Fu colto dal vento, abbattuto al suolo, sollevato a dieci chilometri. (…) Si sciolse per tre volte nell'acqua del mare, una nell'acqua di un torrente in cascata, e ancora fu espulso. Viaggiò col vento per otto anni: ora alto, ora basso, sul mare e fra le nubi, sopra le foreste, deserti e smisurate distese di ghiaccio; poi incappò nella cattura e nell'avventura organica.

**Primo Levi**
(1919 -1987)

- Il sistema periodico -

# Materiale e informazioni

http://elearning.unimib.it/

- Area Scienze
- Lauree magistrali
- Scienze e Tecnologie per l'Ambiente e il Territorio [F7501Q]
- 1° Anno
- Chimica Ambientale → registrarsi e scaricare!!!

# Chimica Ambientale I e II - 12 CFU

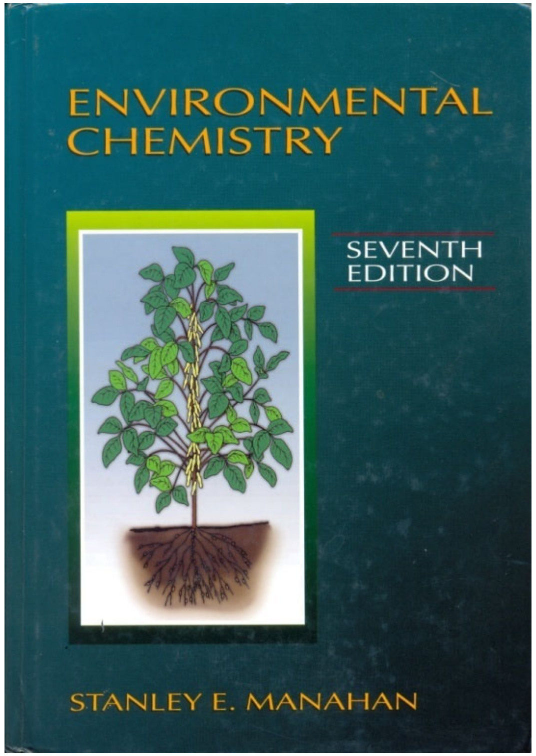
Esame orale in unica soluzione

o

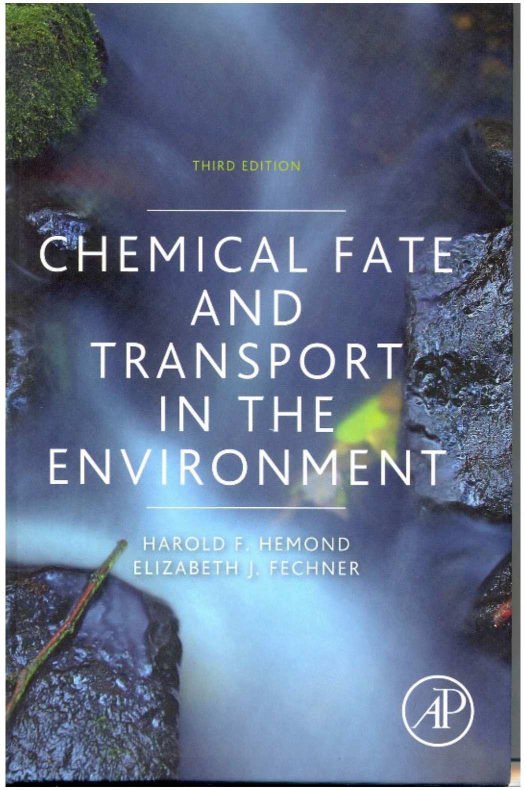
Per agevolare,

- <u>prima parte</u>: febbraio 2023 - giugno 2023
- <u>seconda parte</u>: giugno 2023 - gennaio 2024

