCl \rightarrow HNO_3 + \mathbf{Cl_2}$$
(on the surface of $HNO_3.3\,H_2O$ crystals)

Ozone O_3

2. Halogenated derivatives

- **HO_x**: $HO^\cdot/HO_2^\cdot$ (hydroxyle/perhydroxyle radicals)

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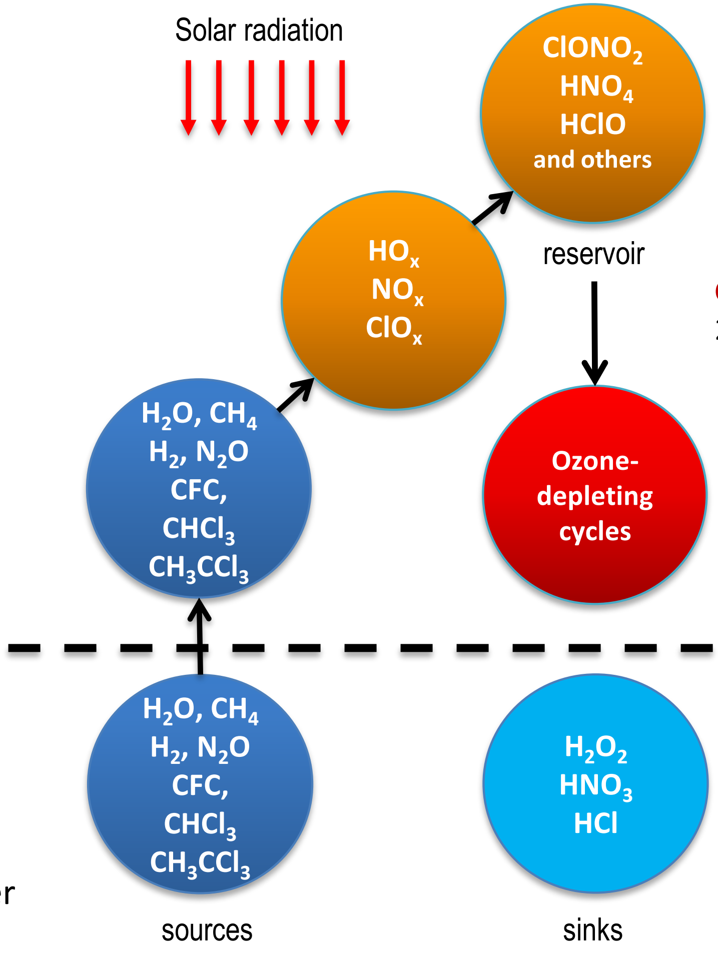


$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$
$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2$
(on the surface of $HNO_3.3\ H_2O$ crystals)

$Cl_2 + h\nu \rightarrow Cl^\cdot + Cl^\cdot$
$2\ HOCl + h\nu \rightarrow ClO^\cdot + HCl + OH^\cdot$

$$O_3 \rightarrow O_2 + O$$
$$Cl^\cdot + O_3 \rightarrow ClO^\cdot + O_2$$
$$ClO^\cdot + O \rightarrow Cl^\cdot + O_2$$
$$2\ O_3 \rightarrow 3\ O_2$$

CFC, HCFC, HFC and others

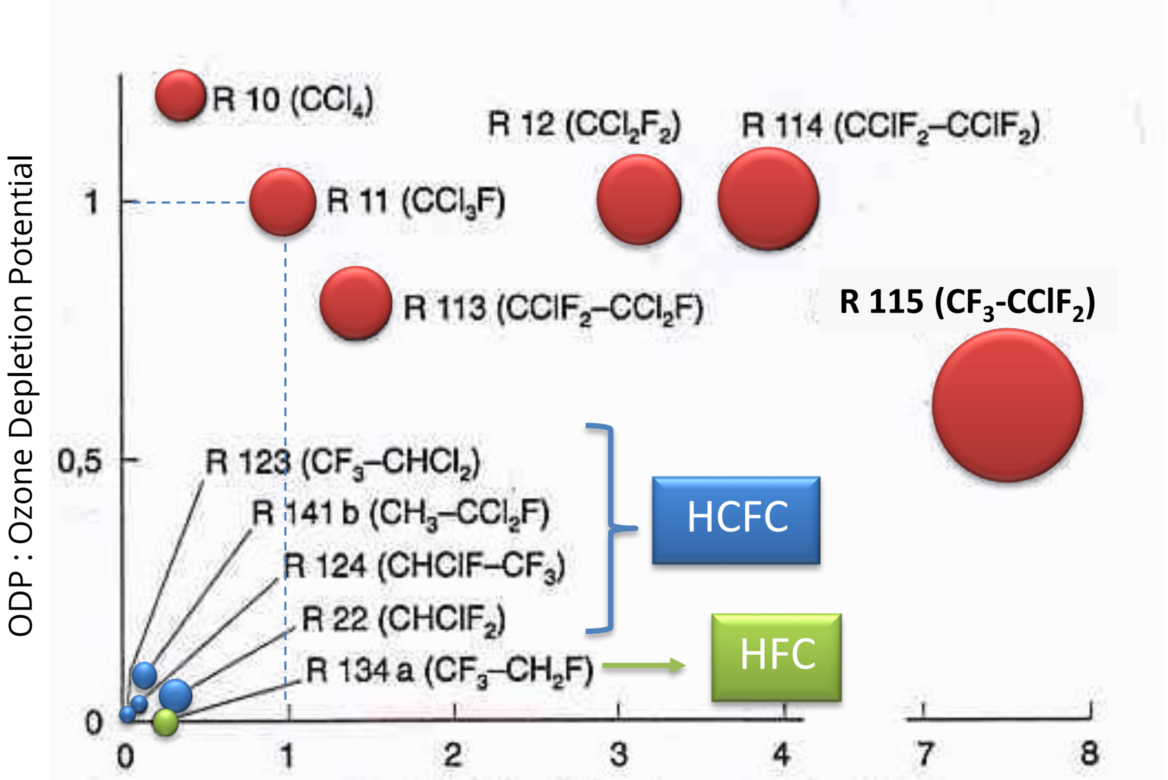
2. Halogenated derivatives

- **CFC (ChloroFluoroCarbons) and Halons***
  - banned Sep. 16, 1987 (Montreal Protocol)
  - Emerging countries: production authorized until 2010
- **HCFC** (**H**ydro**C**hloro**F**luoro**C**arbons)
  - banned Jan. 1st, 2015
- **HFC** (**H**ydro**F**luoro**C**arbons)
  - banned Oct. 15, 2016 (→2025)
- **pentane** & **cyclohexane**
  - foams
- **propane** & **butane**
  - propulsion
- **cyclopentane**
  - cooling systems

Flammable!

* Halon 1211 : CF_2ClBr
Halon 1301 : CF_3Br
Halon 2402 : $C_2F_4Br_2$

- fire retardants and extinguishers
- 10 times worse than CFCs!



GWP: Global Warming Potential

circle size = f(lifetime)

Reference = R11

(but $GWP^{R11} = 4750 \times GWP^{CO_2}$)

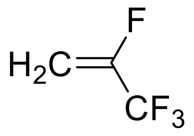
CFC, HCFC, HFC and others

2. Halogenated derivatives

HFO : HydroFluoroOlefins (HCFO : HydroChloroFluoroOlefins)

Example : R-**1234yf** ➡ 2,3,3,3-tetrafluoropropene (HFO-1234yf)

-new refrigerant gas for air conditioning (cars)
-European directive 2006/40/EC (in force since 2011)

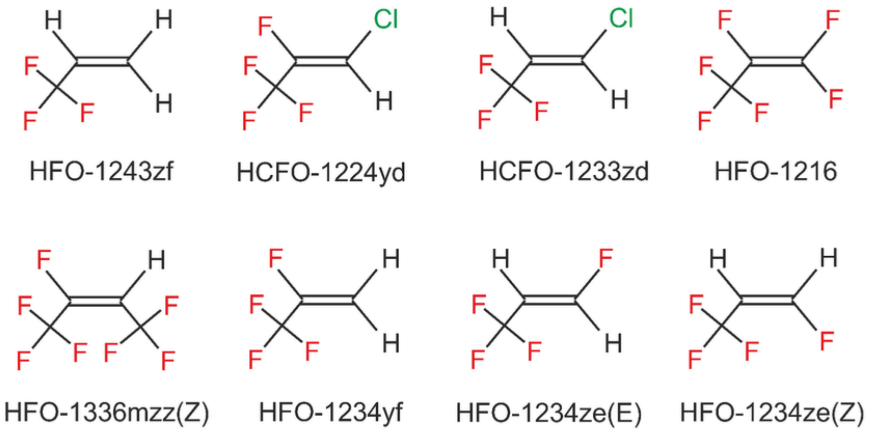


- ODP = 0
- GWP = 4
- t ½ life = 13 days
- flammable

-replace R-134a:

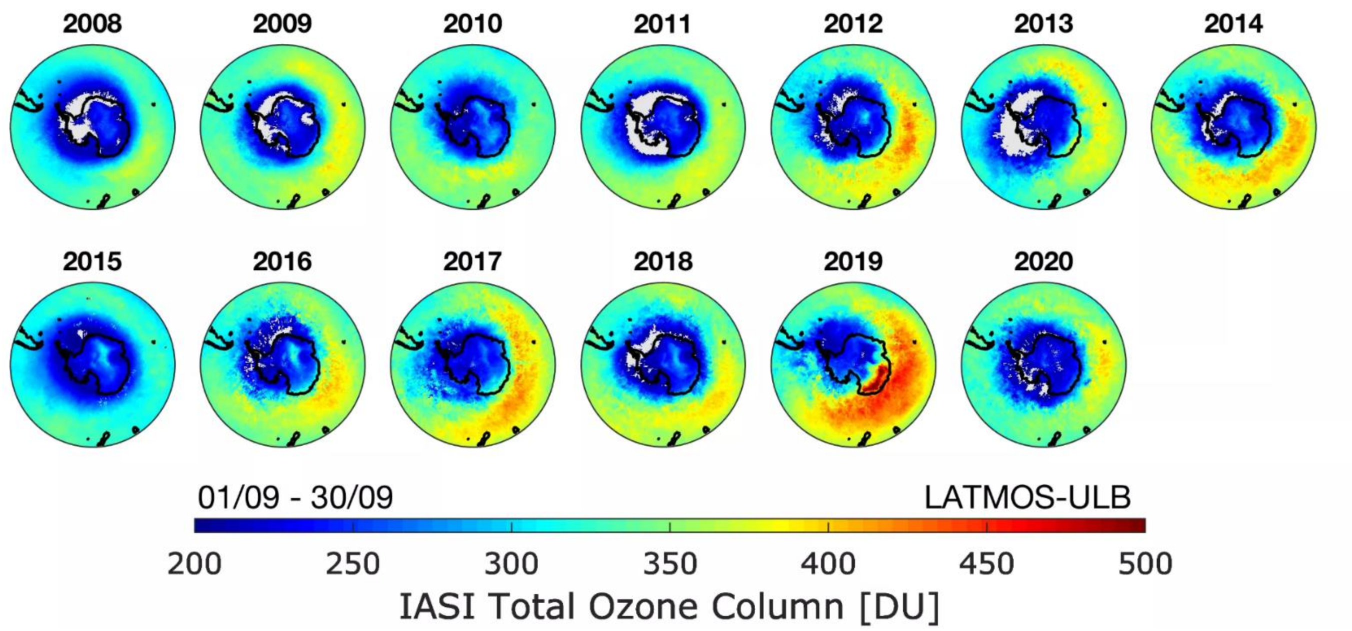
F_3C-CH_2F

- ODP = 0
- GWP = 1340
- t ½ life = 14 years
- flammable



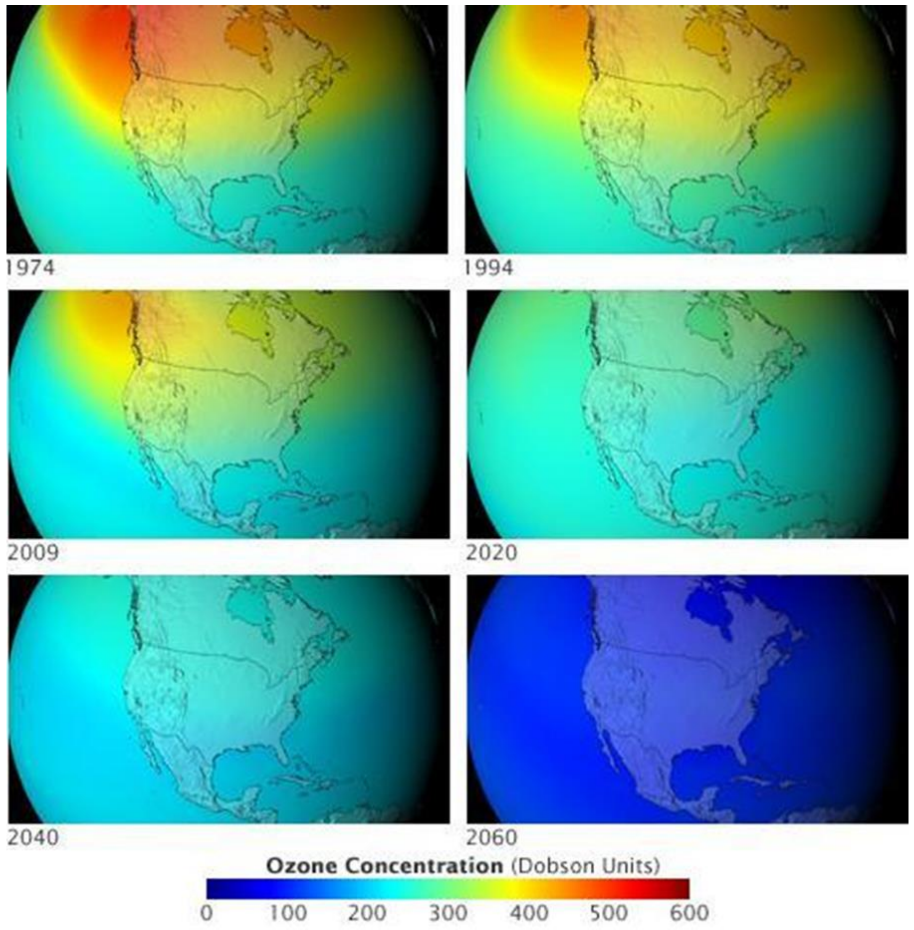
CFC, HCFC, HFC and others

2. Halogenated derivatives



Laboratory « ATMosphères et Observations Spatiales" (LATMOS-IPSL, CNRS/UVSQ-UPSay/Sorbonne Univ./CNES)

If we had done nothing!



