Introduction to Persistent Organic Pollutants (POPs)

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Provision of services related to training, assessment and reduction of PCDD/Fs releases from metallurgical industries in Turkey

Iskenderun Anemon Hotel, Turkey, 22 March, 2017

Introduction to POPs

- POPs - general definition,;
- Understanding of POPs;
- Properties, problems, "Dirty Dozen", new POPs;
- Source of POPs;
- Toxicology and ecotoxicology of POPs;
- POPs aspects of transboundary impact;

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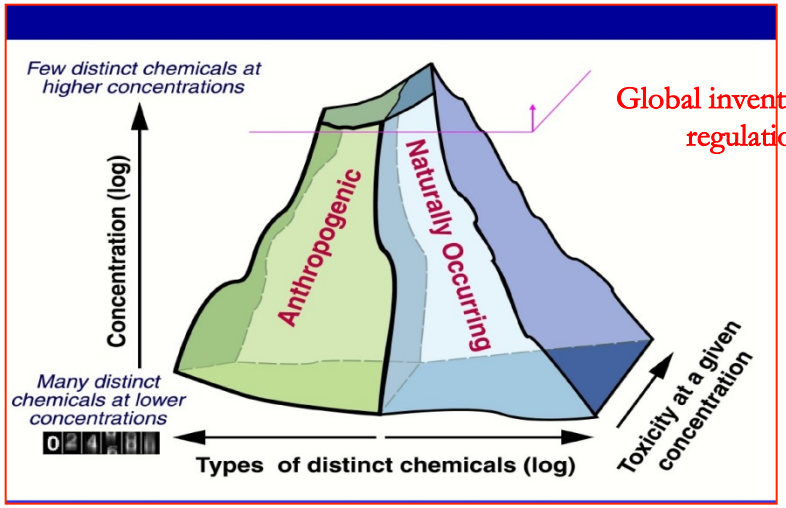
Environmental pollution



Global inventory and regulation

Toxicological relevant chemicals

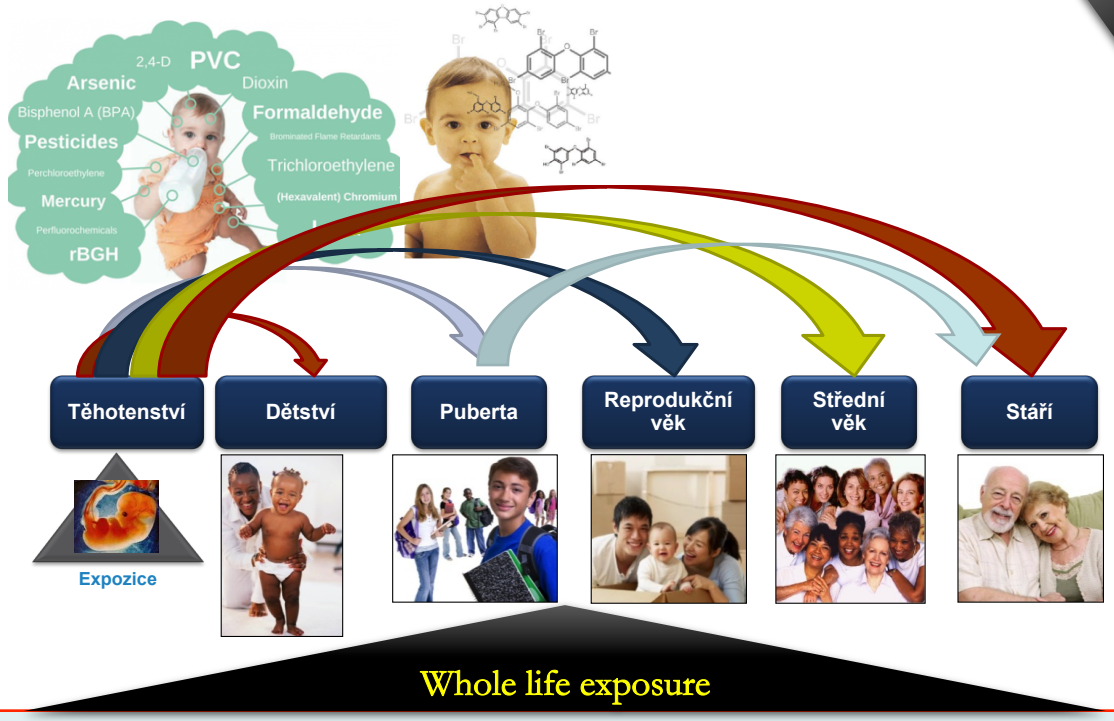
Pesticides

Products of combustion processes

Personnal care products (PCP)

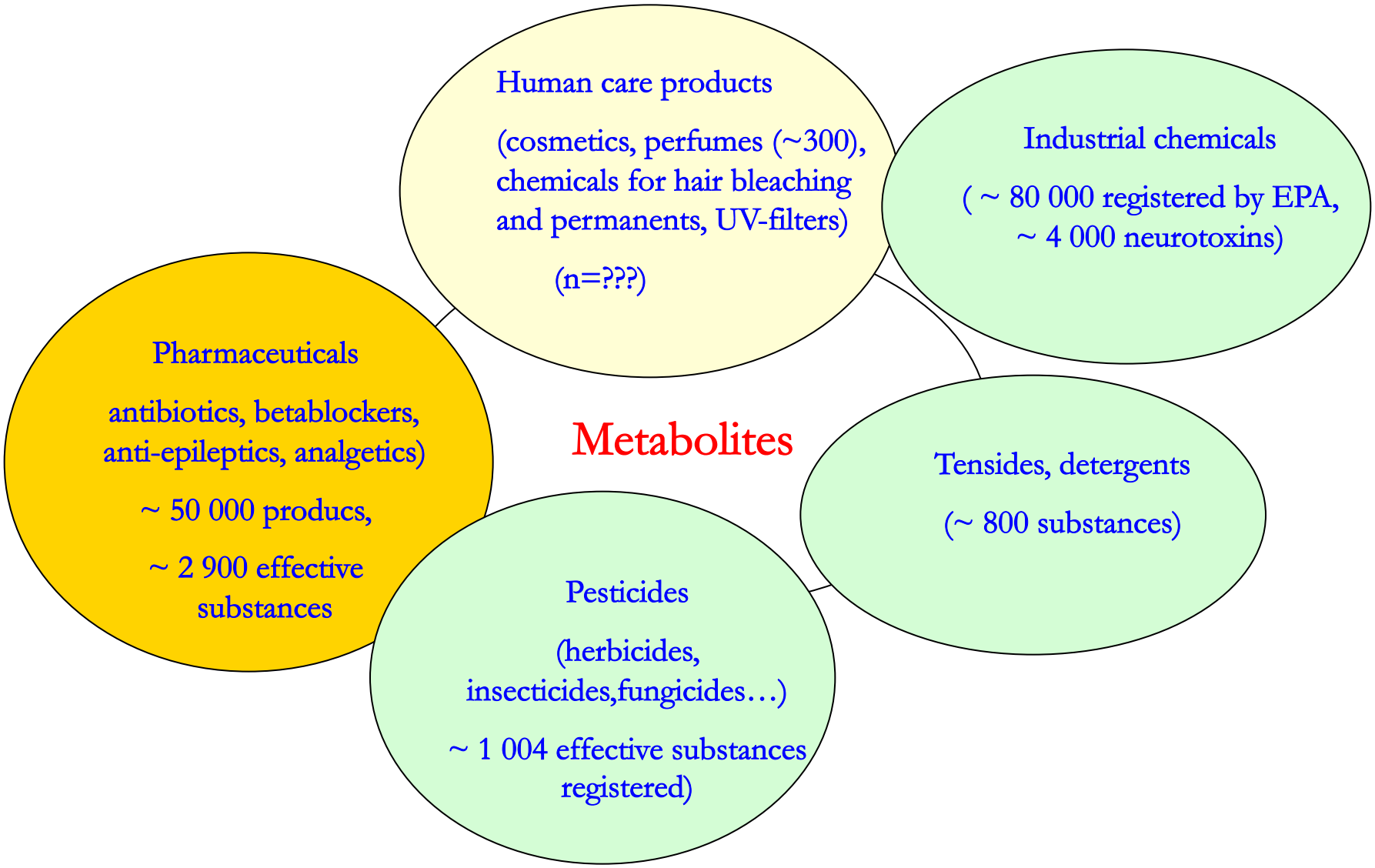
Food packages

Wastes



Environmental occurrence= potenctial possibility of transfer to human organisms
We have to determine the level of exposure in all age categories including prenatal period
Health effects may be delayed until later in life

Nowdays environmental chemicals



What are we talking about ?

- Unintentional releases
- Releases to air, water, soil, waste, products

Of the 5.7 million tons of pollutants released, main part of them were of chemicals considered persistent, bioaccumulative or toxic

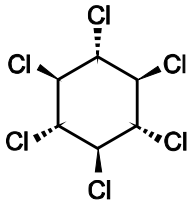
970 000 tons were known or suspected carcinogens and

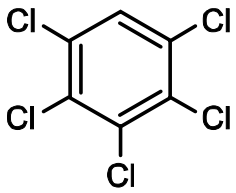
857 000 tons were of chemicals that are considered reproductive or developmental toxicants.

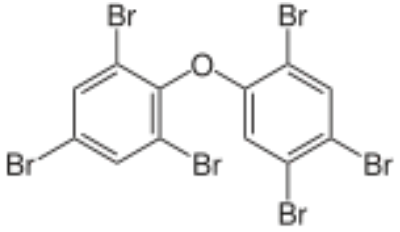
(UNEP Chemicals, 2012)

Risk of POPs

Persistent Organic Pollutants





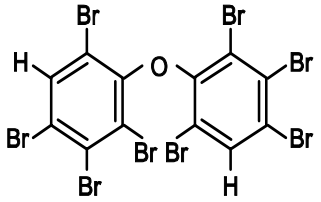


- Persistent
- Bio-accumulative
- Potential of long-range transport
- Pose a risk of causing adverse effects to human health and the environment

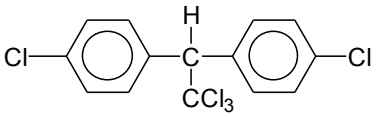
Persistent Organic Pollutants

Main groups:

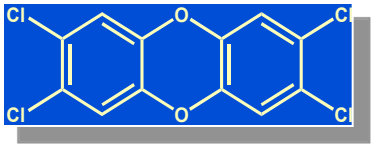
- Technical chemicals



- Pesticides



- Industrial by-products

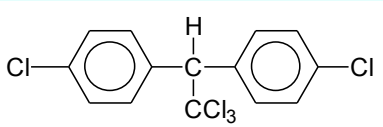


  - Wastes

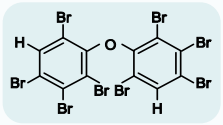
  - Obsolete POPs

  - Contaminated sites

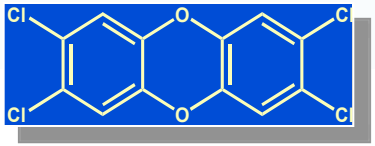
IP and UP POPs



- Intentionally produced (IP): Chlorinated pesticides, transformer/capacitor oils (PCB), polybrominated flame retardants, …



- Unintentionally produced (UP): Dioxins/furans (byproducts in thermal processes)



Elimination of wastes (IP) - destruction (conservation)

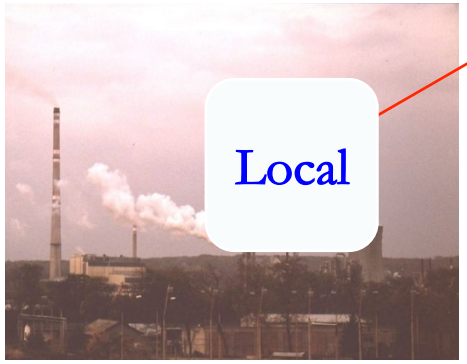
Elimination of stockpiles (IP) - destruction (conservation)

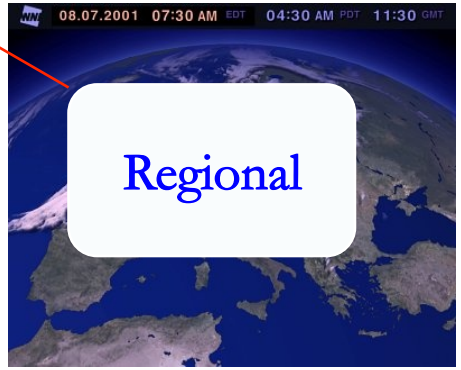
Elimination of byproducts (UP) - prevention and destruction

Decontamination (IP + UP) - remediation of soils, sludges, water, sediments, …

Scale of impacts

Scale of impacts





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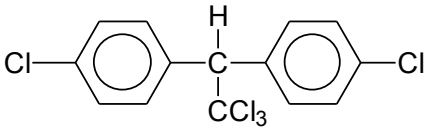
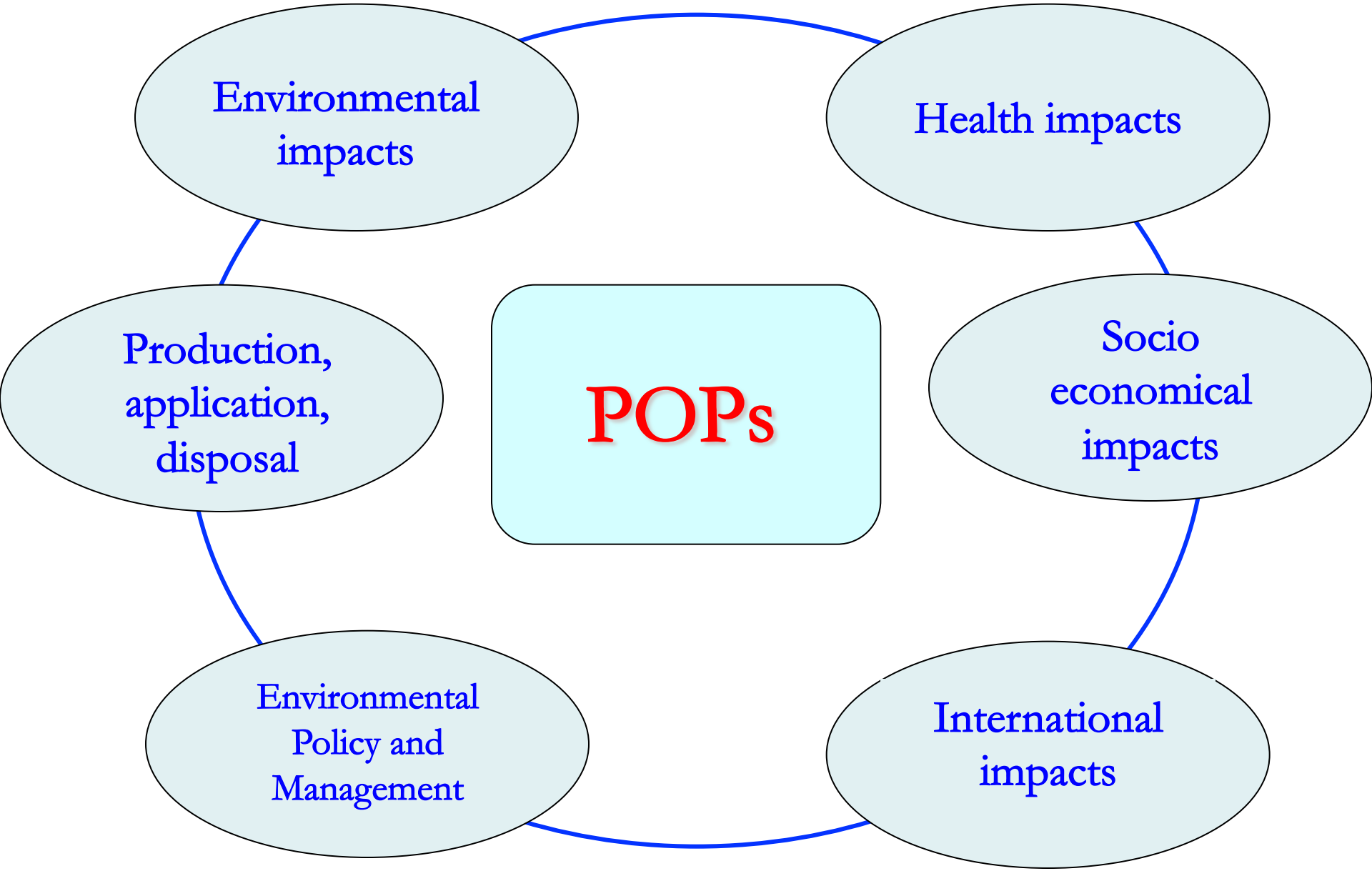
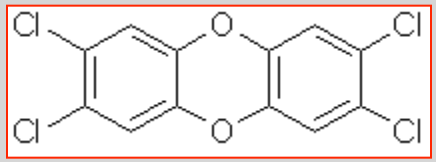
What I mean by understanding ??

- Understanding – physical-chemical properties – which one, sources, fate, effects
- Properties – POPs definition – persistence, hydrophobicity, lipophility, abiotic cummulation/bioaccumulation, long range transport
- Fate – transport, transformations, distribution, equilibria – understandig of environmental behaviour
- Effects – broad range, single compounds, toxic mixtures
- Determination/monitoring – phase distribution, properties
- Technologies – disposal, destruction, remediation
- Decision making process




Environmental impacts
Health impacts
Production, application, disposal
POPs
Socio economical impacts
Environmental Policy and Management
International impacts

POPs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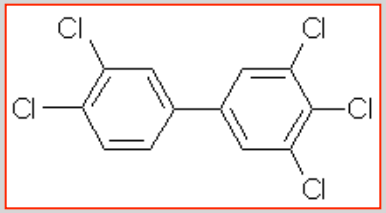
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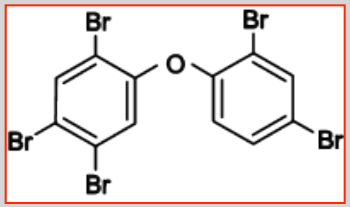
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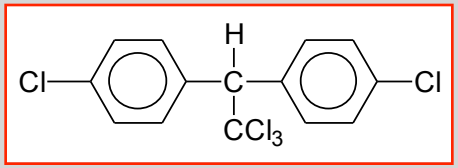
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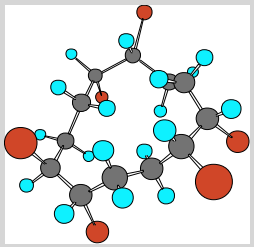

