Environmental Sensors

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Course contents and slides:

http://polysense.poliba.it/index.php/environmental-sensors-mst/

Suggested textbooks

Sensor Systems for Environmental Monitoring – Volume One – Editor: M. Campbell
Sensor Systems for Environmental Monitoring – Volume Two – Editor: M. Campbell

SYLLABUS

1. **Environmental monitoring**.

   Introduction. Main sources of pollution. Contaminants in soil. Water quality monitoring. Physical and chemical variables in water pollutants monitoring.

2. **Contaminants in air**.

   Classification of atmospheric pollutants. Sampling procedures and analysis. Greenhouse effect and global warming. Health risks and indoor monitoring.

3. **Figures of merit for sensing.**

   Data acquisition and sensor classification. Transfer function. Sensor characteristics. Physical principles of sensing. Example: gas sensor calibration.

SYLLABUS

4. **Optical-based sensors for environmental monitoring**.

   Absorption and emission of light. Roto-Vibrational spectroscopy. Fundamentals of absorption spectroscopy. Dispersive and non-dispersive sensor in the infrared. Tunable diode laser spectroscopy. Multipass cells and optical cavities. Photoacoustic spectroscopy. Remote sensing ed hyperspectral imaging.

5. **Non-optical-based sensors for environmental monitoring**.

   Voltametric and amperometric sensors. Potentiometric sensors. Metal-oxide chemoresistive sensors. Gas chromatography. Electrochemical sensors. Smart sensors for environmental monitoring.

6. **Analysis of volatile organic compounds.**

   Classification and sources of VOCs. State-of-the-art: analysis using non-optical sensors. New perspectives: VOCs detection using optical-based sensors.

Chapter 1
ENVIRONMENTAL MONITORING

1.1 INTRODUCTION

The challenge of sensing the environment

In common language the word "**sensing**" defines any of the faculties, such as sight, hearing, smell, taste, or touch, by which humans perceive stimuli originating from outside our bodies.

Sensing, according to this simple definition, **means to detect, perceive, or become aware** of some phenomena external to us.

Our capacity to understand the environment using sensing technologies is strongly dependent on the **type and quality of information** we obtain.

As a **data-driven process**, understanding Earth's environments and unraveling the patterns of interaction between people and the planet have been greatly facilitated by the **increasing number of sensor systems** characterized by different and peculiar features.

1.1 INTRODUCTION
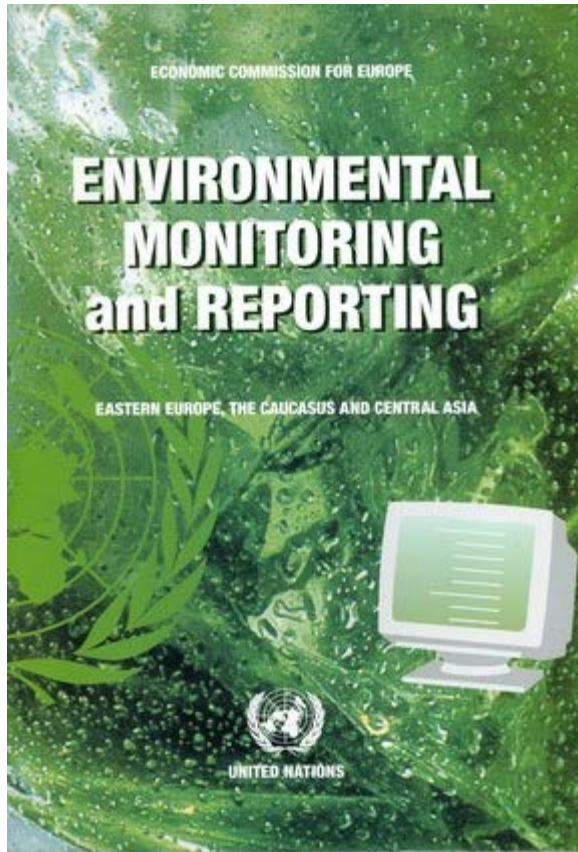
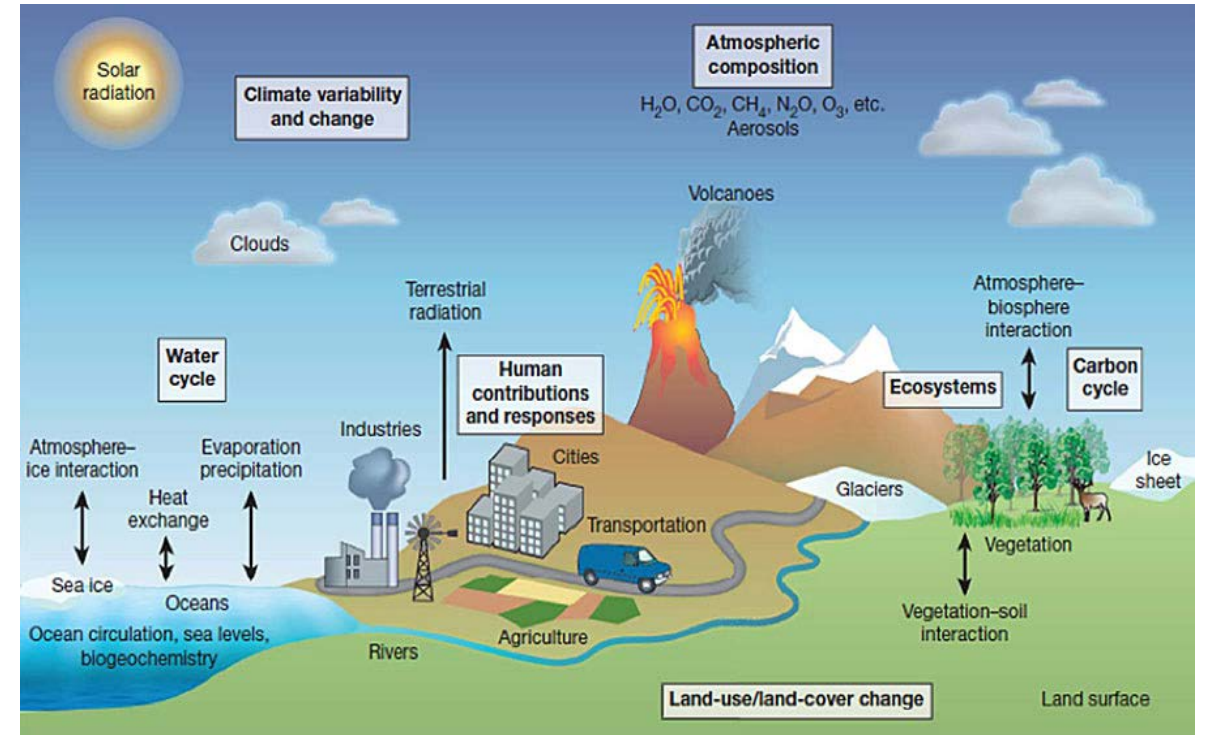**How can "environmental monitoring" be defined?**

According to United Nations Economic Commission for Europe (UNECE):

*Environmental monitoring is a **tool** to assess environmental conditions and trends, support policy development and its implementation, and develop information for reporting to national policymakers, international forums and the public.*

1.1 INTRODUCTION

Why is it important? Because Earth is an interconnected system!

- It is crucial to evaluate what is happening within an ecosystem to prevent and control the consequences on itself and on other ecosystems.

- As human population, industrial activities, and energy consumption continues to grow, the development of advanced, automated monitoring applications and devices is crucial for enhancing the accuracy of environmental monitoring reports.

1.1 INTRODUCTION

Monitoring as a crucial part of environmental science

- Environmental science is defined as *"a table supported by the four legs of **theory, experimentation, cross-site comparisons, and long-term studies"***.

- **Many ecosystems** require long-term study because they **change slowly**, and sustained monitoring of key variables provides the principal record of change.
  Nevertheless, short-term experiments are required for **real-time monitoring** of ongoing processes.

- These two methodologies are **complementary**: long-term monitoring data provide context for short-term experiments and observations.
  For example, suppose an irrigation experiment conducted to determine the effect of water availability on plant production, and no response is observed. If long-term measurements of precipitation indicate that the experiment occurred during the wettest year on record, the monitoring data provide important information for interpreting these unexpected experimental results.

1.1 INTRODUCTION

The role of data science in environmental monitoring

Data science is the **science of extracting meaning from complex data**, hence supporting decision-making in an increasingly complex world (Baesens, *Analytics in a Big Data World*, 2014).

Who needs environmental monitoring?

Gary M Lovett[1*], Douglas A Burns[2], Charles T Driscoll[3], Jennifer C Jenkins[4], Myron J Mitchell[5], Lindsey Rustad[6], James B Shanley[7], Gene E Likens[1], and Richard Haeuber[8]

Environmental monitoring is often criticized as being unscientific, too expensive, and wasteful. While some monitoring studies do suffer from these problems, there are also many highly successful long-term monitoring programs that have provided important scientific advances and crucial information for environmental policy. Here, we discuss the characteristics of effective monitoring programs, and contend that monitoring should be considered a fundamental component of environmental science and policy. We urge scientists who develop monitoring programs to plan in advance to ensure high data quality, accessibility, and cost-effectiveness, and we urge government agencies and other funding institutions to make greater commitments to increasing the amount and long-term stability of funding for environmental monitoring programs.

Front Ecol Environ 2007; 5(5): 253–260

■ **Are monitoring data used effectively?**

We all know of monitoring data that have accumulated in file cabinets (or on hard drives) and gathered dust. These data may be either inaccessible to all but a few, too poor in quality or too poorly documented to be useful, or they may have been collected solely to fulfill a legal requirement, with no real motivation for thorough analysis and interpretation. At the other end of the spectrum are datasets from both individual investigators and large institutional programs that have enormous value to environmental science

- 15 years ago, the role of environmental monitoring within the scientific panorama was still argued
- Dealing with the large amount of data generated by different experiments looked like a giant effort

1.1 INTRODUCTION

The role of data science in environmental monitoring

Nowadays, data science allow an easier management of "big data" compared to just few years ago, but dealing with environmental data is still a non-trivial task

Data Science of the Natural Environment: A Research Roadmap

Gordon S. Blair[1,2]*, Peter Henrys[2], Amber Leeson[1], John Watkins[2], Emma Eastoe[1], Susan Jarvis[2] and Paul J. Young[1,3]

[1] Data Science Institute, Lancaster University, Lancaster, United Kingdom, [2] Centre for Ecology and Hydrology, Lancaster Environment Centre, Lancaster, United Kingdom, [3] Pentland Centre for Sustainability in Business, Lancaster University, Lancaster, United Kingdom

Environmental researches are characterized by **complexity and heterogeneity** of the underlying data sources

Data science is often annotated using the four "V"s of data: **volume, velocity, variety, and veracity** (Jagadish et al., *Big data and its technical challenges. Commun. ACM 57,* 2014).

While in many areas of data science, consideration of volume and velocity dominate, in the environment **variety and veracity (accuracy/precision) are the most important characteristics**.

1.1 INTRODUCTION

The role of data science in environmental monitoring

Environmental data comes from a wide variety of sources, and the amount of data is rapidly increasing together with **new sensing platform and technologies.** Main sources of environmental data are provided by:

- **Historical record**, providing information about the environmental transformation in the last centuries, which can be digitized or not digitized, particularly at a local level.

- **Remote sensing**, where environmental phenomena are observed without contact typically from satellite sensing or aircraft-borne sensing devices, including an increasing use of drones.

- **Earth monitoring systems**, consisting of a range of sensor technologies typically placed close to the observed phenomena. Such sensors will monitor a range of parameters around the atmosphere, lithosphere, biosphere, hydrosphere, and cryosphere.

1.1 INTRODUCTION

Who is in charge for environmental monitoring regulations?

To provide **standard regulations** is a crucial step to reduce the heterogeneity of the data collected by different sensing systems in different environments.

International, national and regional authorities operate and cooperate to perform analysis of the environment, producing certified data and periodical report
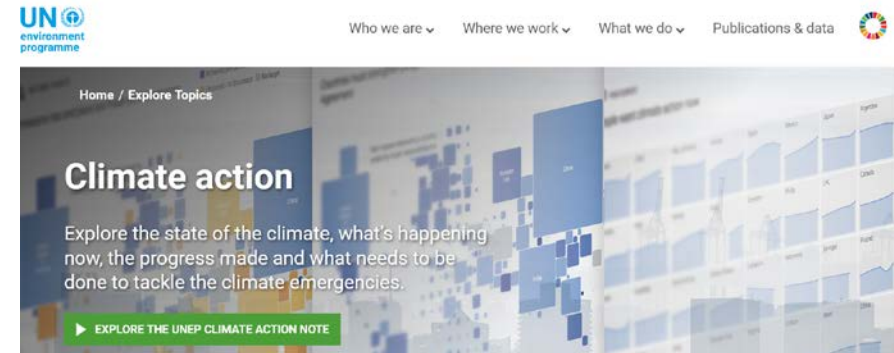
1.1 INTRODUCTION

Who is in charge for environmental monitoring regulations?

Global: United Nation Environment Programme
https://www.unep.org/explore-topics/climate-action

USA: Environmental Protection Agency (EPA)
https://www.epa.gov/power-sector/environmental-monitoring

Resources

Monitoring Networks

- Clean Air Status and Trends Network (CASTNET): CASTNET is a national monitoring program established to assess trends in pollutant concentrations, atmospheric deposition, and ecological effects due to changes in air pollutant emissions. The CASTNET Data Download page provides raw measurement data as well as prepackaged data sets available for download.

- The Long Term Monitoring (LTM) program: LTM tracks changes in surface water chemistry in response to changing air emissions and acid deposition. Data are available for download on the data section of the LTM page.

1.1 INTRODUCTION

Who is in charge for environmental monitoring regulations?

Europe: European Environment Agency (EEA)
https://www.eea.europa.eu/en/about/who-we-are

Italy: Istituto Superiore Protezione Ricerca Ambientale (ISPRA)
https://www.isprambiente.gov.it/en/ispra-services/environmental-services

1.1 INTRODUCTION

Who is in charge for environmental monitoring regulations?