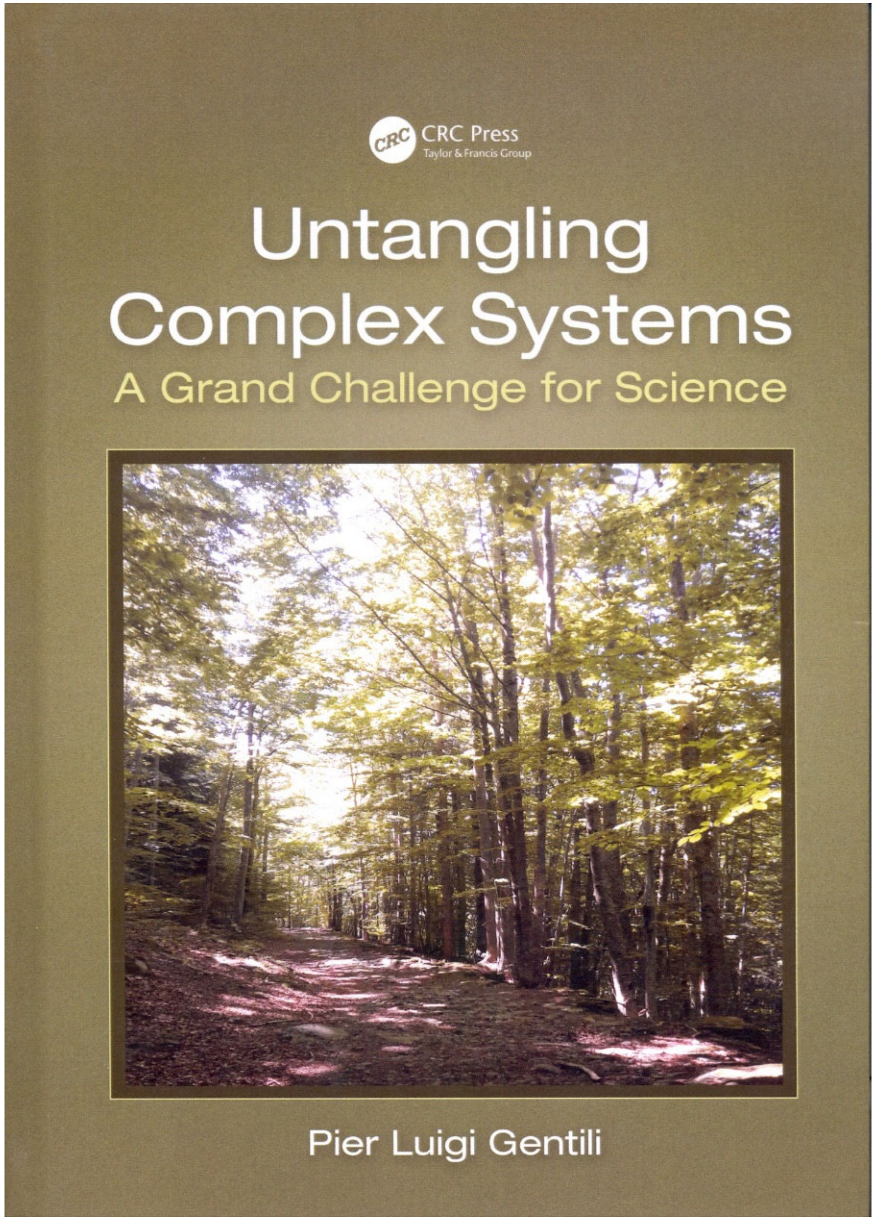
# Testi consigliati







# Testi consigliati



# Chimica Ambientale

- Valutare il comportamento ambientale delle sostanze chimiche (organiche). Impatti di prodotti chimici organici (esistenti o nuovi) per gli esseri umani e gli ecosistemi.

- Comprendere come le interazioni molecolari e i fenomeni di trasporto macroscopico determinino la distribuzione nello spazio e nel tempo delle sostanze chimiche rilasciate in ambienti naturali.
  - Definire i processi che regolano il trasporto / trasferimento e la trasformazione di sostanze chimiche antropogeniche.
  - Struttura chimica e proprietà fisiche e reattività. Processi di trasformazione chimica, fotochimica e biologica
  - Quantificare i processi di trasferimento di fase, trasformazione e trasporto.

- Modelli matematici basati sulla combinazione di tutti gli elementi rilevanti per valutare il comportamento delle sostanze chimiche organiche.

# Chimica Ambientale I e II -12 CFU
# Prof. Ezio Bolzacchini e prof. Marina Lasagni

Primo semestre

## RIPASSO

- Cinetica - esercizi
- Le reazioni radicaliche
- Idrolisi composti organici
- Redox

# Chimica Ambientale I e II -12 CFU
# Prof. Ezio Bolzacchini e prof. Marina Lasagni

- Atmosfera
  - Specie ossidanti
  - reattività
  - Modello Gaussiano di dispersione
  - Modello al Recettore

- Pops
- Pesticidi
- Trattamento acque

# Programma - Chimica Ambientale I e II

## Secondo semestre

- Modelli di fugacità per valutare la persistenza
- Modelli di trasporto nel suolo
- Processi di adsorbimento
- Cinetiche di degradazione biologica
- Esempi di modelli
- La discarica
- Diossine, microplastiche
- Il REACH

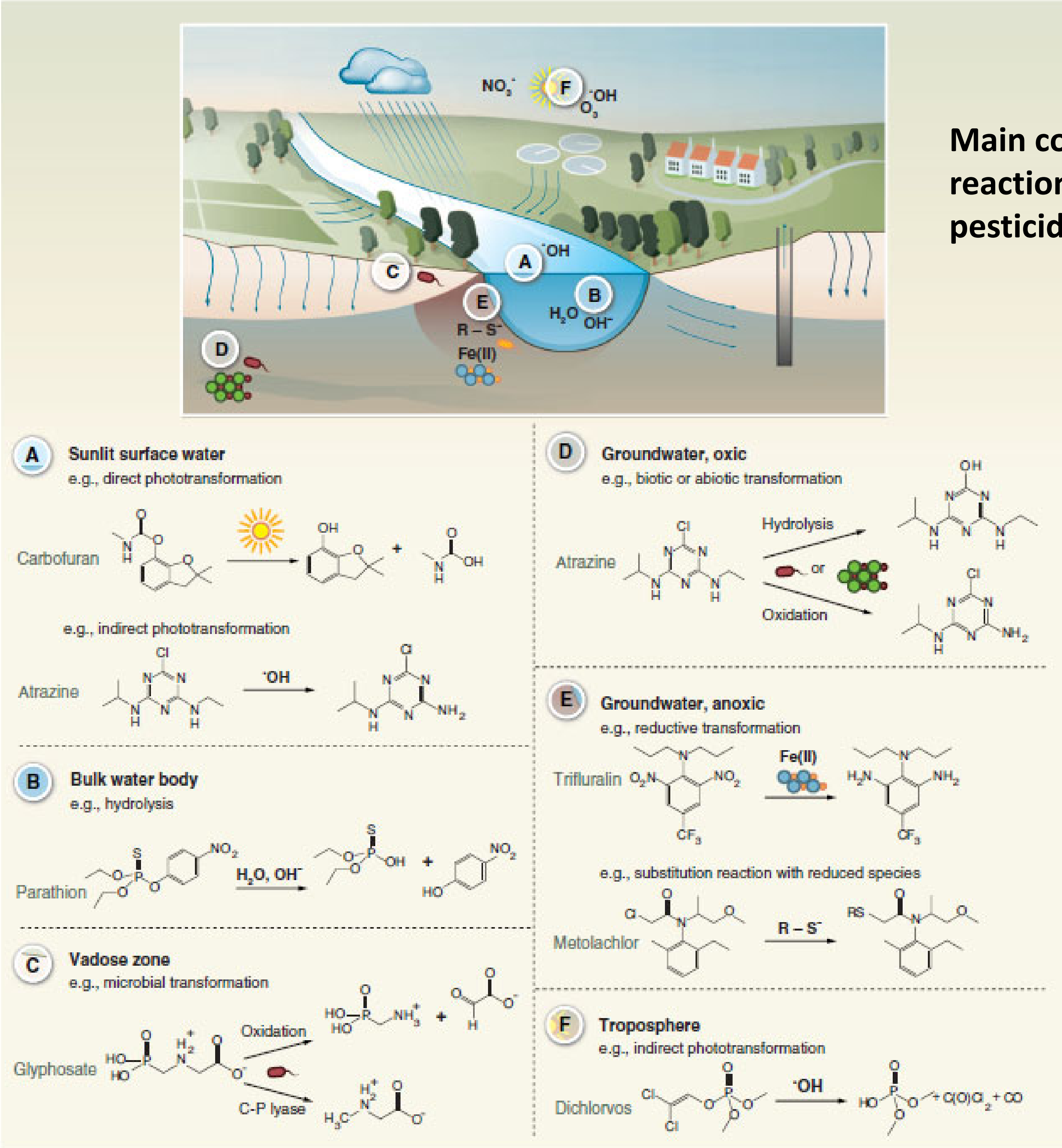
# Environmental Chemistry

- What do we understand as Environmental Chemistry?
- Why is it important that we understand and know Environmental Chemistry?
- What areas of knowledge are related to Environmental Chemistry, and how can we use this concept?