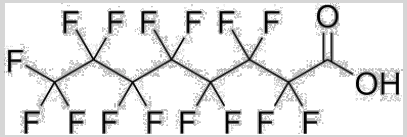
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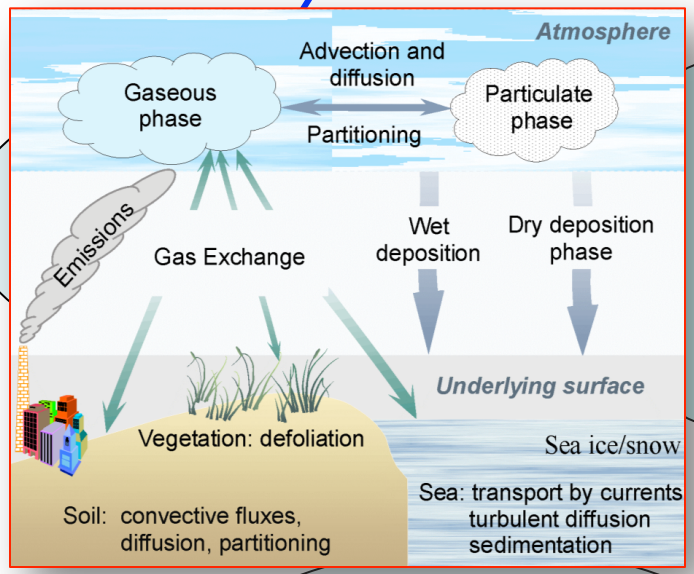
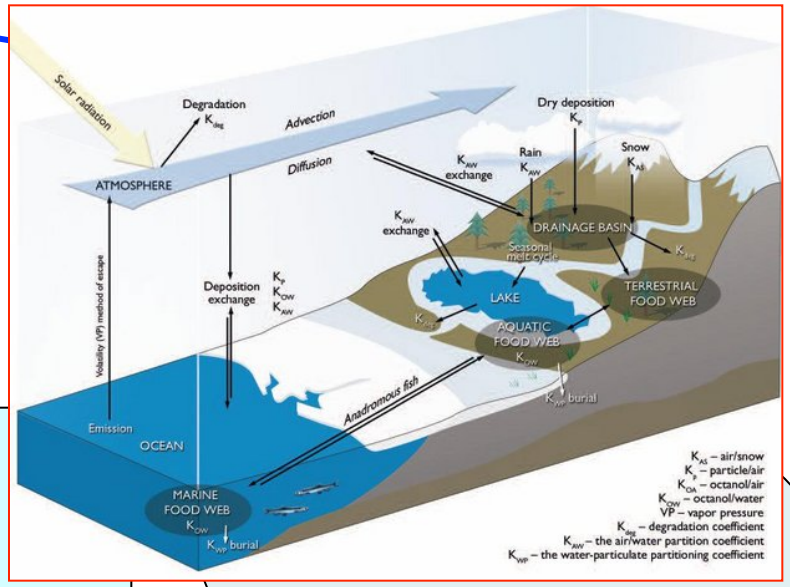
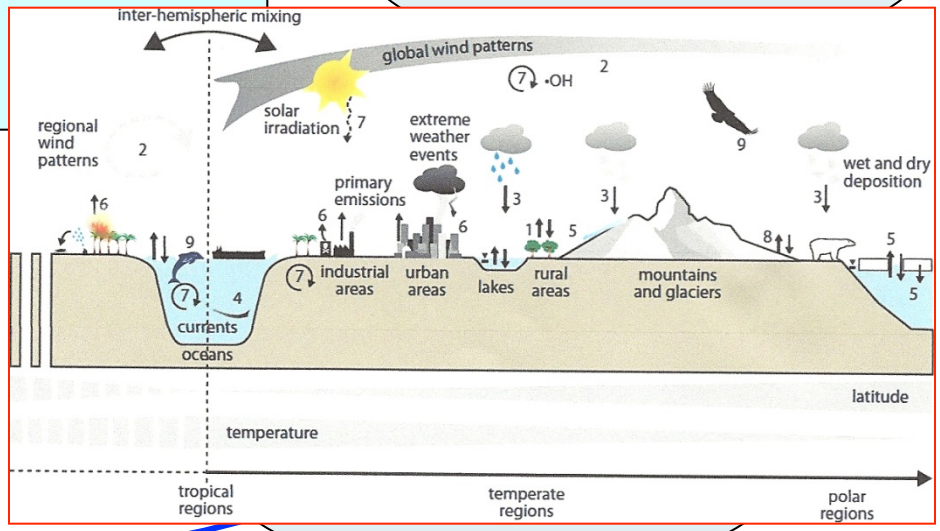
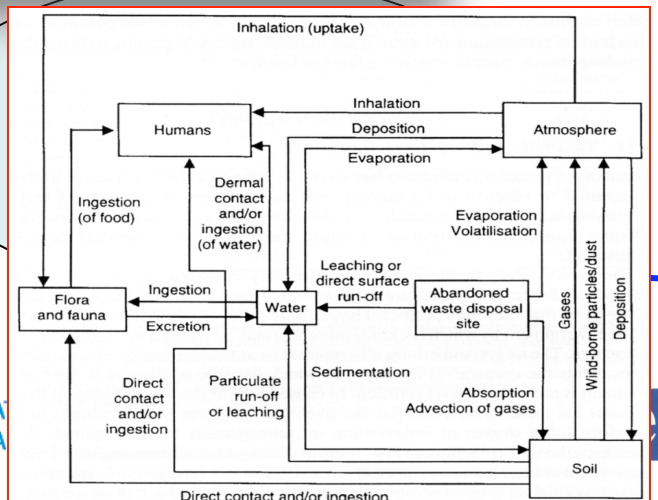
Environmental impacts