Puglia: Agenzia Regionale per la Prevenzione e la Protezione dell'Ambiente (ARPA) - https://www.arpa.puglia.it/

Temi ambientali

ACQUA	AGENTI FISICI	AMBIENTE E SALUTE	AMBIENTI NATURALI	AMIANTO	ARIA
ATTIVITÀ PRODUTTIVE	CAMPI ELETTROMAGNETICI	EMERGENZE AMBIENTALI	INDICATORI AMBIENTALI	MARE	METEO
ODORI	POLO ALIMENTI	POLO RADIAZIONI IONIZZANTI	RADON	RIFIUTI	RISCHI INDUSTRIALI
RUMORE	SNPA	SUOLO E BONIFICHE	TERRE E ROCCE DA SCAVO	VALUTAZIONI	

"If you know the enemy and know yourself, you need not fear the result of a hundred battles.

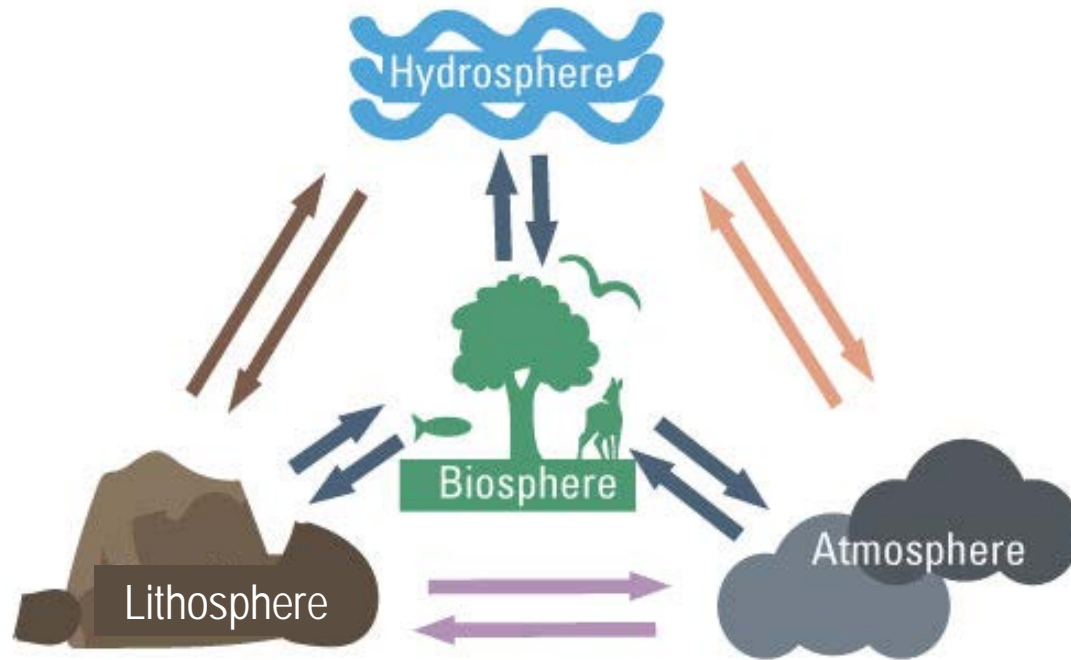*If you know yourself but not the enemy, for every victory gained you will also suffer a defeat.*

If you know neither the enemy nor yourself, you will succumb in every battle."

Sun Tzu – "The art of war"

1.1 INTRODUCTION

Main categories of interest for environmental monitoring


- **Soil monitoring (lithosphere)**

  Contamination, acidification, toxicity,…

- **Water monitoring (hydrosphere)**

  Chemical, biological, quality assessment,…

- **Air monitoring (atmosphere)**

  Contamination, acidification, toxicity,…

Other categories include noise, smell, waste management, and radioactivity.

1.2 MAIN SOURCES OF POLLUTION
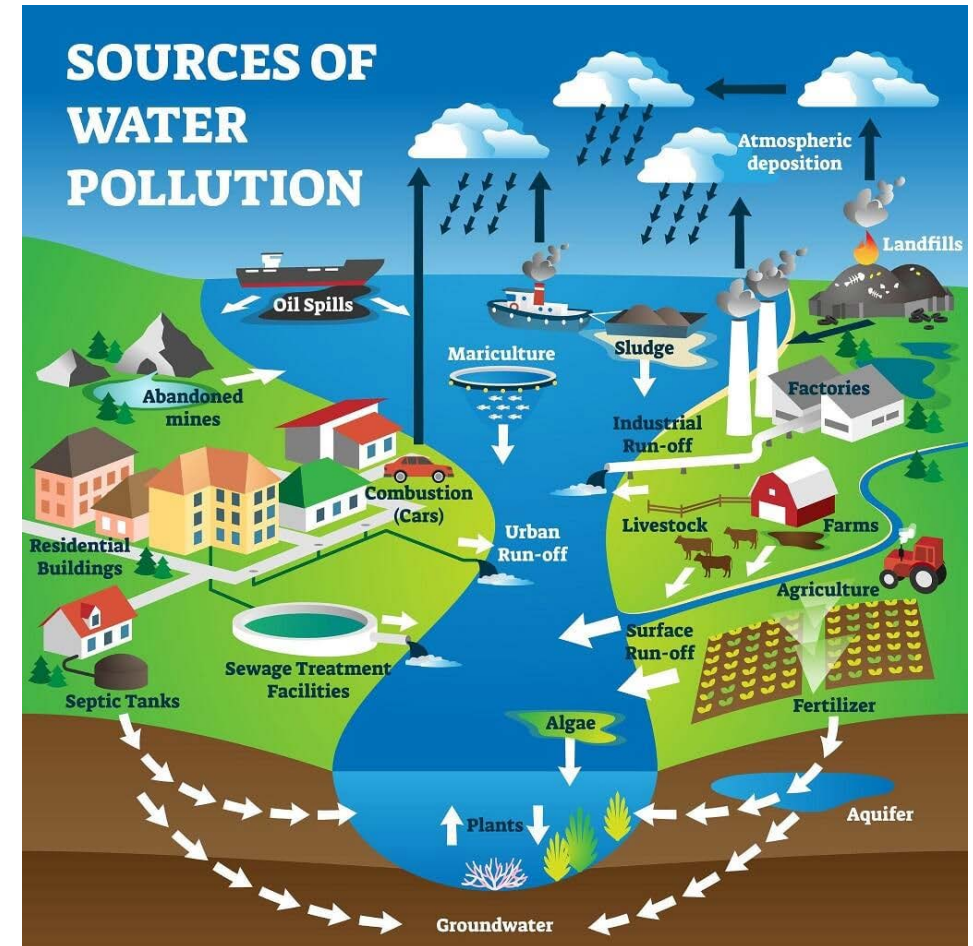
Origin of soil pollutants

- **Industrial Wastes:** harmful substances and dangerous compounds are released and influence the topsoil layer strength

- **Landfills:** wastes gathered in landfills may release toxic and harmful chemical compounds in the nearby soils

- **Fertilizers, pesticides, and manures:** chemical compounds in fertilizers causes contamination and poisoning of the environment

- **Mining Activities:** excavation processes release dusts and chemicals which can spread even far from the mining site

- **Atmospheric deposition:** harmful and toxic compounds in the atmosphere can impact on soil contamination by means of rainwater

- **Plastics and microbeads:** it takes thousands of years to degrade releasing harmful compounds in soil. Burning plastics in landfills produce toxic chemicals that last in soil
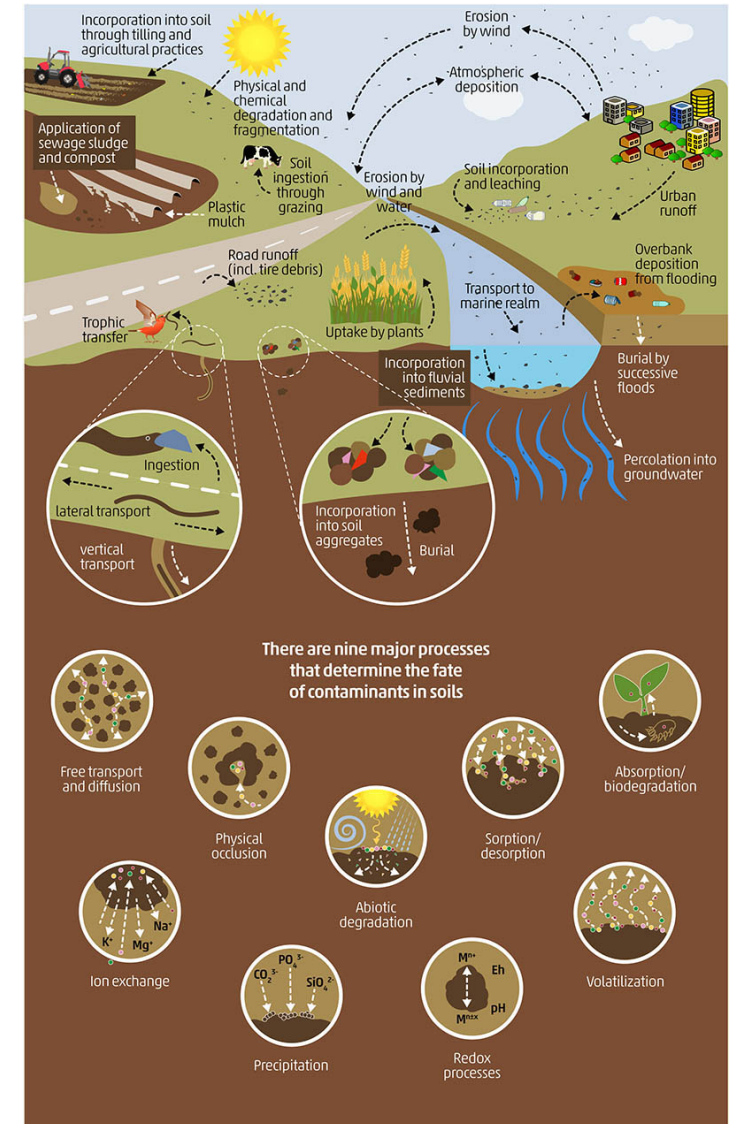
1.2 MAIN SOURCES OF POLLUTION

Origin of water pollutants

- **Industrial Waste:** industrial sites producing waste in the form of toxic chemicals and pollutants

- **Marine Dumping:** dumping garbage into the waters of the ocean

- **Sewage and Wastewater:** harmful chemicals, bacteria and pathogens can be found in sewage and wastewater

- **Oil Leaks and Spills:** large oil spills and oil leaks are a major cause of water pollution. Leaks and spills often are caused by oil drilling operations in the ocean or ships that transport oil

- **Agriculture:** chemicals and pesticides can seep into the groundwater and then mix with rainwater, causing further water pollution

1.2 MAIN SOURCES OF POLLUTION

Origin of air pollutants

- **Mobile sources:** cars, buses, planes, trucks, and trains

- **Stationary sources:** power plants, oil refineries, industrial facilities, and factories

- **Area sources:** agricultural areas, cities, and wood burning fireplaces

- **Natural sources:** wind-blown dust, wildfires, and volcanoes
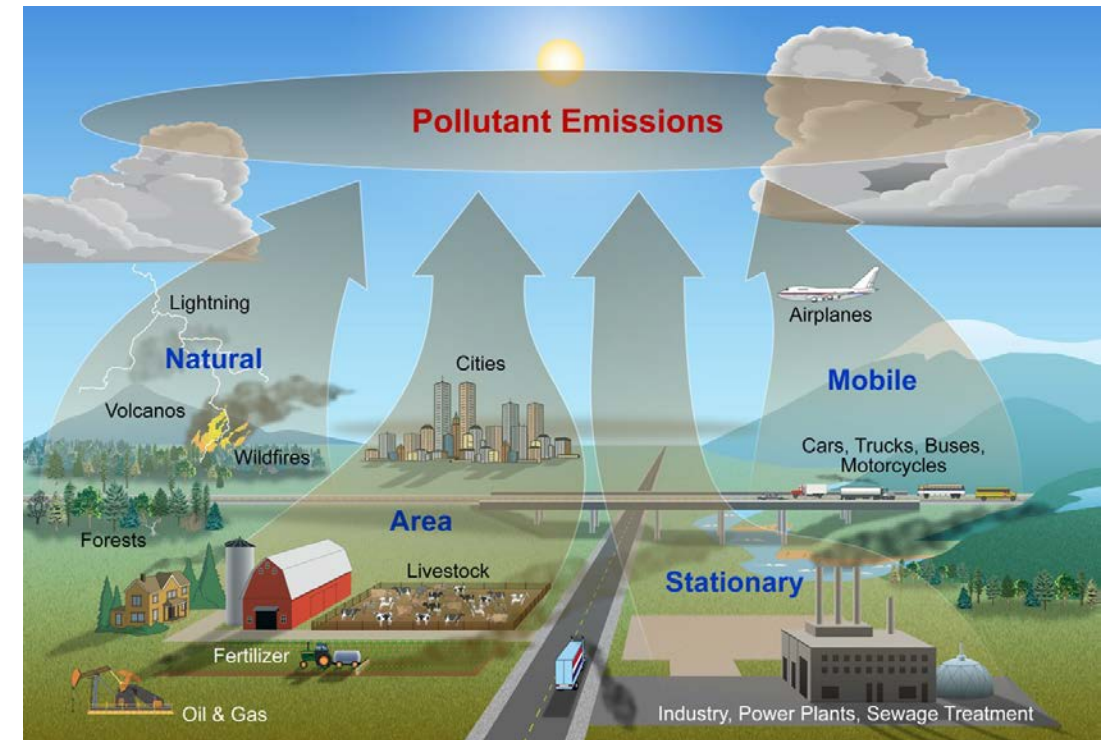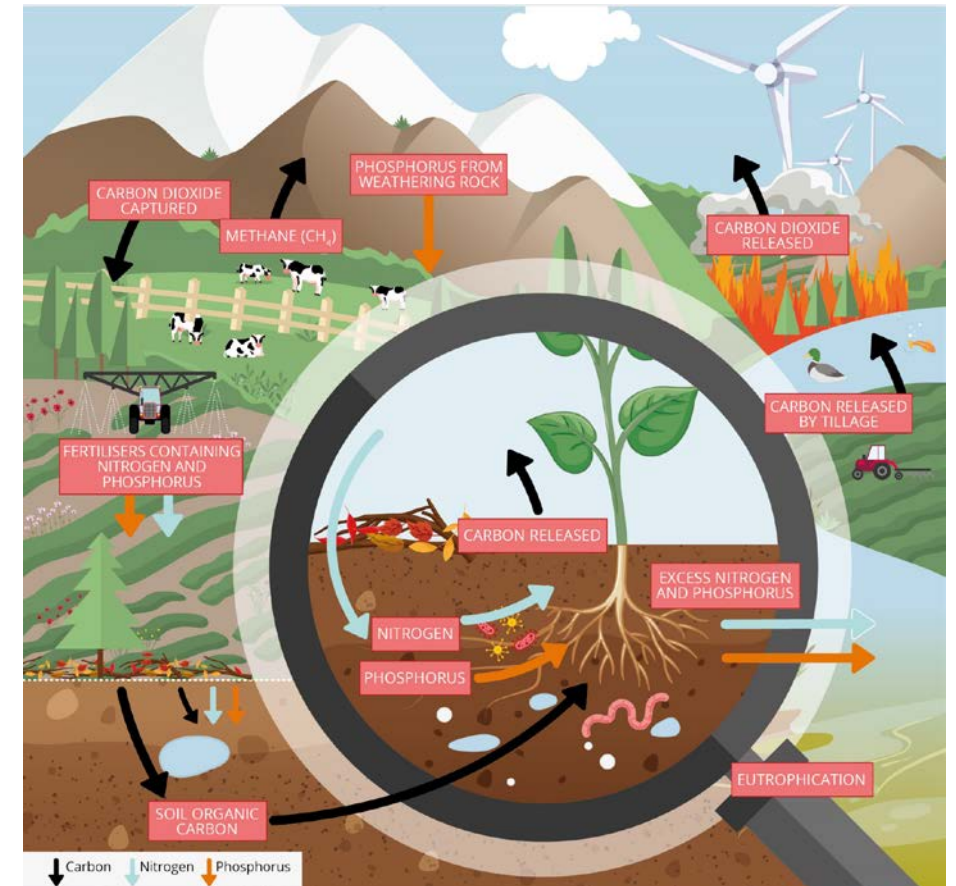
1.3 CONTAMINANTS IN SOIL

Nature and properties of soil contaminants

Soil plays a crucial role in nature's cycles, including the **nutrient cycle**, which involves how much soil organic matter, i.e., carbon, nitrogen and phosphorus, is taken up and stored in soil.