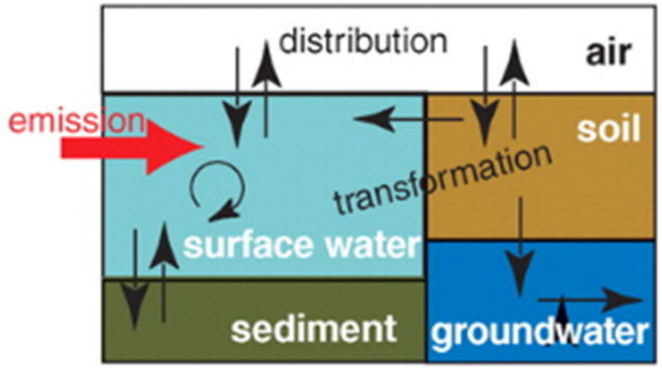
Earth
= reaction vessel, in which complex reactions take place.
= closed system, in which atoms and molecules are neither created nor destroyed, and a balance is maintained.

The atoms and molecules are always located in some environmental compartment, combined in different compounds, present in different physical states, or accumulated in organisms.

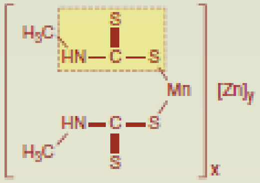
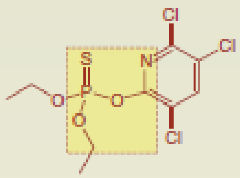
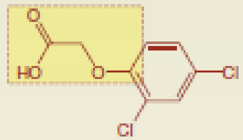
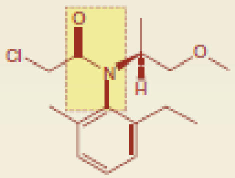
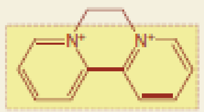
Main compartments and reaction partners for pesticide degradation.

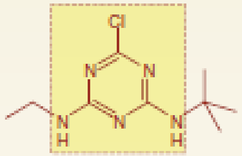
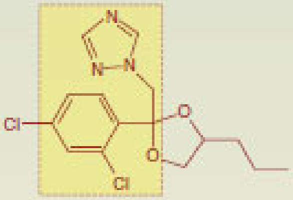
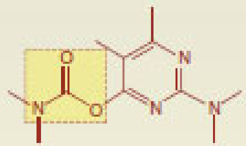
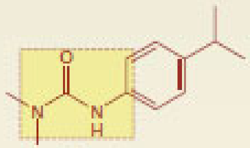
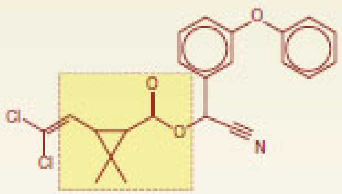