POPs

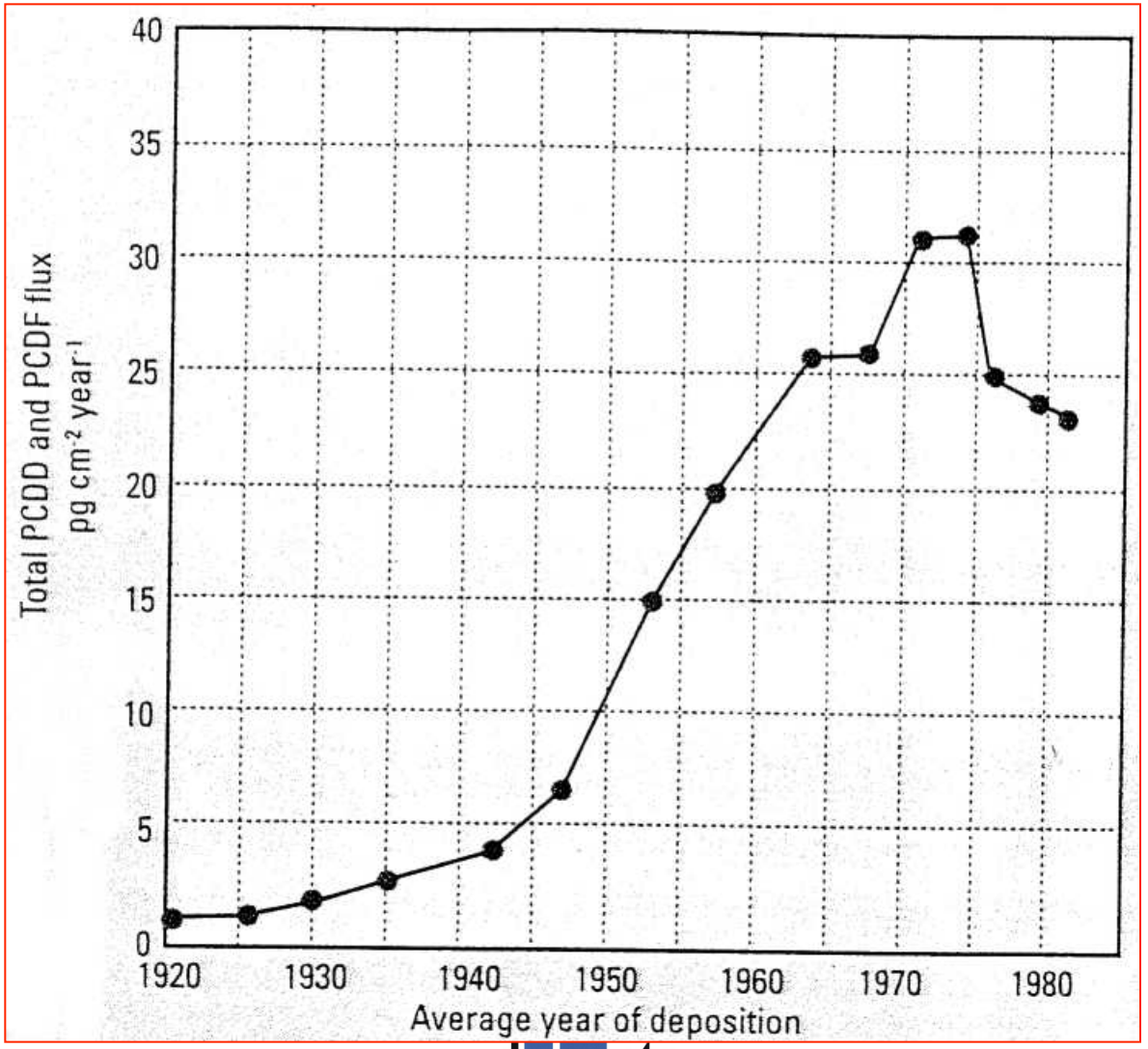






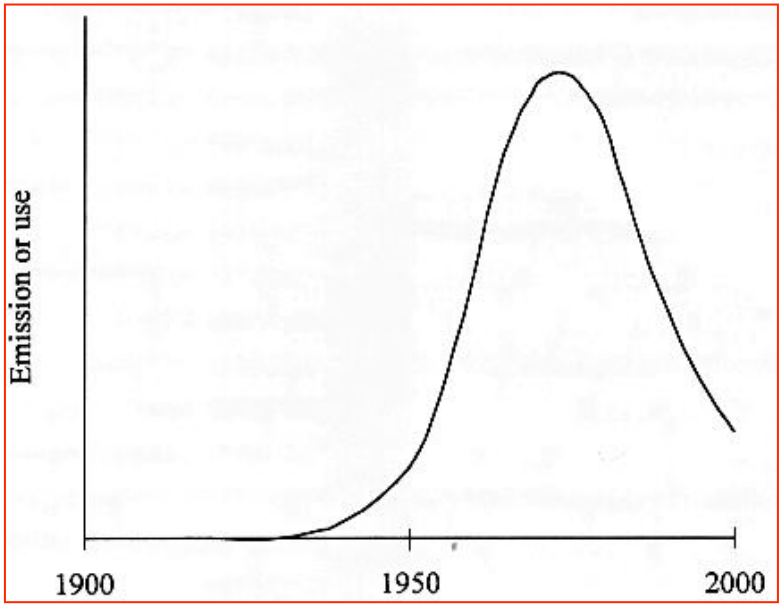


Historical trends of environmental levels of PCDDs/Fs

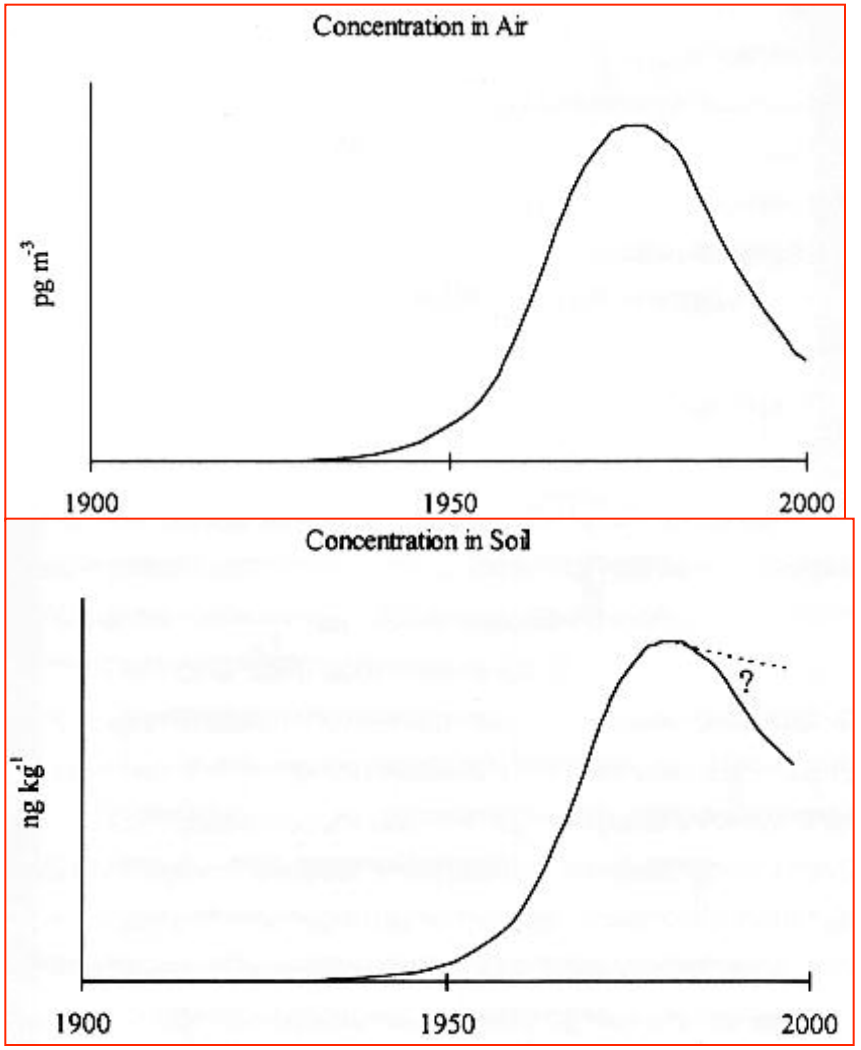


Changes in the temporal trends

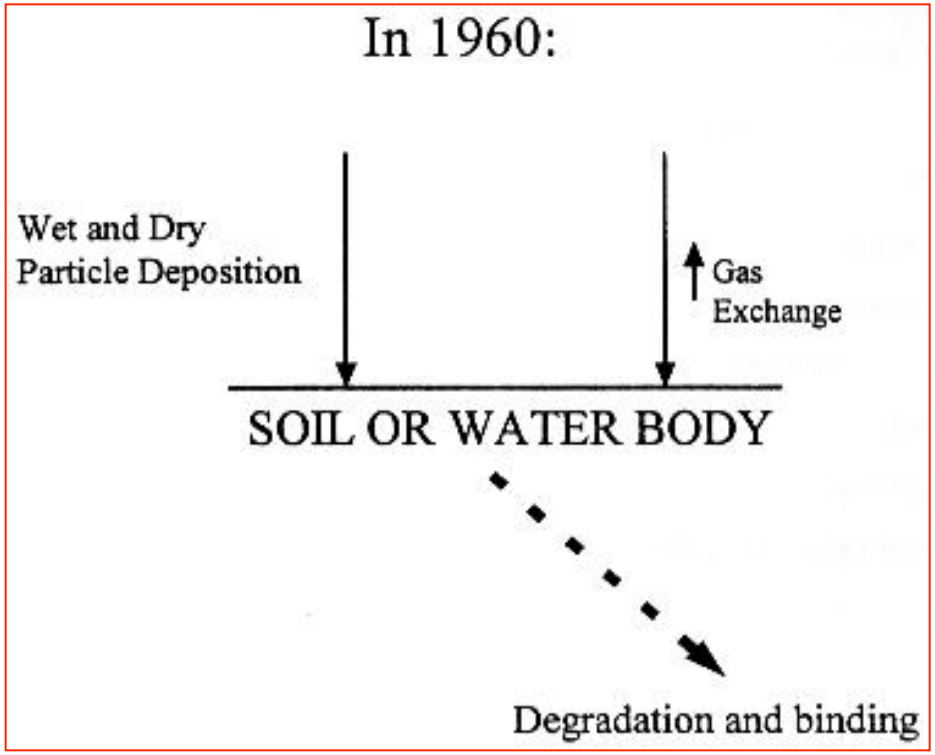
Typical POPs time trend

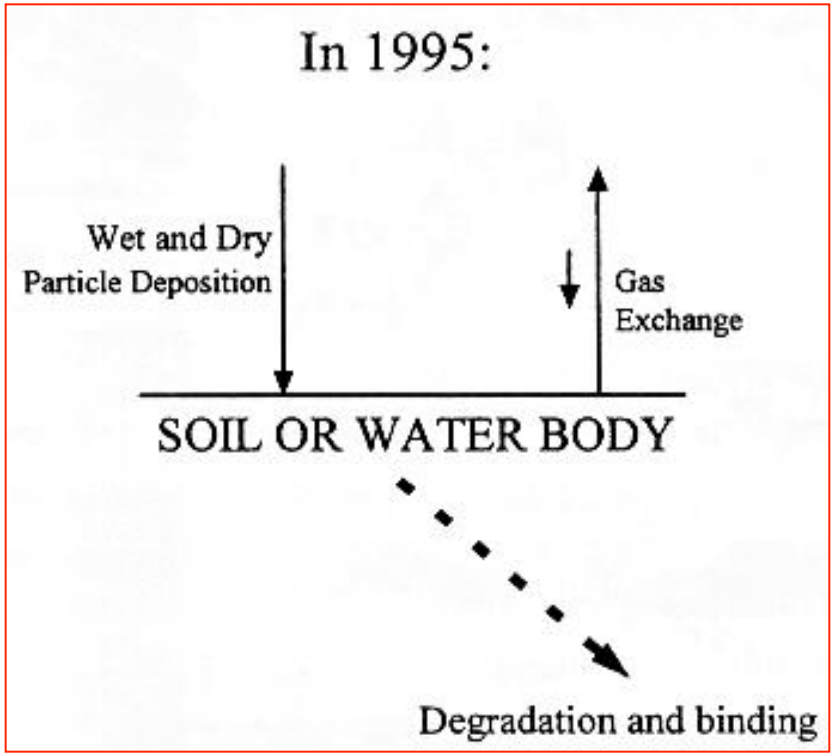


Typical POPs air and soil residues

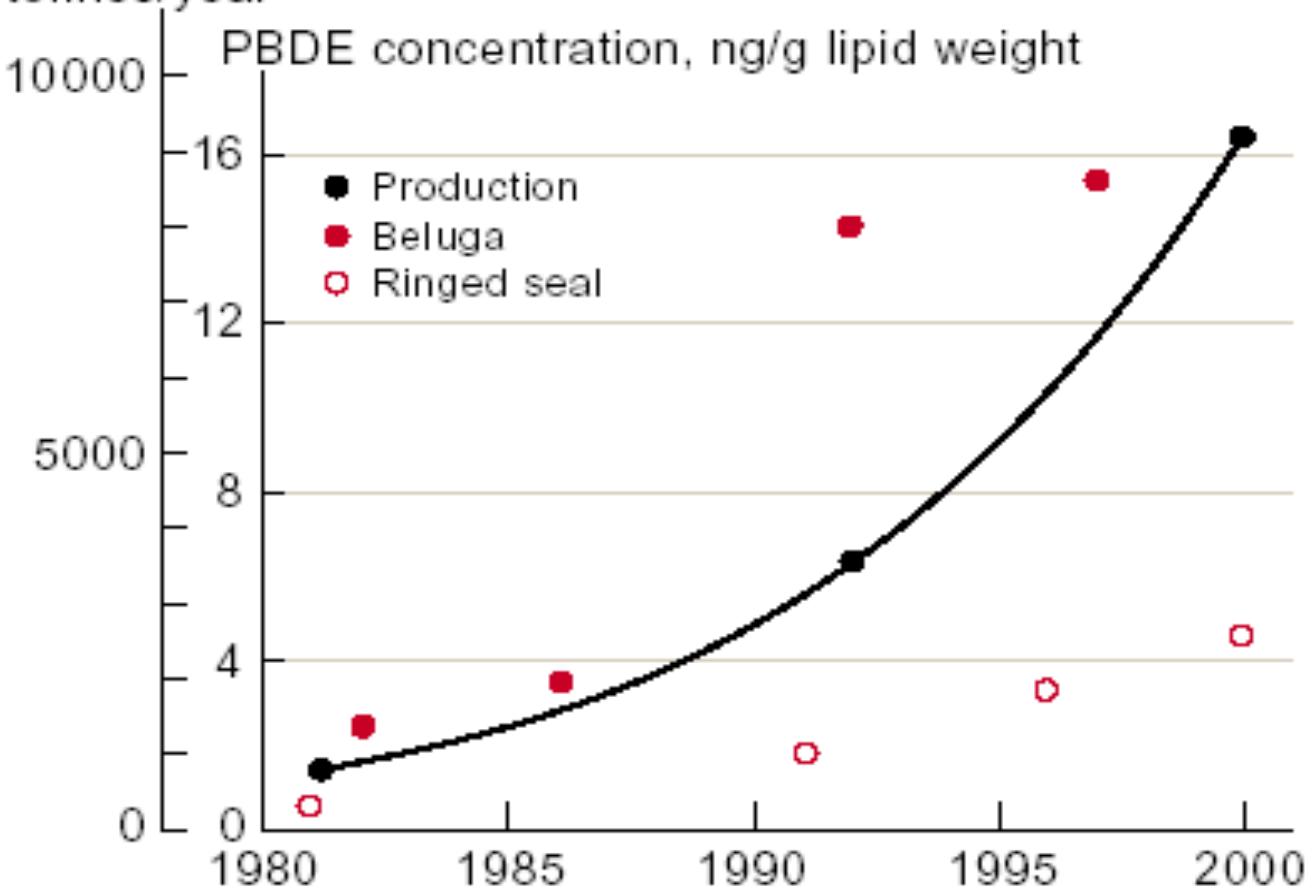


Exchange processes – air – soil - trends

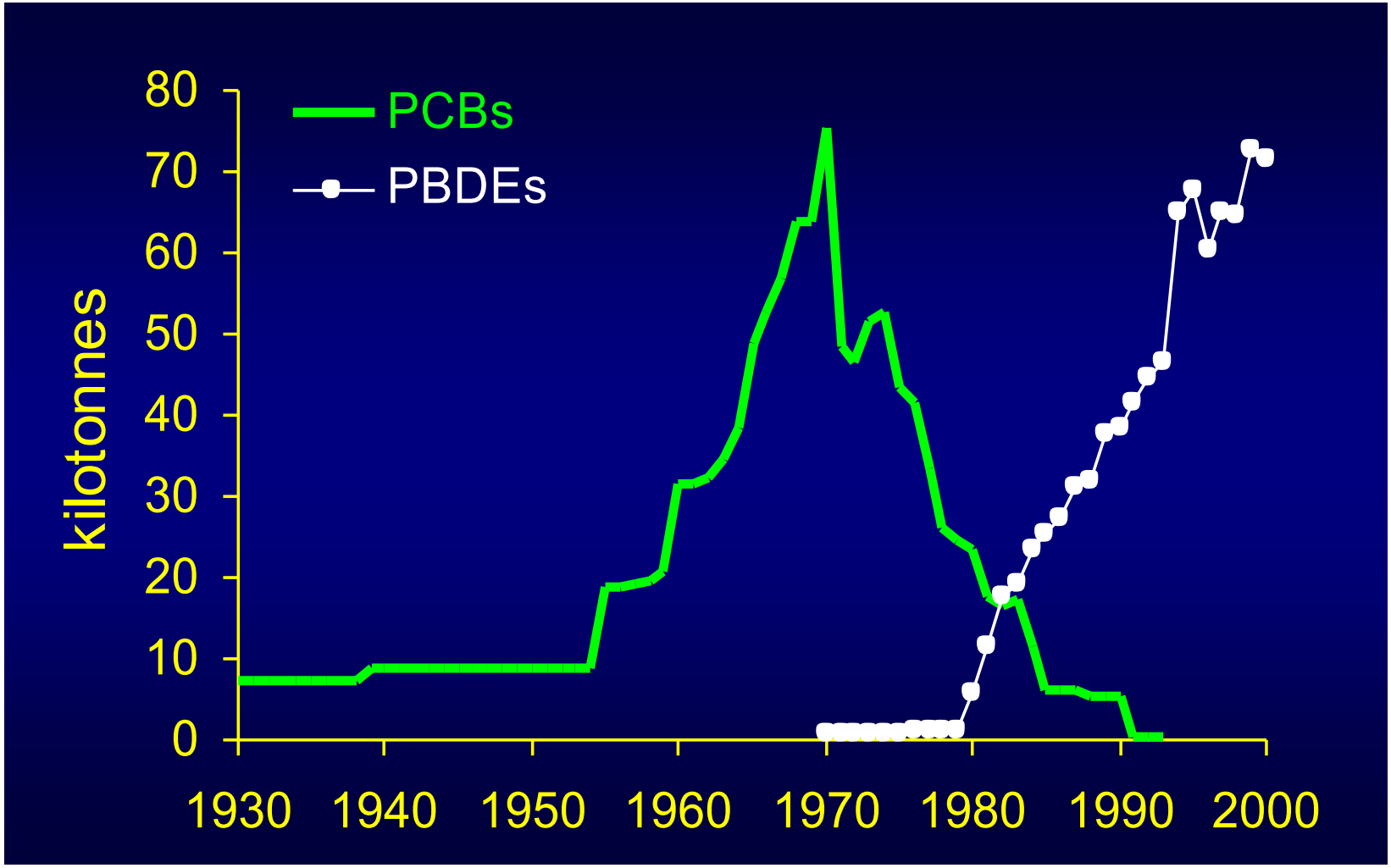




Worldwide PeBDE production and levels of PBDEs in Arctic organisms

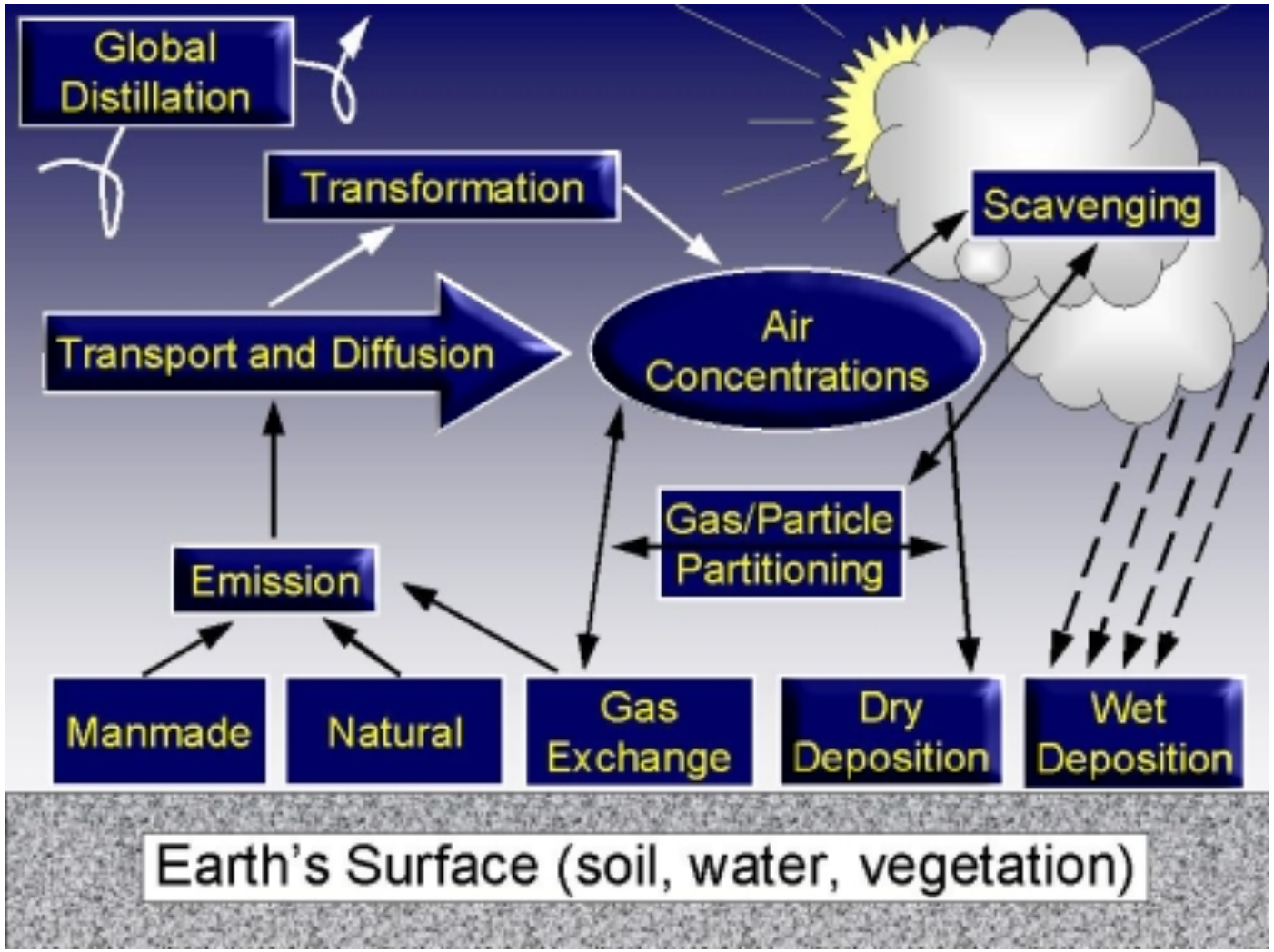


Changes in time trends

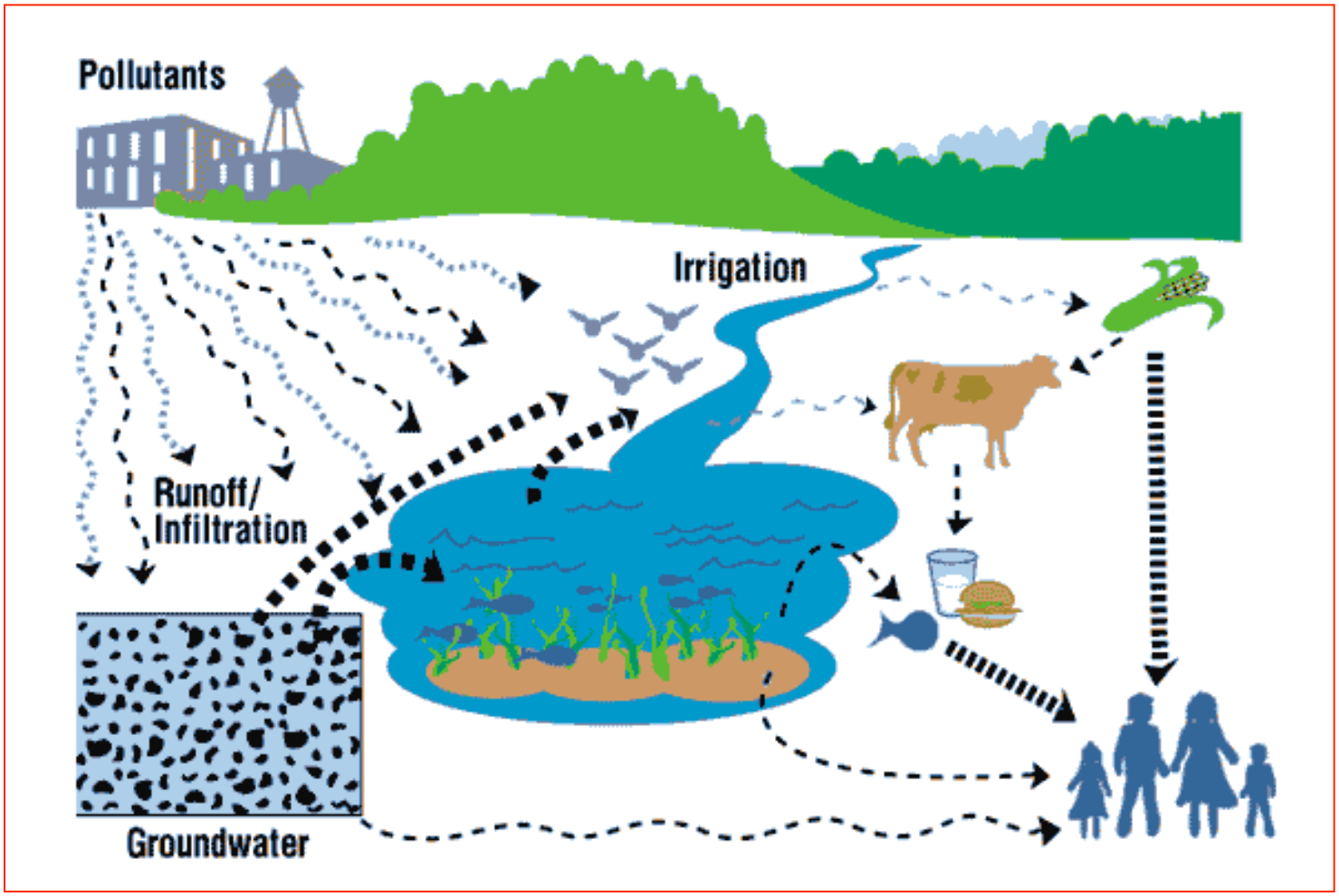


PBDEs: Anna Palm (Pers. Comm.) PCBs: Breivik et al (2002)

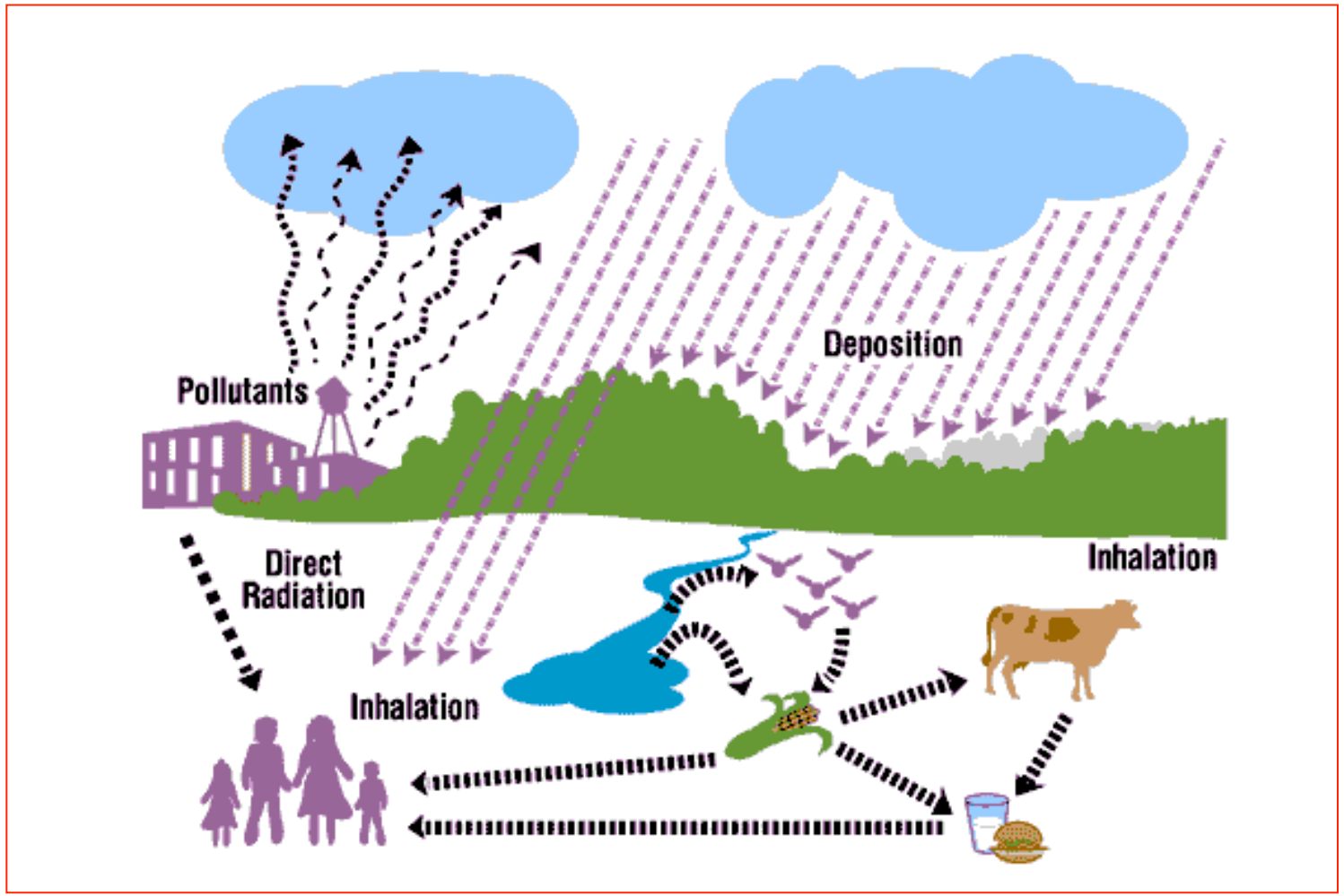
Environmental fate of chemicals



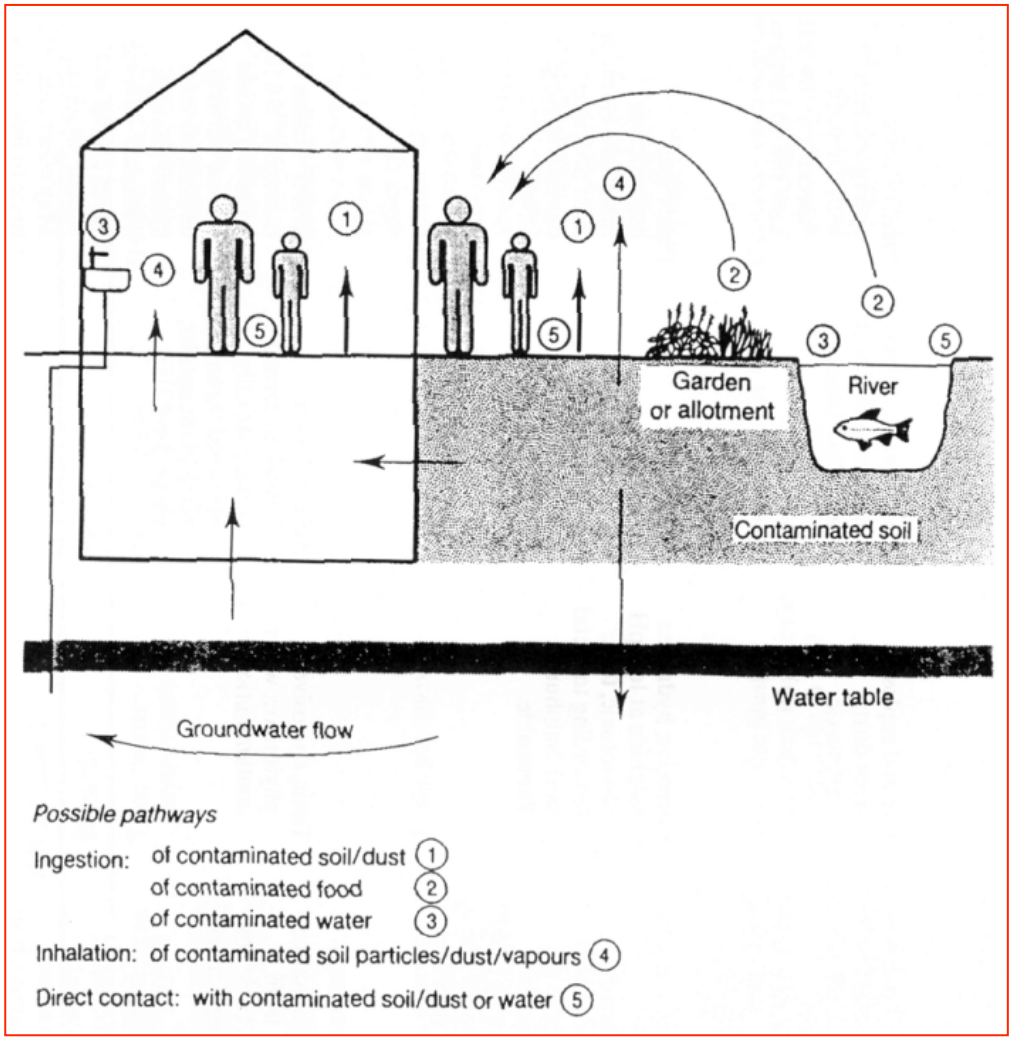
Exposure



Exposure


Pollutants
Deposition
Direct
Radiation
Inhalation
Inhalation

Exposure of human population



Environmental persistence

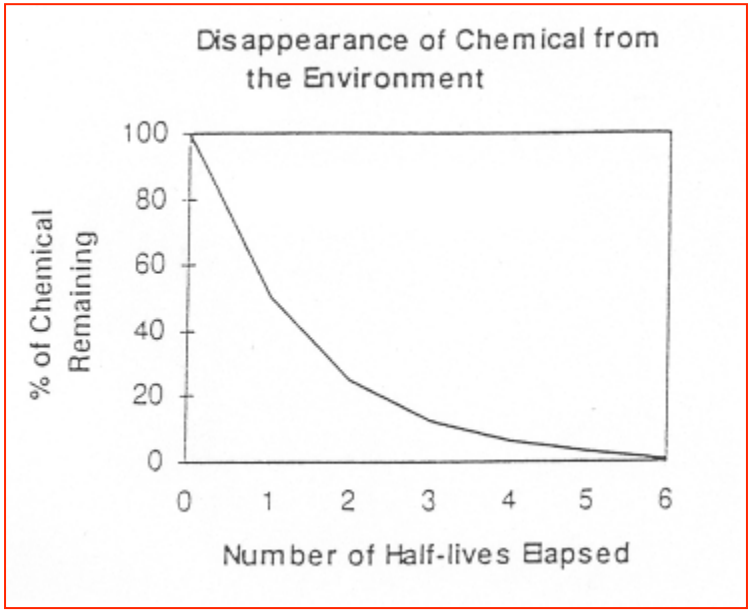
The ability to resist degradation in various media, e.g. air, soil, water, sediment, measured as half-life of the substance in the medium.

Persistence reflects the ability of the substance to resist physical, chemical or biological degradation.

Environmental persistence

Persistence is described by half-live ($t_{1/2}$), when the concentration of compound decreases on the half of original amount in given environmental compartments – after 5 cycles the level decreased on 3 %

Waters - $t_{1/2}$ = 6 days – during 1 months; if $t_{1/2}$ = 70 days, removal during ca 1 year



Biaccumulation – basic definitions

The process by which the chemical concentration in an (aquatic) organism achieves a level that exceeds that in the water (soil), as a result of chemical uptake through all possible routes of chemical exposure (dietary absorption, transport across the respiratory surface, dermal absorption, inhalation).

Bioaccumulation takes place under field conditions.

It is a combination of chemical bioconcentration and biomagnification.