Organic compounds, such as leaves and root tips, are broken down to simpler compounds by organisms living in soil before they can be used by plants.

Some soil bacteria convert atmospheric nitrogen into mineral nitrogen, which is essential for plant growth.

Fertilizers introduce nitrogen and phosphates to induce plant growth but not all amounts are taken up by plants. **The excess can enter rivers and lakes and affect life** in these water ecosystems.

1.3 CONTAMINANTS IN SOIL

Nature and properties of soil contaminants

Every time that potentially hazardous substances are used, treated, processed or disposed, there is a potential for their **release onto land** and hence the **possibility for contamination and pollution.**

This essentially means that **all land under active use by humans is at risk of contamination**.

The number of substances in use is so large that it would be **impossible assess a proper monitoring program for each of these substances**.

A pragmatic approach is to **correlate types of land usage with potential contaminants** relating to that particular use where possible.

Type	Industry/activity
Chemical	Acid/alkali, dyeworks, fertilisers, pesticides, pharmaceuticals, paint works, wood treatment plants/ wood preserving industry
Metals	Metal mines, smelters, refineries, foundries, finishing works, plant and heavy engineering (shipbuilding and shipbreaking, etc.), scrapyards[a]
Petroleum/petrochemicals	Oil refineries (hydrocarbon storage and distribution sites)
Energy	Gasworks[a], power stations
Transport	Docks and railway land (especially large sidings and depots)
Minerals	Asbestos works[a]
Waste disposal	Landfill sites[a], other waste handling/disposal sites
Water supply and sewage treatment	Sewage treatment works[a]
Other	Dry cleaning, hospitals, munitions production and ranges/ testing sites, paper and printing works, tanneries, radioactive material processing installations

1.3 CONTAMINANTS IN SOIL

Nature and properties of soil contaminants

The extent and duration of soil pollution and the risk of harm of a specific contaminant or contaminant class depends on several determinants:

- **chemical nature** of the contaminant (inorganic or organic, radionuclides, asbestos);

- **physico-chemical properties**: volatility, water solubility, lipophilicity, lipophobicity;

- **toxicity** of the compounds in their various forms;

- **source of origin and pathway to the environment**: geogenic versus anthropogenic, direct release or disposal in soil versus atmospheric deposition;

- **soil concentration** and analytical detection values;

- **land use of and sensitivity to receptors in affected areas**: agricultural and forestry activities, recreational, residential or industrial areas.

1.3 CONTAMINANTS IN SOIL

Nature and properties of soil contaminants

Chemicals that act as environmental contaminants in soil and which potentially cause hazards, are either **inorganic or organic compounds.**
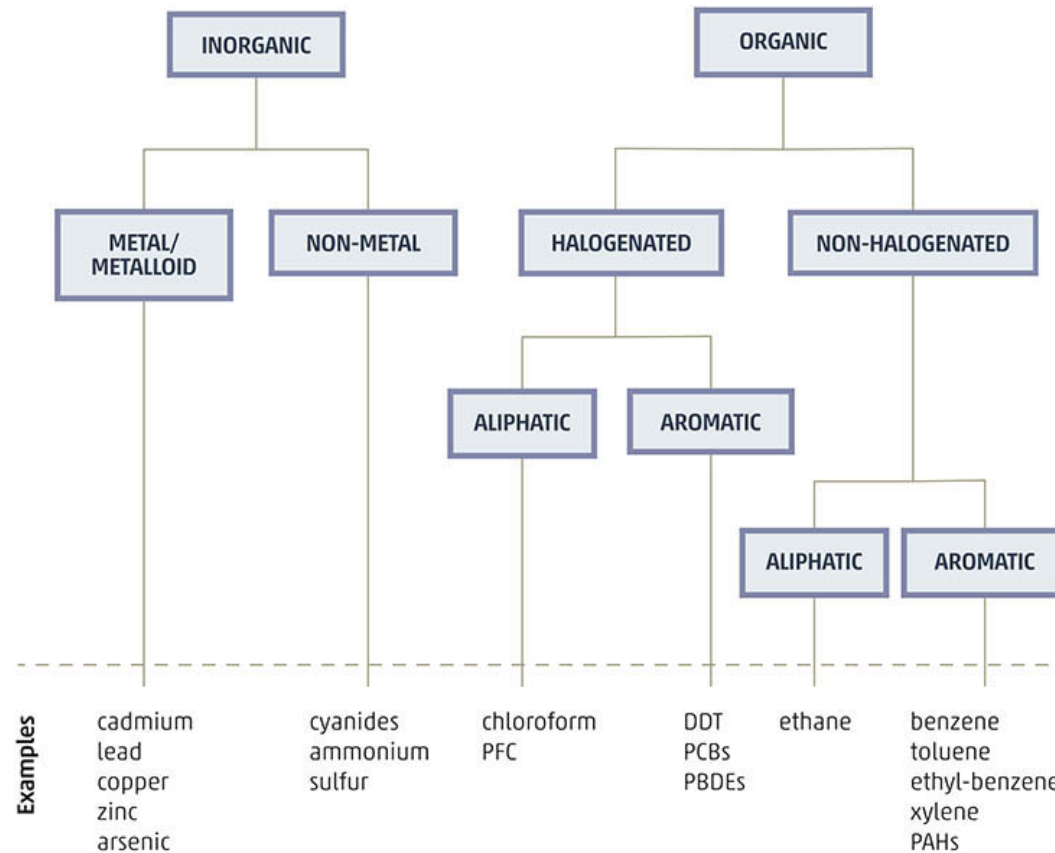
1.3 CONTAMINANTS IN SOIL

Inorganic contaminants in soil

The most commonly occurring inorganic soil contaminants are **trace elements**, i.e., elements that are generally found in soil at low concentrations, less than 100 mg/kg, that are biologically significant.

Biological significance would include **elements that are essential or toxic to any organism** where some elements can be both, depending on their concentration. Many of the trace elements of importance are metals, while others are metalloids, non-metals, and halogens occurring a variety of chemical states (elemental, cations, anions, oxyanions, methylated, etc.).

Despite the natural occurrence of trace elements, hazard to the environment and human health can result if these elements are present at **concentrations** and/or in a **chemical form** that can be toxic for living organisms.

Inorganic contaminants are by nature persistent and can occur in **many different forms** such as salts, oxides, sulphides, or organo-metallic complexes, or may be present in the form of ions dissolved in soil solution, depending on the soil pH.

1.3 CONTAMINANTS IN SOIL

Inorganic contaminants in soil

Differently from organic contaminants, which can be degraded when metabolized by different organisms, **inorganic elements cannot be degraded by metabolic processes**.

Inorganic elements can exist as **different oxidation states** and are characterized by the tendency to form **metal-organic compounds**, which effectively determines the bioavailability and toxicity.

Typical examples are chromium and arsenic which can occur as chromium[III] / chromium[VI] or arsenic[III] / arsenic[V] .

In practice, most assessments of trace elements measure and **report total concentrations** rather than the specific chemical form of the element due to the complexity of analyses and interpretation of sequential extraction methods in laboratories (e.g., chromium is reported instead of discriminating chromium[III] or chromium[VI]).

1.3 CONTAMINANTS IN SOIL

Inorganic contaminants in soil

Trace elements constitute inorganic compounds that are widespread in nature. **Some elements are essential micronutrients** to soil microorganisms, plants, and animals, such as iron (Fe), copper (Cu), zinc (Zn), manganese (Mn), nickel (Ni), boron (B), selenium (Se) and molybdenum (Mo) (Viets, 1962), while **other elements have no known metabolic function**, such as lead (Pb), cadmium (Cd) and mercury (Hg).

Trace element concentrations are expressed on a **weight per unit weight basis**: micrograms or milligrams per kilogram of soil dry weight (µg/kg d.w. or mg/kg d.w.). The abundance of trace elements in soils may range from more than 1000 mg/kg (aluminium, manganese, barium) to less than 1 mg/kg (cadmium, gold, mercury, molybdenum, selenium, silver).

The W.H.O. differentiates between trace elements as:

- **Essential**: chromium, copper, molybdenum, selenium, zinc

- **Probably essential**: manganese, nickel, vanadium

- **Toxic**: aluminium, arsenic, cadmium, lead, lithium, mercury, and tin

Element	Essential	Natural sources	Anthropogenic sources	Uses
Arsenic	No	Dust storms Volcanic eruptions Geothermal/hydrothermal activity Forest fires Arsenic-rich minerals	Metal mining and smelting Coal mining and burning of arsenic-rich coals Pesticide Timber industry Pyrotechnics	Wood preservatives Additive to veterinarian drugs (poultry) Doping agent in semiconductors
Cadmium	No	Zinc and lead minerals Phosphate rocks	Mining waste Electroplating Metal industry (non-ferrous metals and steel) Automobile exhaust Phosphate mineral fertilizer	Battery plants Pigments in paints, ceramics, plastics, etc. Cd impurities in Zn coatings used on metal structures
Chromium	Yes	Chromium minerals	Metal industry Electroplating Industrial sewage	Electroplating Metal alloys Anticorrosive products Pesticides, detergents
Copper	Yes	Sulphides, oxides, carbonates	Domestic and industrial waste, mining waste, animal manures (pig and poultry) Car breaks Metal industry Copper-based fungicides	Electric supplies, electric conductor Electroplating Fungicides Plant residues treated with fungicides used as soil amendments Timber treatment chemicals Copper piping and guttering Vehicle brake linings

Element	Essential	Natural sources	Anthropogenic sources	Uses
Lead	No	Lead minerals	Battery manufacturing facilities Private and industrial waste Rifle ranges and military facilities Leaded paints and leaded fuel addition Insecticides	Batteries Alloys, bullets and other munitions
Mercury	No	Mercury sulphide ores Volcanoes Forest fires Ocean emissions	Artisanal and small-scale gold mining Chemical industry Fossil fuels (coal and petroleum) combustion Nonferrous metals production	Catalysts, electrical switches Batteries, fluorescent lights, felt production, thermometers and barometers Alloys for dental fillings Bright-red paint pigment
Nickel	Yes	Nickel minerals	Metal works, battery plants, electronics, Industrial waste	Metal alloys, batteries, electronics,
Zinc	Yes	Minerals	Battery plants Metal industry Phosphate fertilizers	Batteries Alloys Construction anticorrosive plating Tyre rubber Additives in veterinary drugs and pesticides

1.3 CONTAMINANTS IN SOIL

Organic contaminants in soil

Organic contaminants are defined as chemicals that are carbon based, for example, organic solvents, pesticides, petroleum-based wastage, timber, and gas or liquid phase volatile compounds. These contaminants are anthropogenic in origin but also, to a minor extent, derived from natural processes such as wildfires or volcanic eruptions.

Synthetic organic contaminants include pesticides as dichlorodiphenyltrichloroethane (**DDT**), dieldrin, and hexachlorobenzene (HCB), hexachlorohexane (HCH, lindane), and endosulfan but also **industrial chemicals** such as polychlorinated biphenyls (PCBs) or other halogenated organics and volatile organics (**VOCs**) such as **benzene, toluene, and chloroform**.

Organic contaminants may also be produced unintentionally as by-products such as industrial emissions, frequently from mining and petroleum industries, that release **polycyclic aromatic hydrocarbons** (PAHs).

1.3 CONTAMINANTS IN SOIL

Organic contaminants in soil

Organic contaminants show different behavior in terms of **solubility in water**.

Non-soluble organic contaminants are typically volatile and their low solubility in water results in high absorptive potential to lipids (lipophilicity), **forming stable bonds** with lipids and carbohydrates i**n organisms' tissues** and with **soil organic matter**.

Soluble organic contaminants are designed to be soluble in water and form water-soluble ions. **These are typically used in agrochemicals**.

Another environmentally relevant characteristic of many organic contaminants is **persistence in the environment and potential toxicological effects**. A contaminant is considered persistent in soild if its half-life is at least of 120 to 180 day.
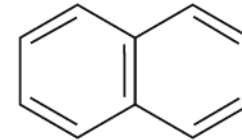
1.3 CONTAMINANTS IN SOIL

Organic contaminants in soil - polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are compounds containing only carbon and hydrogen atoms organized in two or more **annulated aromatic rings that are joined along shared edges**.

Several thousand PAHs are possible in nature being released by **natural events** such as volcano eruptions or forest fires or through a wide range of past and current **anthropogenic activities** such as production and combustion of petroleum and fossil fuels.