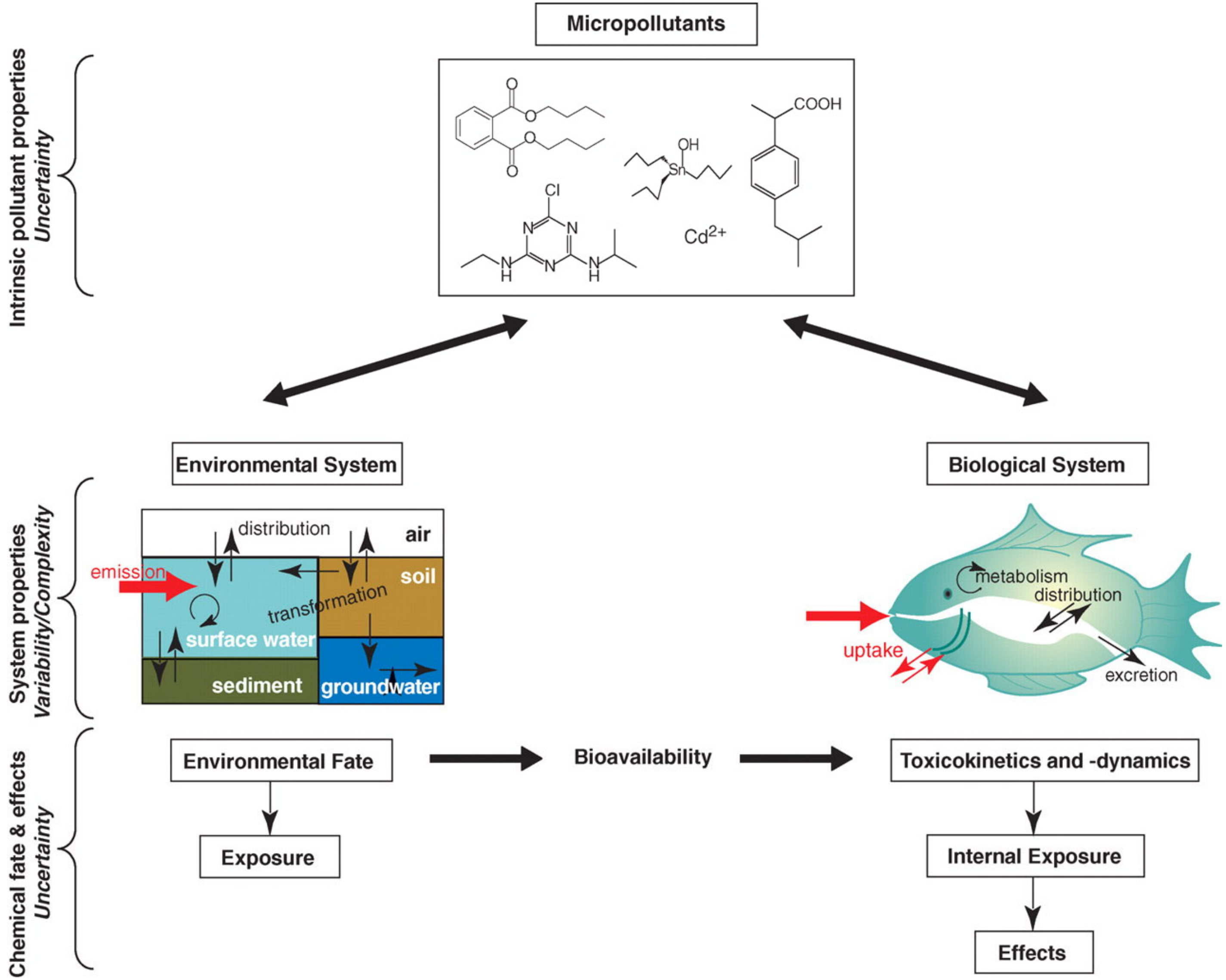

Examples of relevant reactions in each compartment



distribution
air
emission
soil
transformation
surface water
sediment
groundwater

| Pesticide class | Major representative active substance and structural motif | Major use category | Percent of global pesticide use | Main environmental degradation route | Environmental occurrence in secondary compartments (remote regions surface water, groundwater, etc.) |
|---|---|---|---|---|---|
| Dithiocarbamates |  Mancozeb | Fungicides | 7.1 | Acid-catalyzed hydrolysis; formation of potential NDMA precursors (*49*) | Rarely observed |
| Organophosphates |  Chlorpyrifos | Insecticides | 6.7 | Microbial transformation (oxidation and hydrolysis) | Glyphosate and AMPA frequently detected in groundwater (*3*, *50*); chlorpyrifos, diazinon, disulfuton detected in rainwater and remote lake waters (*6*, *51*) |
| Phenoxy alkanoic acids |  2,4-D | Herbicides | 4.7 | Microbial transformation (oxidative dealkylation and aromatic ring cleavage) | Parent compounds frequently detected in groundwater (*3*, *52*) |
| Amides |  S-Metolachlor | Herbicides | 4.2 | Microbial transformation (hydrolysis and glutathione coupling) | Chloroacetanilides and their transformation products oxanilic (OXA) and ethanesulfonic acid (ESA) frequently detected in groundwater (*4*); metolachlor and alachlor detected in remote lake waters (*6*, *51*) |
| Bipyridyls |  Diquat | Herbicides | 3.2 | Only very slowly biotransformed due to strong sorption to soil matrix | Rarely observed; mainly sorbed to sediments and soils |

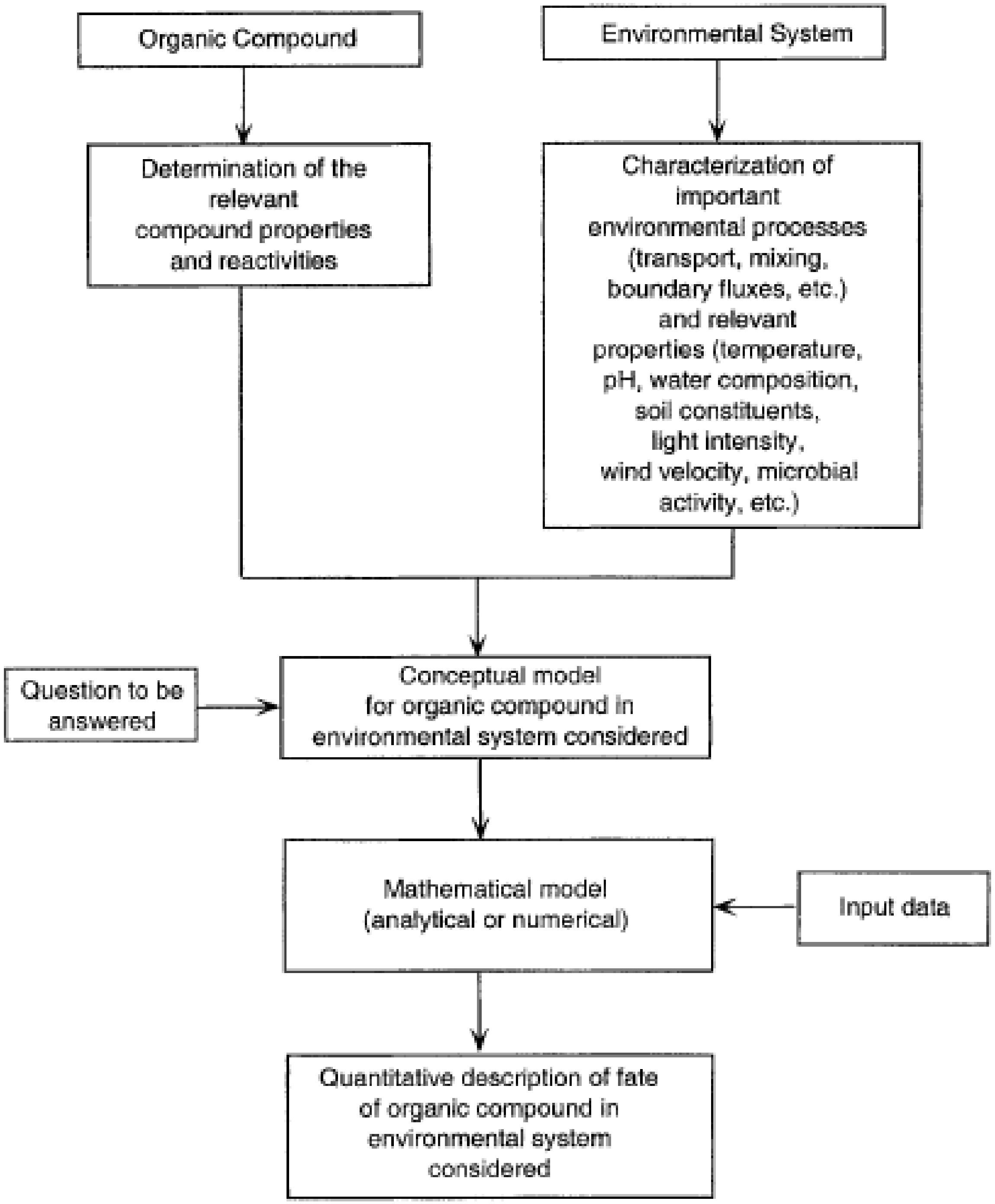
| Pesticide class | Major representative active substance and structural motif | Major use category | Percent of global pesticide use | Main environmental degradation route | Environmental occurrence in secondary compartments (remote regions surface water, groundwater, etc.) |
|---|---|---|---|---|---|
| Triazines |  Terbuthylazine | Herbicides | 2.3 | Microbial transformation (oxidative dealkylation and hydrolysis) | Parent compounds and hydroxy- and dealkylated transformation products frequently detected in groundwater (significantly beyond phase-out period); atrazine and DEA detected in remote lake waters (*6, 51*) |
| Triazoles, diazoles |  Propiconazole | Fungicides | 2.0 | Slow microbial transformation (oxidation); photo-transformation of specific representatives | Flutriafol detected in remote lake waters (*51*) |
| Carbamates |  Pirimicarb | Insecticides/ herbicides | 2.0 | Ready microbial or base-catalyzed transformation (hydrolysis of ester bond); photo-transformation of specific representatives | Rarely observed |
| Urea derivatives |  Isoproturon | Herbicides | 1.7 | Microbial transformation (oxidative dealkylation and hydrolysis) | Parent compounds frequently detected in groundwater (*3*) |
| Pyrethroids |  Cypermethrin | Insecticides | 1.3 | Microbial transformation (hydrolysis, oxidation); photo-transformation (direct and indirect) | Rarely observed; mainly sorbed to sediments and soils |