Biaccumulation

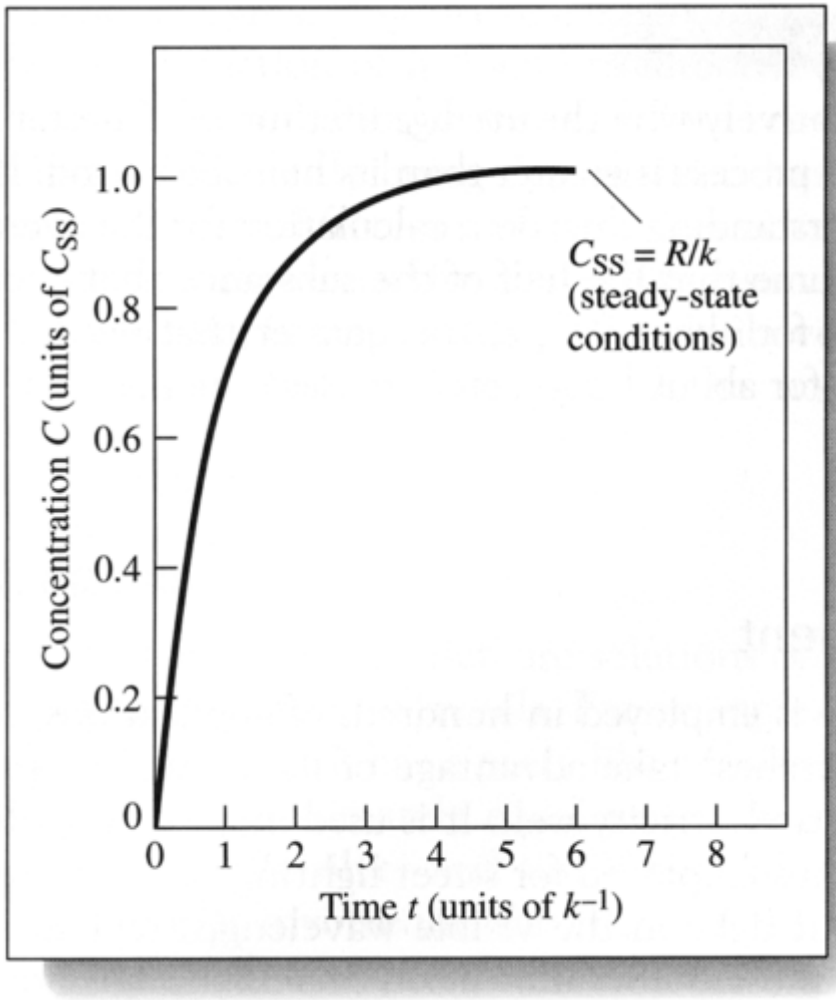
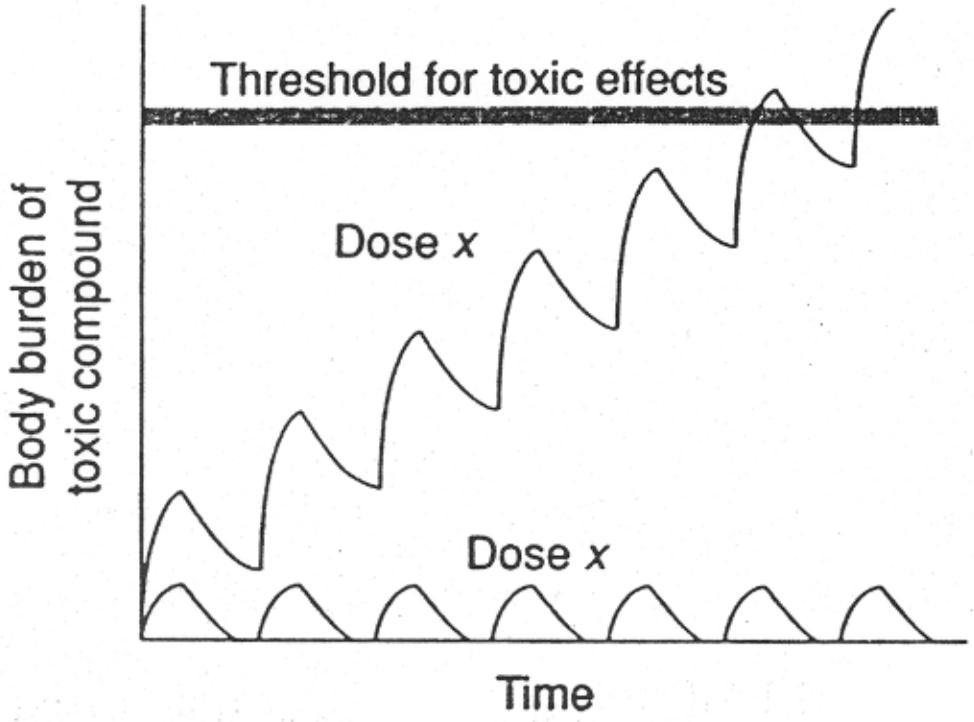


Figure 7-1
Increase in metal concentration with time to reach the steady-state value, C_{ss}.

Bioaccumulation



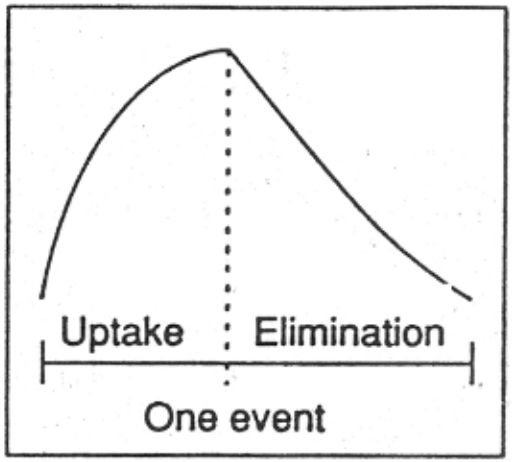


FIGURE 5-5
Effect of dose fractionalization on accumulation of a toxic compound.

Photochemical transformation processes

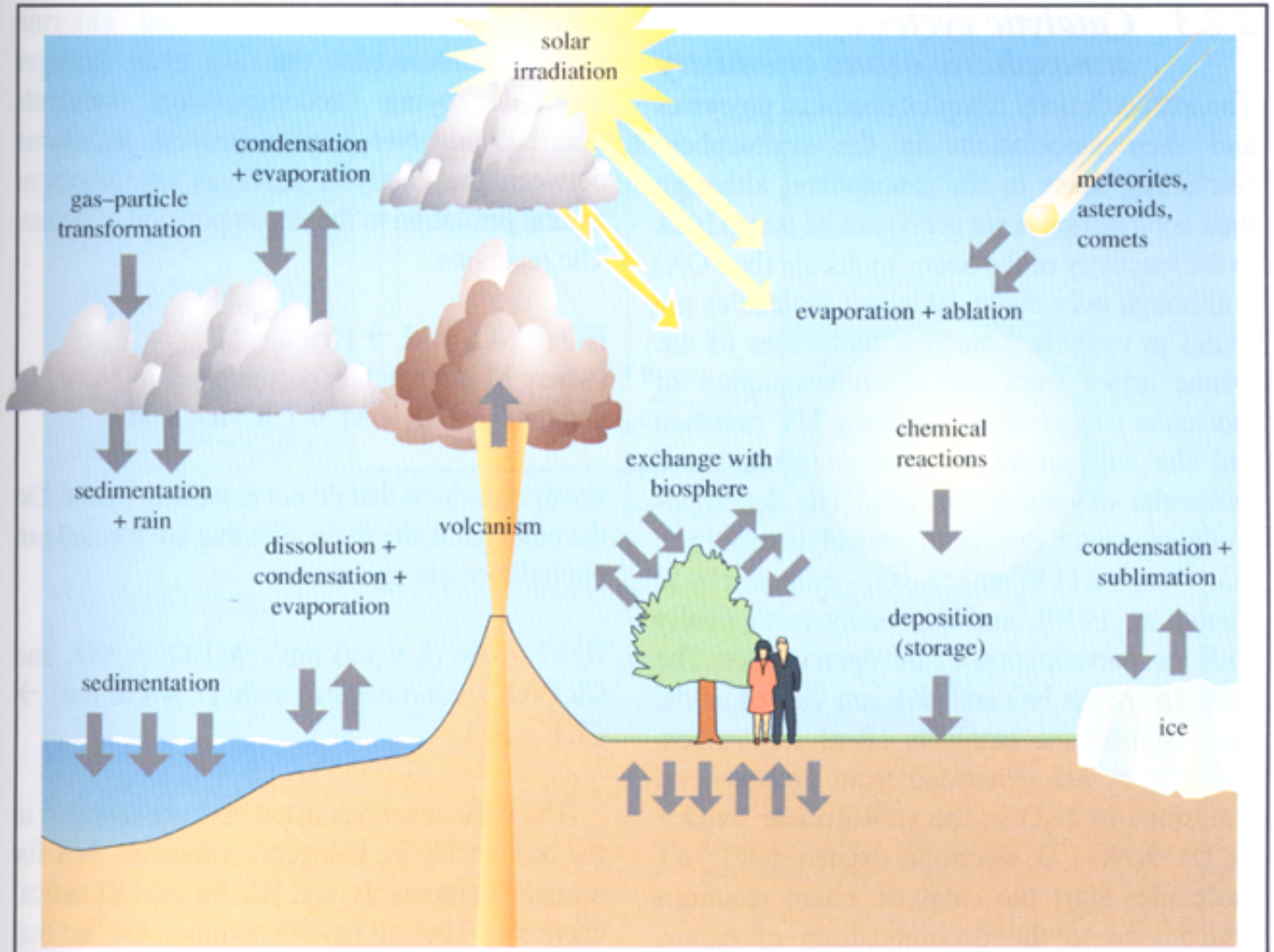


Figure 2.2.1 Chemistry and photochemistry

Biodegradation

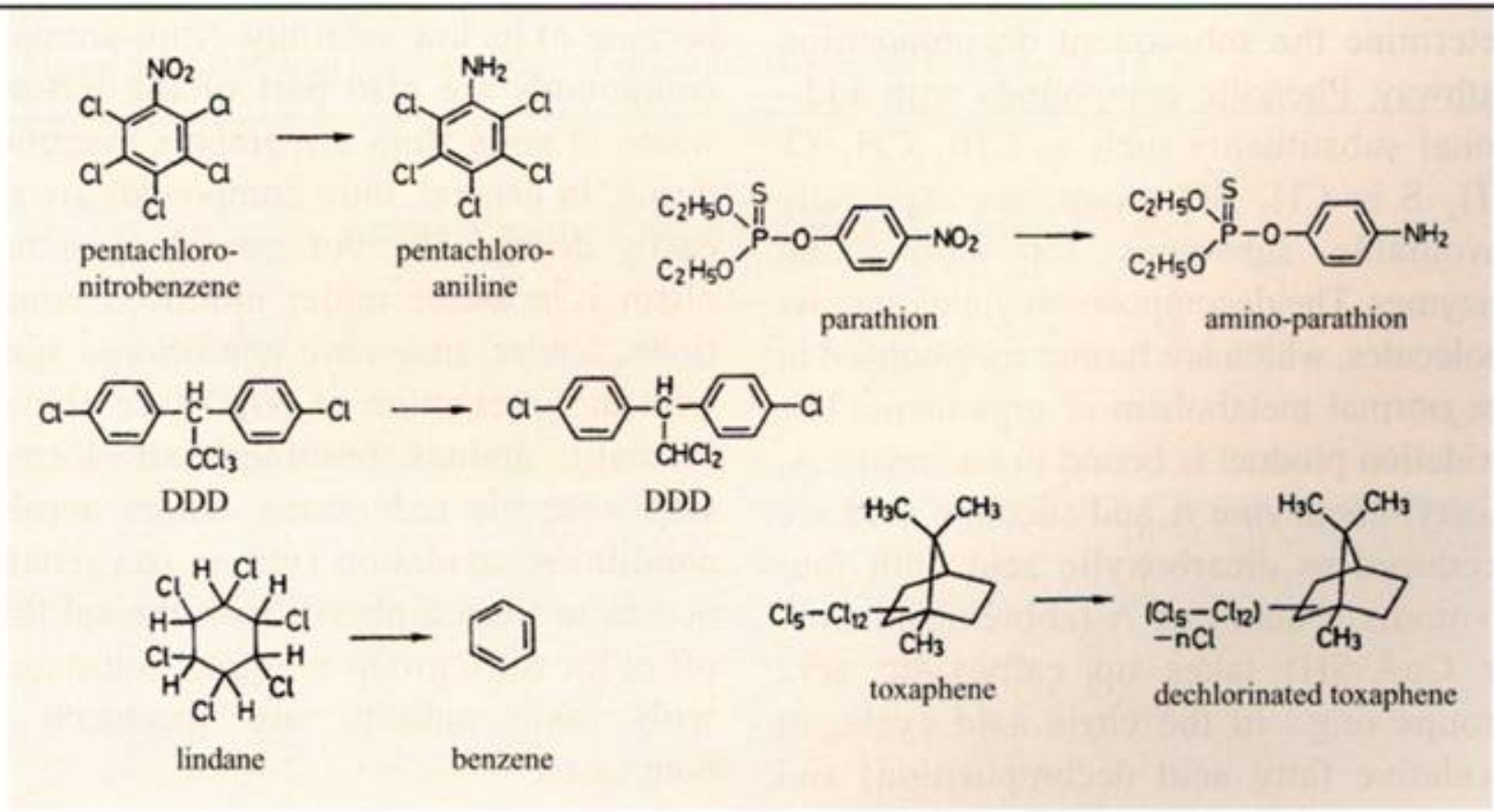


Figure 5.2.2 Reductive (anaerobic) reactions of xenobiotics

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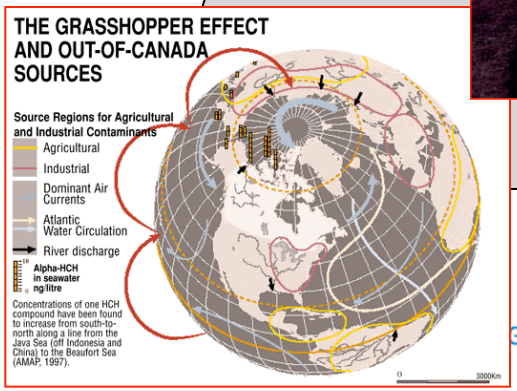
Production, application, disposal

POPs



GANIZATION

The main sources of persistent organic pollutants

(a) Combustion processes;

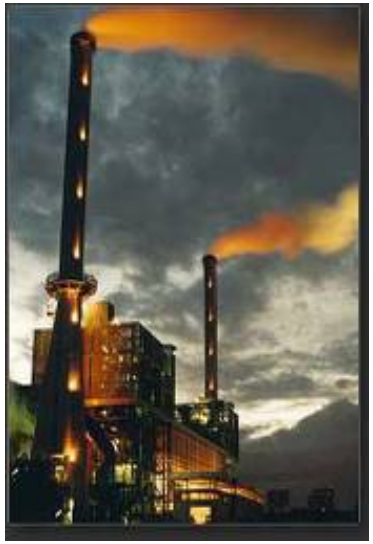
(b) Industrial processes;

(c) Diffusing sources (mobile sources, open burning etc.);

(d) Secondary sources (volatilisation from landfills etc.); and

(e) Accidental sources (industrial accident, transport accident etc.).

(f) Environmental processes



UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

dekonta

Sources of POPs under the SC

- Although most information is available for dioxins and furans, it is assumed that the major sources of PCDD/PCDF are also sources of PCB and HCB.
- The Convention specifies four source categories, which should be addressed with priority:
  - waste incinerators, including co-incineration of municipal, hazardous, medical wastes, and sewage sludge;
  - cement kilns firing hazardous wastes;
  - production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching;
  - thermal processes in the metallurgical industry (secondary copper, sinter plants in the iron and steel industry, secondary aluminum, and secondary zinc).

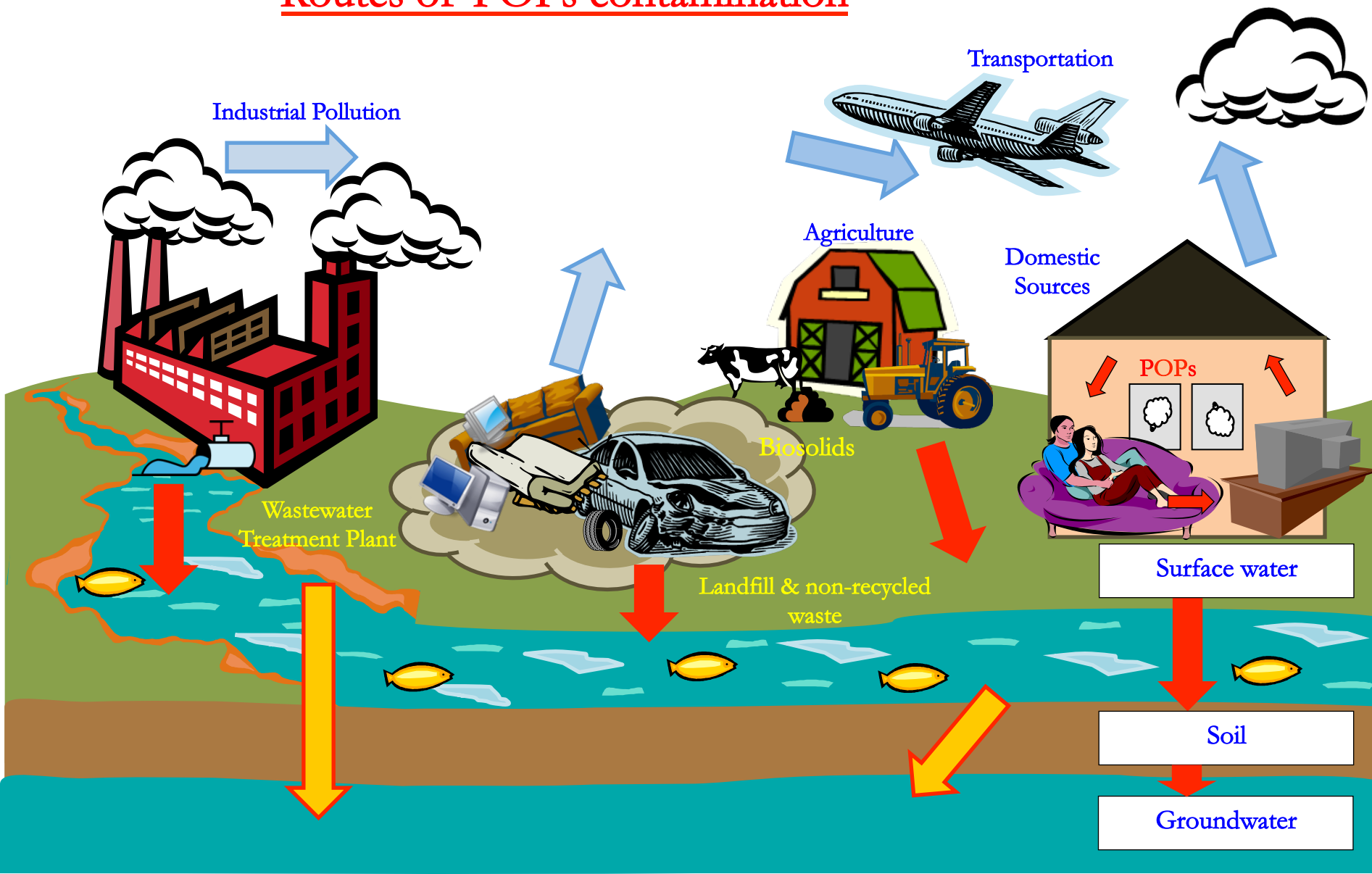
Sources of POPs under the SC

An additional list of 13 other sources contains 11 more combustion sources, which also can release POPs byproducts; *e.g.*

- open burning,
- residential combustion sources,
- fossil-fuel utility boilers,
- crematoria,
- cable smouldering, *etc.*
- but also textile and leather dyeing (with chloranil)
- and finishing (with alkaline extraction).