Polycyclic aromatic hydrocarbons are also produced during **cooking** of certain food items, such as grilled vegetables, toasted bread, and meat and smoked foods.
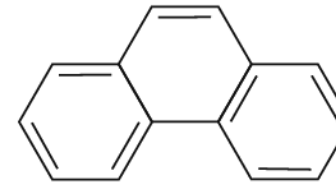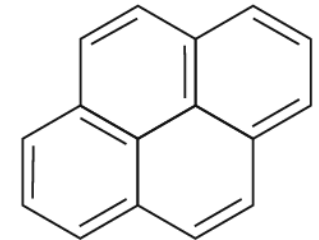
Naphthalene

Anthracene
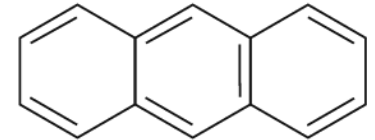
Phenanthrene

Pyrene

1.3 CONTAMINANTS IN SOIL

Organic contaminants in soil - polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons are solid at room temperature and **are not soluble in water but are generally lipophilic.** Therefore, they easily bind to organic material, soil organic matter and fatty tissue, or dust particles.

The properties of the individual PAH homologues depend on the number of hydrocarbon rings: **the smaller the molecule, the smaller the lipophilicity and the higher the volatility**. Smaller PAH homologues show increased long-range-transport potential, and the larger and heavier homologues accumulate in organic matrices and the fatty tissue in living organisms including humans.

Many PAHs are carcinogenic, mutagenic and/or toxic for reproduction. The United States of America Environment Protection Agency (**US EPA**) has identified 16 PAHs as *Priority Pollutants* which were selected as representative PAHs for regulation.
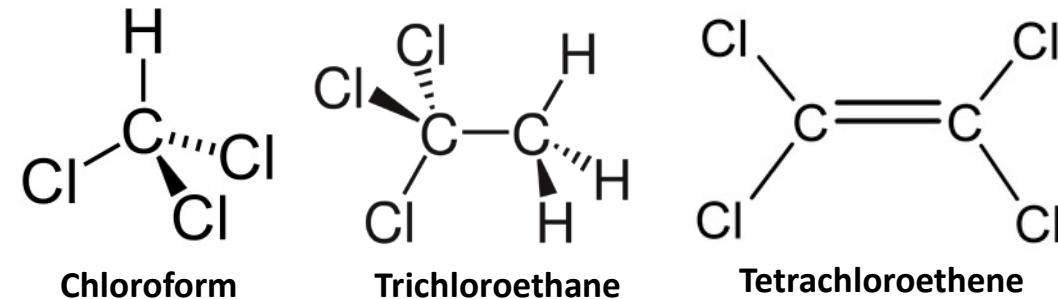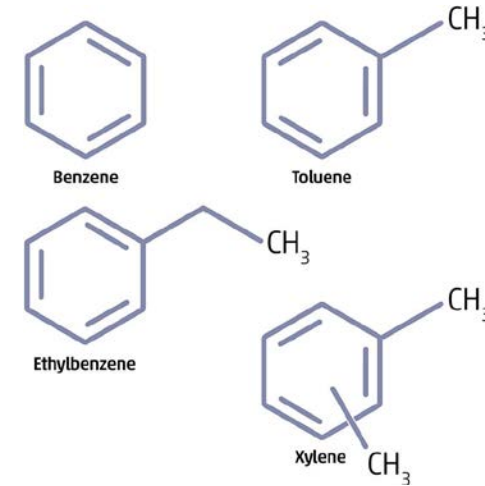
1.3 CONTAMINANTS IN SOIL

Organic contaminants in soil – volatile organic compounds

The **volatile organic compounds** (VOCs) encompass a range of chemical classes, aliphatic and aromatic, that exist primarily as liquids that are highly volatile or even gases at room temperature.

Monocyclic aromatics commonly encountered in soils are the **BTEX compounds** (benzene, toluene, ethyl benzene and xylene)

Halogenated aliphatic compounds are vinyl chloride, chloroform, trichloroethane (TCE) and tetrachloroethene (PCE).

Benzene Toluene

Ethylbenzene

Xylene

Chloroform   Trichloroethane   Tetrachloroethene

These compounds exhibit a range of toxic effects, with some promoting **carcinogenic, mutagenic and teratogenic responses**, and are not easily degradable but volatilization is an important loss process.

1.3 CONTAMINANTS IN SOIL

Organic contaminants in soil – volatile organic compounds

Many **VOCs are used widely as organic solvents in industry**, for example in degreasing, dry cleaning, printing and painting operations, and are important contaminants at industrial sites. The **BTEX** compounds are associated with **petroleum**, especially gasolines, and are also used as solvents in many industrial processes.

The VOCs are **one of the most significant categories of contaminants** that are encountered at polluted sites, typically as mixtures. Their **volatility** leads to a **difficult quantitative determination** of the concentration in soil.

Depending on their behavior in soils and groundwater, hydrophobic organic liquids are often grouped as **non-aqueous phase liquids (NAPLs)**.

These compounds are subdivided into:

- **light** non-aqueous phase liquids (LNAPLs), less dense than water and thus **floating** (**BTEX**);

- **dense** non-aqueous phase liquids (DNAPLs), denser than water and thus **sinking**.
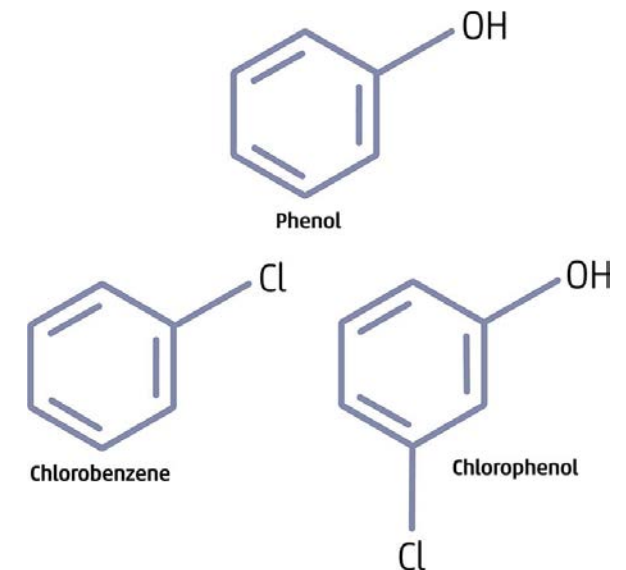
1.3 CONTAMINANTS IN SOIL

Other organic contaminants in soil

- **Petroleum hydrocarbons (PHCs)**
  Mixtures of organic compounds found in or derived from geological substances such as oil, bitumen and coal. The PHCs are usually released into the soil environment due to accidental spills or leakages from oil storage containers, pipelines or vehicles.

- **Phenols, chlorobenzenes and chlorophenols**
  Chlorinated derivatives of benzene and phenol. Chlorobenzenes are cyclic aromatic compounds in which one or more hydrogen atoms of the benzene ring are substituted by a chlorine atom. These compounds can cause toxic effects to humans and other organisms, representing a risk for ecosystems as potential precursors of dioxins.

OH
Phenol

Cl
Chlorobenzene

OH
Chlorophenol
Cl

1.3 CONTAMINANTS IN SOIL

Other organic contaminants in soil

- **Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)**
  PCDDs are composed of two benzene rings joined by two adjacent oxygen bridges (C-O-C bonds), respectively, with varying degree of chlorine substitution on each benzene ring. PCDFs are similar with the benzene rings joined by one C-O-C bond and one direct bond without a bridging atom (C-C bond).

  The formation of PCDDs and PCDFs occurs as a by-product of industrial processes associated with the chlorine and organochlorine industry, incomplete combustion during incineration processes including improper waste incineration, and burning of waste, and in particular electronic waste

  Currently, **a large proportion of the European population is considered exposed to greater that the tolerable intake values of the European Food Safety Authority**, which has been set at 70 pg/kg bw/month (picograms per kilograms of body weight per month) and even low exposures can produce birth defects in small mammals, interact with DNA, and may cause carcinogenicity.
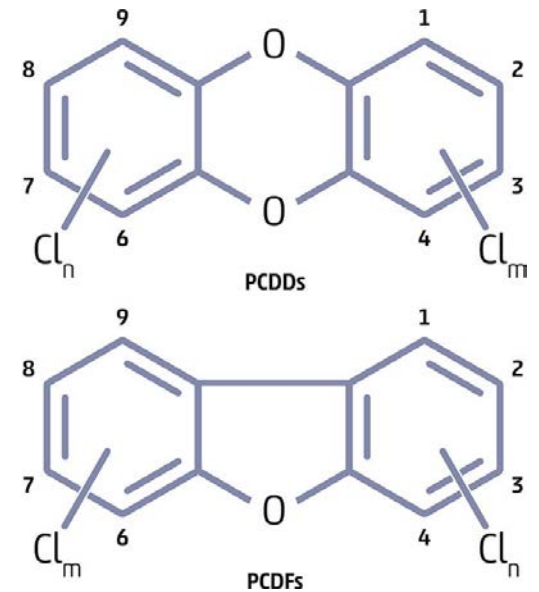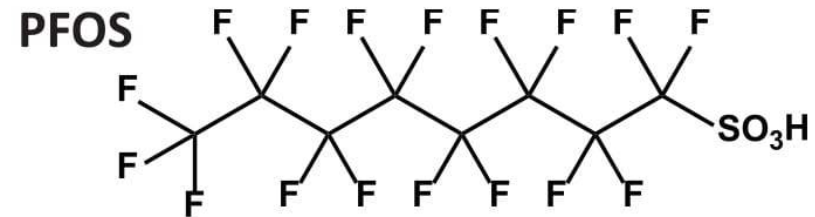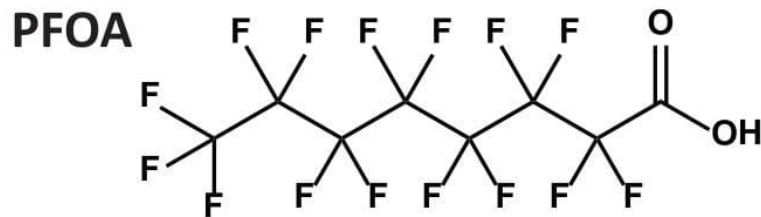
Other organic contaminants in soil

- **Perfluoroalkyl and polyfluoroalkyl substances (PFASs)**
  PFAS is a family of synthetic molecules composed of a carbon chain that can be linear or branched, and partially or fully fluorinated. Perfluoroalkyl and polyfluoroalkyl substances normally present high thermal, chemical and biochemical stability, low aqueous surface tension and amphiphilic behavior, although many homologues exist. **The PFAS family may include between 5000 and 10000 different chemicals and therefore the range in behavior highly different.**
  PFASs are persistent in the environment, toxic to both animals and humans, and highly mobile in aquatic environments, especially in the case of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) , which are the most frequently detected PFASs.
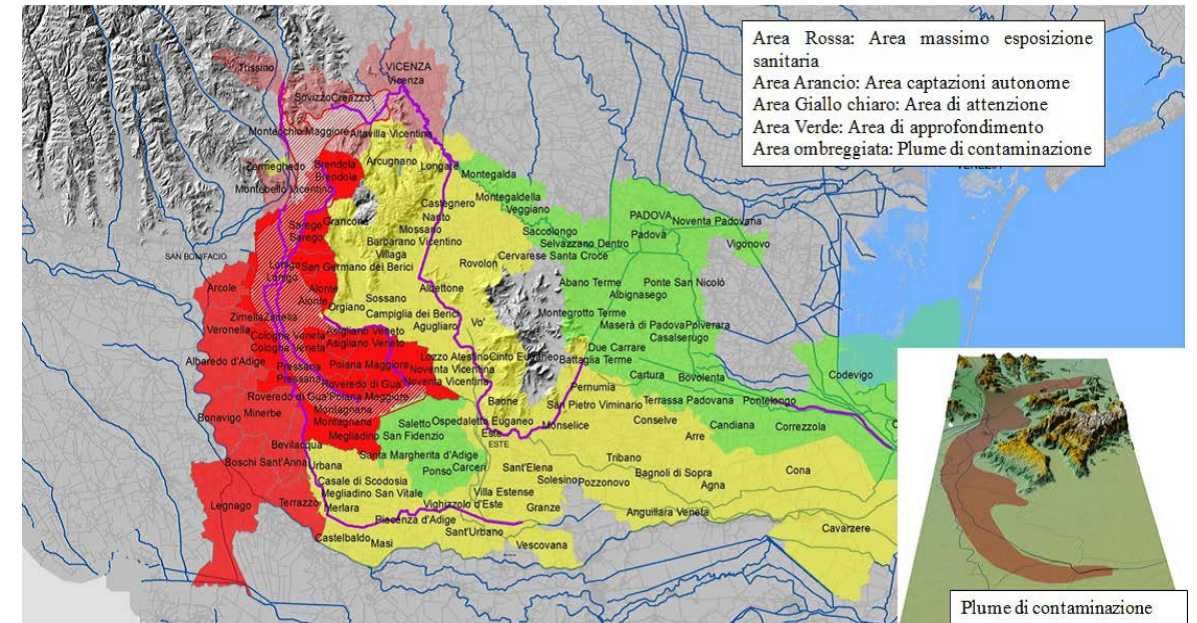
1.3 CONTAMINANTS IN SOIL

Other organic contaminants in soil

PFASs became a hot topic in Italy in 2011 when a research study discovered a strong contamination by perfluoroalkyl substances related to the industrial activities of a chemical industry located in Trissino, nearby Vicenza.

Starting from the sixties, this industry has been producing fluorinated compounds, and the industrial wastewater have been responsible for a contamination of soils and groundwater

Area Rossa: Area massimo esposizione sanitaria
Area Arancio: Area captazioni autonome
Area Giallo chiaro: Area di attenzione
Area Verde: Area di approfondimento
Area ombreggiata: Plume di contaminazione

Plume di contaminazione

The area interested by the pollutants is about **180 km²** around Vicenza, Verona and Padova, affecting an estimated population of **300k inhabitants.**

1.3 CONTAMINANTS IN SOIL

Other organic contaminants in soil

- **Pesticides**
The term "pesticide" includes active substances, or mixtures of substances, used for preventing, destroying or controlling any pest causing harm to humans or interfering with human activities such as production, processing, storage, transport or marketing of food, wood and wood products, fibres and other agricultural commodities.

  Today, there are about 1000 different pesticides in use composed of more than 800 active ingredients and the number is still increasing.