- 37 years after Montreal: successful mobilization (stabilization since 1995)
- But it will take a long time to get back to where we were:
  - the average residence time of CFCs/halons in the atmosphere is very long
  - some manufacturers are still using CFCs/halons despite the ban*
  - global warming interferes with ozone regeneration

**An unexpected and persistent increase in global emissions of ozone-depleting CFC-11.*
James W. Elkins et al., *Nature* (2018) *557*, 413–417

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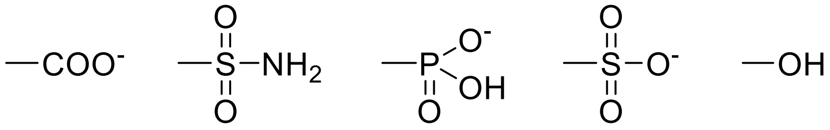
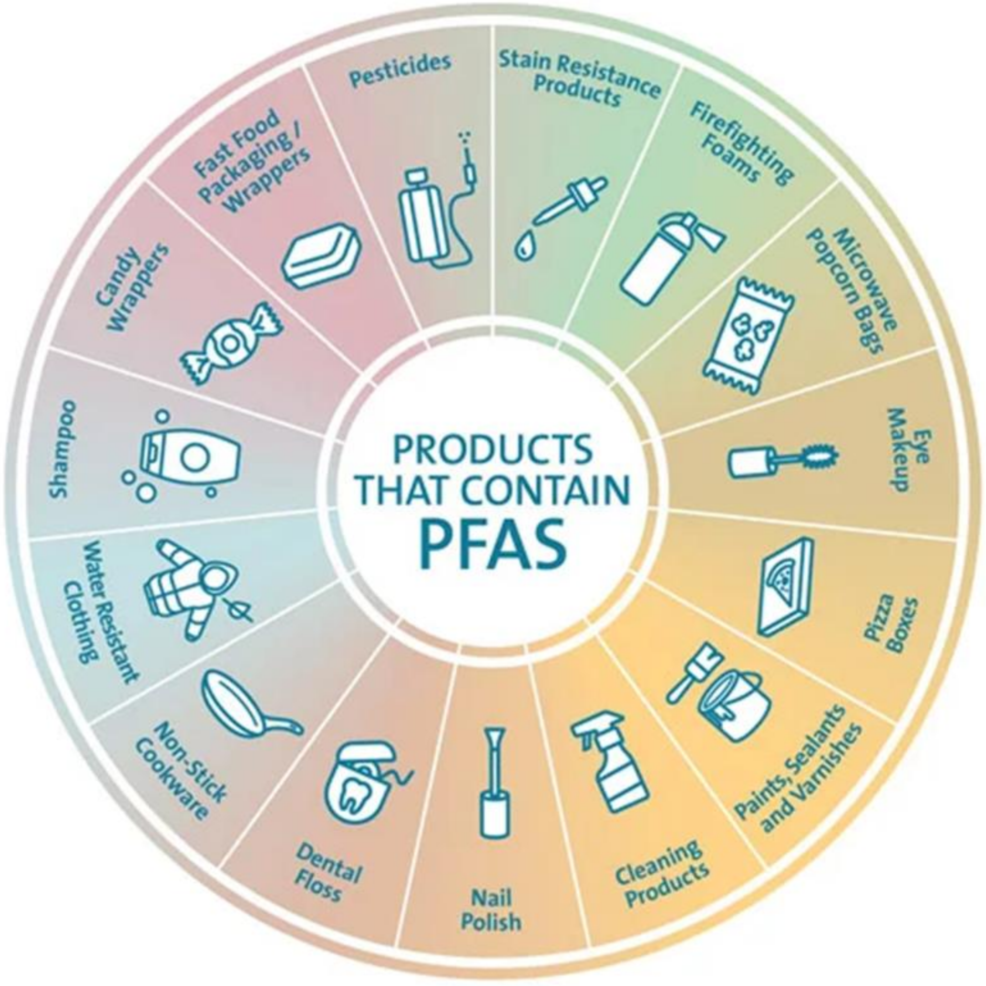
2. Halogenated derivatives

Per/poly-fluoroalkyl substances PFAS

- generic term for highly fluorinated aliphatic substances
- consisting of at least one fully fluorinated carbon atom (-CF_2-)
- partially or fully fluorinated alkyl chain
- generally contains a terminal functional group: carboxylate, sulfonamide, phosphonate, sulfonate, alcohol...



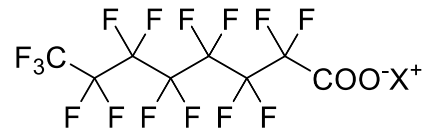
- approx. *5,000* different PFAS currently on the market
- non-stick, heat-resistant and waterproofing properties
- categories: short chains (< C6), long chains...
- thermodynamically *stable C-F bond* (up to 130 kcal/mol)
- highly resistant to:
    - hydrolysis, metabolism, photolysis, general degradation (POPs)
    - non-flammable
- used in many everyday products
- variable toxicity, bioaccumulable, biomagnifiable
- surface-active properties for the most part
- currently unregulated in France
- only a few PFAS are banned under the Stockholm Convention



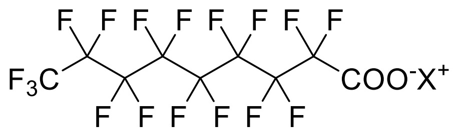
2. Halogenated derivatives

Per/poly-fluoroalkyl substances PFAS

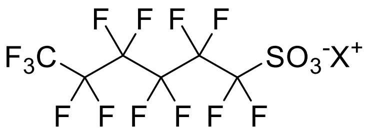
- PFASs
  - Non-polymers
    - **Perfluoroalkyl acids (PFAAs)** CnF2n+1R
      - Perfluoroalkyl carboxylic acids (PFCAs)
      - Perfluoroalkane sulfonic acids (PFSAs)
      - Perfluoroalkyl phosphonic acids (PFPAs)
      - Perfluoroalkyl phosphinic acids (PFPIAs)
    - **Perfluoroalkane sulfonyl fluoride (PASF)** CnF2n+1SO2F → **PASF-based derivatives** CnF2n+1SO2-R, R = NH, NHCH2CH2OH, etc.
    - **Perfluoroalkyl iodides (PFAIs)** CnF2n+1I → **Fluorotelomer iodoes (FTIs)** CnF2n+1CH2CH2I → **FT-based derivatives** CnF2n+1CH2CH2-R, R = NH, NHCH2CH2OH, etc.
    - **Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives** – Polyfluoroalkyl ether carboxylic acids
  - Polymers
    - **Fluoropolymers** — Polytetrafluoroethylene (PTFE), Polyvinylidene fluoride (PVDF), Fluorinated ethylene propylene (FEP), Perfluoroalkoxyl polymer (PFA), etc.
    - **Side-chain fluorinated polymers** — Fluorinated (meth)acrylate polymers, Fluorinated urethane polymers, Fluorinated oxetane polymers
    - **Perfluoropolyethers**