**René P. Schwarzenbach et al. Science 2006;313:1072-1077**

Consistent exposure and effect assessment is possible if processes in the environmental system and in the organisms (biological system) are treated with the same modeling structure and tools. Within this concept, pollutants interact with environmental and biological systems according to their intrinsic physicochemical properties and reactivities, yielding a characteristic pattern of environmental and internal exposure concentrations for each pollutant. Final exposure and effect assessment according to this concept will always be subject to uncertainty due to inherent variability and complexity of both environmental and biological systems. Quantification and explicit communication of irreducible uncertainties therefore need to be an integral part of exposure and effect assessment.

# General scheme for evaluation of the environmental behavior of anthropogenic organic compounds



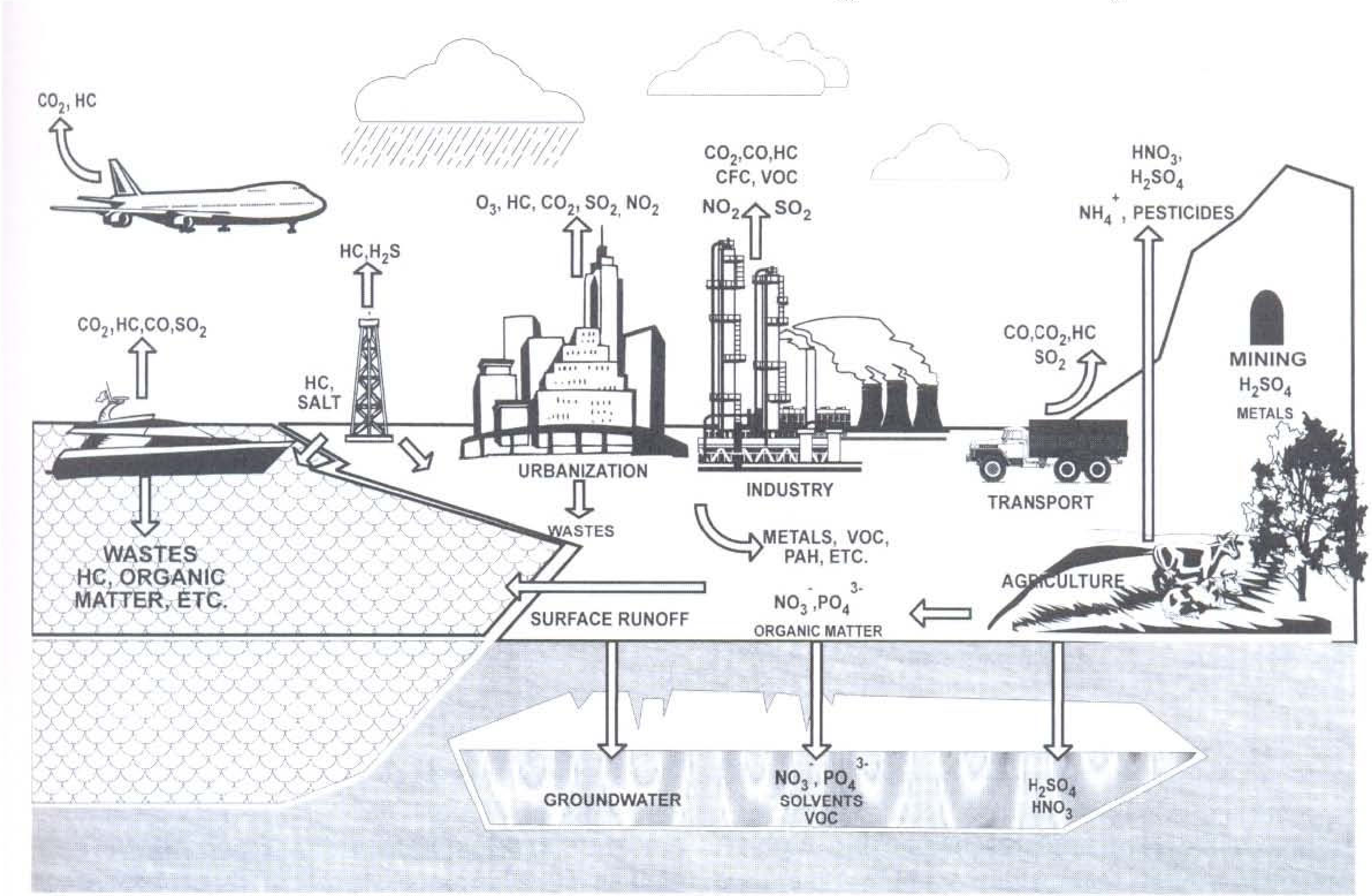
# Chemistry Associated with Pollution Processes

Mankind has increased the discharge of substances and extraction of resources, thereby increasing the pollution of the environment.

Cycling of the natural chemical species has been altered by human action through the discharge into environmental compartments of excessive amounts of compounds that cannot be assimilated, moved, or transformed at the same rate as before.

Some *xenobiotics* have been introduced into the environment deliberately and discharged into the environment either by accident or as wastes.

Example of how human activity has affected or contributed to the alteration or modification of the natural biogeochemical cycles



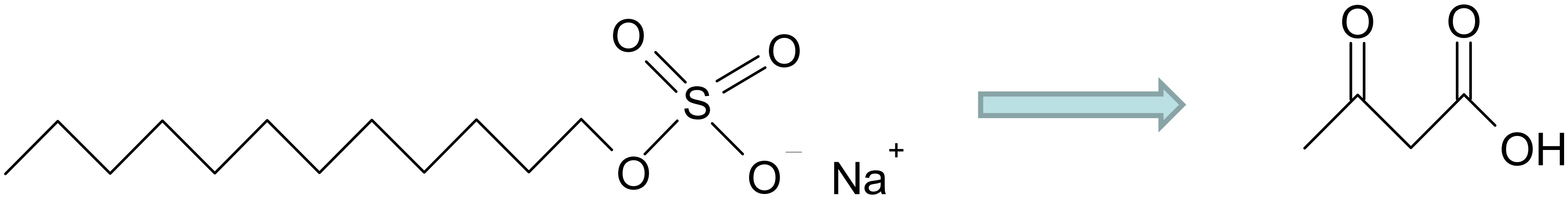
The pollutants discharged into the environment undergo abiotic or biotic transformations in innocuous or toxic compounds and may undergo partial transformations that result in even more toxic derivatives.