Contaminated sites

Routes of POPs contamination



PCDDs/Fs sources

a) Production processes involving chlorine (production, use and disposal):

- Chlorination of phenols
- 2,4,5-trichlorophenol
- Pentachlorophenol
- Friedel-Crafts synthesis with aluminium or ferrous chloride
- Pesticides especially those based on chlorophenoxyacetic acid
- PCBs
- Chlorine with graphite anodes
- Chloroamine
- Metal chlorides
- Pulp chlorobleaching
- Water disinfection
- Use of coagulants with a chloride base

PCDDs/Fs sources

(b) Thermal processes:

- Incineration of:
  - municipal wastes
  - industrial wastes
  - hazardous wastes
  - hospital wastes

- Metallurgical processes:
  - production of iron and steel
  - production of copper
  - production of aluminium
  - production of nickel
  - production of magnesium
  - metal reclamation especially of copper or aluminium
  - use of old iron in steel production

PCDDs/Fs sources

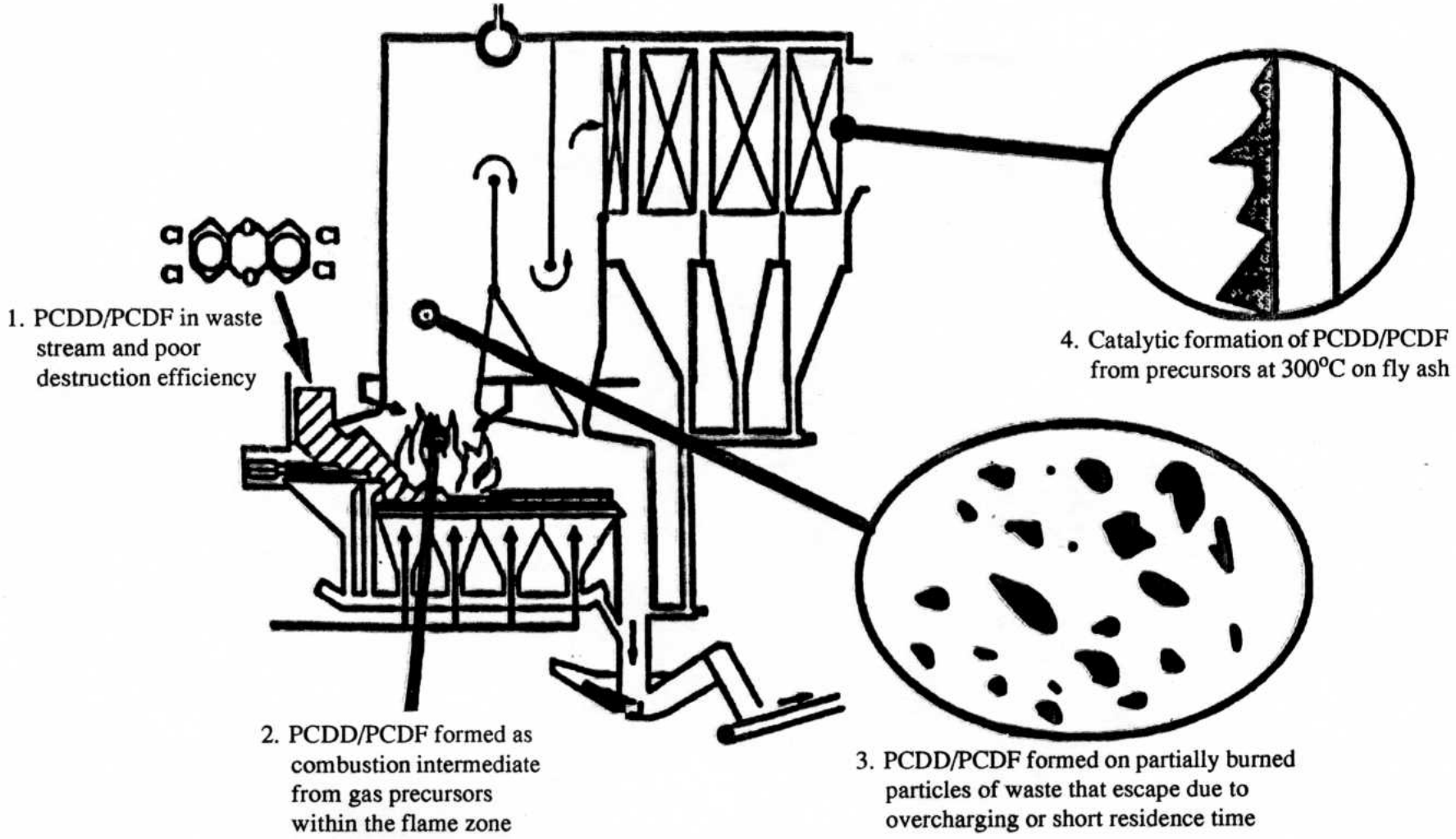
(c) Other processes:

- Motor vehicles using unleaded petrol
- Domestic heating systems
- Production of heat and electricity
- Domestic waste burning
- Uncontrolled fires in landfills
- Building fires (dwellings and factories)
- Dry cleaning

(d) Diffusive sources:

- Use of sewage sludges in agriculture
- Volatilisation from landfills (flared and unflared)
- Use of products with content of PCDDs/Fs or their precursors
- Use of pesticides based on chlorophenoxyacetic acid with impurities of PCDDs/Fs

PCDDs/Fs formation



Sources of PCBs

Closed Applications

Dielectric Fluids
- Transformers
- Capacitors
- Microwave ovens
- Air conditioners
- Electric motors

Electrical Light Ballasts
Electromagnets

Partially Closed Applications

Hydraulic Fluids
Heat Transfer Fluids
Switches
Voltage Regulators
Circuit Breakers
Vacuum Pumps
Electrical Cables

Open Applications

Inks
Lubricants
Waxes
Flame Retardant
Adhesives
Surface Coatings
Insulating Materials
Pesticides
Dyes
Paints
Asphalt
Condensate from Pipelines
Plasticisers

Waste

Fluff
Inadvertent Production
Navigational Dredging
Spills
Decommissioned Equipment
Building Demolition

Recycling Operations

Oil (Mineral Oil Market)
Carbonless Copy Paper
Plastics

Interim Storage/Permanent Disposal

Temporary Storage Facilities
High Temperature Incineration
Underground Storage Facilities
Chemical Decontamination
Hydrogenation

Industrial Dumpsites

Landfills

Products Made with Recycled Materials

Soil

Air

Water

Food

OCPs sources

- Production
- Use as a pesticide
- Environmental contamination
- Disposal of wastes and materials containing DDT
- Volatilisation from landfills (flared and unflared)
- Use in livestock treatment
- Use in wood and seed applications
- Use as intermediate

PAHs sources

(a) production
(b) use as intermediates
(c) production of carbon black
(d) combustion of fossil fuels
- production of heat and electricity
- motor vehicles

(e) production and use of coke
(f) production and use of asphalt
(f) production and use of coal tars
(g) catalytic cracking
(h) heat coal conversion processes
(i) waste waters
(j) food technologies

PAHs sources

(k) production of aluminium
(l) production of iron and steel
(m) volatilisation from landfills (flared and unflared)
(n) combustion of various types of wastes
(o) cement production in both dry and wet process kilns
(p) petroleum refineries
(r) crematoria
(s) forest and prairie fires
(t) volcanic eruptions
(u) smoking

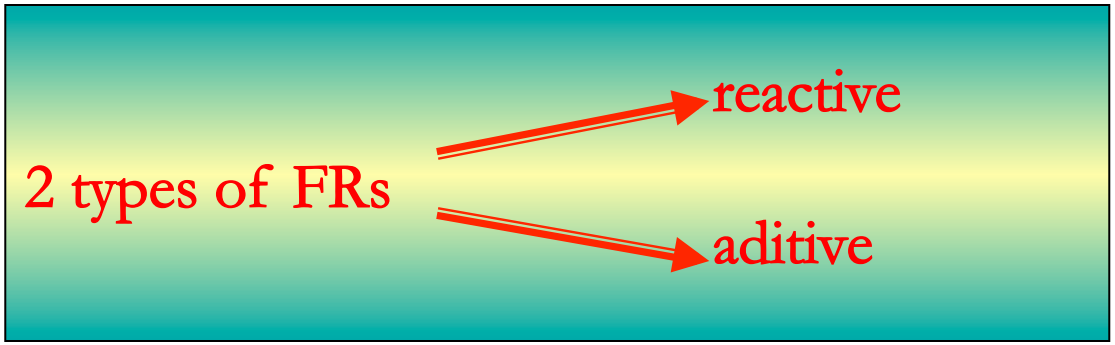
Brominated Flame Retardants (BFRs)

- PBDEs: added into plastics or as impregnation of fabrics, technical mixtures of various bromination degree
- vastly used in North America and Asia
- their use was banned, however EU regulation ALLOWS use of recycled plastics containing PBDEs (Directive 2002/95/EC, ammended)
- HBCDDs: additives in polystyrene foams (EPS, XPS), extensive use in Europe
- more isomers, α, β, γ, δ, ε, used again as technical mixture, where γ-HBCDD prevails

Mechanism of flame retardancy

Heat (increasion of tempareture) → destruction of FRs (early than destruction of polymer matrice) → input of products protected/retard the fire

Ideal situation: retardant is destroyed round temperature round 50 °C than polymer – brominated flame retardants (BFRs) in combination with many polymers cover this consideration



How does BFRs work?

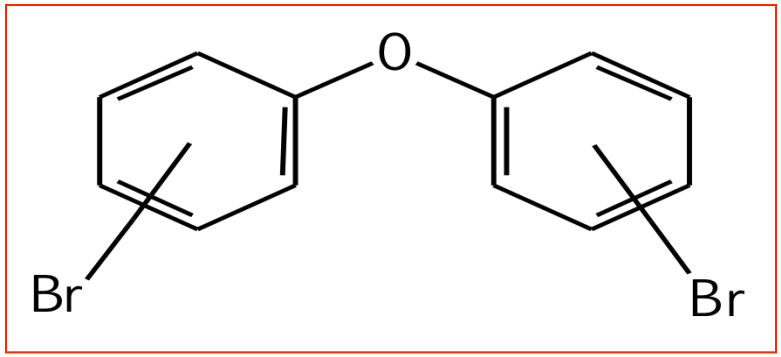
- They are thermally labile
- Break down with heat – give off HBr (g)
- HBr 'quenches' flame
- Increases 'flash-over' time - More time to escape
- BFRs save lives, but are toxic and persistent!

Non-flame retarded:

Treated with: PBDEs:

Aditive flame retardants

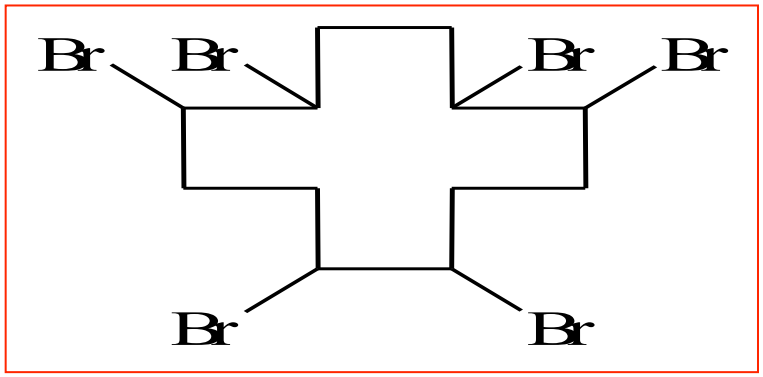
PBDEs



(DeBDE - 75 %)

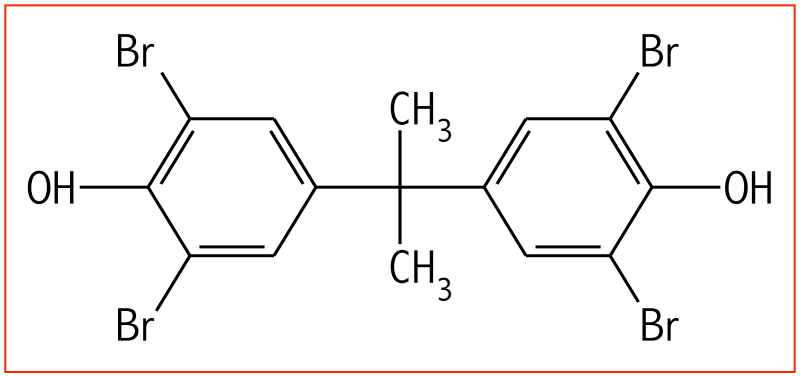
Commercial technical mixtures conteins PBDEs: BROMKAL 70, DE - 71, FR 1205....)

HBCD



Reactive flame retardants

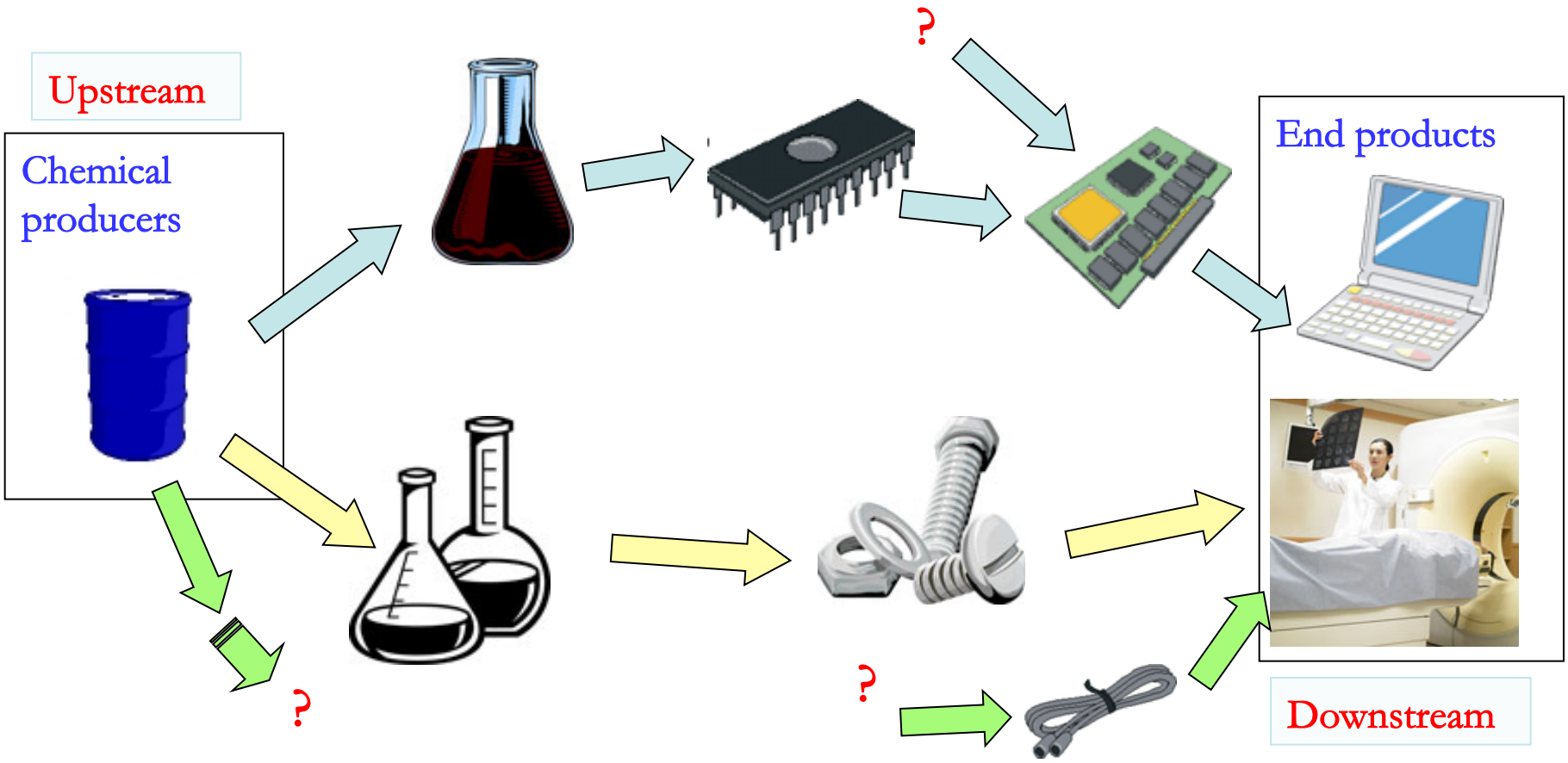
TBBPA



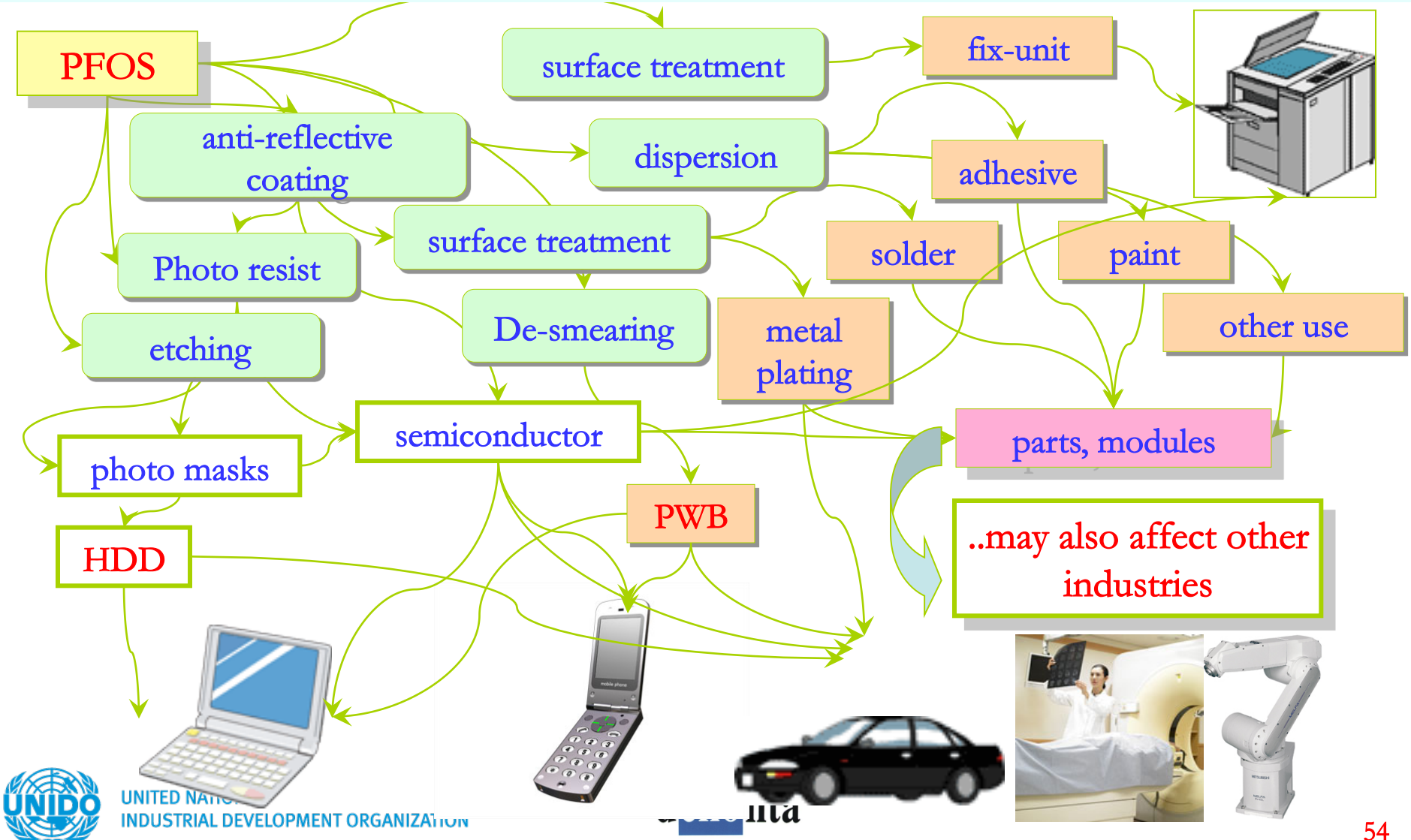
Main use of tetrabromobisphenol (TBBPA):

- Epoxy resins
- Phenol resins

Special care needed for industrial chemicals like PFOS because: Used in numerous processes and parts



Special care needed for industrial chemicals like PFOS because: Long supply-chain, involve many producers/ users



Using of PFOS

PFOS use areas with possible relevance:

- Fire fighting foams
- Chromium plating and other plating industry
- Oil extraction
- Synthetic carpets (production and use)
- Textile industry;
- Paper industry
- Imported textile and paper
- Other specific industrial applications (listing in the POPRC document)
- Pesticides (Sulfluramid); aviation fluids air plains
- Detergents and impregnations

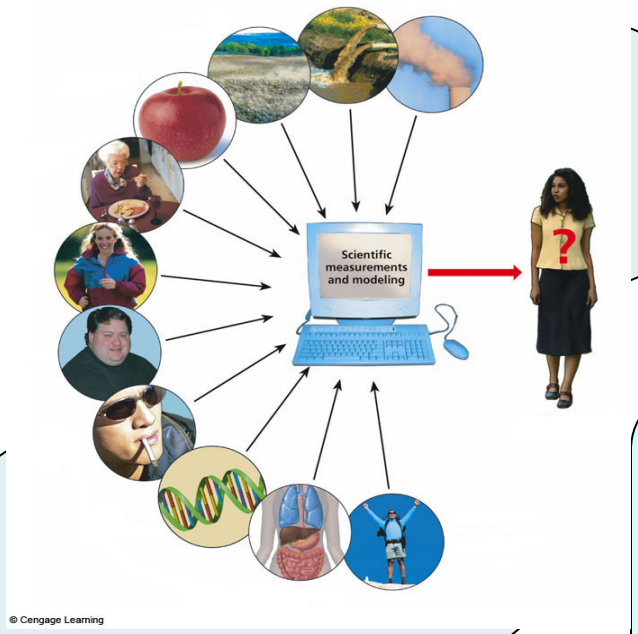
Recycling of PFOS containing materials:
Recycling synthetic carpets, PFC paper, PFC textiles?

Emission of PCDDs/Fs and PAHs from uncontrolled burnings

Introduction to POPs

- POPs - general definition,
- Understanding of POPs
- Properties, problems, "Dirty Dozen", new POPs;
- Source of POPs;
- Toxicology and ecotoxicology of POPs;
- POPs aspects of transboundary impact;

Health impacts



POPs

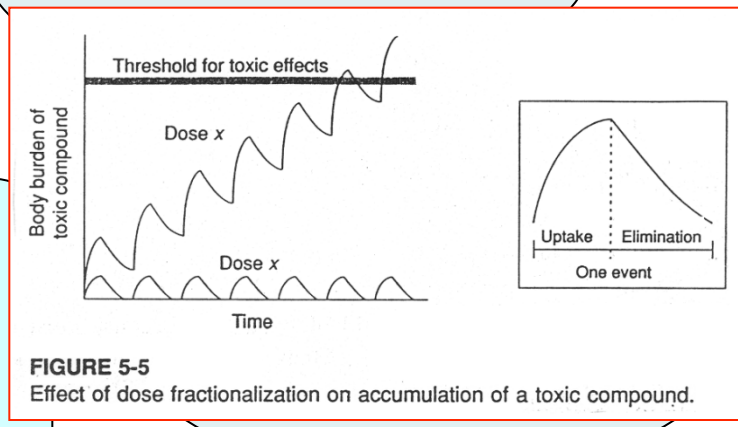


FIGURE 5-5
Effect of dose fractionalization on accumulation of a toxic compound.