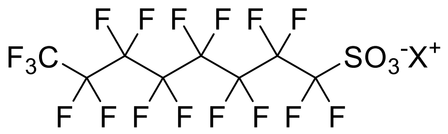
PFOA



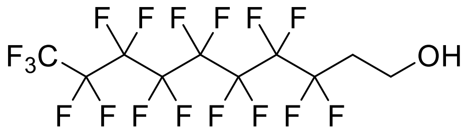
PFNA



PFHxS



PFOS



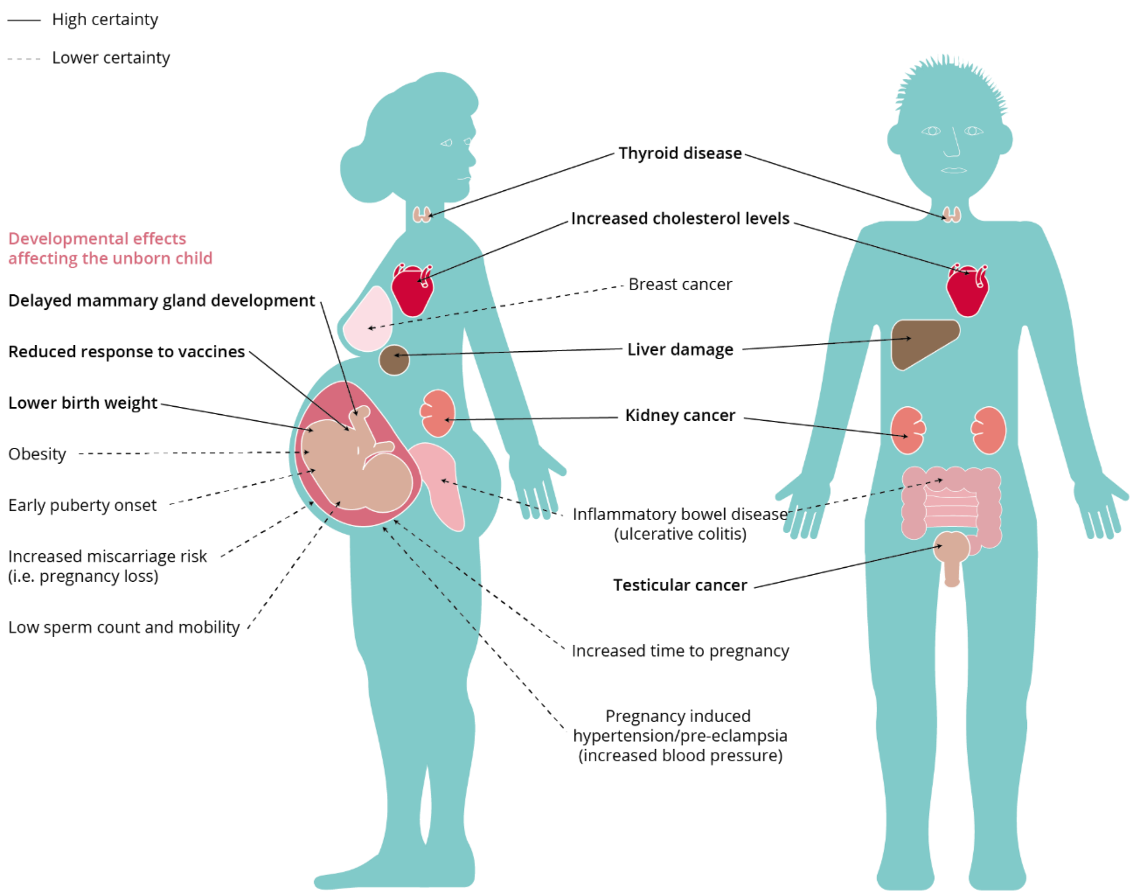
8:2 FTOH

Source : EOCD 2013, UPDS 2021

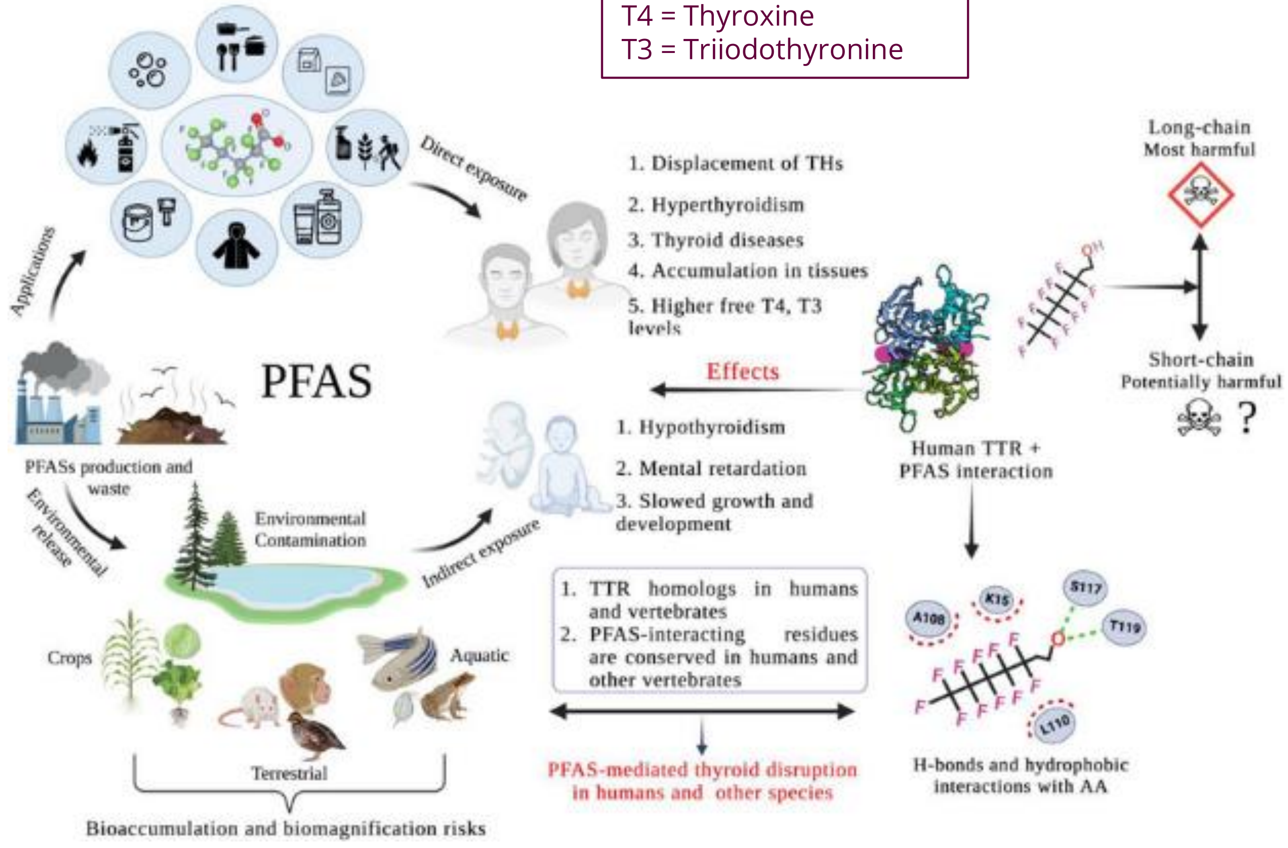
2. Halogenated derivatives

Per/poly-fluoroalkyl substances PFAS

THs = Thyroid hormones
TTR = Transthyretin
T4 = Thyroxine
T3 = Triiodothyronine



Sources : US National Toxicology Program (2016), C8 Health Project Reports (2012), CIRC OMS (2017)



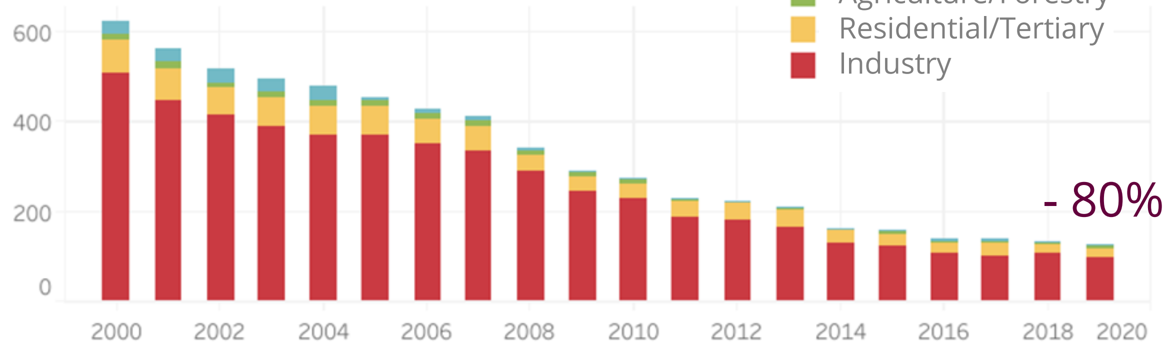
Source : *Archives of Toxicology* **2023**, *97*, 755-768

Metallurgy and SO_2

3. Metallurgy and Trace Metallic Elements

- Extractive metallurgy:
  - all the physical, chemical, calorific and electrolytic treatments that ores undergo to extract metals.
- Pyrometallurgy:
  - *thermal treatment* of minerals and metallurgical ores to enable recovery of valuable metals (roasting/smelting).
  - *metal sulfides* ➞ release of SO_2 ➞ toxicity, acid rains, soil acidification...

Atmospheric SO_2 emissions by sector in France in kt



- ➢ Helsinki Protocole (1985): emission of sulfur compounds
- ➢ Oslo Protocole (1994): acid rain control

$$Fe_2O_3 + 3\,CO \xrightarrow{1300\,°C} 2\,Fe + 3\,CO_2$$
hematite

$$PbS + \frac{3}{2}O_2 \xrightarrow{1000\,°C} PbO + SO_2$$
galena

$$ZnS + \frac{3}{2}O_2 \xrightarrow{1000\,°C} ZnO + SO_2$$
blende

$$HgS + O_2 \xrightarrow{1000\,°C} Hg^0 + SO_2$$
cinnabar

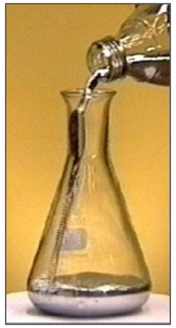
Great Smog of London, Dec. 1952 ➞ 12,000 death

Mercury

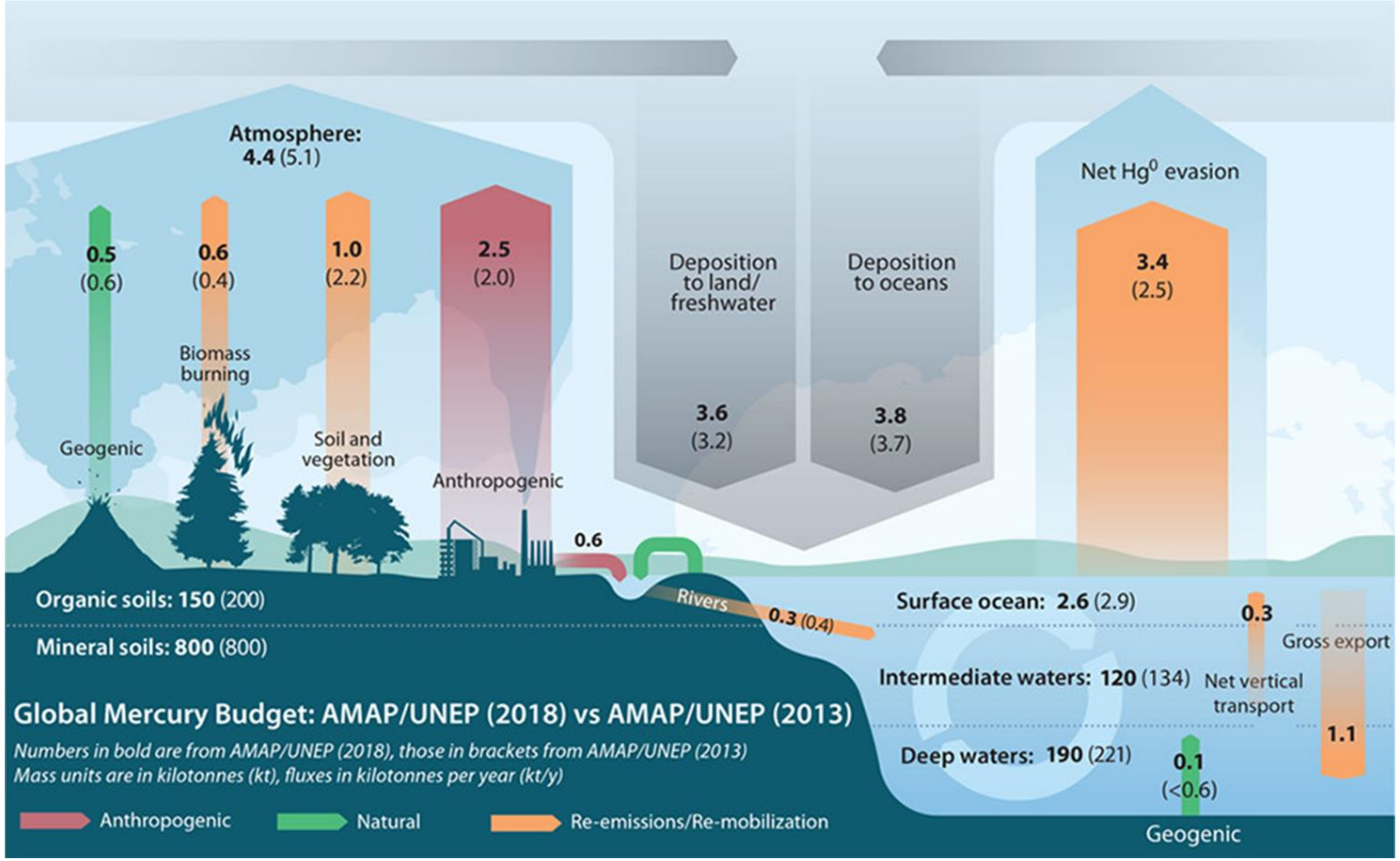
3. Metallurgy and Trace Metallic Elements

- Trace metalllic elements (TME/ETM):
  - historically: heavy metals
  - metal in low concentration
    - terrestrial crust: < 1‰
    - living being: < 0.1‰
  - toxicity = f(nature, speciation, oxidation state)
  - most toxic TME for plants/animals: **Hg**, **Pb**, **Cd**

- **Mercury (Hg)**
  - only liquid metal at room temperature
  - very volatile
  - highly toxic for living beings:
    - VME $Hg^0/HgO/HgCl_2$ (inhalation): 20 µg/m³
    - lifetime : brain = 1 yr, body = 30-60 days
    - VME $Hg^{+/2+}$ (oral):
      - 0.1 µg/kg/day (alkyl cpds)
      - 2.0 µg/kg/day (inorganic cpds)
    - Concentration:
      - volcanic fumes = 40 µg/m³
      - clean atmosphere = 2.5 µg/m³
      - coal = 0.3 ppm, oil = 3.5 ppm
      - clean soil = 0.1-2 ppm



Global mercury cycle (2018)

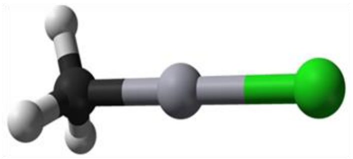


Mercury

3. Metallurgy and Trace Metallic Elements

MINAMATA CONVENTION ON MERCURY

10 Oct. 2013

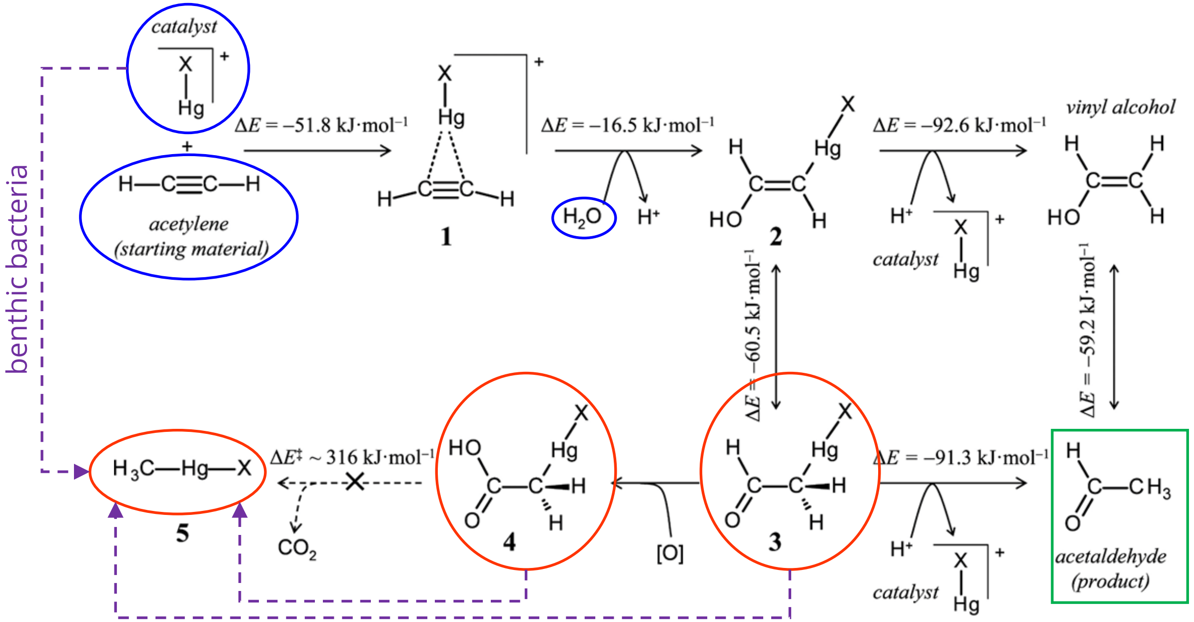


Methylmercury : CH_3Hg^+, X^-

Increase of the concentration of a toxic substance:

- in an organism ➔ **bioaccumulation** (bioconcentration)
- throughout the trophic chain ➔ **Biomagnification** (bioamplification)
  - biomagnification factor up to 10^6!