  Different classifications of pesticides have been proposed by different organizations depending on chemical composition and the chemical families to which they belong or on toxicological effects.

Other organic contaminants in soil

- **Plastics**
  Plastic polymers consist of very large **macromolecules**, characterized by average molecular weights of millions of grams per mole (from 1000 to 10000 atoms per molecule), and a **long repetitive chain-like molecular architectur**e. This material mainly originates from the processing of **crude oil and natural gas**, and in some cases from other raw materials.

  Plastic items and residues are commonly found in all environmental compartments and can be ingested by organisms, causing damage and possibly mortality, but may also **be transferred across the food chain**.

  Moreover, **fugitive emission of potentially toxic solvents**, eluents and other chemicals as monomers during plastic production, as well as **the use of toxic catalysts in production**, and particulate emissions can also represent an important burden of pollution, impairing human health and ecosystems.

1.3 CONTAMINANTS IN SOIL

Other organic contaminants in soil

- **Plastics**
  Plastics can be partially broken down by mechanical action (agricultural machinery, garbage collection trucks and treatment plants) or weathering, including UV-radiation of sunlight.
  Macroplastics are generally defined as having a **size > 1 mm**, whereas **microplastics** refers to particles **< 1 mm**.

  Microplastics can be formed by the chemical and physical weathering of plastics (secondary microplastics) or have a primary source. Due to the small size, microplastics are not completely removed by wastewater facilities, and are **easily dispersed into the environment.**

  Microplastics **can absorb and subsequently leach toxic compounds** such as trace metals, PCBs, PBDEs, nonylphenols and pesticides, increasing their pollutant effect.

1.4 WATER QUALITY MONITORING

Water as fundamental constituent of life

Water is a vital natural resource that forms the basis of all life. Further, water is a key resource in all economic activities ranging from agriculture to industry. With ever increasing pressure of human population, there is **severe stress on water resources**.

Many developmental projects as well as industrial and urbanization programs, are likely to have both qualitative and quantitative effects on both the surface and ground water environment (rivers, lakes, estuaries, oceans), which may result in considerable impacts on aquatic faunal or floral species and aquatic ecosystems. The release of complex and diverse industrial wastes impairs the quality of the environment and poses a threat to **human health directly or indirectly.**

Respect to soil pollution, water pollution represents a closer threat to human health due to its crucial role in everyday life, from drinking to domestic uses.

1.4 WATER QUALITY MONITORING

Classification of pollution sources

Sources of water pollution can be classified in:

- **Point sources**
  A point source is a single, identifiable source of pollution, such as a pipe or a drain. Industrial wastes are commonly discharged to rivers and the sea in this way.

- **Non-point sources**
  Non-point sources of pollution are often termed 'diffuse' pollution. They refer to inputs and impacts which occur over a wide area and are not easily attributed to a single source. They are often associated with particular land uses, as opposed to individual point source discharges.

1.4 WATER QUALITY MONITORING

Point pollution sources

Point-source pollutants in surface water and groundwater are usually found in a **plume** that has the highest concentrations of the pollutant nearest the source, such as the end of a pipe or an underground injection system and diminishing concentrations farther away from the source.

The various types of point-source pollutants found in waters are as varied as the types of business producing them: **industry, agricultural, and urban sources**.

Examples: organics or metals entering surface water as a result of wastewater discharge from a manufacturing plant; animal feeding operations, animal waste treatment, pesticides, fertilizers, and petroleum; wastewater treatment plants, landfills, utility stations, motor pools, and fleet maintenance facilities.
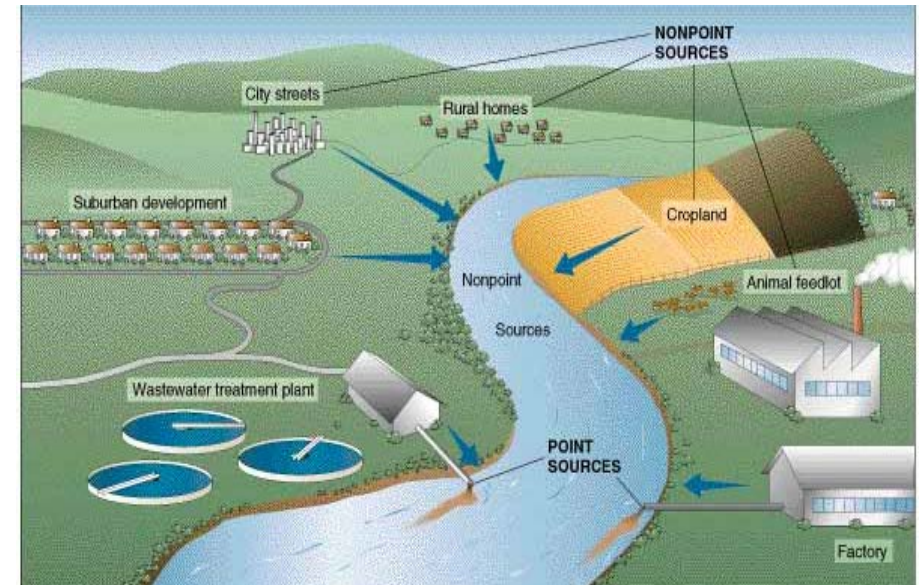
1.4 WATER QUALITY MONITORING

Non-point pollution sources

Non-point sources (NPS) of pollution generally results from **land runoff, precipitation, atmospheric deposition, drainage, seepage or hydrologic modification**. NPS pollution, unlike pollution from industrial and sewage treatment plants, comes from **many diffuse sources**. NPS pollution is caused by rainfall or snowmelt moving over and through the ground. As the runoff moves, it picks up and carries away natural and human-made pollutants, finally depositing them into lakes, rivers, wetlands, coastal waters and ground waters.

NPS pollution includes:

- Excess fertilizers, herbicides and insecticides from agricultural lands and residential areas

- Oil, grease and toxic chemicals from urban runoff and energy production

- Bacteria and nutrients from livestock, pet wastes and faulty septic systems

- Atmospheric deposition and hydromodification

1.4 WATER QUALITY MONITORING

Major Types of Pollutants in water

- **Oxygen-demanding wastes**: decomposition by aerobic bacteria depletes level of dissolved oxygen in water; flora and fauna perish; further decomposition by anaerobic bacteria produces foul-smelling toxic substances such as hydrogen sulfide.

- **Plant nutrients:** algal blooms; death of submerged vegetation; production of large amounts of dead organic matter with subsequent problems of oxygen depletion

- **Acids**: Acidification of natural waters; sharp decline in species richness; fish killed; concomitant increase in level of toxic metals in solution, for example, aluminum

- **Toxic metals (Hg, Pb, Cd, Zn, Sn)**: Biomagnification of toxic metals with each successive stage of food chain; threat to consumers including humans

- **Oil**: Contamination of the aquatic environment, death of birds and mammals

- **Pesticides**: Biomagnification; top carnivores at risk; very persistent in the environment, effects on human health
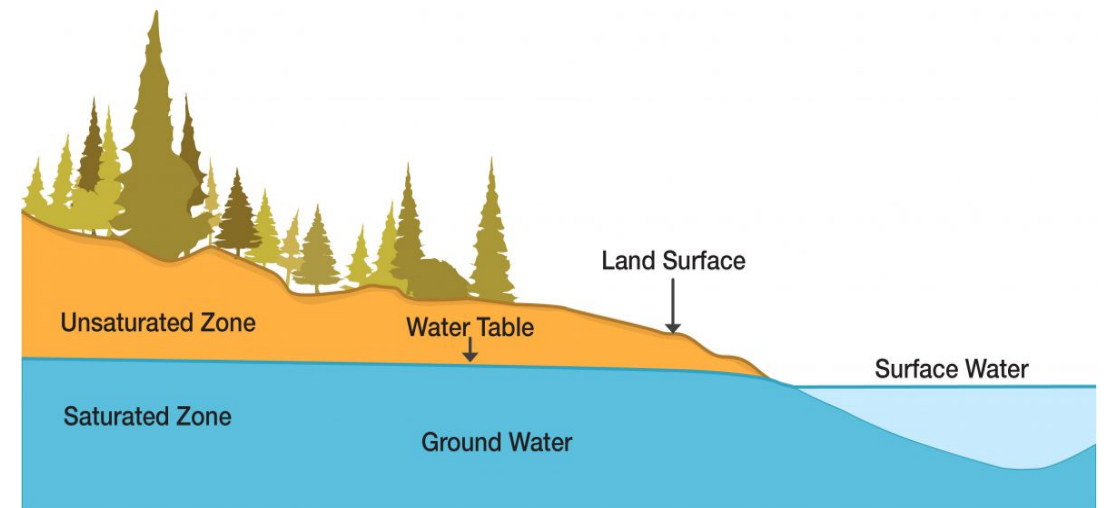
1.4 WATER QUALITY MONITORING

Surface water and groundwater

Source water refers to bodies of water providing water to drinking-water supplies and wells. Water sources include **surface water** (i.e., lakes, rivers, reservoirs) and **groundwater** (i.e., aquifers)

Surface water collects on the ground or in a stream, river, lake, reservoir, or ocean. Surface water is constantly evaporating out of water bodies, seeping into ground water supplies, and being replenished by rain and snow. A spring is where ground water comes to the surface and becomes surface water.

Ground water is located below the surface of the earth in spaces between rock and soil. Ground water is naturally filtered, which might remove some germs and chemicals depending on the water's depth and the area's local geology. Water coming from a well is ground water.

1.4 WATER QUALITY MONITORING

Surface water pollution

The effects of pollution sources on surface water are heterogeneous and dependent on the type and concentration of pollutants.

Soluble organics, as represented by high biochemical oxygen demand wastes, cause depletion of oxygen in the surface water. This can result in fish kills, undesirable aquatic life, and undesirable odors.

Suspended solids decrease water clarity and hinder photosynthetic processes; if solids settle and form sludge deposits, changes in benthic ecosystems result. **Oils and floating materials** are of concern because of their possible influence on water clarity and photosynthetic processes.

Excessive nitrogen and phosphorous can lead to algal overgrowth, with water treatment problems resulting from algae decay and interference with treatment processes.

Chlorides cause a salt taste to be imparted to water, and in sufficient concentration, limitations on water usage can occur.

Acids, alkalis, and toxic substances have the potential to cause fish kills and create other imbalances in stream ecosystems.

Groundwater pollution

Groundwater contamination commonly results from human activities where pollutants, **susceptible to percolation are stored and spread on or beneath the land surface**.

The amount of water available for infiltration, either from precipitation or the wastewater itself, is a primary factor in carrying pollutants down through a soil profile. Water from the surface passes downward through the unsaturated zone and disperses in an aquifer in a manner depending on site conditions. **Dispersion of a contaminant is influenced both physically by soil porosity and hydraulically by the rate of water movement**.
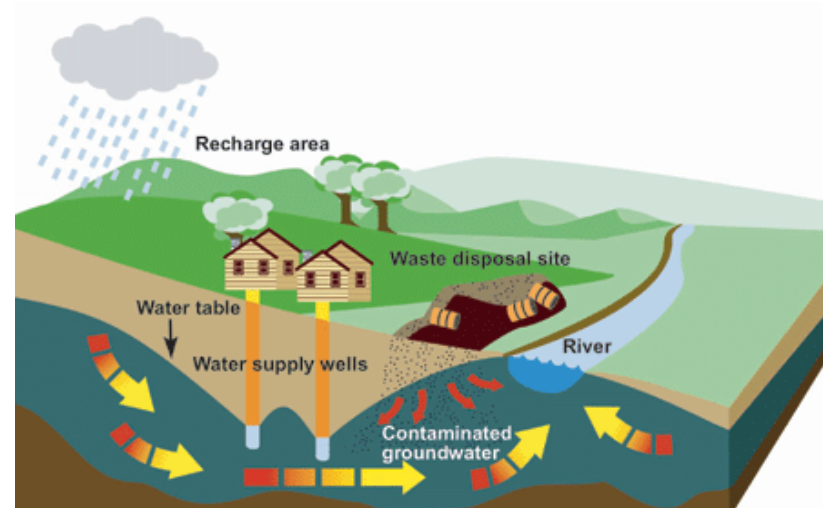
1.4 WATER QUALITY MONITORING

Groundwater pollution

Groundwater pollution can be **persistent underground for years, decades, or even centuries**. This is in marked contrast to surface water pollution. Reclaiming polluted groundwater is usually much more difficult, time consuming, and expensive than reclaiming polluted surface water.

The principal natural chemicals found in groundwater are **dissolved salts, iron and manganese, fluoride, arsenic, radionuclides, and trace metals**. Both geologic and climatic conditions influence mineral composition. In arid regions with limited water recharge, slow percolation results in mineralized poor-quality water high in sodium chloride.

1.4 WATER QUALITY MONITORING

Monitoring techniques: sampling vs. continuous

Water quality variables exist relatively continuously in position within the water body and in time, but one can never measure at every place and at every instant of time.

- **Sampling** can be necessary in order to reduce the data collection procedure and to avoid excessive amounts of data. However, if the sampling is too sparse, valuable information may be missed and so a compromise has to be reached.

- **Continuous monitoring** is preferable to sampling for two reasons: first, measurements are available in ' real time' and, second, the signal is continuous.

Different sensing system can be used depending on the monitoring techniques adopted.

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Criteria for water quality

Three types of water quality variable are typically considered:

- **Physical**: temperature, conductivity, salinity, turbidity, total suspended solids, and color

- **Chemical**: dissolved oxygen, pH, acidity, alkalinity, anions, cations, hydrocarbons and petrochemical, oil and grease, and pesticides.

- **Biological**: algae, bacteria, viruses, toxins, biocides, biochemical oxygen demand, populations and diversity of aquatic and benthic flora and fauna.

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Physical variables in water monitoring: temperature

Temperature sensors for water monitoring should be characterized by **high accuracy, linearity and small time constant**.

In making measurements in water, the range of measurement will be from just below 0°C to about 40°C and the required accuracy might range from a relative accuracy of ±0.01°C for depth profiles to an absolute accuracy of between 0.1 and 0.5°C for characterizing water bodies.

Some fish and plants species are sensitive to water temperatures just a few degrees above 20°C, and many organisms have an optimum temperature range, above and below which their growth rates are reduced.

Commonly used sensing systems for temperature monitoring include resistive sensors, thermocouples, thermistors, semiconductor junctions, thermometers (standard or IR).