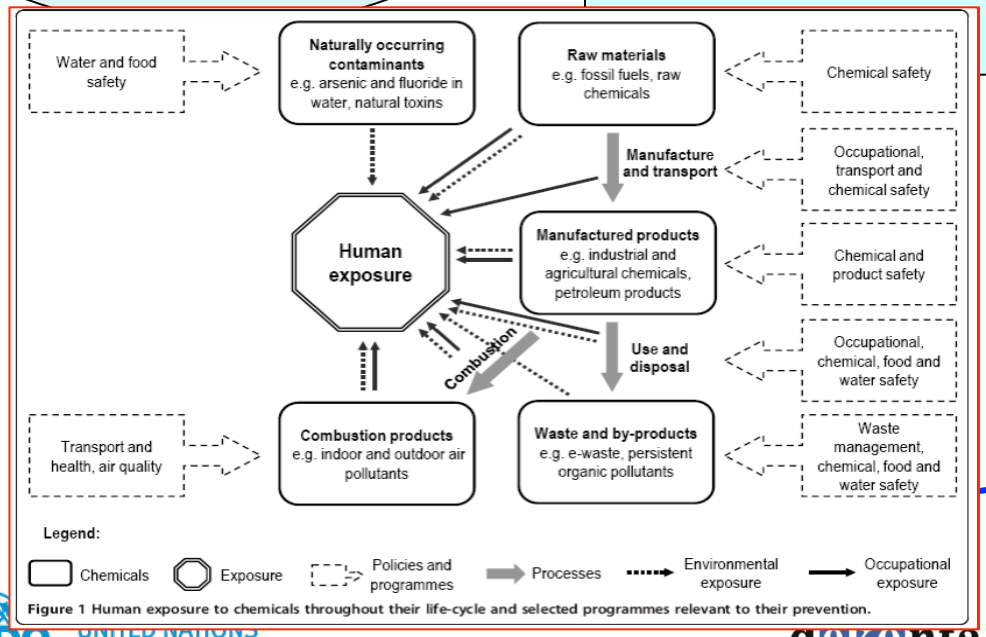


Figure 1 Human exposure to chemicals throughout their life-cycle and selected programmes relevant to their prevention.

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Effects of POPs

The most important effects:

- Induction of AHH receptors
- Neurotoxicity
- Imunotoxicity
- Endocrinne disruption:

  - estrogens/antiestrogens
  - antiandrogens
  - thyroid hormones

Biotransformations

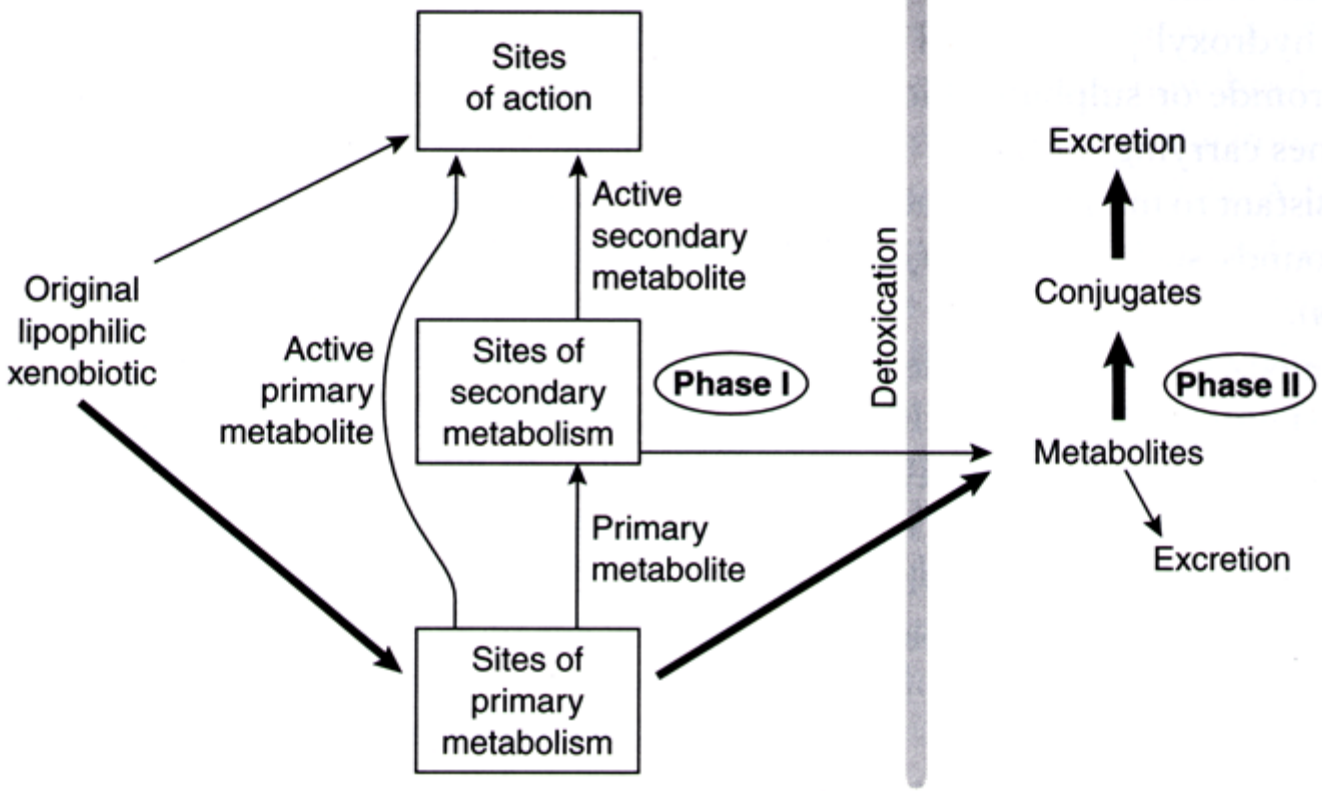


FIGURE 2.2 *Metabolism and toxicity.*

Biotransformations

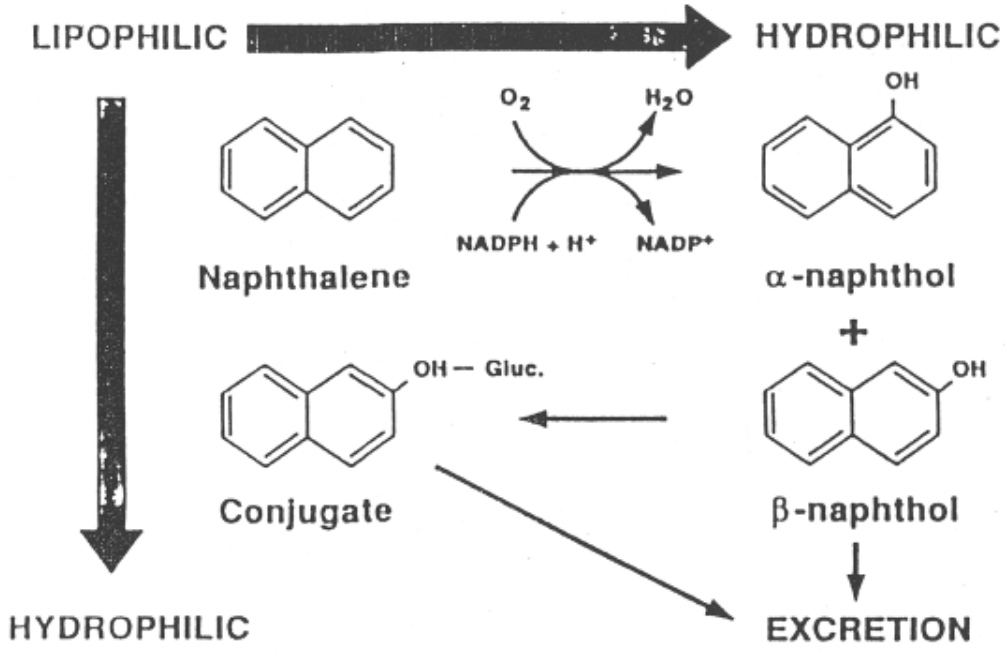
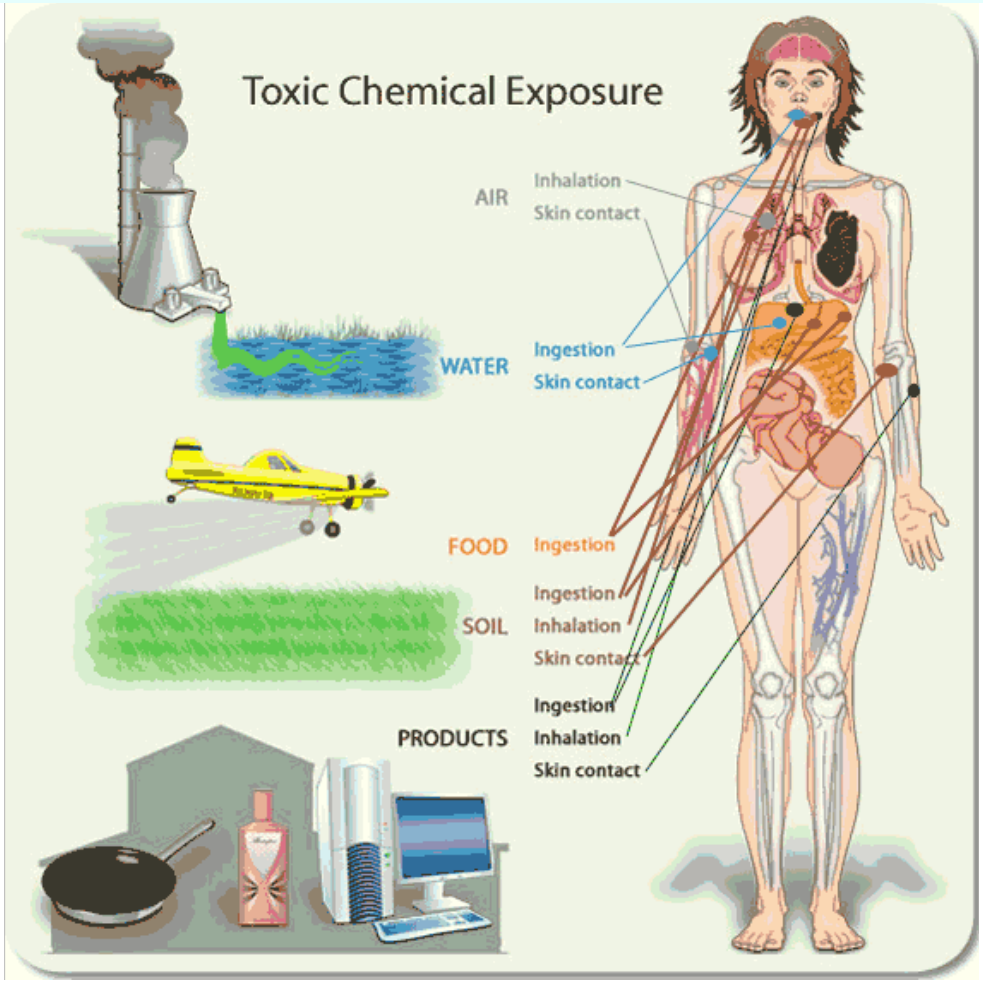


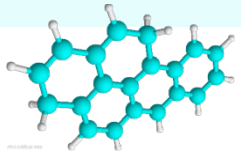
Figure 1. The cytochrome P-450 mixed function oxidase system facilitates excretion of lipophilic organic substrates in terrestrial and aquatic animals by producing metabolites that are more water soluble than the parent compound. Common metabolites of naphthalene are shown (after 2).

Environmental chemicals exposure



WHO World Health Organization

EXPOSURE



- Only in the case of contact
- Exposure pathways have a lot natural and active function barriers
- After transfer to organism some chemicals can have negattive effects

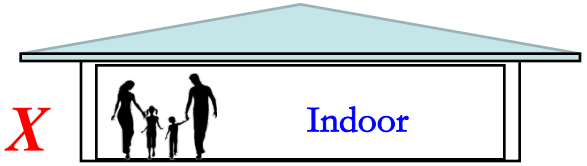
EXPOSURE PATHWAYS

Inalation

Dermal exposure

Oral exposure

Outdoor X



Source of contamination → Environment → Exposure → Health effects on population

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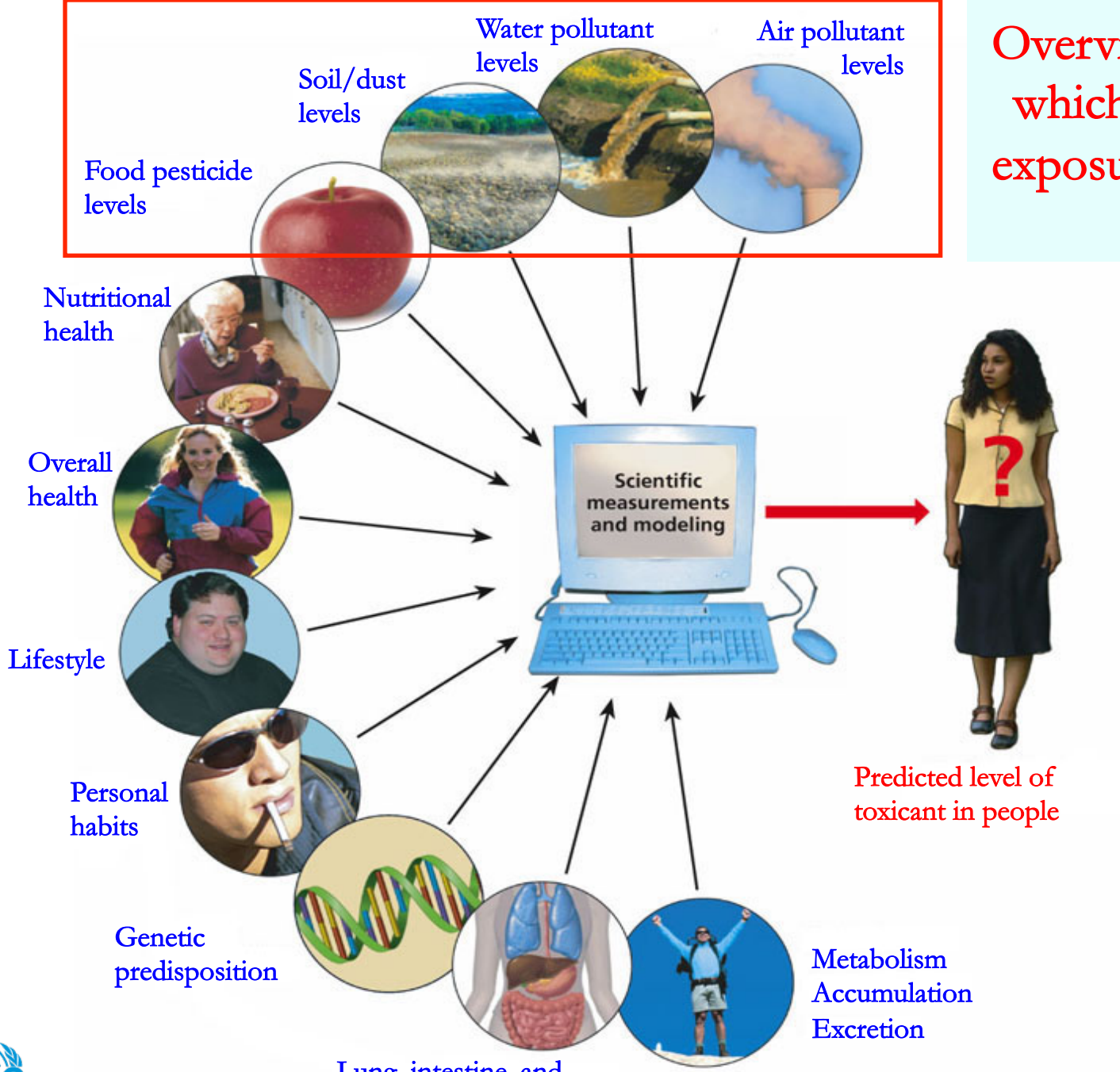
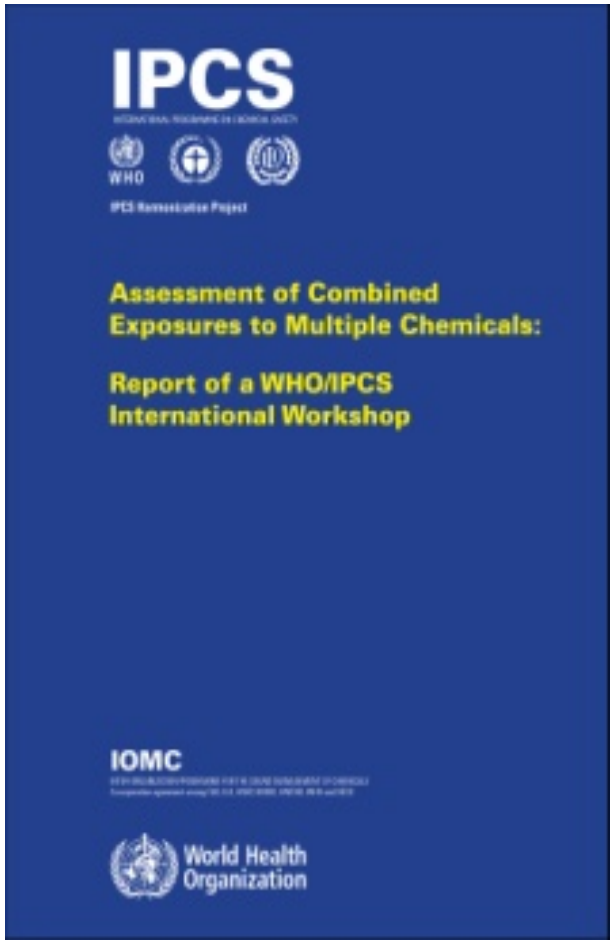
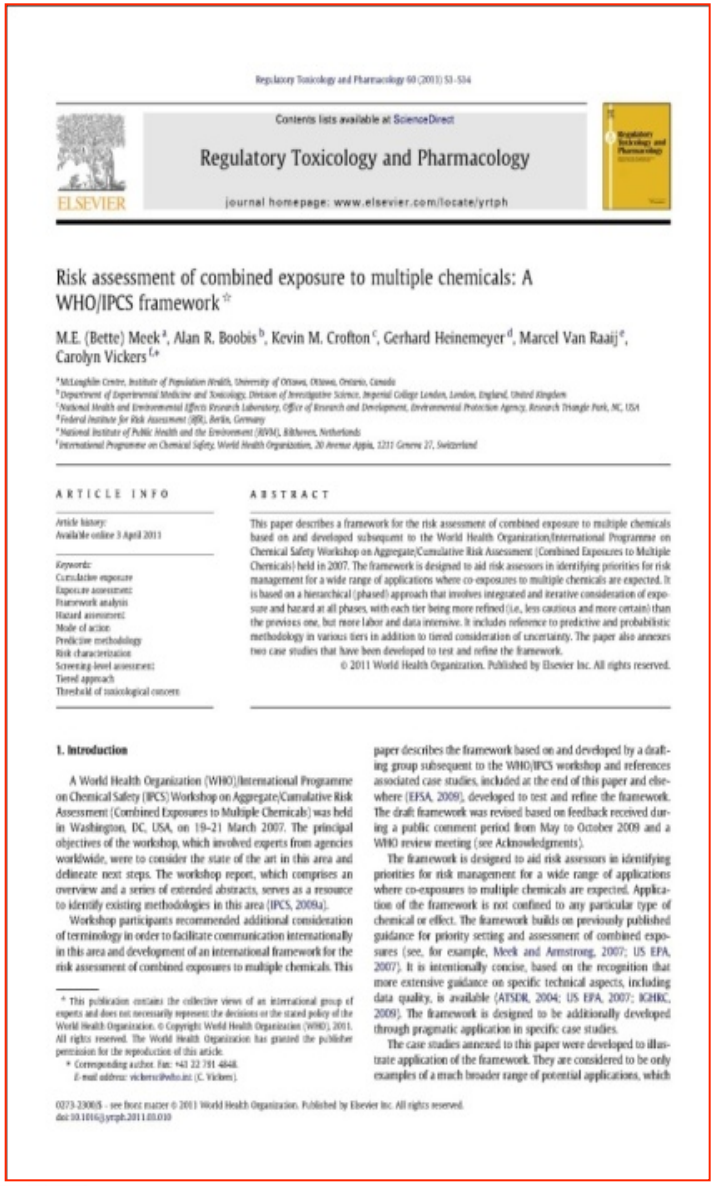
Overview of factors, which can affected exposure and human risks



Toxic interactions





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Risk assessment of combined exposure to multiple chemicals: A WHO/IPCS framework ☆

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Screening-level assessment
Tiered approach
Threshold of toxicological concern

ABSTRACT

This paper describes a framework for the risk assessment of combined exposure to multiple chemicals based on and developed subsequent to the World Health Organization/International Programme on Chemical Safety Workshop on Aggregate/Cumulative Risk Assessment (Combined Exposures to Multiple Chemicals) held in 2007. The framework is designed to aid risk assessors in identifying priorities for risk management for a wide range of applications where co-exposures to multiple chemicals are expected. It is based on a hierarchical (phased) approach that involves integrated and iterative consideration of exposure and hazard at all phases, with each tier being more refined (i.e., less cautious and more certain) than the previous one, but more labor and data intensive. It includes reference to predictive and probabilistic methodology in various tiers in addition to tiered consideration of uncertainty. The paper also annexes two case studies that have been developed to test and refine the framework.

1. Introduction

A World Health Organization (WHO)/International Programme on Chemical Safety (IPCS) Workshop on Aggregate/Cumulative Risk Assessment (Combined Exposures to Multiple Chemicals) was held in Washington, DC, USA, on 19–21 March 2007. The principal objectives of the workshop, which involved experts from agencies worldwide, were to consider the state of the art in this area and delineate next steps. The workshop report, which comprises an overview and a series of extended abstracts, serves as a resource to identify existing methodologies in this area (IPCS, 2009a).