Minamata tragedy (Japan, Chisso plant, 1956-1966)



Environ. Sci. Technol. **2020**, *54*, 2726

Direct anthropogenic atmospheric emissions of Hg^0 (1960 t, 2010) :

- **Gold panning :** 37% (725 t)
- **Combustion of fossil fuels (coal/oil):** 25% (490 t)
  - -coal: 0.2 mg Hg/kg (essential emissions)
  - -oil: 3.5 mg Hg/kg ➔ 60 t/a of eq. Hg in the atmosphere
- **Metal industry:** 18% (353 t)
- **Cement and chlorine industries:** 10% (196 t)
  - -limestone : 0.2 to 2.3 mg Hg/kg
- **Combustion of household waste :** 5% (98 t)
- **Dental office rejects/Cremations (!) :**
  - -dental amalgam ban in France... ?
  - (Minamata convention, 2013)

Lead

3. Metallurgy and Trace Metallic Elements

- Lead (Pb)
  - highly toxic to living organisms:
    - daily human intake: 0.35 mg/day
    - lifetime in blood: 15-30 days
    - lifetime in the skeleton: 20 days
    - Mean exposure value (VME): 0.15 mg/m^3
  - sources:
    - natural = 70 Kt/yr (volcanos, soils, biomass…)
    - anthropic = 130 Kt/an

Galena (PbS)

- Pb metal
  - accumulators and batteries (80%!)
  - water pipes (replaced…)
  - tin solder alloys (Sn 62%, Pb 32%)
  - roofing materials: cf ND de Paris!
  - hunting lead (alloy: 1.5% Sb, 0.8% As)

→ Water pollution
Risk of direct poisoning

- Inorganic compounds
  - anti-rust paint for Pb_3O_4 (minium) steels
  - paint, varnish, mastic and PVC colorants: $Pb(OH)_2.PbCO_3$, $PbCrO_4$, $PbMoO_4$, PbO
  - leaded glass, crystal: PbO
  - tobacco (lead arsenate)
  - fertilizers (impurities in superphosphates)

→ banned for professionals in 1949…but used until 1993 (official ban)

- Organic compounds
  - Tetraethyl lead: $PbEt_4$ (anti-knock product in gasoline)

→ Air pollution, then water and sediment (rivers, estuaries, oceans)

Spectacular consequence of the $PbEt_4$ ban in US (1996) and Europe (2000)

Cadmium

3. Metallurgy and Trace Metallic Elements

- Cadmium (Cd)
  - highly toxic to living organisms:
    - daily human intake: 3 µg/day
    - lifetime in liver and kidneys: 10 years
    - lifetime in the skeleton: 20 days
    - VME: 0.05 mg/m^3

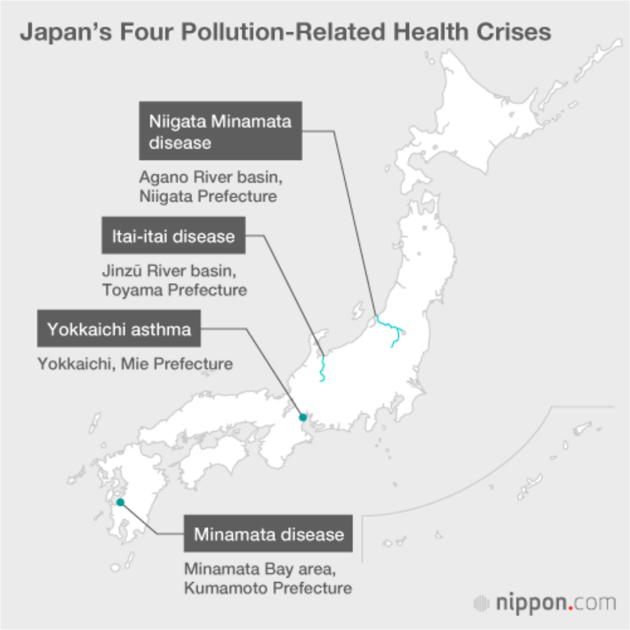
  - absorption into the body:
    - food (fish, shellfish, offal, cereals, vegetables)
    - natural presence of Cd in soils and **fertilizers**; accumulation in **leaves** (cabbage, lettuce, tobacco...)
    - tobacco: 20 cigarettes = 2 µg Cd (75% dose day)

  - Use of cadmium metal
    - rechargeable Ni-Cd batteries (86%!)
    - plating (surface treatment)
    - brazing alloys (Ag 50%, Cd 18%, Zn 16%, Cu 15%)
    - fuse alloy (Bi 50%, Pb 27%, Sn 13%, Cd 10%)
    - electronics and electrical engineering industry

→ Water pollution
Risk of direct poisoning → Disaster in Itai-itai (Toyoma, Japan, 1955)

- Inorganic compounds
  - paint and PVC colorants (CdS, CdSe)
  - plastic stabilizers (cadmium stearate)
  - impurity in phosphate fertilizers
  - spreading sludge

EC 2014: discussions on banning Cd pigments
REACH (4/2016): < 0.01% w/w (< 0.1% w/w if > 10% Zn)



III. Third cause of pollution: agricultural activities

1. Fertilizers
2. Pesticides

1. Fertilizers

Nitrogen cycle

- To be assimilated in **biomass**, nitrogen must be fixed (NH_3 or NO_3^-)
  - 3 biotic processes regulate the N cycle:
    - *fixation, nitrification, denitrification*
  - 2 physical processes are involved:
    - *volcanism, thunderstorms*
  - 1 chemical process developed:
    - *Haber process*

Atmospheric N_2 fixation

$N_2 + 8\,H^+ + 8\,e^- + 16\,ATP \rightarrow 2\,NH_3 + H_2 + 16\,ADP/P$

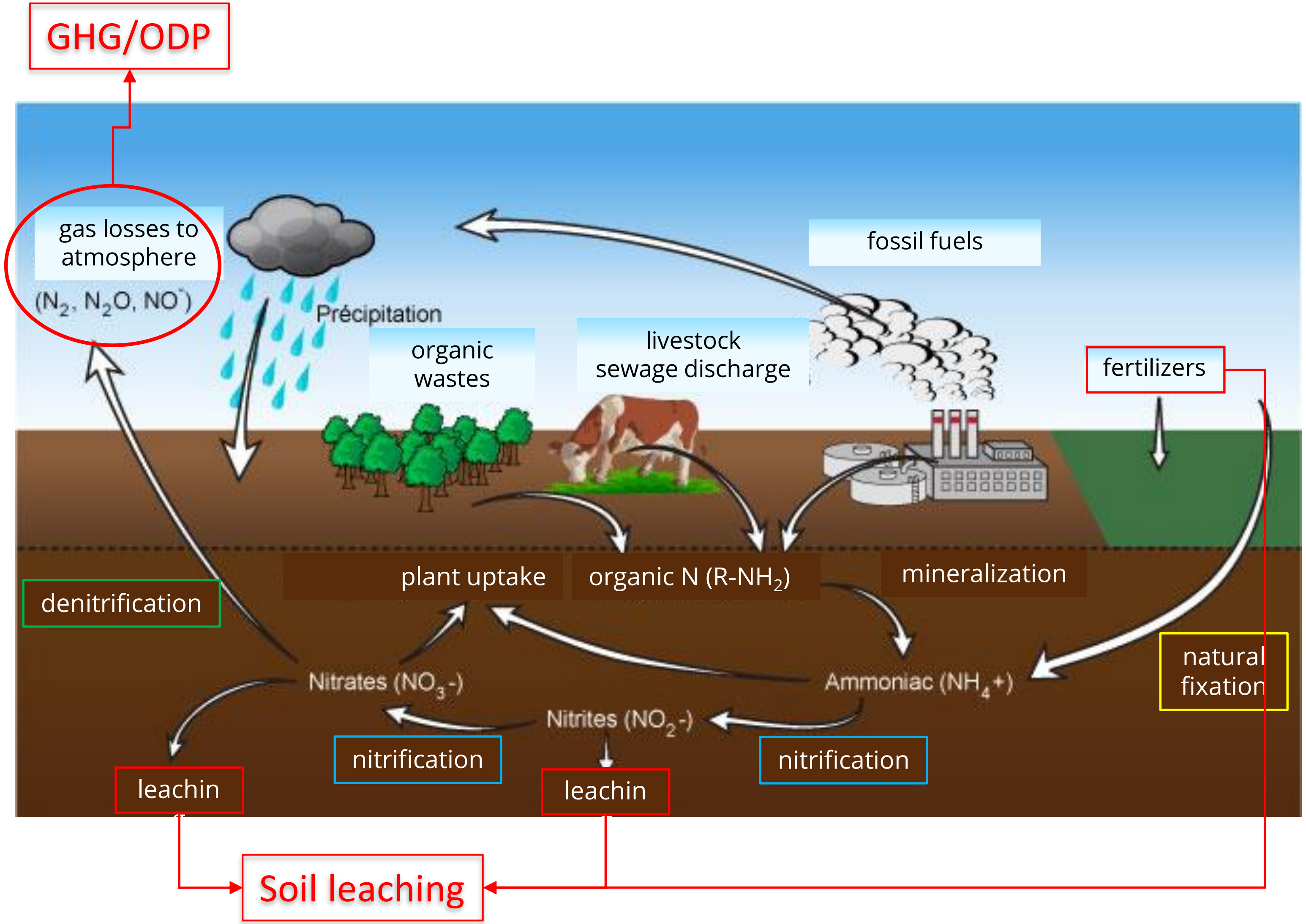
Nitrification

$NH_3 + O_2 \rightarrow NO_2^- + 3\,H^+ + 2\,e^-$

$NO_2^- + H_2O \rightarrow NO_3^- + 2\,H^+ + 2\,e^-$

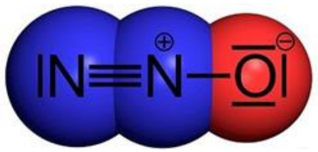
Denitrification

$NO_3^- \rightarrow NO_2^- \rightarrow NO\cdot \rightarrow N_2O \rightarrow N_2$



Source : Visionlearning 2000-2009

Nitrogen protoxide



1. Fertilizers

- nitrous oxide
- euphoric gas, anesthetic, oxidizer rocket engine
- results from biological reactions (denitrification in anoxia)
- stable in the troposphere (as destroyed by photolysis at $\lambda < 400$ nm)
- GHG ($GWP_{100\ years} = 265$)
- decomposes in the stratosphere:

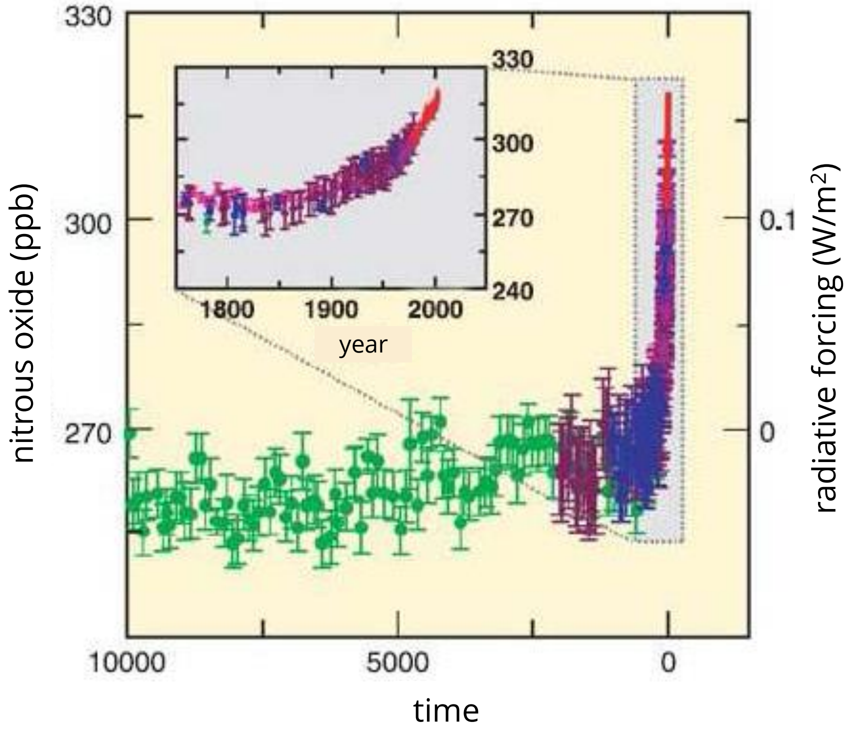
$$N_2O + h\nu \longrightarrow N_2 + O^{1D}$$

$$N_2O + O^{1D} \longrightarrow N_2 + O_2 \quad 95\%$$

$$N_2O + O^{1D} \longrightarrow 2\,NO^{\cdot} \quad 5\%$$

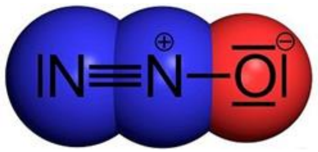
vs O_3 stratos. !