Many of the products that accumulate in organisms *(bioaccumulation)* or are metabolized have *genotoxic effects* (i.e., they affect cellular reproduction) and may even cause death.

TABLE 1.1. Transformation and characteristics of different toxic pollutants

| Parent compound | Dangerous characteristics | Biotic and abiotic transformations | Final products | Dangerous characteristics of final or intermediate products |
|---|---|---|---|---|
| (RDX) 1,3,5-Cyclotrimethylene nitroamine or "cyclonite" (used as an explosive) | Explosive, neurotoxicant, possible carcinogen | Anaerobic reduction and photolysis | 1,1-Methylhydrazine, 1,2-Dimethylhydrazine | Possible carcinogens and mutagens, neuro-, nephro-, and hepatotoxicants |
| Benzo(*a*)pyrene (found in cigarette smoke) | Carcinogen | Metabolic oxidation | Benzo(*a*)pyrene-hydroquinone | Highly carcinogenic |
| $Hg^0$ (used in industrial processes) | Toxic vapor (neuro- and nephrotoxicant) | Abiotic oxidation and microbial transformation in aerobic or anaerobic conditions | $Hg^{2+}$ and methyl mercury | Toxic compounds, nephro- and neurotoxicants, affect reproduction and digestive processes, probable carcinogens |
| (DDT) Dichlorodiphenyl trichloroethane (pesticide) | Neuro- and hepatotoxicant, causes reproductive alterations, probable carcinogen | Photolysis and microbial transformation | Dichlorodiphenyl dichloroethylene (DDE) | Neurotoxicant, reproductive alterations, probable carcinogen |

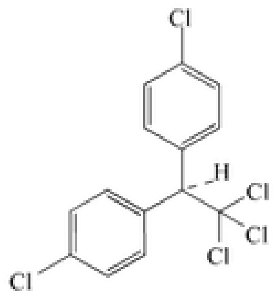
Metabolic biotic transformation of the dodecylsulfate detergent into acetoacetic acid.




Generation of chloroform (or other organochlorine compounds or *trihalomethanes)* in treated water.

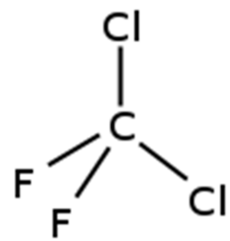
More stable xenobiotic compounds may be transported, without major changes to sites very far from the original discharge point, and exposed to unpredictable conditions that may produce a serious environmental or health impact.

**DDT and the CFCs (chlorofluorocarbons).**

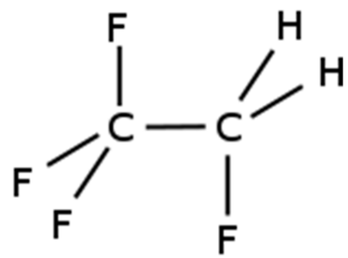



In the case of **DDT**, although it has been banned since ‘70, its negative effects are still present.
It has been detected in the Arctic Circle where no DDT was ever applied.

**CFCs** their high volatility and low reactivity allow their movement to the stratosphere and the destruction of the protective ozone layer through an initial photolytic reaction caused by ultraviolet (UV) radiation




Dichlorodifluoromethane
(CFC-12)




1,1,1,2-Tetrafluoroetha
(HFC-134a)

# Issues of anthropogenic chemicals in the environment

- DDT (dichlorodiphenyltrichloroethane)

- Synthesized first in 1874
- organochlorine insecticide
- great success in the second half of World War II to control malaria and typhus
- The Swiss chemist Paul Hermann Müller was awarded the Nobel Prize in Physiology or Medicine in 1948 “for his discovery of the high efficiency of DDT as a contact poison against several arthropods”.
- After the war, DDT was made available for use as an agricultural insecticide and produced massively (40,000 tons per year)

## Issues of anthropogenic chemicals in the environment

- Acute contamination (chemical accidents, spills, waste dump sites etc)

2007 South Korea oil spill

# Issues of anthropogenic chemicals in the environment

- Chronic contamination (everyday use in industry, household etc)

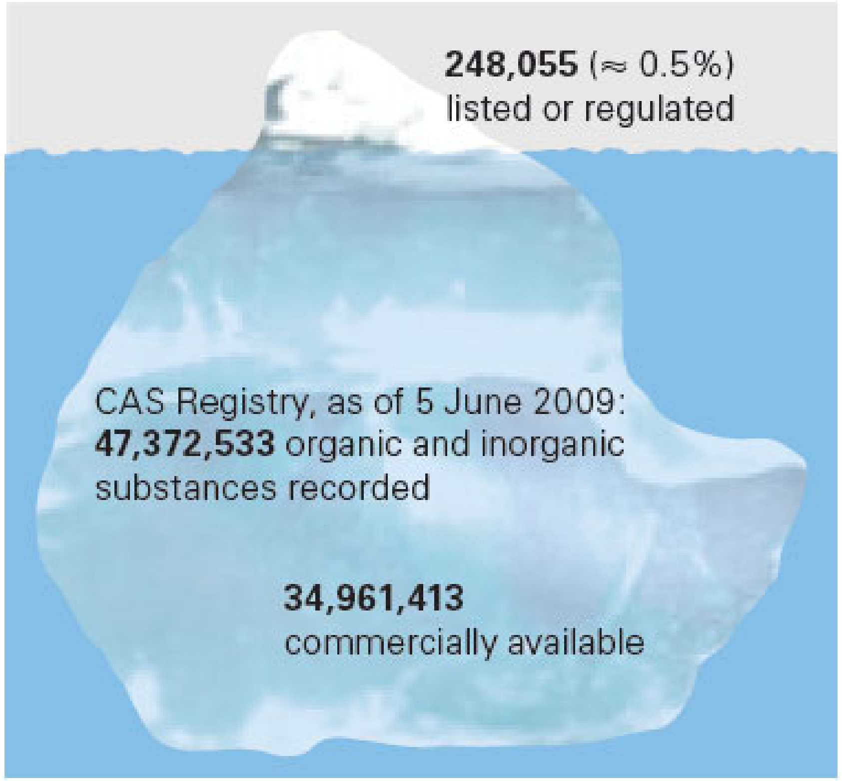



Fig. 1: The roughly 250,000 substances listed or regulated are only the tip of the iceberg. CAS = Chemical Abstracts Service.