Workshop participants recommended additional consideration of terminology in order to facilitate communication internationally in this area and development of an international framework for the risk assessment of combined exposures to multiple chemicals. This paper describes the framework based on and developed by a drafting group subsequent to the WHO/IPCS workshop and references associated case studies, included at the end of this paper and elsewhere (EFSA, 2009), developed to test and refine the framework. The draft framework was revised based on feedback received during a public comment period from May to October 2009 and a WHO review meeting (see Acknowledgments).

The framework is designed to aid risk assessors in identifying priorities for risk management for a wide range of applications where co-exposures to multiple chemicals are expected. Application of the framework is not confined to any particular type of chemical or effect. The framework builds on previously published guidance for priority setting and assessment of combined exposures (see, for example, Meek and Armstrong, 2007; US EPA, 2007). It is intentionally concise, based on the recognition that more extensive guidance on specific technical aspects, including data quality, is available (ATSDR, 2004; US EPA, 2007; ICHRC, 2009). The framework is designed to be additionally developed through pragmatic application in specific case studies.

The case studies annexed to this paper were developed to illustrate application of the framework. They are considered to be only examples of a much broader range of potential applications, which

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Endocrine Disruptors (EDs)

= exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub) populations (IPCS, 2002)

- a variety of chemical classes - natural and synthetic hormones, pesticides, compounds used in the plastics industry and in consumer products, and other industrial by-products and pollutants
- often widely dispersed in the environment
- some are persistent, can be transported long distances across national boundaries, and have been found in virtually all regions of the world (e.g. POPs)
- others are rapidly degraded in the environment or human body or may be present for only short periods of time but at critical periods of development (e.g. phthalates)
- Interfere with reproduction, immune functions, neurobehaviour, development of cancer, at all levels of biological organization and at key stages of life cycles

Obesogens

Obesity = a major global health problem

- Associated with many serious health risks
- Fundamental basis = an imbalance of energy intake and expenditure
- the early life experience (= quality of intrauterine life) being the important risk factor in obesity development.

.....the role of *in utero* and early life exposures to synthetic chemicals (e.g. EDs) that may have the capacity to disrupt energy balance, in the development of obesity and related metabolic diseases

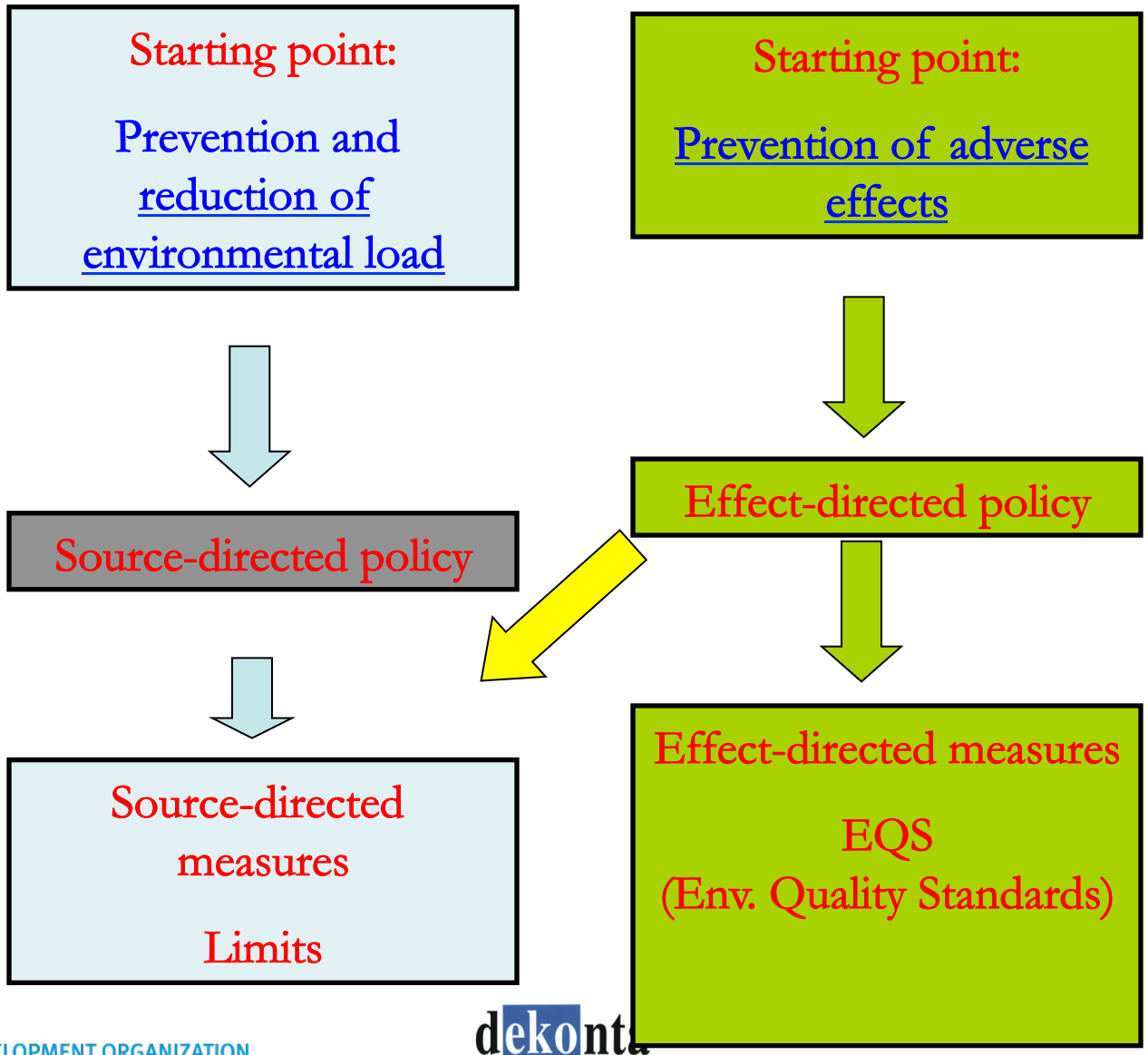
Obesogens

Obesogens = chemical agents with ED properties that inappropriately regulate and promote lipid accumulation and adipogenesis to favour weight gain and obesity (Grun and Blumberg, 2007).

- exposure to dietary and environmental chemicals, may further exacerbate the effects of imbalances in diet and exercise, resulting in an increased susceptibility to obesity and obesity-related disorders.

A first set of candidate obesogens – e.g. persistent organic pollutants (POPs), perfluoroalkyl compounds, bisphenol A, and phthalates.

Environmental policy: Limitations of sources and effects



Risk assessment & management

'Hazard' identification

Data compilation

Exposure assessment

PEC

Effect assessment

PNEC

Risk characterisation

HI = PEC/PNEC

Environmental quality standards / criteria

Hazard index

HI

< 1

> 1

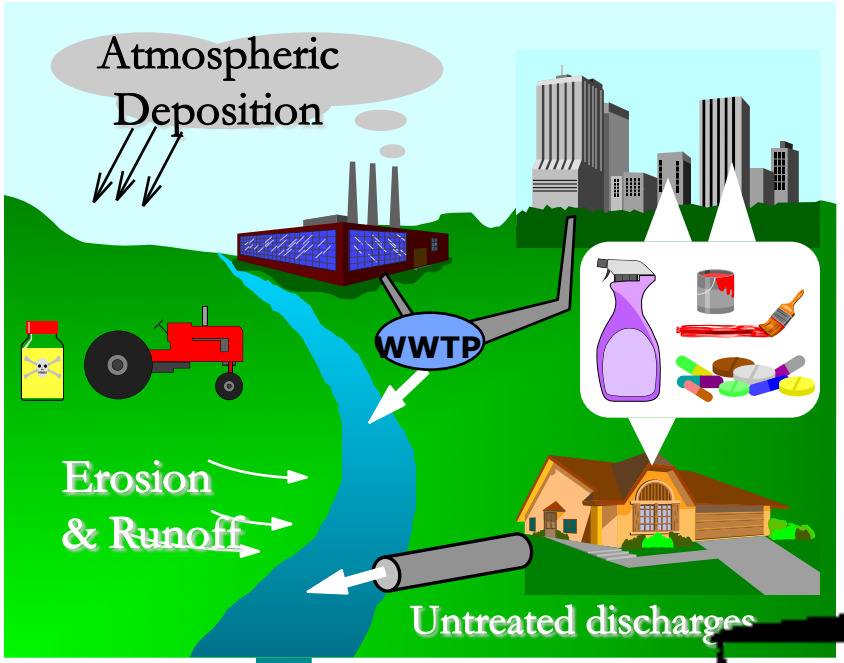
Risk management

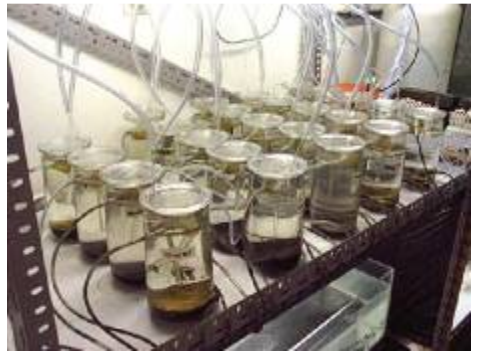
Risk assessment

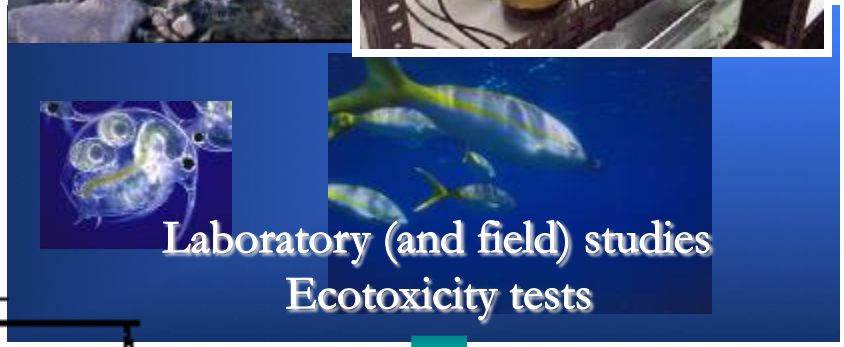
Exposure

Effects

EUSES European Union System for the Evaluation of Substances







Predicted Exposure Concentration (PEC)

Predicted No Effect Concentration (PNEC)

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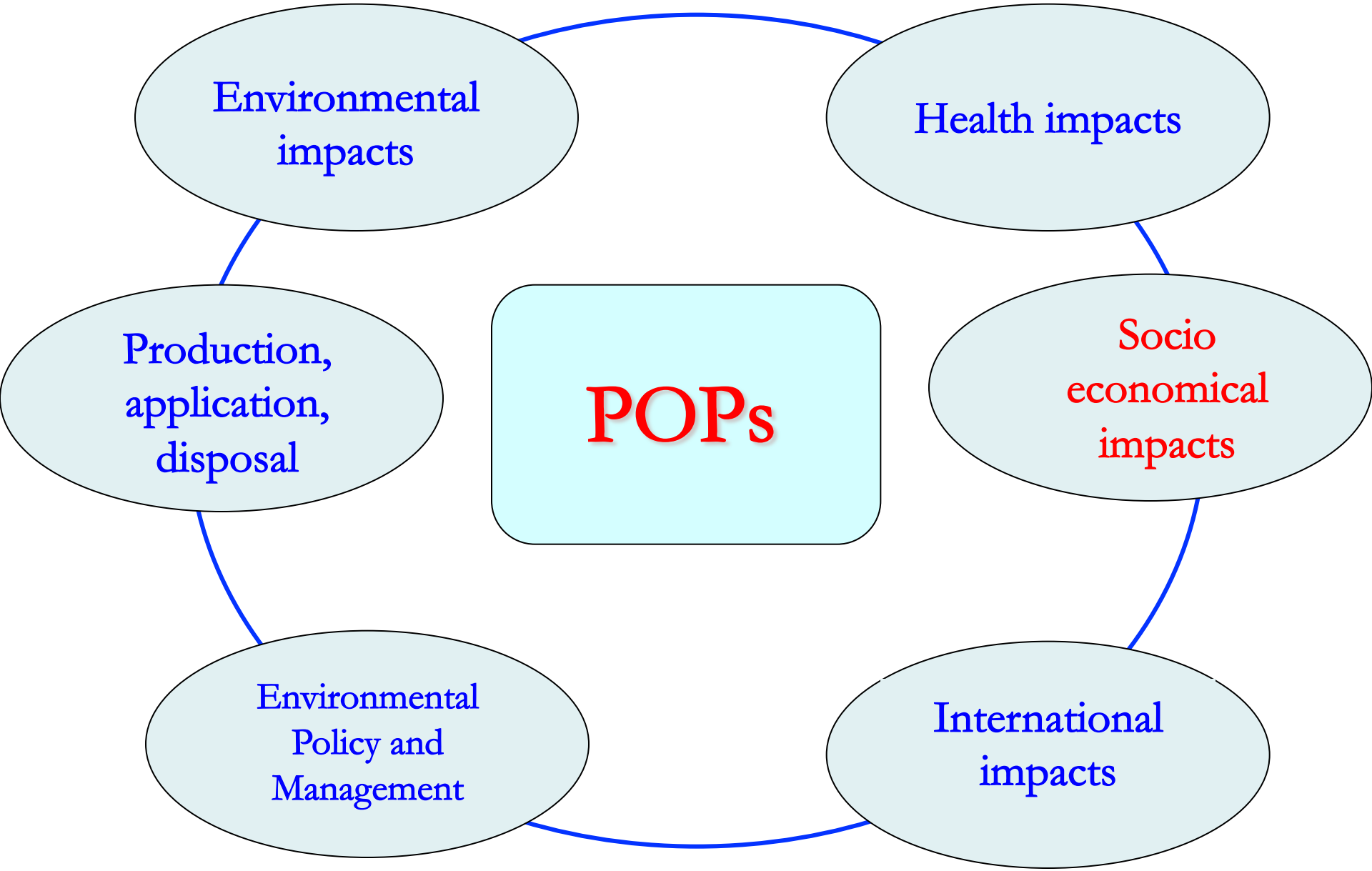
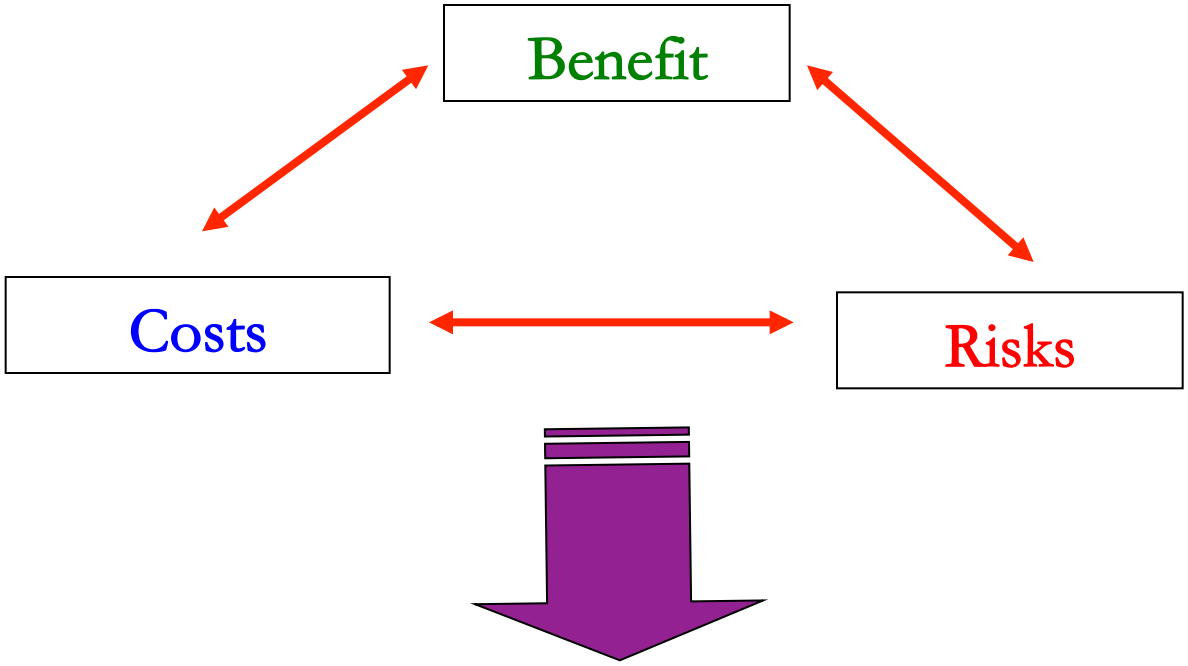

Environmental impacts
Health impacts
Production, application, disposal
POPs
Socio economical impacts
Environmental Policy and Management
International impacts

Basic definitions

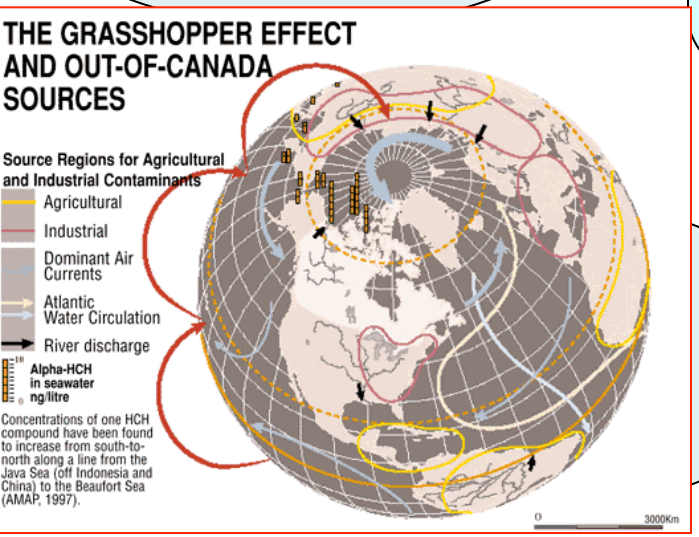


None from this element could not be changed without changes of other

Alternative evaluation have to include relationship between benefit and risk, which can be done due to some remediation