N_2O sources	TgN / yr
Natural sources:	**6.5**
-soils	4.5
-oceans	2
Anthropic sources:	**8**
-fossil fuels	1.2
-biomass combustion	0.5
-fertilization	6.3
Total	**14.5**



- $[N_2O]$ increases by 0.8 ppbv/year (intensive use of nitrogen fertilizers since 1950)

Nitrogen protoxide



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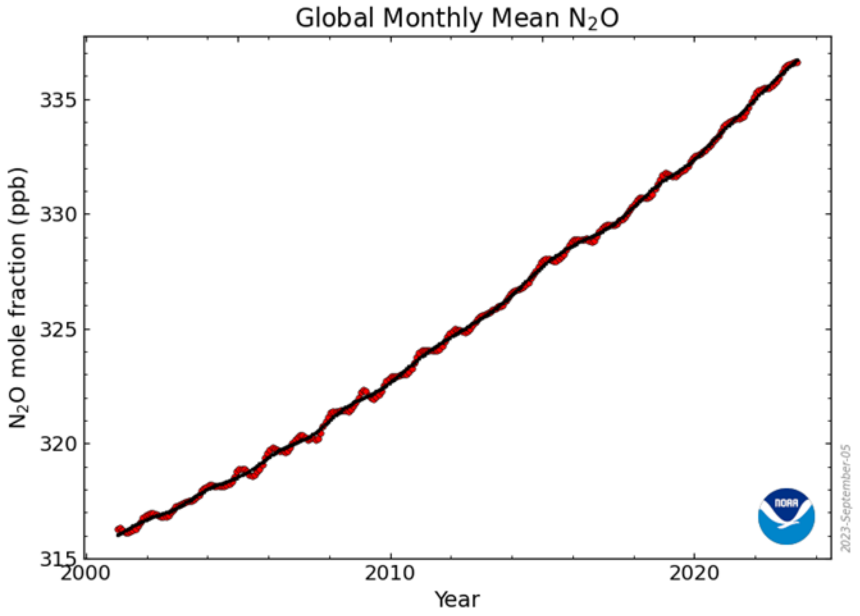

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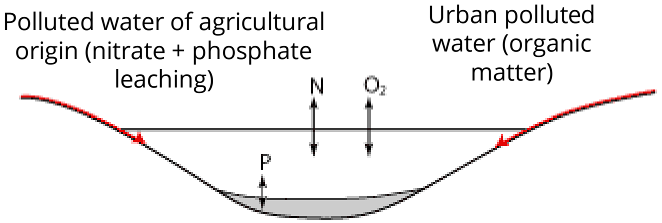
Phosphorous cycle – Eutrophisation/Dystrophisation

1. Fertilizers

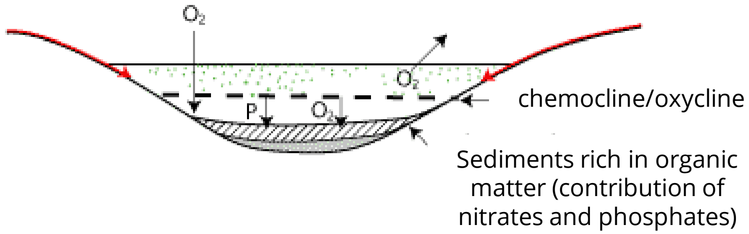
- element P is present in low concentrations in the biosphere (limiting factor in ecosystems)
- eutrophisation:
  - natural enrichment of an aquatic ecosystem with nutrients (nitrates, phosphates...)
  - *kinetic*: tens of thousands of years
- dystrophisation (or hyper-entrophication):
  - anthropogenic enrichment of an aquatic ecosystem with nutrients
  - *kinetic*: decades

Proliferation of algae and higher aquatic plants: green/red tide

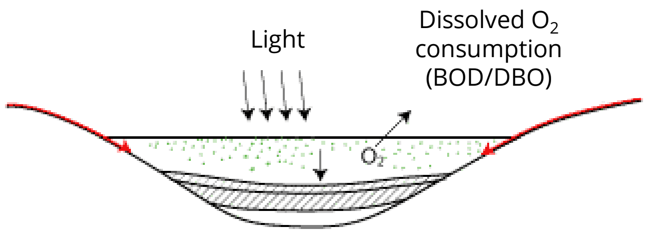
* Phenomenon favoured by:
- high temperatures
- high light levels
- low current
- homogeneous living conditions



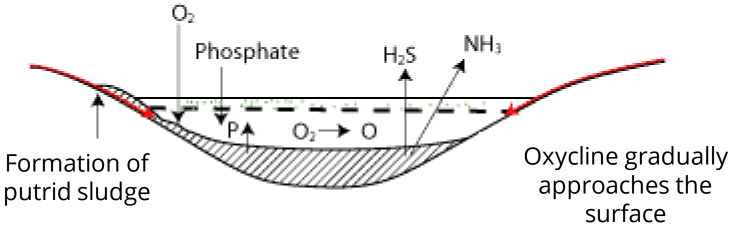
1. Nutrient supply



3. Death and aerobic decomposition of algae on the bottom



2. Algae bloom on the surface



4. Anaerobic fermentation: H_2S, NH_3

1. Fertilizers

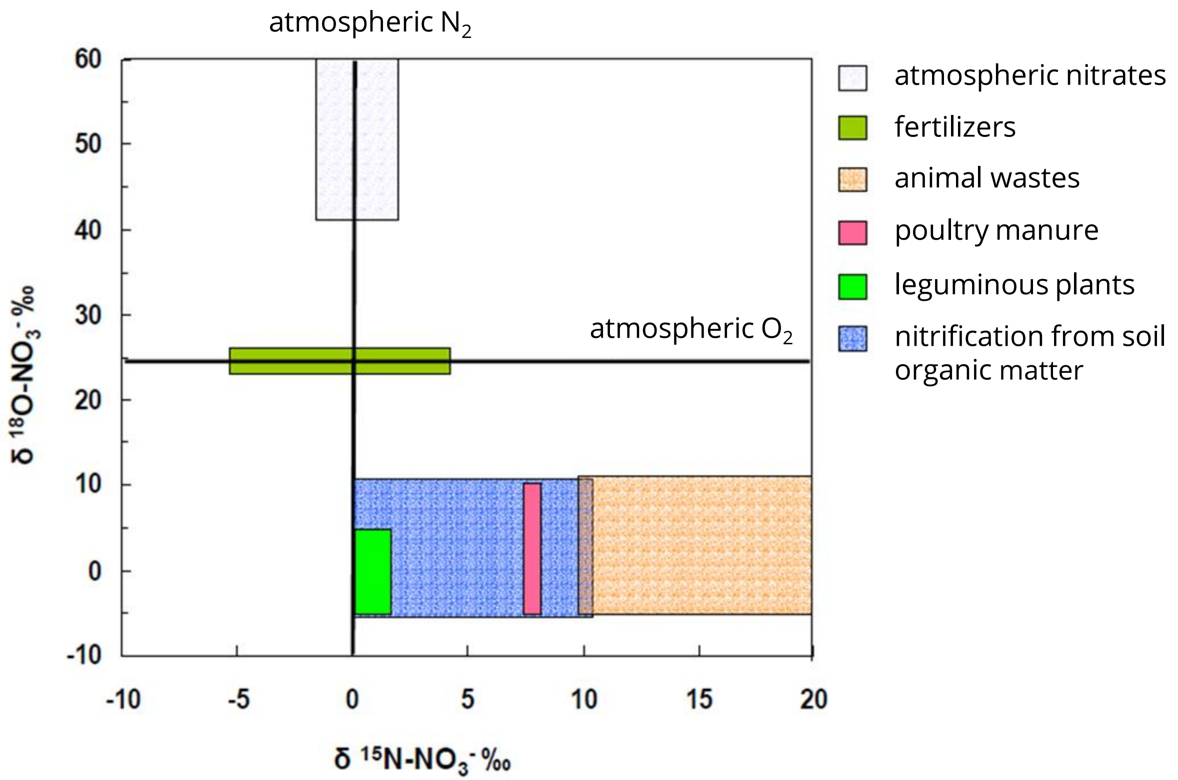
How do you know whether nitrates in surface water come from fertilizers or not?

$$\delta_{15N} = \left(\frac{[^{15}N]/[^{14}N]_{échantillon}}{[^{15}N]/[^{14}N]_{air}} - 1 \right) \times 1000$$

$$\delta_{18O} = \left(\frac{[^{18}O]/[^{16}O]_{échantillon}}{[^{18}O]/[^{16}O]_{air}} - 1 \right) \times 1000$$

Nitrates (**fertilizers**):
δ_{15N} = -5/+5‰
δ_{18O} = 23.5‰

Nitrates (**natural**):
δ_{15N} = 0/+20‰
δ_{18O} = -5/+10 ‰



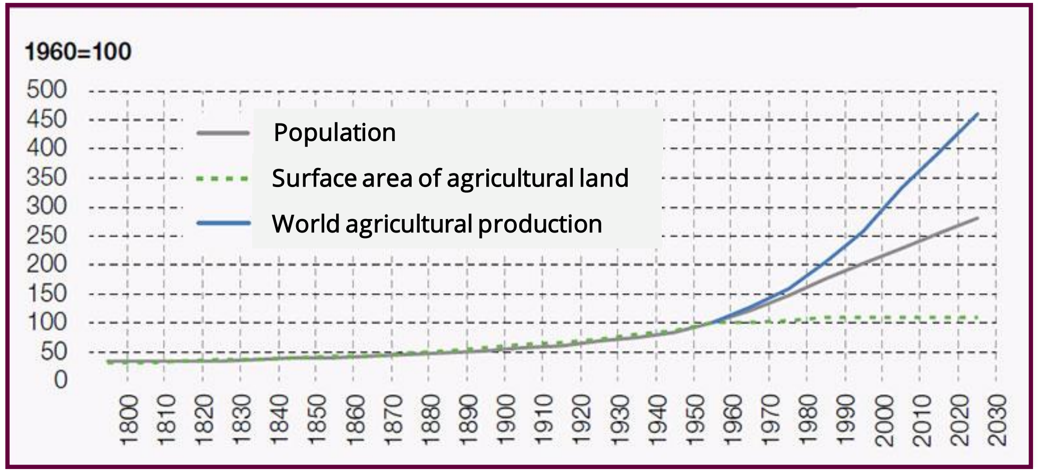
Intensive use of fertilizers – Environmental impacts

1. Fertilizers

- Nitrogen fertilizers:
  - NH_4NO_3, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, urea
- Phosphate fertilizers:
  - $Ca(H_2PO_4)_2$ (superphosphates), Thomas meal (bone, dried blood)
- Potassium salts:
  - KCl, K_2SO_4

- Fertilizers production:
  - energy consumption
  - consumption of non-renewable raw materials
  - large quantities (storage: AZF accident; transport)
- Fertilizers use:
  - dystrophization
  - soil pollution by TME

Global trends: agricultural production set to grow faster than population, with almost the same surface area



Source : OCDE (2019)

NO_3^- sources	Fixed N Gt NO_3^- / yr
Natural sources: -bacteria, lightstorms	140
Anthropic sources: -nitrated fertilizers -nitrifying crops (carrots, beets…) -biomass combustion -fossil fuel combustion -land clearing -drainage of wetlands	210 80 40 40 20 20 10

Alternatives

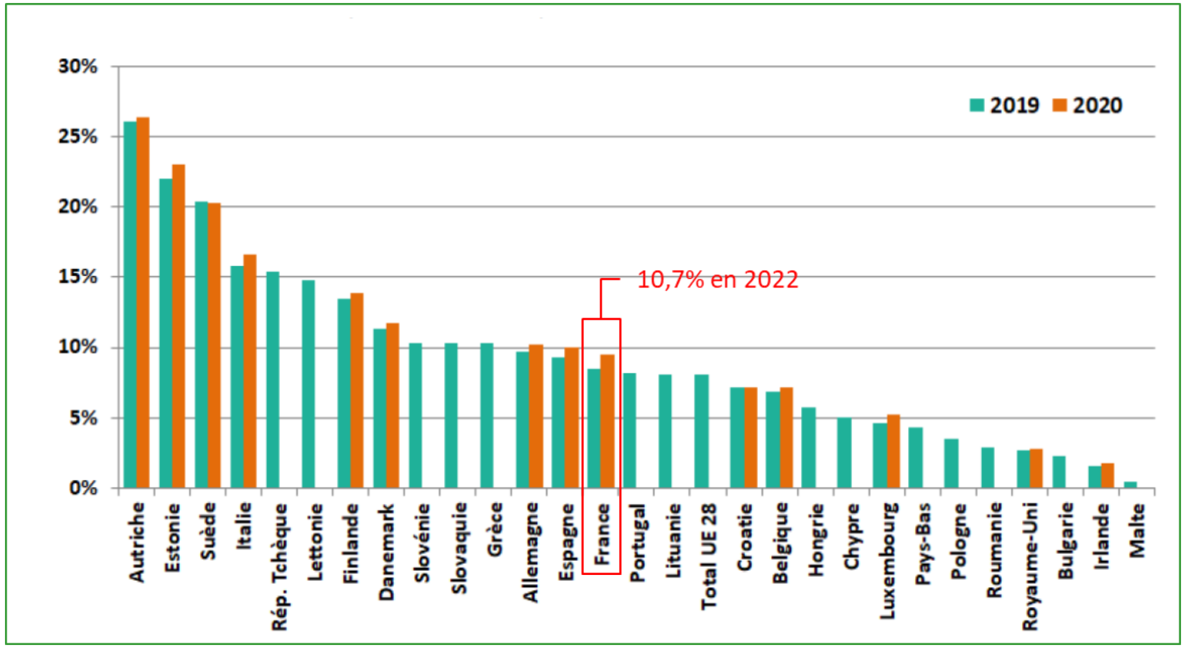
1. Fertilizers

- Organic/biological farming:
  - agricultural production system based on *rational soil management* for quality, balanced, more autonomous, more economical and non-polluting production:
    - respecting biological cycles and the environment
    - takes account of ecological knowledge

- Organic farming in France in 2022:
  - over 200,000 direct jobs
  - organic market :
    - + 50% vs 2015
    - - 4.6% vs 2021
  - sales = 12 billions €
  - useful agricultural area = 10,7%

- Rational/reasoned fertilization:
  - '*the right dose in the right place*'
  - part of the integrated agriculture
  - ≠ organic farming!