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Physical variables in water monitoring: conductivity

The conductivity of water is a measure of its ability to carry an electric current and arises from the movement of the ions within the water when an electric field is applied.

Pure water contains only relatively few hydrogen and hydroxyl ions produced by the dissociation of water and **has a very low conductivity** (0.037 $\mu S \cdot cm^{-1}$ at 18°C).

Dissolved inorganic compounds will generally be dissociated into their respective anions and cations and these ions provide additional charge carriers and hence **increase the conductivity**.

The measured **conductivity** of a given solution **depends on its temperature**, thus the measurements should be made at, or standardized to, 25 ± 0.1°C.

It is also usual to **calibrate instruments** against 0.01 moles of potassium chloride (KCl) solution, which has a known conductivity of 1413 $\mu S \cdot cm^{-1}$ at 25°C.
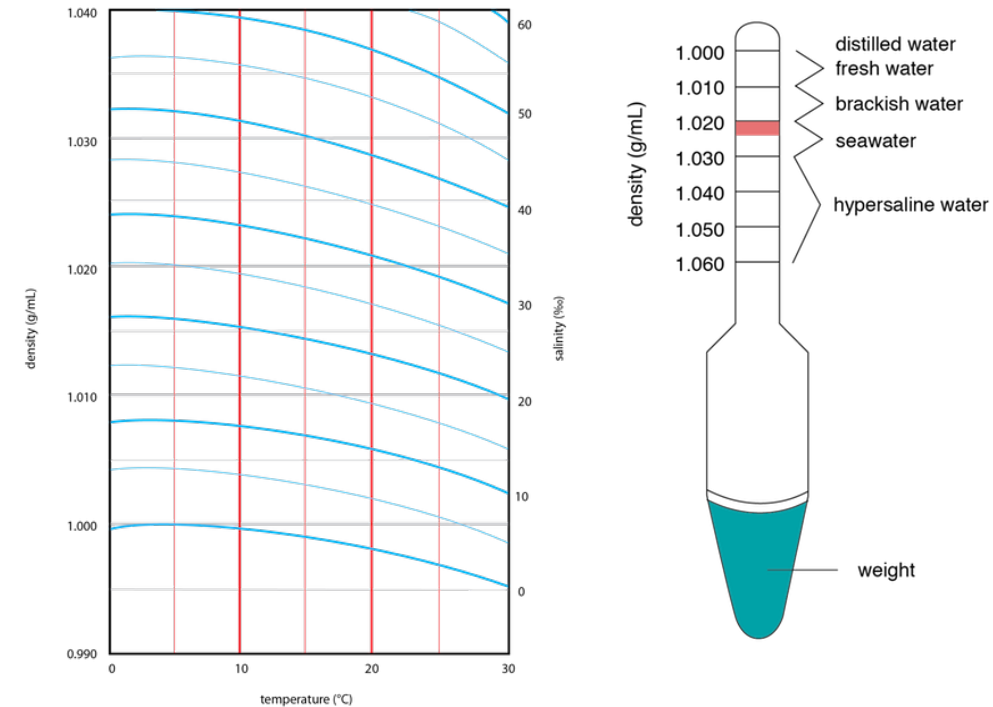
Physical variables in water monitoring: salinity

Salinity is the dissolved salt content of a body of water and helps determine many aspects of the chemistry of natural waters and the biological processes within them. **Dissolved ions increase salinity as well as conductivity, therefore the two measures are related**. The salts in sea water are primarily sodium chloride (NaCl). However, other saline waters owe their salinity to a combination of dissolved ions including sodium, chloride, carbonate and sulfate.

Both temperature and salinity affect density. **The more dissolved salts there are in a body of water, the greater the density of the water.** If the density and temperature of a water sample are known, salinity can be determined.

The units of measurements of salinity are parts per thousand (‰) or grams per kilograms (adimensional) or grams per liter (1 L of pure water weights 1 kg). The salinity level in seawater is about 35‰ (35,000 mg/L), while brackish estuaries may have salinity levels between 1 and 10 ‰.

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Physical variables in water monitoring: salinity

Salinity can be derived from electrical conductivity measurement. To relate those two quantities, a "**practical salinity**" was defined. Practical salinity of a sample of water is defined in terms of the ratio between the electrical conductivity of the water sample at a temperature of 15°C and a pressure of one atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is $32.4356 \cdot 10^{-3}$ (32.4356 g KCl in a mass of 1 kg of solution), at the same temperature and pressure. This ratio is referred as K_{15}.

The practical salinity is adimensional and its unit of measurement is referred as **practical salinity unit** (PSU). **K_{15} equal to 1** corresponds by definition to a **practical salinity equal to 35**, representing the **standard salinity for seawater**. The practical salinity is defined in terms of ratio K_{15} by the following equation:

$$S = a_0 + a_1 K_{15}^{1/2} + a_2 K_{15} + a_3 K_{15}^{3/2} + a_4 K_{15}^2 + a_5 K_{15}^{5/2} + \Delta S$$

$$\Delta S = \frac{T-15}{1+k(T-15)}(b_0 + b_1 K_{15}^{1/2} + b_2 K_{15} + b_3 K_{15}^{3/2} + b_4 K_{15}^2 + b_5 K_{15}^{5/2})$$

$a_0 = 0.008$ $b_0 = 0.0005$
$a_1 = -0.1692$ $b_1 = -0.0056$
$a_2 = 25.3851$ $b_2 = -0.006$
$a_3 = 14.0941$ $b_3 = -0.0375$
$a_4 = -7.0261$ $b_4 = 0.0636$
$a_5 = 2.7081$ $b_5 = -0.0144$
$k = 0.0162$

Physical variables in water monitoring: turbidity

Turbidity is the measure of relative clarity of a liquid. It is an optical characteristic of water and is a measurement of the amount of **light that is scattered by material** in the water when a light is shined through the water sample. The higher the intensity of scattered light, the higher the turbidity. Turbidity arises mainly from suspended particulate and colloidal matter, and from microorganism.

Turbidity can be measured using light-based techniques exploiting **transmission** of light, **side-scattering** of light, and **back-scattering** of light.
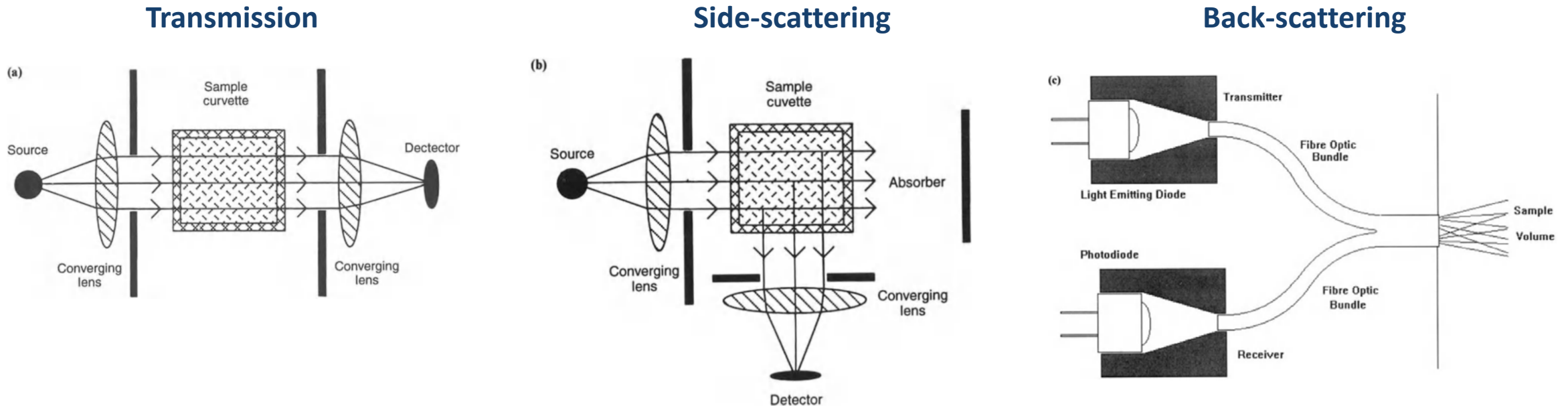
Transmission   **Side-scattering**   **Back-scattering**

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Physical variables in water monitoring: turbidity

For low turbidity, side-scattering instrument (nephelometer) are typically preferred. For high turbidity, the transmission measurements are usually preferred. Back-scattering instruments would also be used for high turbidities.

The first known measure of turbidity was called the Jackson Candle Method (JCU), which used a vertical glass tube over a candle. A sample was poured into the tube until the user could no longer see the distinct image of the candle flame. The final height of the sample which was added resulted in the corresponding turbidity measurement.

Today, **Nephelometric Turbidity Units (NTU) and Formazin Nephelometric Units (FNU) are the common units used for nephelometers**. These scales are referred to standardized reference: USEPA Method 180.1 and ISO 7027, respectively.

Formazin Attenuation Units (FAU) is the common unit for transmission measurements, measuring the decrease in transmitted light through the sample at an angle of 180 degrees to the incident light. This type of measurement is not considered a valid turbidity measurement by most regulatory agencies.

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Physical variables in water monitoring: total suspended solids

The term total suspended solids (SS) refers to the mass (mg) or concentration (mg L^{-1}) of inorganic and organic matter, which is held in the water column of a stream, river, lake or reservoir by turbulence. **TSS are typically fine particulate matter with a diameter larger than 2 microns and smaller than ~60 μm. Anything smaller than 2 microns (average filter size) is considered a dissolved solid.** Most suspended solids are made up of inorganic materials, though bacteria and algae can also contribute to the total solids concentration.

TSS are quantified by means of **gravimetric analysis.** Gravimetric analysis is a quantitative method for accurately determining the amount of a substance by selective precipitation of the substance from an aqueous solution. The precipitate is separated from the remaining aqueous solution by filtration and is then weighed.

Buchner funnel — Filter paper

Vacuum flask — To vaccuum source
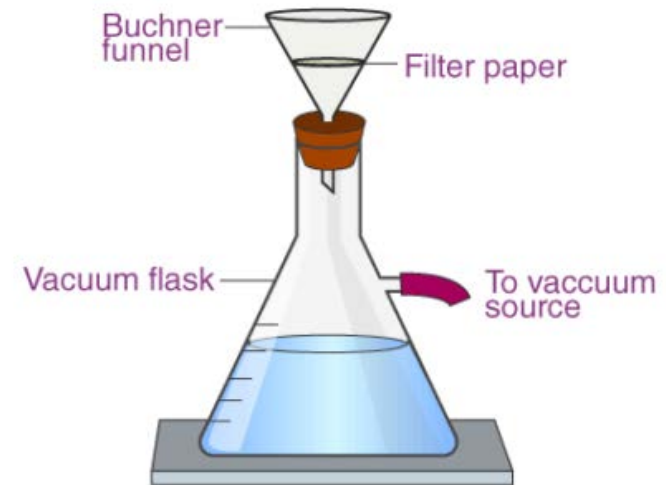
**Gravimetric Analysis Apparatus**

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Physical variables in water monitoring: TSS and turbidity

Turbidity is related to the concentration of scatterers thus it is related to the concentration of TSS and has often been considered as a surrogate for their measurements. However, the two quantities and their sensing systems are different.

Turbidity is visual properties of water based on light scattering and attenuation, which can be monitored continuously. Conversely, TSS can be quantified only by means of sampling operations.

Turbidity can then be used to estimate the total suspended solids concentration, within suitable approximation. Turbidity does not include any settled solids or bedload and its measurements may be affected by colored dissolved organic matter. While this dissolved matter is not included in TSS measurements, it can cause artificially low turbidity readings as it absorbs light instead of scattering it.
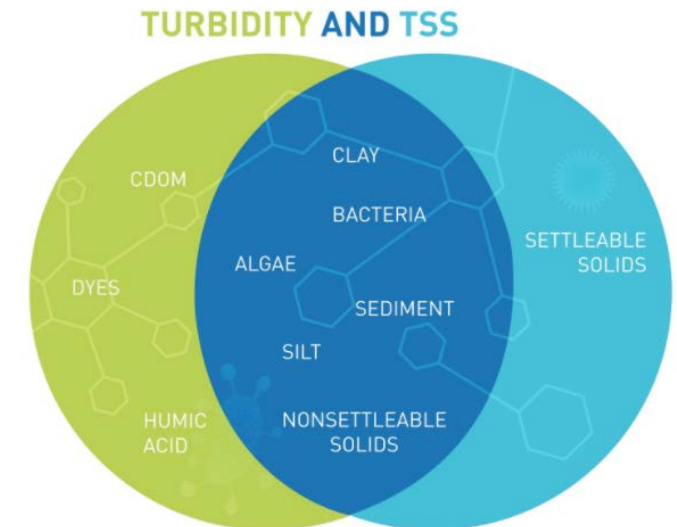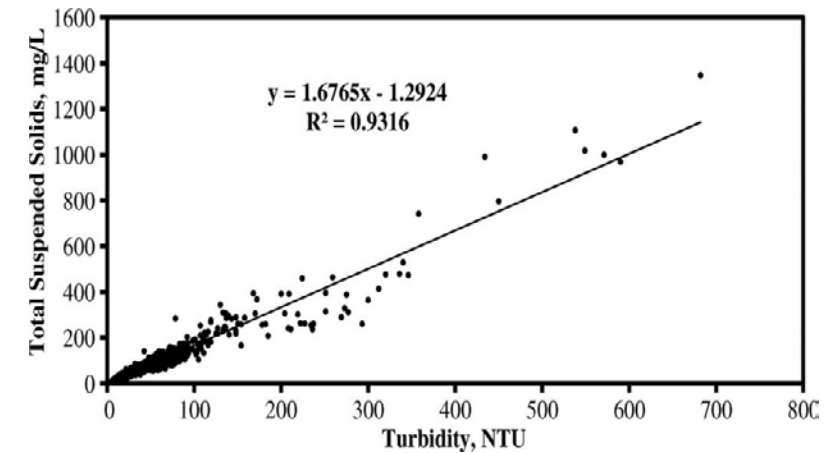
$y = 1.6765x - 1.2924$
$R^2 = 0.9316$

TURBIDITY AND TSS

Physical variables in water monitoring: color

Color in natural water may arise from organic matter or from metal ions, particularly iron and manganese.

Suspended matter influences the **'apparent' color** of the water (influenced by both dissolved and suspended components) compared with the **'true' color** of a filtered sample.