POPs

LRTAP
Long-range Transboundary Air Pollution



International impacts

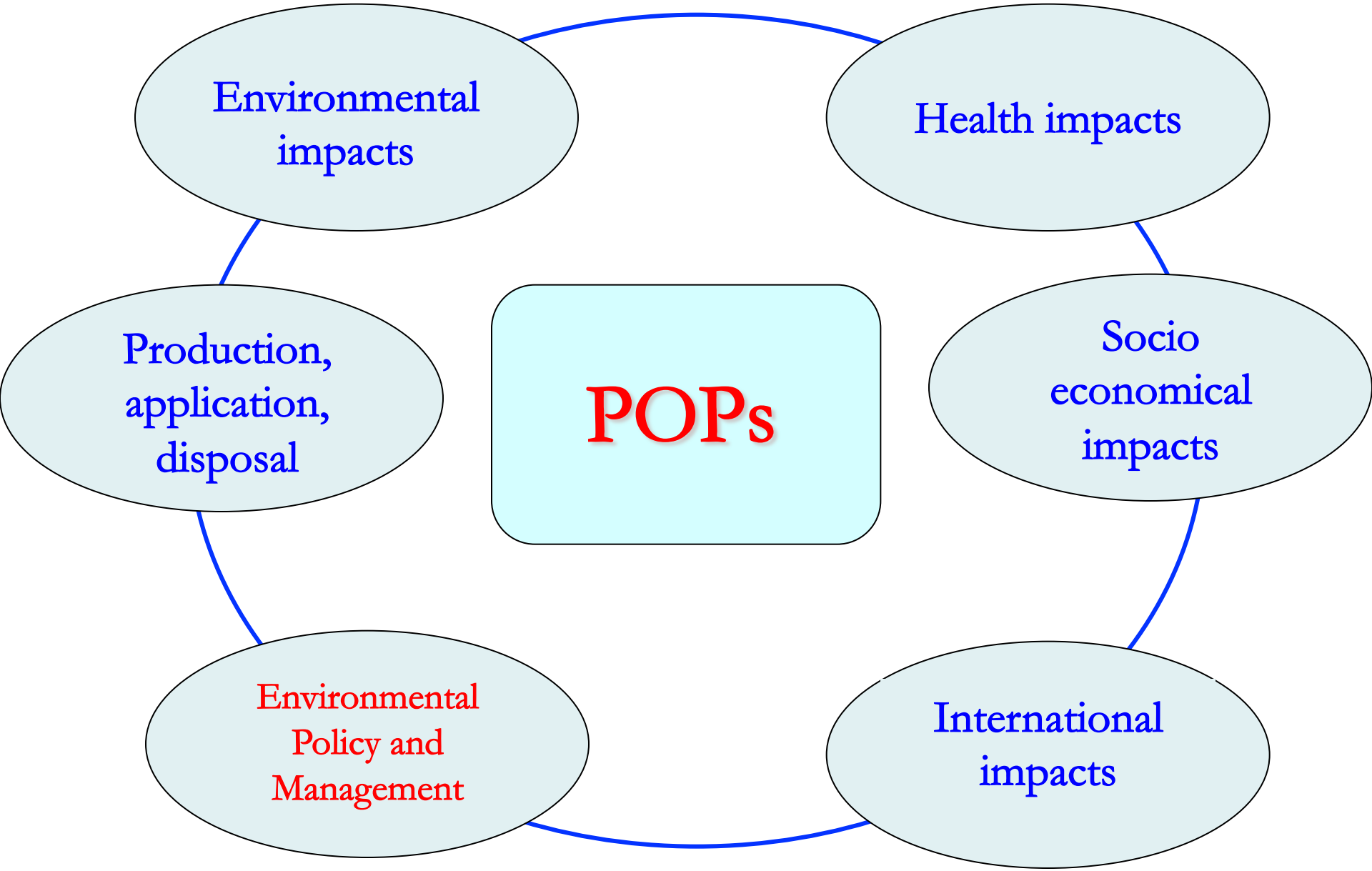
UNEP

FAO

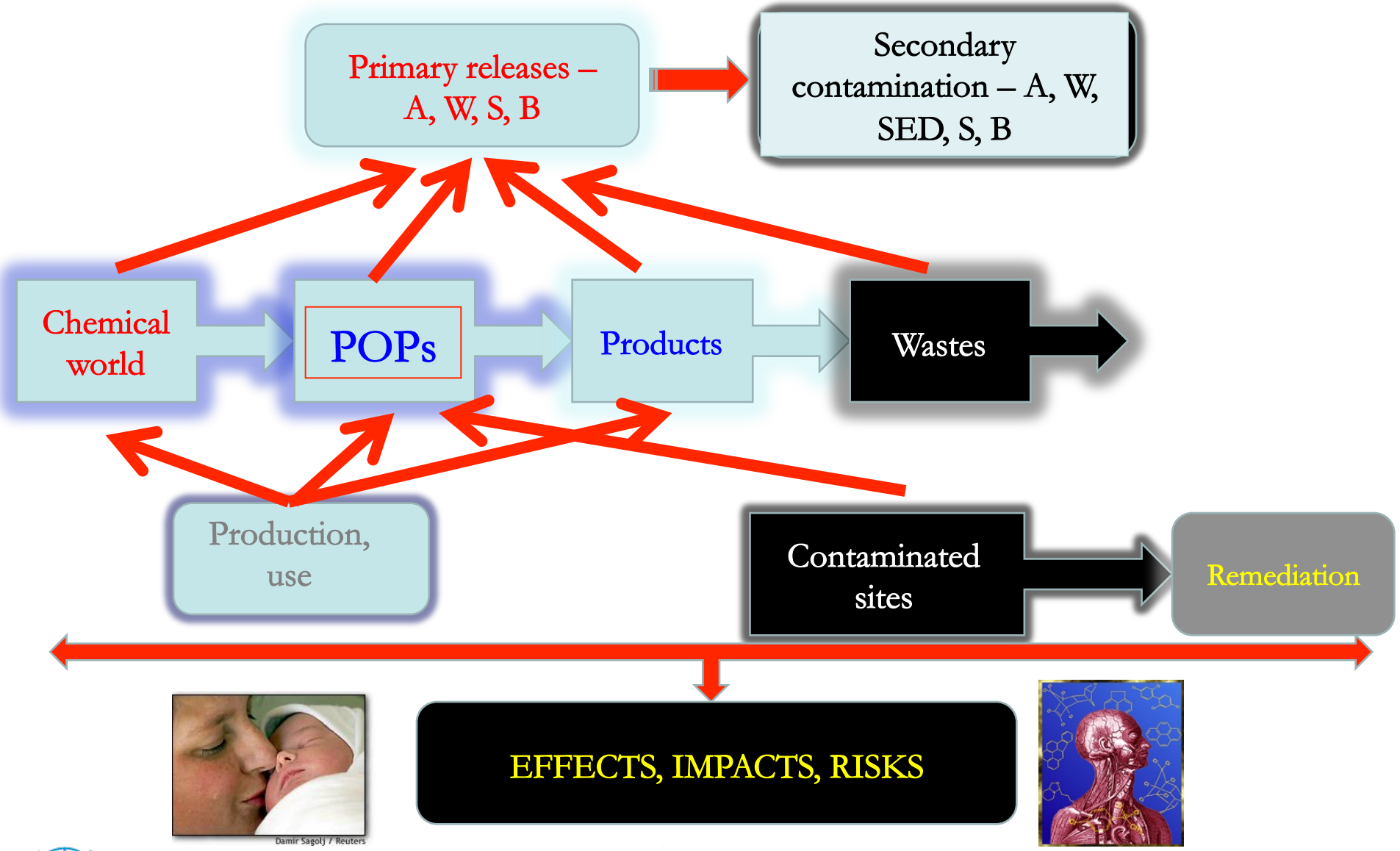
BASEL CONVENTION

ROTTERDAM CONVENTION

STOCKHOLM CONVENTION


Environmental impacts
Health impacts
Production, application, disposal
POPs
Socio economical impacts
Environmental Policy and Management
International impacts

Summary of chemical problems

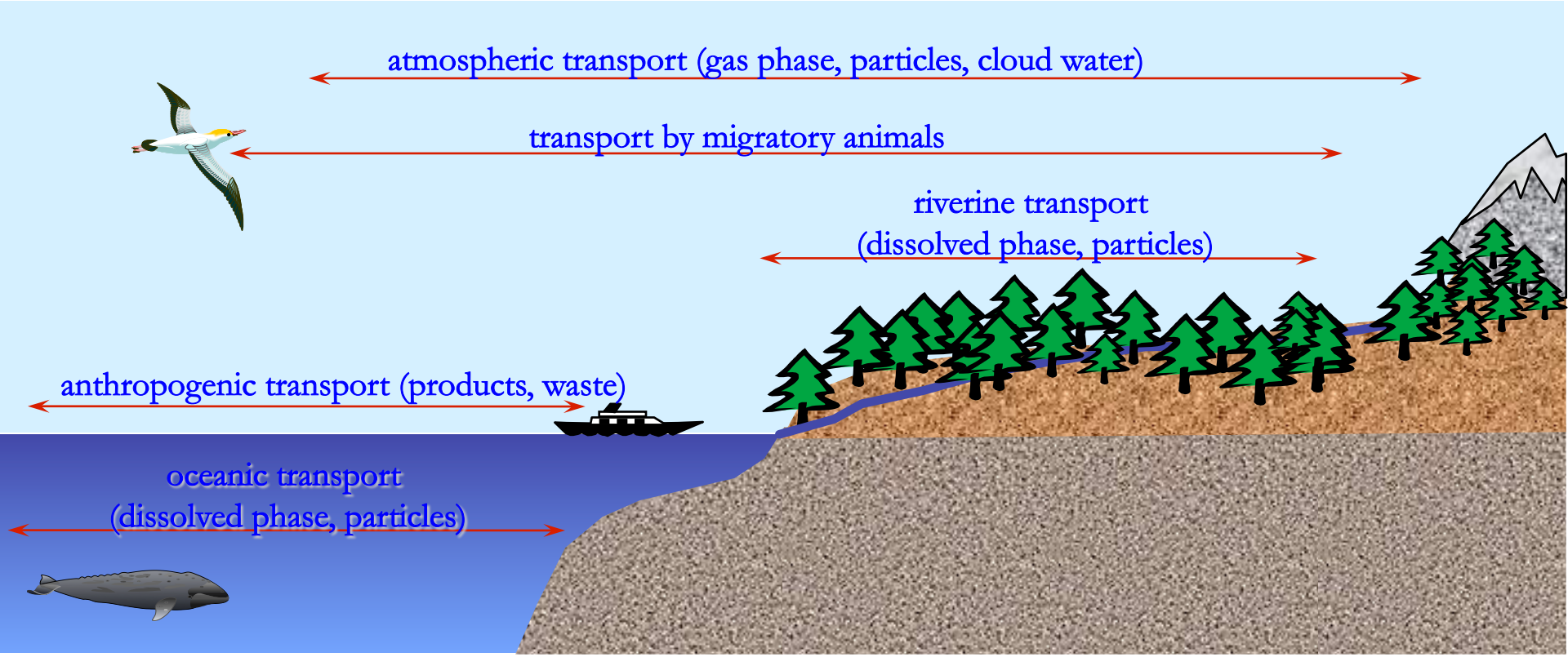


Introduction to POPs

- POPs - general definition,
- Understanding of POPs
- Properties, problems, "Dirty Dozen", new POPs;
- Source of POPs;
- Toxicology and ecotoxicology of POPs;
- POPs aspects of transboundary impact;

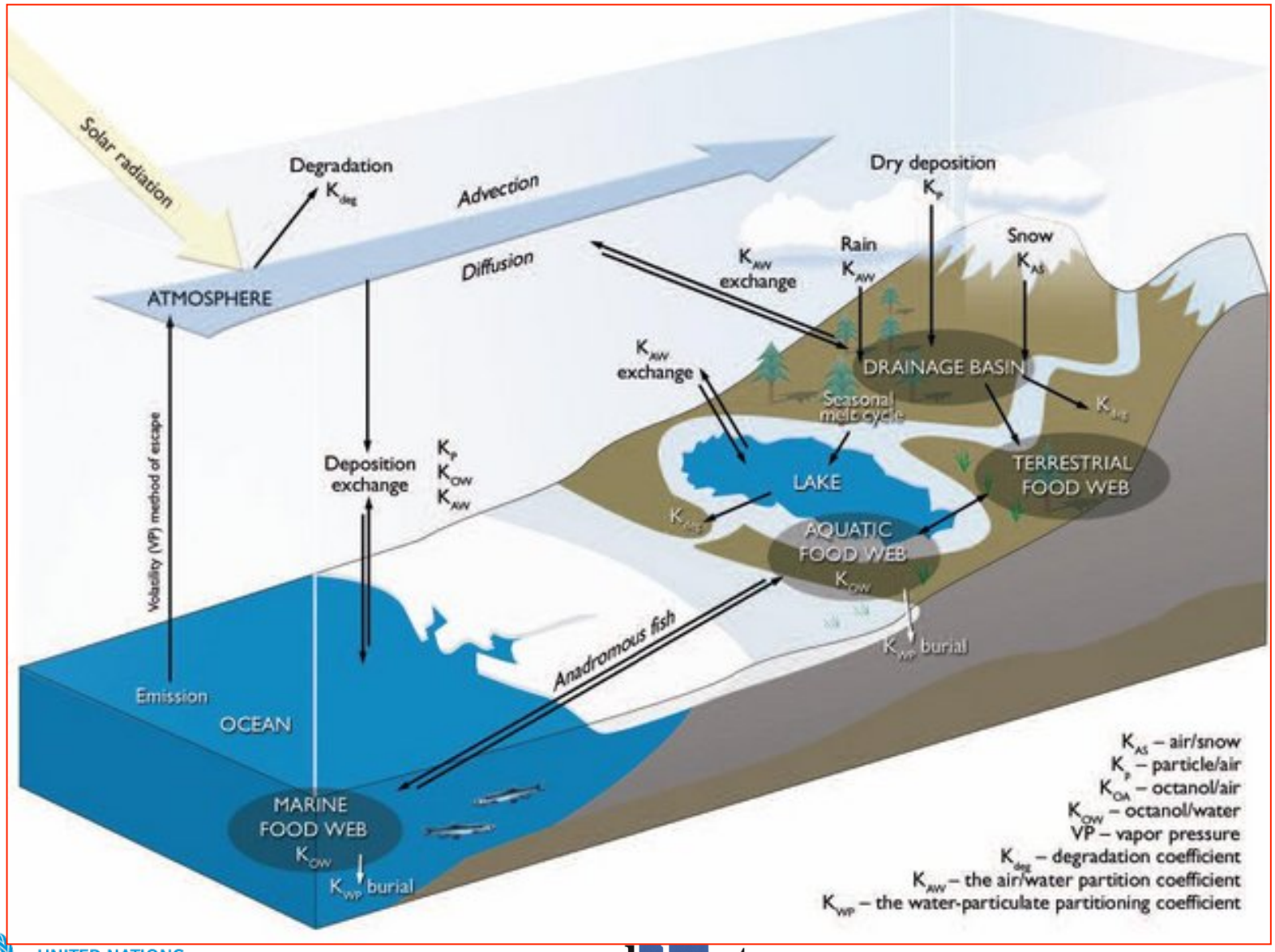
PTS Transport Pathways

- persistence increases the relative importance of transport relative to transformation in controlling a contaminant's fate
- distribution characteristics leading to significant presence in different environmental media (air, water, soil)



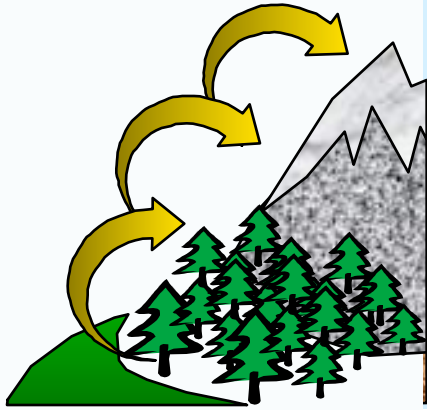
F. Wania

Long-range transport of POPs

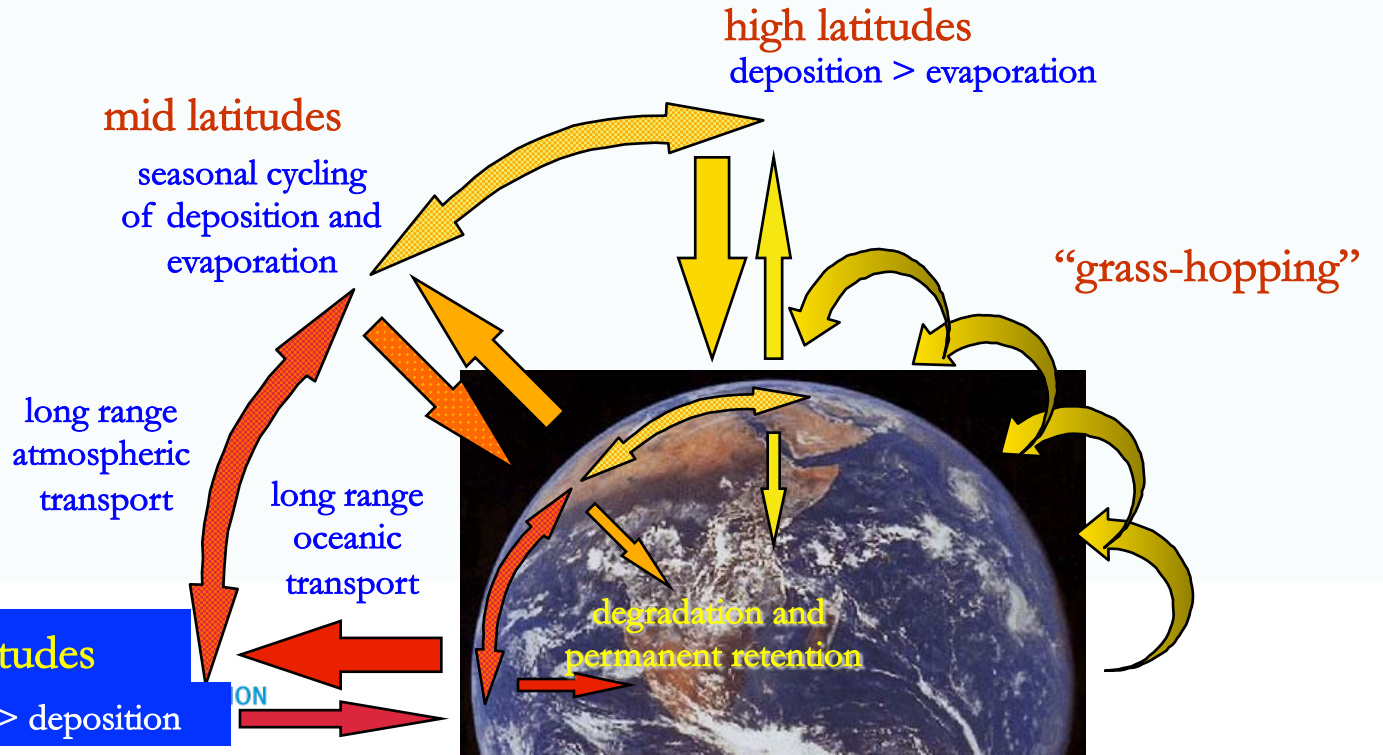


Long-range transport of PTS

Because rates of deposition and evaporation are temperature-dependent, hopping is enhanced by periodic temperature changes

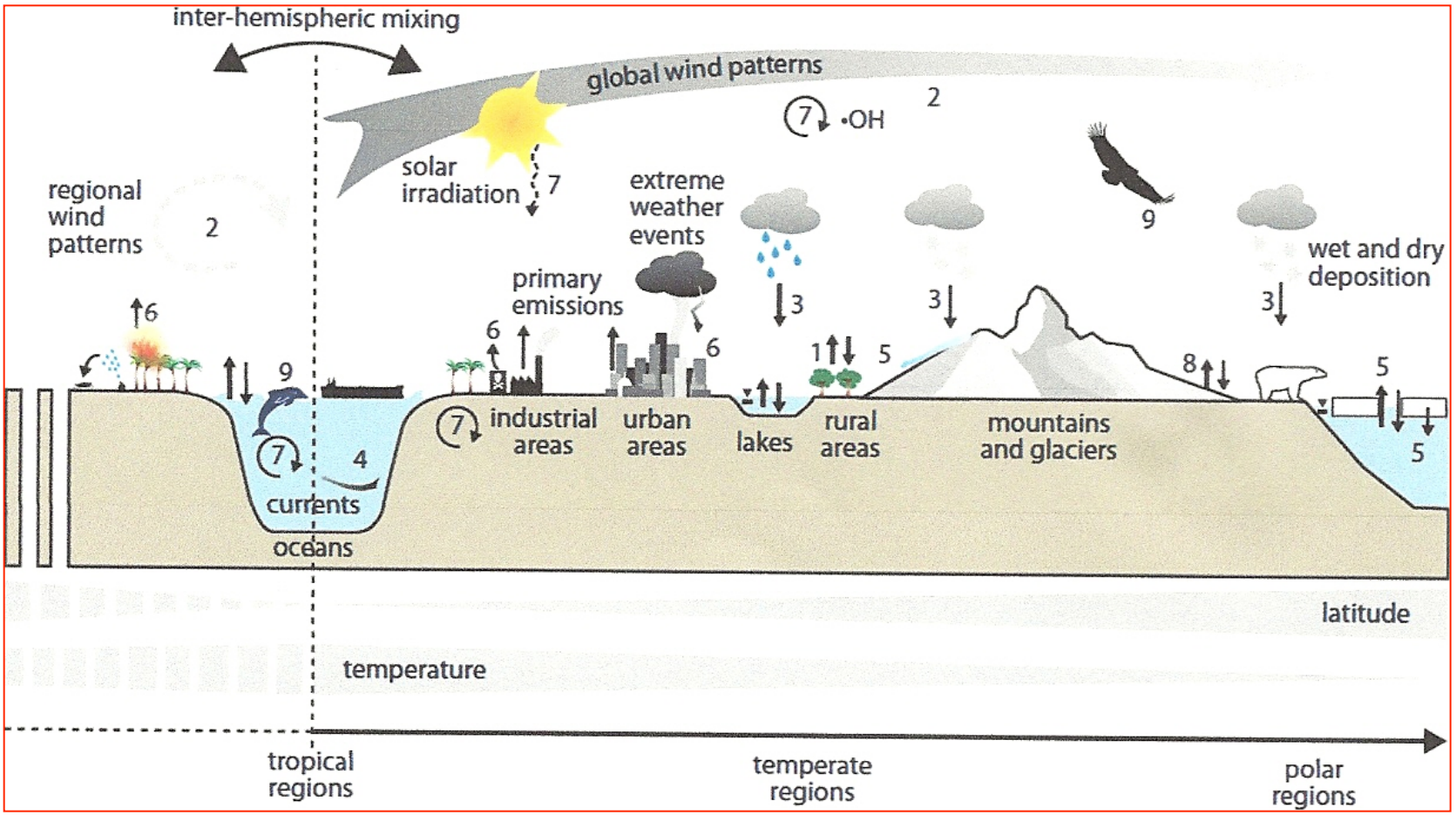


Temperature gradients in space in combination with atmospheric mixing will favour gradual transfer from warm to cold regions on both global and regional scales



F. Wania

Climate change and POPs – Predicting the impacts



Conceptual representation of key factors influencing the environmental fate and transport of POPs under a climate change scenario. Numbers in the Figure correspond to enumerated items in the text, including climate-change-induced modifications in (1) strength of secondary re-volatilization sources, (2) wind fields and wind speed, (3) precipitation, (4) ocean currents, (5) melting of polar ice caps and mountain glaciers, (6) frequency of extreme events, (7) degradation and transformation of chemicals, (8) environmental partitioning of chemicals, and (9) biotic transport of chemicals. Note that the processes depicted for the Northern hemisphere are the same in the Southern hemisphere.

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