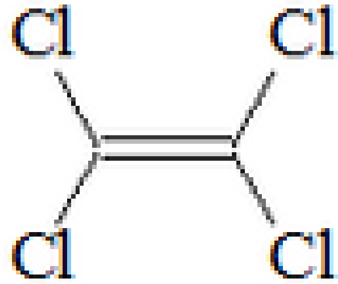
Eawag News 67e/October 2009

- Petroleum chemicals
- Solvents
- Polymers
- Pesticides/insecticides
- Pharmaceuticals
- Nanomaterials
- ….
- >300 million tons

# Issues of anthropogenic chemicals in the environment

- **REACH**, European Union Regulation of 18 December 2006
- Registration, Evaluation, Authorisation and Restriction of Chemical
- addresses the production and use of chemical substances, and their potential impacts on both human health and the environment
- Requires all companies manufacturing or importing chemical substances into the European Union in quantities of one ton or more per year to register these substances with a new European Chemicals Agency
- the strictest law to date regulating chemical substances and will affect industries throughout the world

# Perchloroethylene:

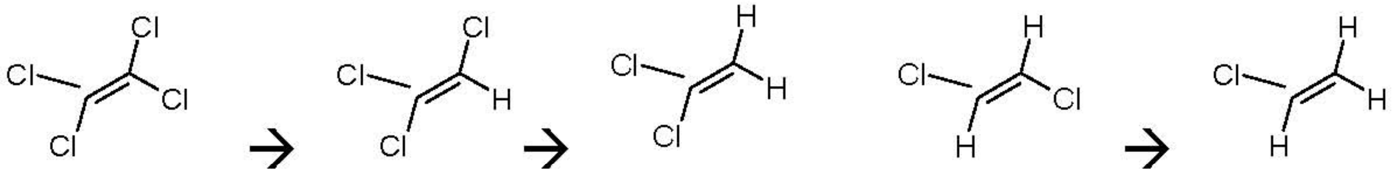



discharged into the atmosphere from dry-cleaning processes and industrial degreasing of parts, or from seepage from a leaking storage tank in an industrial site.

Its vapors will move along with air and can be transported by rainfall into land and surface water.

Seepage from a storage tank will partially vaporize, and the rest can seep into groundwater or surface water. If retained in the groundwater or in the sediments of aquatic bodies, it can undergo sequential anaerobic biotic transformations or cometabolic dechlorination. In other media, it can undergo abiotic elimination reactions that will result in other compounds, all of them toxic.

PCE (perchloroethylene) → TCE (trichloroethylene) → DCE (dichloroethylene) → vinyl chloride



Such a transformation process will affect its mobility and increase its toxicity. This we can see in the corresponding data.

| Compound | Reference dose (mg/kg·d) | Carcinogenic slope factor [(mg/kg·d)$^{-1}$] | Solubility (mg/L at 25°C) | Vapor pressure (mm Hg at 25°C) |
| --- | --- | --- | --- | --- |
| Perchloroethylene (tetrachloroethylene) | 0.171 (inh)<br>0.01 (oral) | 0.175 (inh)<br>0.052 (oral) | 150 (at 20°C) | 18.47 |
| Trichloroethylene | 0.01 (inh)<br>0.0003 (oral) | 0.4 (inh)<br>0.011 (oral) | 1366 | 74 |
| 1,1-Dichloroethylene | 0.057 (inh)<br>0.05 (oral) | 0.175 (inh)<br>0.6 (oral) | 2500 | 591 |
| Vinyl chloride | 0.0286–0.01 (inh)<br>0.003 (oral) | 0.03 (inh)<br>1.5 (oral) | 2763 | 2660 |

*Sources:* http://www.atsdr.cdc.gov/toxprofiles/, EPA Toxic Profiles.
http://www.epa.gov/iris/subst/, IRIS (EPA Integrated Risk Information System).
http://www.epa.gov/ttn/atw/hlthef/, EPA Technology Transfer Network Air Toxics Website.
http://risk.lsd.ornl.gov/cgi.bin/tox/, RAIS (EPA Risk Assessment Information System).

If these pollutants reach a certain exposure level for a community who breathes contaminated air or consumes polluted water, its members will be at risk.

## Chemistry Applied to the Analysis of Pollutants and Natural Compounds

- What is the quality of the water that we drink or of the air that we breathe?
- How clean is the water in the lake?
- What types of toxic wastes are there in a nearby dumpsite or in an aquifer, and what are their concentration levels?
- What causes certain algae blooms for the death of fish?
- How safe is it to eat fish from a body of water? Do the fruits and vegetables we eat contain pesticides?

Technicians have to find the best chemical analytical tools that identify potential and existing pollutants.
They also need to determine their properties, particularly those affecting the fate, transport, bioavailability, toxicity, and stability or degradation of the chemical constituents in a sample.

**Tools such as these may be considered a part of Environmental Chemistry.**

*Environmental Chemistry is related to the methods required to determine, in a complex sample, the presence of pollutants and their transformation products, from high to very dilute or trace concentrations*.

- ✓ It should have a truly representative environmental sample.
- ✓ It should identify and avoid possible sources of sample contamination.
- ✓ It often needs a highly effective method of extraction or separation, and concentration to reach detection levels, especially when measuring extremely low concentrations or trace amounts of the analyte
- ✓ It should separate or identify a target compound from an array of a complex mixture of compounds or matrix, taking into account innumerable interactions with other compounds present in the sample and considering that they may interfere with the method.
- ✓ Because many of the analyses have to be normalized, it is almost certain that validation of the results will be necessary.

# Chemistry Applied to the Treatment and Remediation of Pollution

Environmental Chemistry can also be applied to treat wastes, and to prevent and reduce the impact of certain discharges into the environment.

A basic knowledge of chemistry will allow for a more detailed understanding of processes such as water and wastewater treatment, air pollution control, and waste management.

# Green Chemistry

Green Chemistry is the chemical tool used to design a reaction, a process, or a new material benign to the environment.
Chemistry applied in pollution prevention and waste minimization.