Percentage of useful agricultural area cultivated organically in the EU



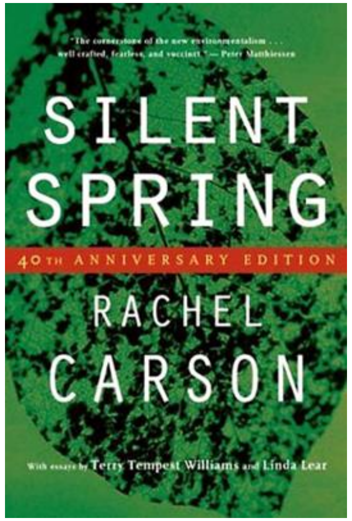
http://www.agencebio.org

Introduction

2. Pesticides

- pesticide:
  - chemical substance used to prevent, destroy, repel or mitigate animal and plant pests
- phytosanitary product:
  - a pest control product for agricultural and related uses designed to protect and/or cure plants
- biocide:
  - substance hazardous to all living organisms

- **insecticide**
- **herbicide**
- **fongicide**
- helicide
- corvicide
- nematocide
- rodonticide
- acaricide
- antimicrobial
- algicide
- anti-fooling agent



1962

Rachel CARSON
1907-1964
Biologist and writer

State of the art:

- pesticides are the only class of chemical pollutants deliberately dispersed in terrestrial ecosystems because of their toxicity!
- **90%** of pesticides applied do not reach their target! They are transferred to the air (**10%**), water (**5%**) and soil (**75%**).
- Specifications (challenge!) for a pesticide: selective in toxicity and rapidly degradable beyond its time of action.
- 468 authorized active ingredients (Europe, April 2021) in around 4,000 commercial specialties
- No. 1 consumer of crop protection products on the European market (18%): 100 to 61 kt (2001 to 2020)
- Europe's 10th-largest consumer in kg/Ha (3.4 kg/Ha in 2020)

➢ insecticide: carbamates – neonicotinoids
➢ herbicide: organochlorines – aminophosphate (glyphosate)

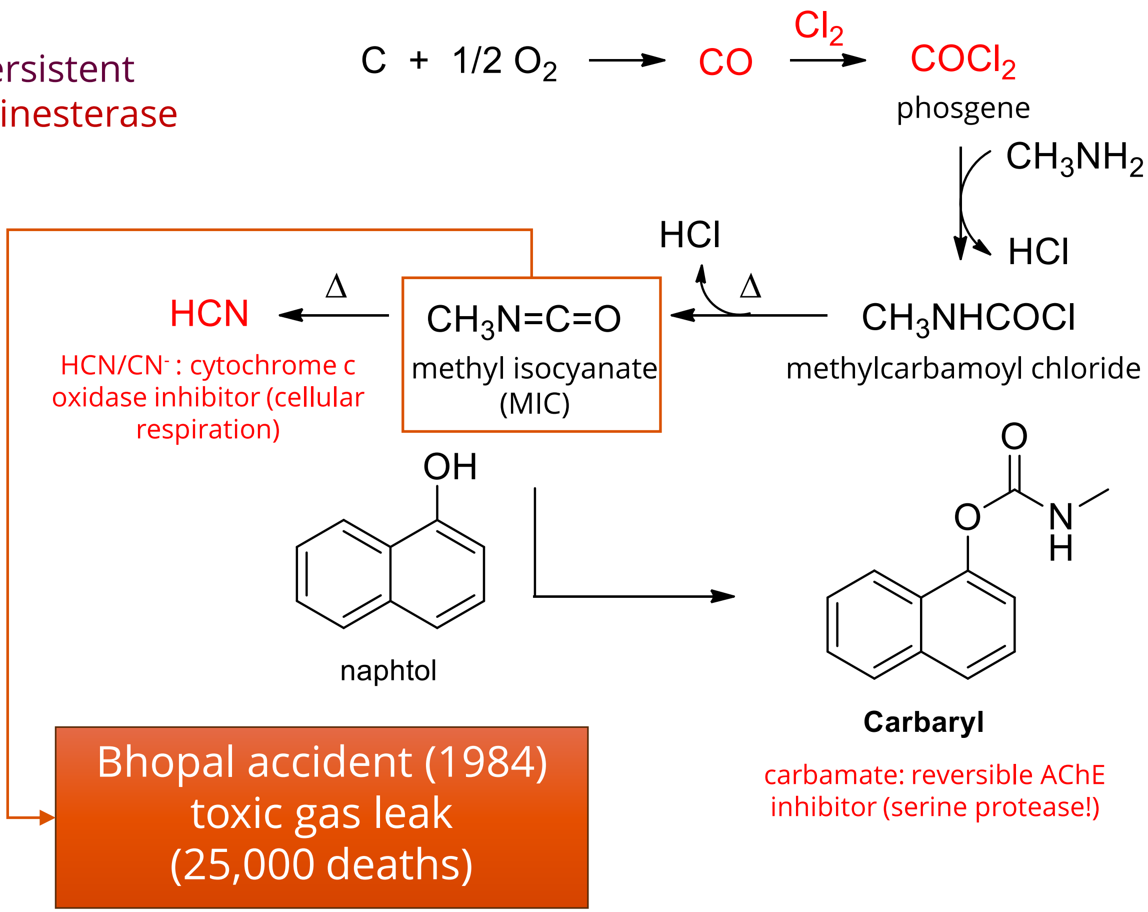
Insectides

2. Pesticides

- carbamates:
  - carbamic acid derivatives (RNHCOOR’)
  - relatively selective, do not accumulate in fat, not very persistent
  - toxic through action on the CNS: inhibition of acetylcholinesterase
  - toxic to mammals, kill bees (banned in Europe in 2007)

UNION CARBIDE / DOW Chemical

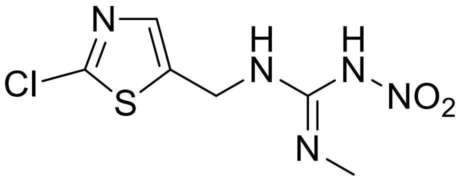
Carbaryl synthesis (Sevin)



Insectides

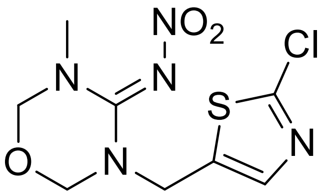
2. Pesticides

- neonicotinoids:
  - antagonist of nicotinic cholinergic receptors
  - neuronal hyperactivation and insect death
  - suspected of causing a decline in the honeybee population
  - ban in France in 2018, derogation in 2020, new ban in 2023 (EC justice)



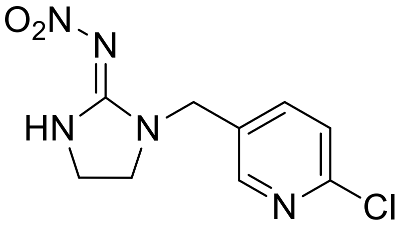
Clothianidine

Poncho®: never authorized in France



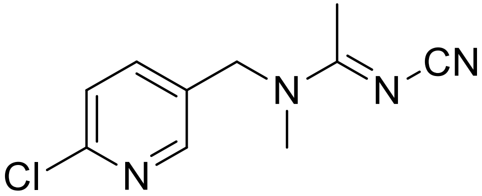
Thiamethoxam

Cruiser® : banned for colza in 2012



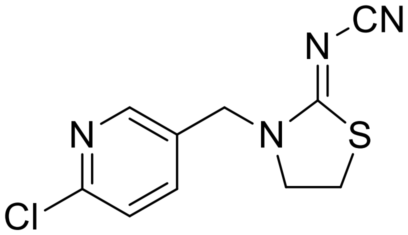
Imidaclopride

Gaucho®: banned for sunflowers in 1999, for corn in 2004



Acetamipride

Chipco®: authorized (toxic to bees)



Thiaclopride

Proteus®: authorized (toxic to bees)
Thiacloprid + Deltamethrin

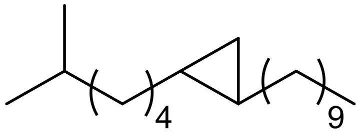
Alternatives to conventional chemical insectides

2. Pesticides

- pheromones:
  - Chemical substance secreted by animals to stimulate a physiological or behavioral response in another member of the same species (communication)
  - the most interesting (but expensive) are "sex-attractive" pheromones

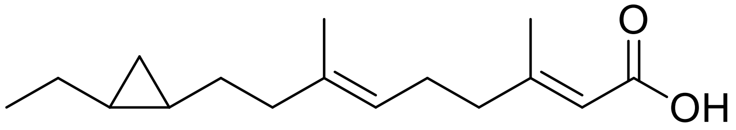
$CH_3(CH_2)_7CH{=}CH(CH_2)_{12}CH_3$

Common fly pheromone



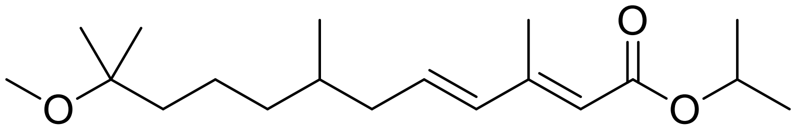
Moth pheromone

- growth hormones:
  - Chemical substance secreted by animals to promote the development of young individuals
  - Production of the hormone is naturally halted to allow the adult to mature



a natural juvenile hormone

  - Search for analogues of these compounds with more interesting properties and at a more affordable cost

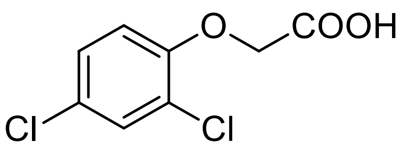


Metoprene

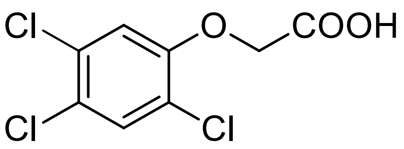
Herbicides

2. Pesticides

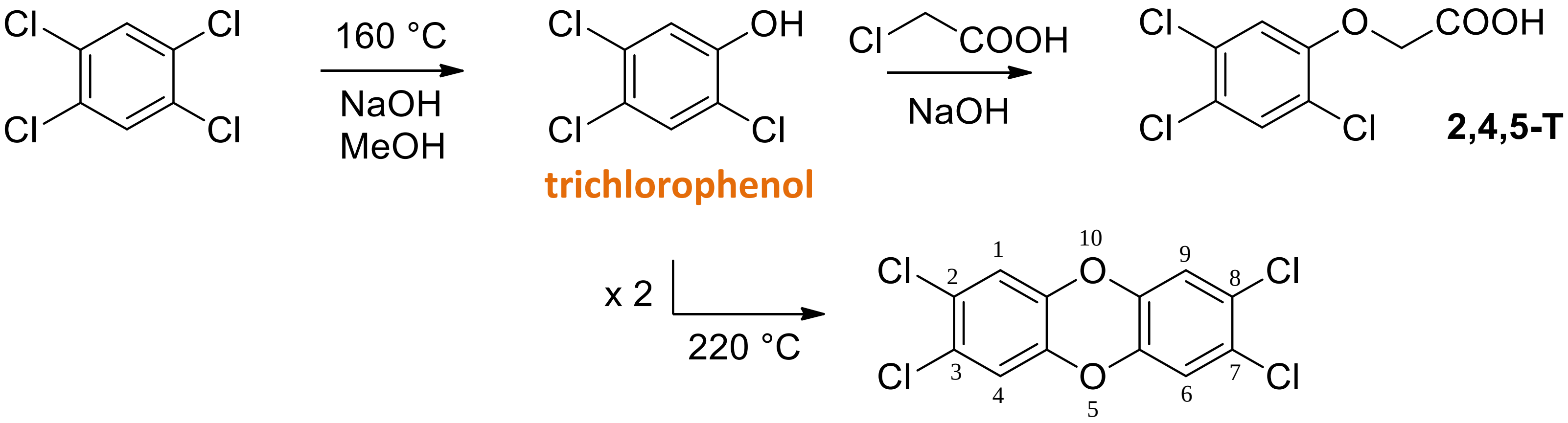
- organochlorides:
  - 2,4-D and 2,4,5-T
  - defoliating properties (leaf drop)
  - "Orange agent"
  - Teratogenic! Banned in 1985



2,4-D
2,4-dichlorophenoxyacetic acid



2,4,5-T
2,4,5-trichlorophenoxyacetic acid



2,3,7,8-tétrachlorodibenzo-*p*-dioxine
« Seveso dioxin»
2,3,7,8-TCDD

Seveso directives

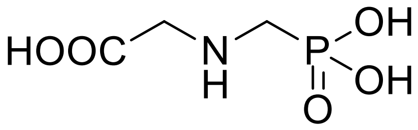
Seveso (Milan) – 1976
Trichlorophénol production:
Contamination of several thousand hectares

Herbicides

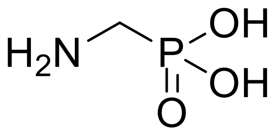
2. Pesticides

- aminophosphates - Glyphosate:
  - Foliar and root herbicide, widely used
  - Inhibition of amino acid synthesis enzymes (Tyr, Phe, Trp)
  - Not selective: eliminates all vegetation
  - Very rapidly degraded to AMPA (aminomethylphosphonic acid)
  - Very low toxicity to warm-blooded animals:
    - LD50 (rat) = 4900 mg/kg

5-EnolPyruvyl-Shikimate 3-Phosphate Synthase (EPSPS) :
- absent in mammals
- does not mean that Round-up (glyphosate) is non-toxic!