The pH also influences the color of water samples.

Color of pure liquid water is generally referred as light cyan, due to **water absorption in the red part of the visible spectrum**.
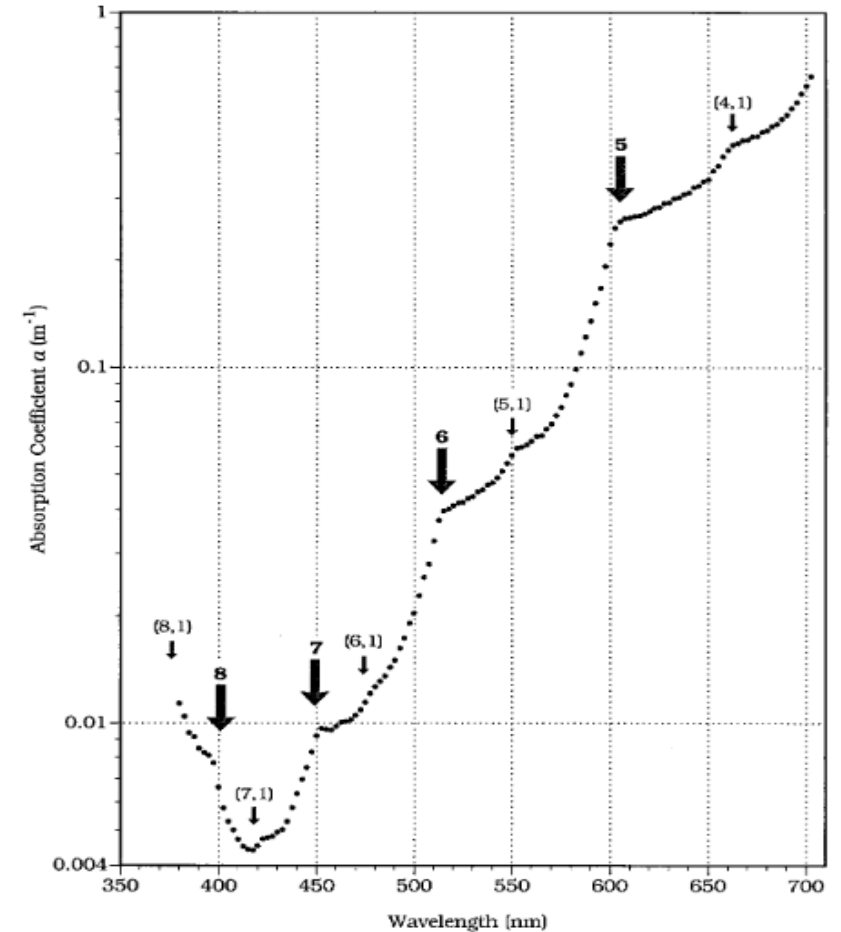
1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Physical variables in water monitoring: color

Color of water is typically measured by means of visual comparison technique, based on standard references.

The commonly employed scale is the **APHA color scale** (named after the American Public Health Association) or Hazen scale (from the name of the chemist which firstly developed this scale). This scale is also referred as **Platinum-Cobalt (Pt-Co) color scale** as this visual color scale is based on stable liquid color standards made from chloroplatinate solutions.

The scale ranges from distilled water at 0 ("water-white") to a stock solution of 500 (parts per million of platinum cobalt to water). Intermediate Pt-Co color standards are made by dilution of the Pt-Co stock solution.
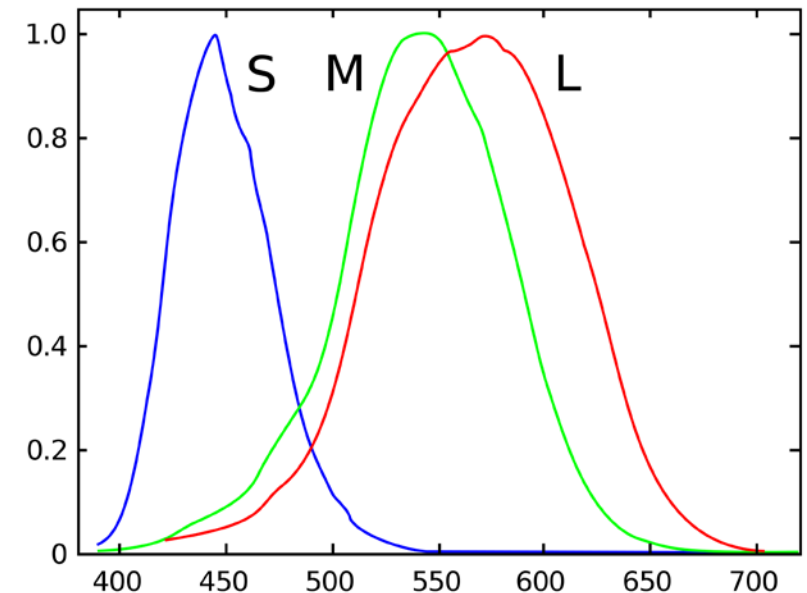
Physical variables in water monitoring: color

Modern instruments employ **colorimetric technique** to evaluate color of liquid samples which are then referred to the APHA scale.

The human eye is characterized by three kinds of cone cells which allow human color perception in conditions of medium and high brightness. These cells are characterized by different spectral sensitivities, peaking at different wavelength:

- **Short wavelengths ("S", 420 nm – 440 nm)**

- **Middle wavelengths ("M", 530 nm – 540 nm)**

- **Long wavelengths ("L", 560 nm – 580 nm)**

Each color produce a stimulus for each cone cell which can be identified by three parameters (tristimulus colorimetry). These parameters identify a 3-dimensional vector space, labelled LMS color space.
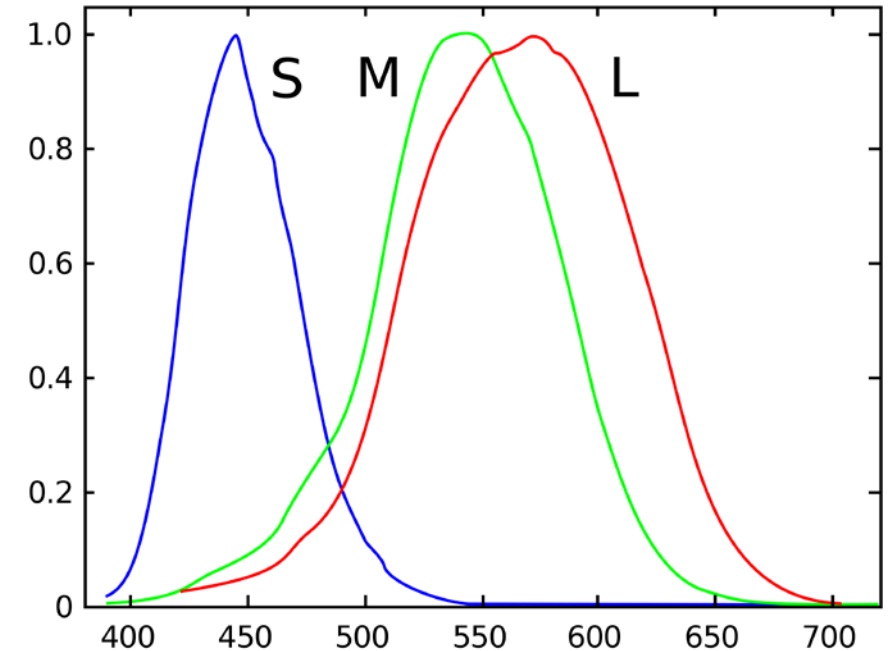
1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Physical variables in water monitoring: color

LMS color space is defined by the spectral sensitivities of the cone cells and to their distribution, thus is **device-dependent**. Moreover, even if LMS color space can **represent any perceivable colors** it is not particularly suitable for some technical applications.

In particular, it is not immediately apparent **how to generate light which creates the color impression related to a particular point in LMS color space**; we cannot directly address the different receptors in the eye because of their spectral **sensitivity curves overlap substantially**.

For example, is not possible to have a non-zero M value combined with L and S being zero because the spectral response curves of the three receptors are substantially overlapping.

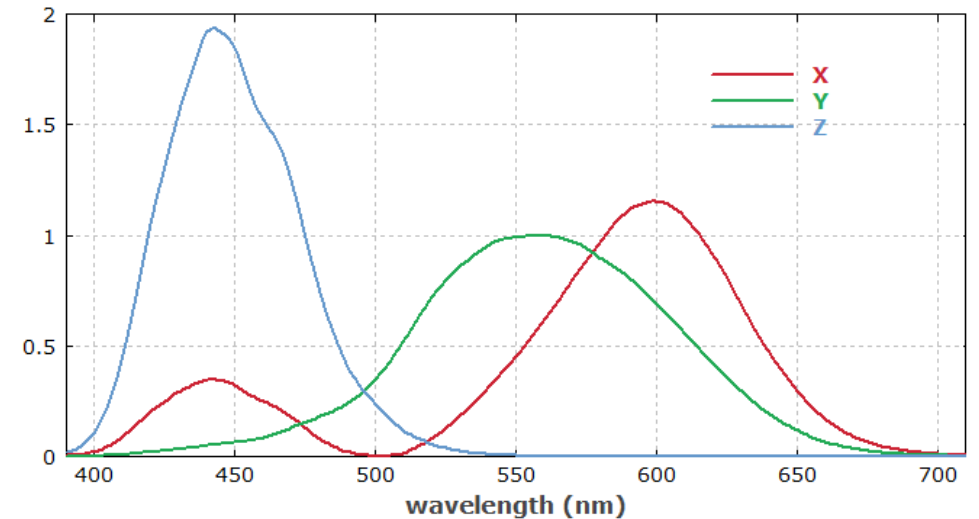# 1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Physical variables in water monitoring: color

To remove these limitations, a different color space is typically used. In 1931, the CIE (Commission Internationale de l'Éclairage) has defined its **XYZ color space.**

The CIE color model takes the **luminance** (as measure for perceived brightness) as one of the three color coordinates, calling it **Y**. This coordinate is usually normalized to 1 or 100.

The coordinate **Z** responds mostly to **shorter-wavelength** light, while **X** responds **both to shorter- and longer-wavelength light**.

XYZ coordinates can be related to LMS coordinates by means of a transfer matrix, where Z coordinate corresponds to S, Y coordinate include both L and M, while X coordinate accounts for all three cones.

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 1.910\,20 & -1.112\,12 & 0.201\,91 \\ 0.370\,95 & 0.629\,05 & 0 \\ 0 & 0 & 1.000\,00 \end{bmatrix} \begin{bmatrix} L \\ M \\ S \end{bmatrix}$$
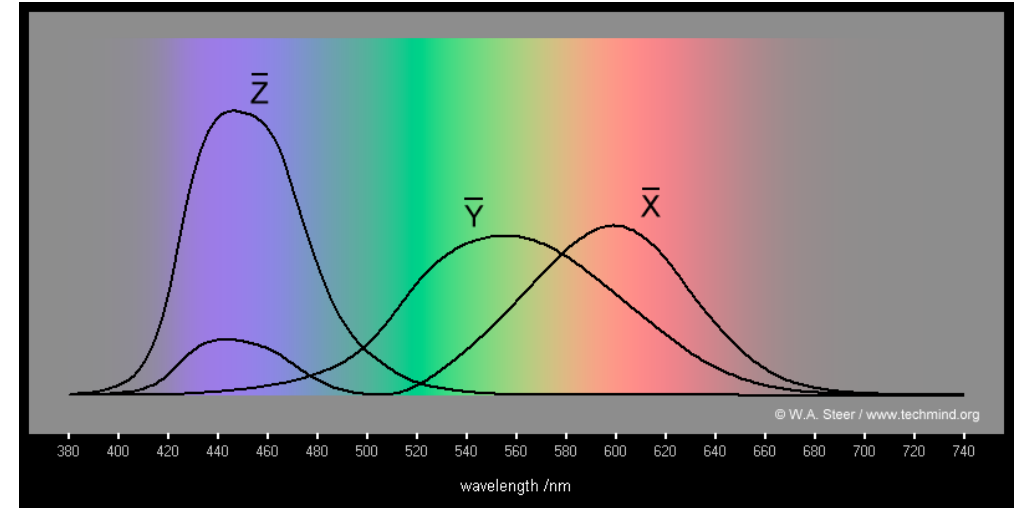
Physical variables in water monitoring: color

X, Y and Z can be regarded as red, green and blue, owing to their wide band and substantial overlap, but this is quite an approximation.

Because of the overlap of the functions, **they are not fully independently stimulable**, i.e., no physical light source can stimulate one channel while maintaining zero in the other two.

A "color" is defined by the relative stimulus of the eye's XYZ channels (the actual magnitudes will define the brightness or intensity). It makes sense therefore to define a color by an **xyz triplet which are normalized versions of XYZ.**

By definition now, **$x + y + z = 1$**. Therefore, only two out of the three *xyz* coordinates are needed to uniquely define a color.

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$$x = \frac{X}{X + Y + Z}$$

$$y = \frac{Y}{X + Y + Z}$$

$$z = \frac{Z}{X + Y + Z} = 1 - x - y$$

Physical variables in water monitoring: color

The representation of color gamut covered by human eye is usually expressed in **xy coordinates**.

The CIE chromaticity diagram would ideally display the true color tones for all pairs in the perceivable range of colors, which corresponds to a horseshoe-shaped part of XYZ color space.

The **inverted-U shaped locus boundary represents monochromatic light**, or spectral colors. The lower boundary of the gamut, called the line of purples, basically represent some mixtures of red and violet, which cannot be reached with monochromatic light. **White light** with a flat power spectrum corresponds to the point with $x = y = 1/3$.