In the design and development of new products and processes, key environmental requirements that should be observed or are a priority in Green Chemistry are:

- utilization of reusable or recyclable materials, thus avoiding consumption of nonrenewable natural resources as material inputs
- reduction and replacement of some of the traditionally harmful reagents and solvents in industry
- reduction in energy consumption
- reduction in dissipative loss of waste materials, aiming for zero discharges
- lessening of threats to the ecology and to human health
- lowering of safety risks

# Importance of Environmental Chemistry

As indicated above, knowledge of Environmental Chemistry is essential for understanding what happens in nature and for predicting the fate and the chemical reactions that natural compounds and artificial pollutants may undergo; for understanding their interactions, and for predicting what may happen to certain compounds if discharged into the environment, and if organisms (human or not) come into contact with them.

Reactions such as dissolution, hydrolysis, precipitation, photolysis, adsorption/ desorption, oxidation-reduction, ion exchange, complexation, biodegradation, polymerization, and others taking place in the environment, may affect the solubility of pollutants and therefore their mobility, speciation and toxicity. This, in turn, can define to a great extent the dispersion, bioavailability, and risk associated with them.

Examples of the above include the following:

- The solubility of Fe(II) and Mn(II) compounds can be greatly decreased by oxidizing them to Fe(III) and Mn(IV), respectively.
- The bioavailability and toxicity of copper, selenium, and arsenic for some aquatic organisms is higher in their inorganic form, but not in the presence of certain chelating ligands or metal-organic complexes.
- The toxicity of Cr(VI) compounds can be greatly decreased by simply reducing it to a lower oxidation state, Cr(III).
- Iron oxides in minerals or in deposits can be dissolved by the action of light in the presence of certain compounds (ligands), but not in their absence.

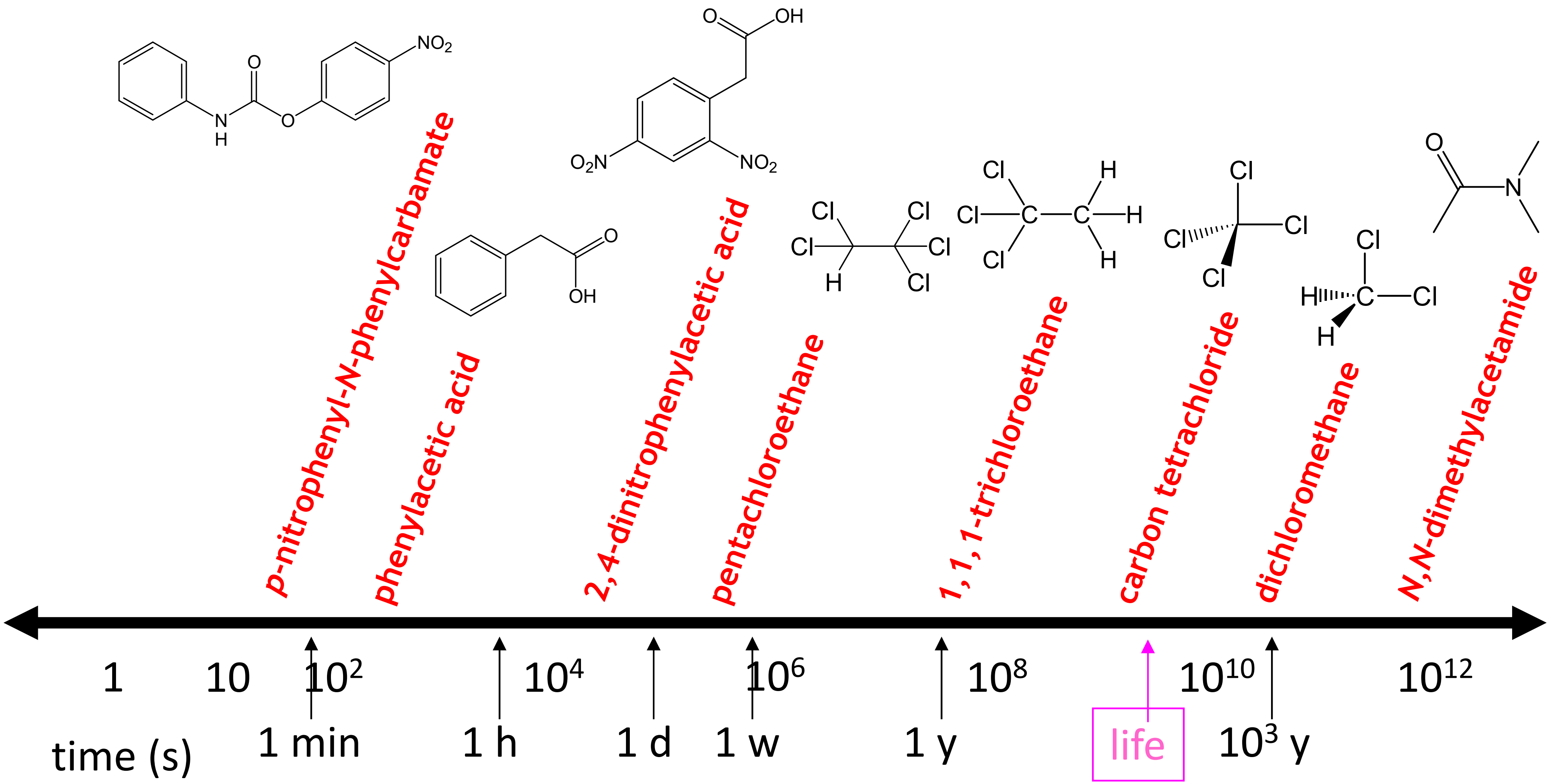
Provides data input for risk assessment and treatability studies, and determines the required level of environmental quality or control needed in a system. All of these factors are particularly important when making cost-effective decisions about discharge treatments or risk-management decisions, or in determining environmental-impact mitigation or remediation measures.

# Kinetics


- how fast?
  - central question to environmental fate and transport prediction
- what mechanism?
  - understanding for designing remediation techniques
- effect of solution chemistry?
  - what aspects of solution chemistry affect rates?
- effect of temperature?
  - key variable in predicting fate and transport

# Kinetics

## Kinetics – time scales



# AVVISO

## Presentazione dei piani di studio

## novembre 2022 per tutti

Per i 12 CFU a scelta dello studente:

- ❑ Se scelti 2 insegnamenti tra quelli proposti dal nostro CdS – pre-approvato
- ❑ Se esterni → in commissione – attendere approvazione