Round-up®
(glyphosate + adjuvants…)



AMPA

Potential toxic effects of glyphosate and its commercial formulations below regulatory limits.
R. Mesnage, N. Defarge, J. Spiroux de Vendômois et G.-E. Séralini, *Food Chem. Tox.* **2015**, 84, 133-153

2. Pesticides

Food and Chemical Toxicology 84 (2015) 133–153

Contents lists available at ScienceDirect

Food and Chemical Toxicology

journal homepage: www.elsevier.com/locate/foodchemtox

Review

Potential toxic effects of glyphosate and its commercial formulations below regulatory limits

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[b] CRIIGEN, 81 rue de Monceau, 75008 Paris, France

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Roundup
GMO
Endocrine disruption
Toxicity
Pesticide

A B S T R A C T

Glyphosate-based herbicides (GlyBH), including Roundup, are the most widely used pesticides worldwide. Their uses have increased exponentially since their introduction on the market. Residue levels in food or water, as well as human exposures, are escalating. We have reviewed the toxic effects of GlyBH measured below regulatory limits by evaluating the published literature and regulatory reports. We reveal a coherent body of evidence indicating that GlyBH could be toxic below the regulatory lowest observed adverse effect level for chronic toxic effects. It includes teratogenic, tumorigenic and hepatorenal effects. They could be explained by endocrine disruption and oxidative stress, causing metabolic alterations, depending on dose and exposure time. Some effects were detected in the range of the recommended acceptable daily intake. Toxic effects of commercial formulations can also be explained by GlyBH adjuvants, which have their own toxicity, but also enhance glyphosate toxicity. These challenge the assumption of safety of GlyBH at the levels at which they contaminate food and the environment, albeit these levels may fall below regulatory thresholds. Neurodevelopmental, reproductive, and transgenerational effects of GlyBH must be revisited, since a growing body of knowledge suggests the predominance of endocrine disrupting mechanisms caused by environmentally relevant levels of exposure.

2. Pesticides

Environmental Toxicology and Pharmacology 46 (2016) 292–300

Contents lists available at ScienceDirect

Environmental Toxicology and Pharmacology

journal homepage: www.elsevier.com/locate/etap

Glyphosate induces cardiovascular toxicity in *Danio rerio*

Nicole M. Roy *, Jeremy Ochs, Ewelina Zambrzycka, Ariann Anderson

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Cardiac
Vasculature

ABSTRACT

Glyphosate is a broad spectrum herbicide used aggressively in agricultural practices as well as home garden care. Although labeled “safe” by the chemical industry, doses tested by industry do not mimic chronic exposures to sublethal doses that organisms in the environment are exposed to over long periods of time. Given the widespread uses of and exposure to glyphosate, studies on developmental toxicity are needed. Here we utilize the zebrafish vertebrate model system to study early effects of glyphosate on the developing heart. Treatment by embryo soaking with 50 µg/ml glyphosate starting at gastrulation results in structural abnormalities in the atrium and ventricle, irregular heart looping, *situs inversus* as well as decreased heartbeats by 48 h as determined by live imaging and immunohistochemistry. Vasculature in the body was also affected as determined using *fli-1* transgenic embryos. To determine if the effects noted at 48 h post fertilization are due to early stage alterations in myocardial precursors, we also investigate cardiomyocyte development with a Mef2 antibody and by *mef2ca in situ* hybridization and find alterations in the Mef2/*mef2ca* staining patterns during early cardiac patterning stages. We conclude that glyphosate is developmentally toxic to the zebrafish heart.

JECH Online First, published on March 3, 2016 as 10.1136/jech-2015-207005

2. Pesticides

Differences in the carcinogenic evaluation of glyphosate between the International Agency for Research on Cancer (IARC) and the European Food Safety Authority (EFSA)

Christopher J Portier,[1] Bruce K Armstrong,[2] Bruce C Baguley,[3] Xaver Baur,[4] Igor Belyaev,[5] Robert Bellé,[6] Fiorella Belpoggi,[7] Annibale Biggeri,[8] Maarten C Bosland,[9] Paolo Bruzzi,[10] Lygia Therese Budnik,[11] Merete D Bugge,[12] Kathleen Burns,[13] Gloria M Calaf,[14] David O Carpenter,[15] Hillary M Carpenter,[16] Lizbeth López-Carrillo,[17] Richard Clapp,[18] Pierluigi Cocco,[19] Dario Consonni,[20] Pietro Comba,[21] Elena Craft,[22] Mohamed Aqiel Dalvie,[23] Devra Davis,[24] Paul A Demers,[25] Anneclaire J De Roos,[26] Jamie DeWitt,[27] Francesco Forastiere,[28] Jonathan H Freedman,[29] Lin Fritschi,[30] Caroline Gaus,[31] Julia M Gohlke,[32] Marcel Goldberg,[33] Eberhard Greiser,[34] Johnni Hansen,[35] Lennart Hardell,[36] Michael Hauptmann,[37] Wei Huang,[38] James Huff,[39] Margaret O James,[40] C W Jameson,[41] Andreas Kortenkamp,[42] Annette Kopp-Schneider,[43] Hans Kromhout,[44] Marcelo L Larramendy,[45] Philip J Landrigan,[46] Lawrence H Lash,[47] Dariusz Leszczynski,[48] Charles F Lynch,[49] Corrado Magnani,[50] Daniele Mandrioli,[51] Francis L Martin,[52] Enzo Merler,[53] Paola Michelozzi,[54] Lucia Miligi,[55] Anthony B Miller,[56] Dario Mirabelli,[57] Franklin E Mirer,[58] Saloshni Naidoo,[59] Melissa J Perry,[60] Maria Grazia Petronio,[61] Roberta Pirastu,[62] Ralph J Portier,[63] Kenneth S Ramos,[64] Larry W Robertson,[65] Theresa Rodriguez,[66] Martin Röösli,[67] Matt K Ross,[68] Deodutta Roy,[69] Ivan Rusyn,[70] Paulo Saldiva,[71] Jennifer Sass,[72] Kai Savolainen,[73] Paul T J Scheepers,[74] Consolato Sergi,[75] Ellen K Silbergeld,[76] Martyn T Smith,[77] Bernard W Stewart,[78] Patrice Sutton,[79] Fabio Tateo,[80] Benedetto Terracini,[81] Heinz W Thielmann,[82] David B Thomas,[83] Harri Vainio,[84] John E Vena,[85] Paolo Vineis,[86] Elisabete Weiderpass,[87] Dennis D Weisenburger,[88] Tracey J Woodruff,[89] Takashi Yorifuji,[90] Il Je Yu,[91] Paola Zambon,[92] Hajo Zeeb,[93] Shu-Feng Zhou[94]

SUMMARY

The IARC WG concluded that glyphosate is a 'probable human carcinogen', putting it into IARC category 2A due to *sufficient evidence* of carcinogenicity in animals, *limited evidence* of carcinogenicity in humans and *strong* evidence for two carcinogenic mechanisms.

- The IARC WG found an association between NHL and glyphosate based on the available human evidence.
- The IARC WG found significant carcinogenic effects in laboratory animals for rare kidney tumours and hemangiosarcoma in two mouse studies and benign tumours in two rat studies.
- The IARC WG concluded that there was strong evidence of genotoxicity and oxidative stress for glyphosate, entirely from publicly available research, including findings of DNA damage in the peripheral blood of exposed humans.

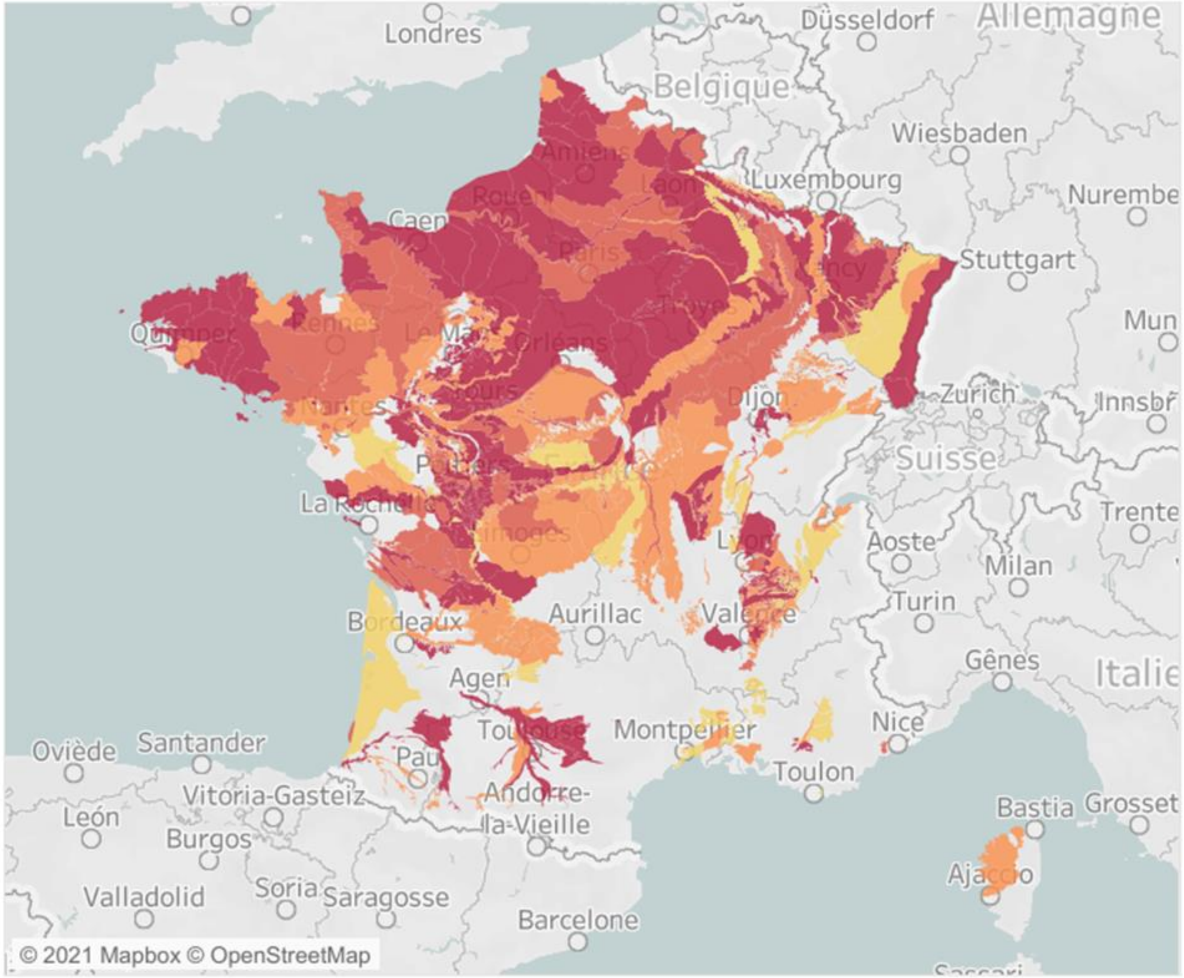
The RAR concluded[5] (Vol. 1, p.160) that 'classification and labelling for carcinogenesis is not warranted' and 'glyphosate is devoid of genotoxic potential'.

- EFSA[4] classified the human evidence as 'very limited' and then dismissed any association of glyphosate with cancer without clear explanation or justification.
- Ignoring established guidelines cited in their report, EFSA dismissed evidence of renal tumours in three mouse studies, hemangiosarcoma in two mouse studies and malignant lymphoma in two mouse studies. Thus, EFSA incorrectly discarded all findings of glyphosate-induced cancer in animals as chance occurrences.
- EFSA ignored important laboratory and human mechanistic evidence of genotoxicity.
- EFSA confirmed that glyphosate induces oxidative stress but then, having dismissed all other findings of possible carcinogenicity, dismissed this finding on the grounds that oxidative stress alone is not sufficient for carcinogen labelling.

The most appropriate and scientifically based evaluation of the cancers reported in humans and laboratory animals as well as supportive mechanistic data is that glyphosate is a *probable human carcinogen*. On the basis of this conclusion and in the absence of evidence to the contrary, it is reasonable to conclude that glyphosate formulations should also be considered likely human carcinogens. The CLP Criteria[18] (Table 3.6.1, p.371) allow for a similar classification of Category 1B when there are 'studies showing limited evidence of carcinogenicity in humans together with limited evidence of carcinogenicity in experimental animals'.

Groundwater quality, France 2017

2. Pesticides



Cliquer sur la carte pour avoir plus d'informations

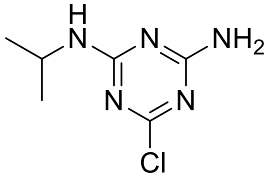
Taux des points des mesure avec la présence du pesticide en 2017

Champ: France entière. Eaux souterraines.

Sources: Système d'information sur l'eau - https://www.eaufrance.fr/. Traitements: SDES, 2019

Pesticide choice

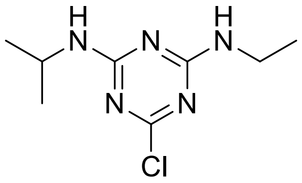
desethyl atrazine



Detection rate

- less than 25%
- between 25% and 50%
- between 50 and 75%
- between 75 and 100%

Atrazine: banned since 2003!



https://ree.developpement-durable.gouv.fr/themes/risques-nuisances-pollutions/pollution-de-l-eau-douce/pesticides/article/les-pesticides-dans-les-eaux-souterraines

Conclusion and alternatives to conventional pesticides

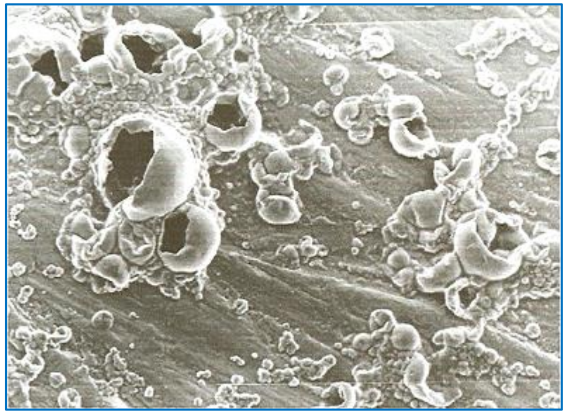
2. Pesticides

Plants suffer from over **80,000** diseases, **30,000** species of weeds, **3,000** species of nematodes and around **10,000** species of insect pests. More than **1,000** active compounds are used as pesticides worldwide.

- Impact of pesticides on health and the environment:
  - Lack of *selectivity* and excessive *stability*
    - water and soil pollution
    - toxicity and ecotoxicity
  - Virtually no structural *eco-design* taken into consideration to date

- Alternatives to conventional pesticides:
  - organic/biological farming
  - reasoned (integrated) farming (seed coating)
  - changes in eating habits (meat consumption)
  - genetically-modified plants
    - What are the impacts of GM plants on the environment and health?
  - nanocides = encapsulation of a pesticide in a nanoparticle
    - specific pesticide release (temperature, pH, contact...)
    - What are the impacts of NP on the environment and health?
  - eco-design of pesticides (and medecines) !!!

- GM 'Mon' corn resist to Round'up (Monsanto/Bayer)
- GM"Bt" corn with insecticidal properties (Novartis)



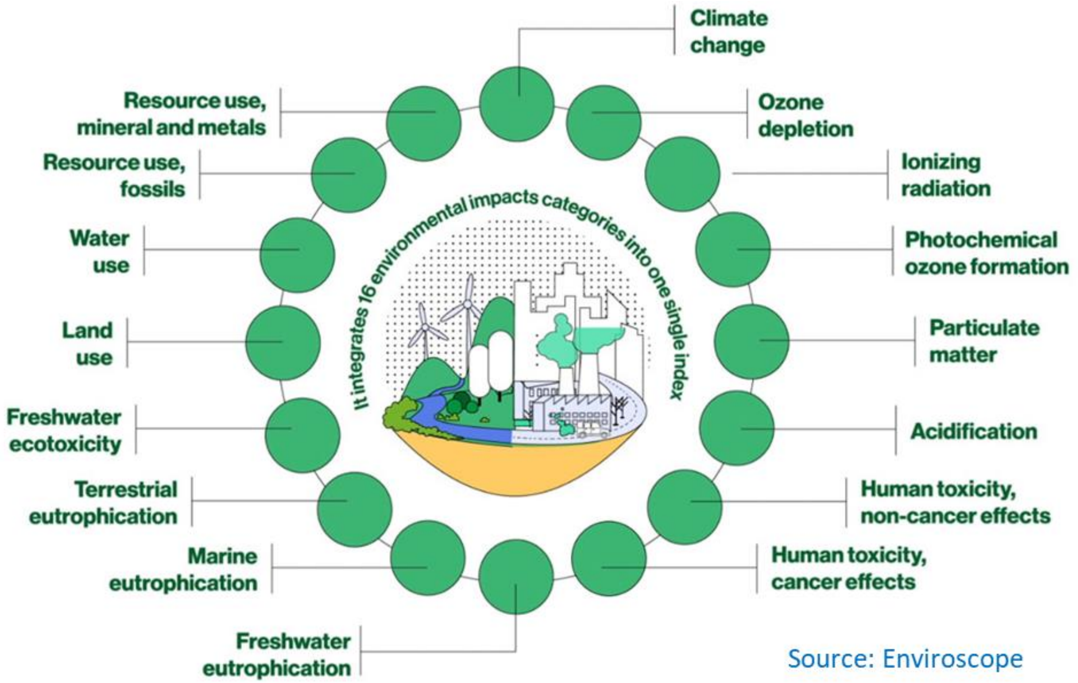
Karate Zeon (Syngenta...)
Insecticide : λ-cyhalothrin

4. Sustainable development and challenges for the chemical industry and research

Sustainable development, United Nations

Challenges for the chemical industry and research

- reduce the environmental impact of a chemical product and its synthesis:
  - product, synthetic process, energy, waste
  - LCA of product and process
    - up to 16 environmental impacts evaluated…
    - … over the different steps of its life
      - extraction PM, production, transport, use, end of life
    - cf. Module 2 (C. Cannizzo and P. Tardiveau)
  - includes chemical waste management and circular economy
    - cf. Module 3 (S. Henry-Daguerre)

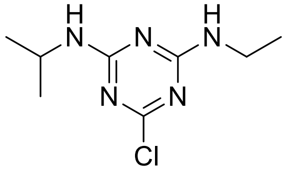


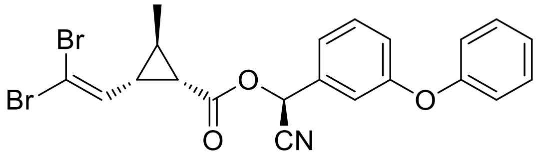
Source: Enviroscope

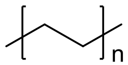
Challenges for the chemical industry and research

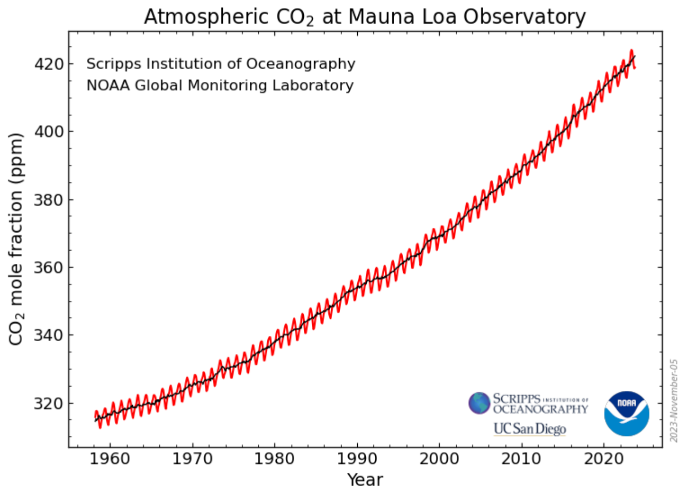
- reduce the environmental impact of a chemical product and its synthesis:
  - product, synthetic process, energy, waste
  - LCA of product and process
    - up to 16 environmental impacts evaluated…
    - … over the different steps of its life
      - extraction PM, production, transport, use, end of life
    - cf. Module 2 (C. Cannizzo and P. Tardiveau)
  - includes chemical waste management and circular economy
    - cf. Module 3 (S. Henry-Daguerre)
  - includes the 12 principles of green chemistry
    - cf. Modules 2 (C. Cannizzo) and 4 (M.-C. Scherrmann)
  - includes chemical and environmental regulations
    - cf. Module 5 (M. Boivin)
  - includes environmental performance assessment (EPA) in chemistry
    - cf. Module 6 (M.-C. Scherrmann)

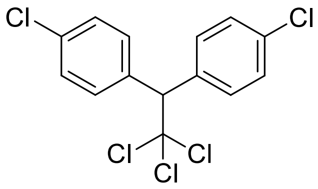
Respecting one or more of the 12 principles of green chemistry does not necessarily mean that your chemistry is sustainable! → **LCA (EPA)!**

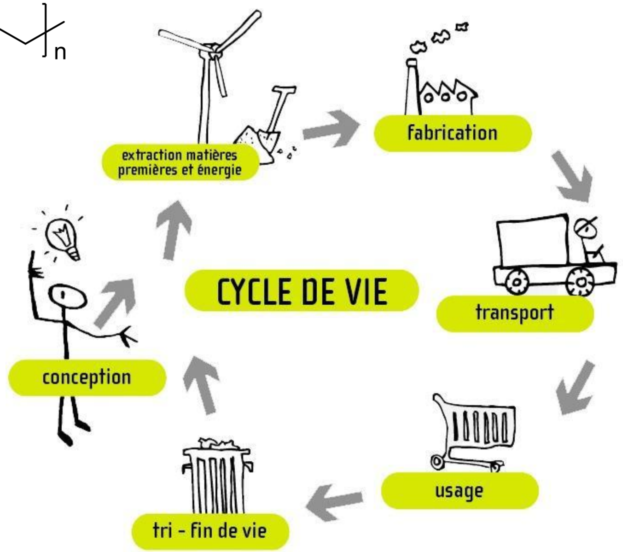


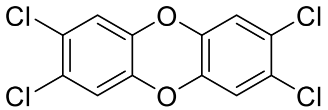


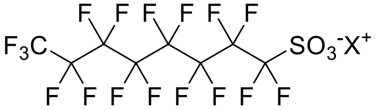


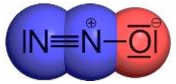


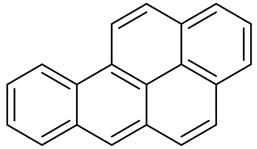


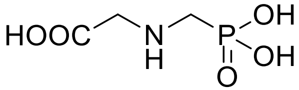




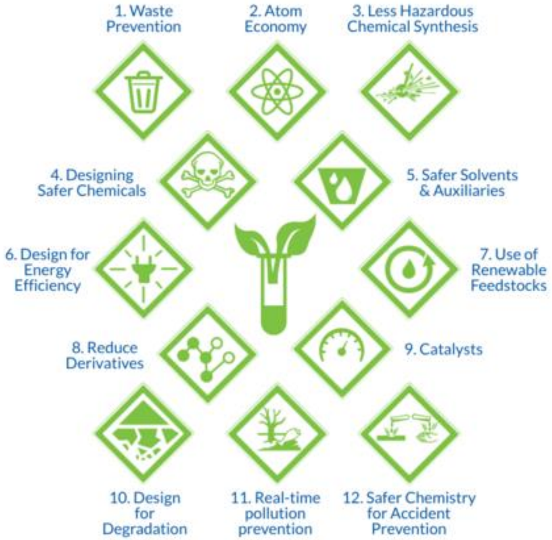








$$PMI = \frac{\text{total mass in a process or process step}}{\text{mass of product}}$$



Thank you for your attention!

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Calendar

Date	Horaire	Lieu	Module	Nom module	Intervenant
January 9, 2024	17h30-19h	Henri Moissan *amphi O. Kahn*	Module 1	Introduction to SD in chemistry	L. SALMON (UPSay)
January 16, 2024	17h30-19h	UEVE *Amphi Up*	Module 2.1	ACV-Ecoconception	C. CANNIZZO (UEVE/CEA)
January 23, 2024	17h30-19h	UVSQ *amphi Bertin*	Module 2.2	ACV-principles and methodology	P. TARDIVEAU (UPSay)
January 30, 2024	17h30-19h	Henri Moissan *amphi H. Daniel*	Module 3	Chemical waste management and circular economy	S. HENRY-DAGUERRE (VEOLIA)
February 6, 2024	17h30-19h	UEVE *amphi Up*	Module 4	Renewable and bio-sourced chemistry	M.-C. SCHERRMANN (UPSay)
February 13, 2024	17h30-19h	UVSQ *amphi Bertin*	Module 5	Environmental regulations and chemical standards	M. BOIVIN (UPSay)
February 20, 2024	17h30-19h	Henri Moissan *amphi O. Kahn*	Module 6	Environmental performance assessment in chemistry	M.-C. SCHERRMANN (UPSay)