Monitors and displays can reproduce only a limited part of color gamut (sRGB, AdobeRGB, etc.)
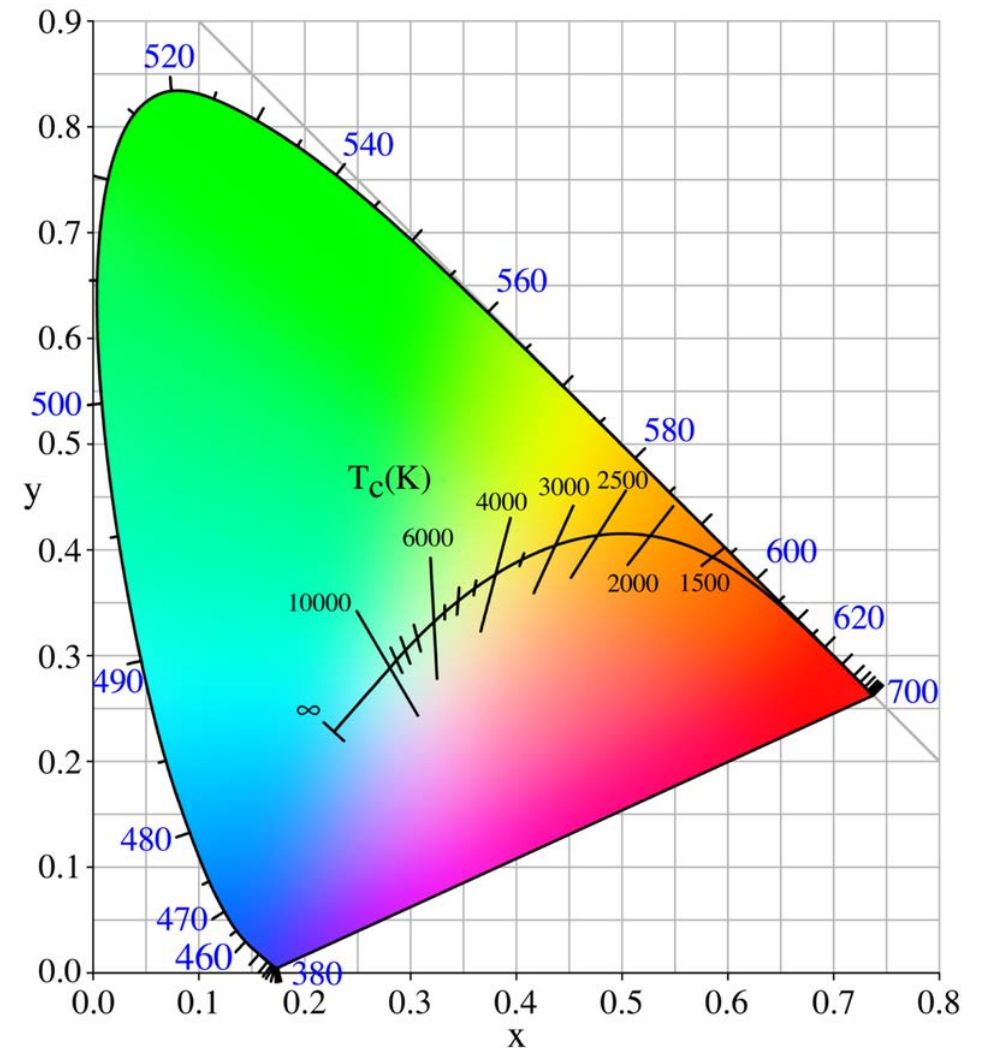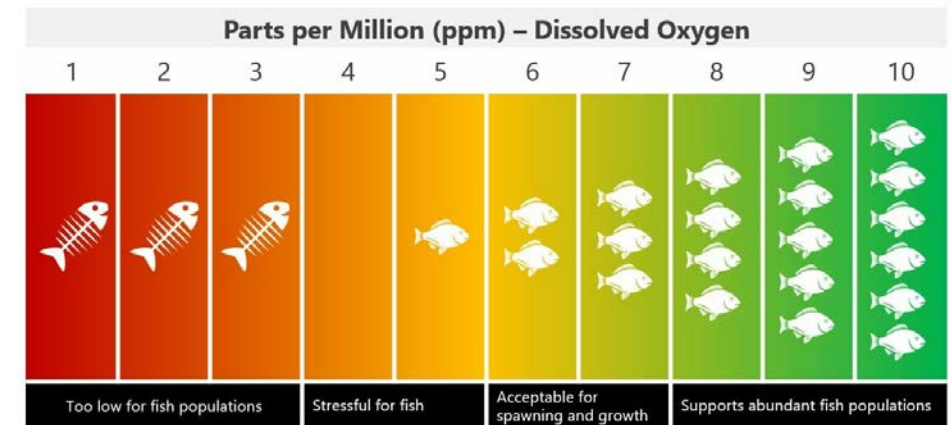
1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Chemical variables in water monitoring: dissolved oxygen

Dissolved oxygen (DO) is the oxygen concentration dissolved in the water. This represents the amount of oxygen available to living aquatic organisms.

The decomposition of organic wastes by bacteria and the sewage fungi requires an input of oxygen, and this is taken from the DO in the water. If the DO concentration in the water is reduced below its equilibrium (or saturation) value there will be a **transfer of oxygen from the air to the water** via the surface, by processes of turbulent diffusion both in the air and in the water. DO plays a crucial role in photosynthesis processes by phytoplankton and aquatic plants, regulating also the concentration of dissolved carbon dioxide.

However, in heavily polluted water, re-aeration from the air to the water surface **cannot match the net uptake of oxygen** caused by decomposition processes and so the DO concentration in the water will be reduced.

Parts per Million (ppm) – Dissolved Oxygen

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |

Too low for fish populations   Stressful for fish   Acceptable for spawning and growth   Supports abundant fish populations

Chemical variables in water monitoring: dissolved oxygen

Atmospheric oxygen dissolves in water to establish a saturation concentration, according to Henry's law stating that: when a gaseous species applies a pressure on a liquid surface, it will be dissolved until a pressure equal to those applied from the outside will be reached inside the liquid.

The saturation value of DO concentration in water, Cs (mg l^{-1}), depends on atmospheric pressure, p, temperature, T (°C), and salinity, S (‰), according to the empirical formula:

$$C_s = \left(\frac{p - p_s(T)}{p_0 - p_s(T)} \right) \left(\frac{461.7 - 2.53\,S}{30.7 + T} \right)$$

Where $p_s(T)$ is the saturation vapor pressure of water at temperature T, and p_0 is the standard atmospheric pressure (101.3 kPa)

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Chemical variables in water monitoring: dissolved oxygen

Several different sensor types can be used to measure dissolved oxygen in water, mainly divided in electrochemical and optical sensors.

- **Polarographic sensors**: DO passes through a membrane and is involved in a redox reaction in voltametric configuration. The generated electric current is proportional to the partial pressure of the DO and thus to its concentration.

- **Luminescent sensors**: DO is measured exploiting the interaction among oxygen and luminescent dyes after the exposure to blue light. The sensor is immersed in the water sample and oxygen crosses a membrane interacting with the dye. This reduces the intensity and change the lifetime of the dye's luminescence, which is measured by the photodetector and used to calculate the DO concentration. Dye's lifetime is measured by means of the induced phase shift respect to the modulated reference signal, induced by oxygen interaction.

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Chemical variables in water monitoring: acidity, alkalinity, and pH scale

The term "acidity" describes the amount of acid in a substance. An acid is a chemical that gives off hydrogen ions (H^+ or hydronium) in water. Acidity is measured on a scale called the **pH scale**. pH measures the relative amount of free hydrogen and hydroxyl ions in the water. On this scale, a pH value of 7 is **neutral**, a pH value of less than 7 to 0 shows increasing **acidity**, while a pH value higher than 7 points out increasing **alkalinity** (basic pH).

Acidity is a very important water quality variable and is routinely monitored.
Natural fresh water tends to be **near neutral**, whereas seawater and estuary water are naturally alkaline.
Rain and other forms of precipitation are naturally **slightly acidic** because of dissolved carbon dioxide, but **polluted rain** can be **highly acidic**, containing sulphuric, nitric and hydrochloric acids derived from fossil fuel combustion.
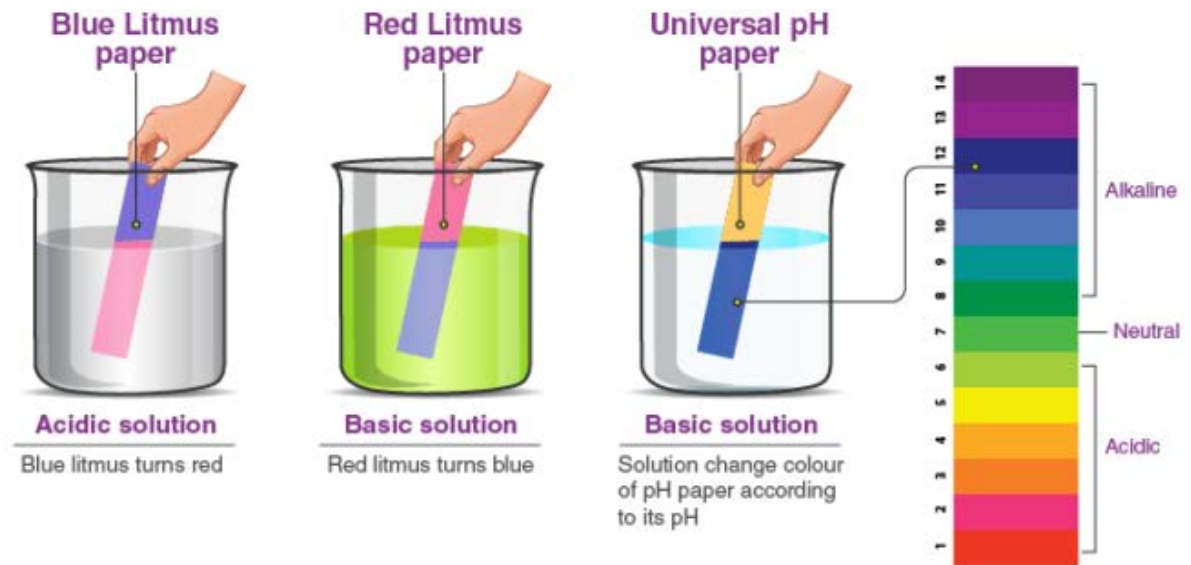Other acidic inputs to water bodies are industrial discharges and mine drainage, which also need to be monitored.

Chemical variables in water monitoring: acidity, alkalinity, and pH scale

Two main methods are employed in the determination of pH value of water:

- **Colorimetric Method:** pH value is determined employing universal indicator exhibiting color changes depending on the pH values.
Typically, universal indicators consist of water, 1-propanol, phenolphthalein, sodium hydroxide, methyl red, bromothymol blue, sodium bisulfite, and thymol blue. These indicators can be either liquid or in paper form (e.g., litmus paper)


Blue Litmus paper

Red Litmus paper

Universal pH paper

Acidic solution
Blue litmus turns red

Basic solution
Red litmus turns blue

Basic solution
Solution change colour of pH paper according to its pH

Alkaline

Neutral

Acidic

Chemical variables in water monitoring: acidity, alkalinity, and pH scale

Two main methods are employed in the determination of pH value of water:

- **Electrometric Method:** pH value is determined by means of a measurement of electric potential among a glass electrode and silver-silver chloride reference electrode (potentiometric sensor). When the glass electrode is placed in solution, hydrogen ions from the solution move to the thin glass membrane and their charge causes a potential difference between the solution outside and the hydrochloric acid contained within the glass bulb. The reference electrode, also in contact with the solution, completes the electrical circuit so that a potential difference between the two electrodes can be measured.
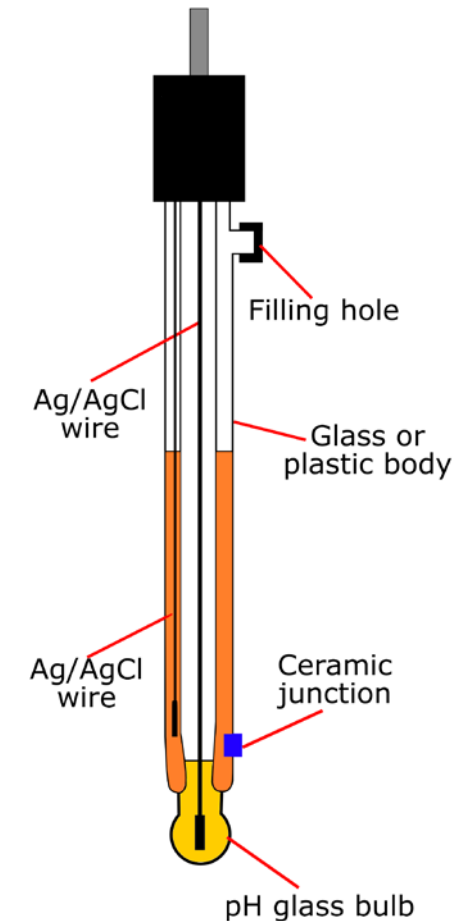
1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Chemical variables in water monitoring: anions

The most abundant **dissolved constituents** in water measured are the **major ions**, which can be both positively charged (**cations**) and negatively charged (**anions**). Because of the requirements of electroneutrality, cations and anions are present at equal concentrations in water and comprise most of the dissolved solids in water.

The most abundant anions in water are bicarbonate (HCO_3), chloride (Cl^-), and sulfate (SO_4). Other anions of interest include nitrite, nitrate, phosphate and silicate.

Anions concentration is evaluated by means of wet chemistry **gravimetric and volumetric methods** as well as **colorimetric methods**. However, these methods require pre-treating of samples to avoid selectivity. Electrochemical sensors can be used for many of the common anions. The general term used to describe them is the **ion-selective electrode**, which is used in conjunction with a reference electrode to produce an electric field proportional to the selected ion activity.
The more modem technique of **ion chromatography** offers considerable advantages, especially for determination of a range of anions.

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Chemical variables in water monitoring: cations

Most important cations in water are metals, which exist in water in ionic form in various oxidation states and in complexes. The so-called **'heavy metals'**, such as cadmium, chromium, lead and mercury, are of particular concern since they may be concentrated in food chains to reach toxic levels. Aluminum, although not a heavy metal, is also of interest because it affects respiration in fish.

Metals in water can be detected using different techniques such as atomic absorption spectrometry (AAS) or colorimetry. In AAS, a solution containing the target analyte is introduced into a flame. The flame converts samples into free ground state atoms that can be excited. A lamp emitting light at a wavelength resonant with the atomic transition is passed through the flame, and as the light energy is absorbed, the electrons in the atoms are elevated to an excited state. The absorbed light is then related to the analyte concentration.

Electrochemical techniques are also used, mainly ion-selective electrodes used potentiometrically, and anodic stripping voltammetry, the latter being extremely sensitive for certain trace (heavy) metals.

1.5 PHYSICAL AND CHEMICAL VARIABLES IN WATER MONITORING

Chemical variables in water monitoring: petrochemical oils and pesticides

Oil leakage from oil rigs, oil tankers and shipping in general causes considerable pollution of coastal waters, even apart from catastrophic accidents.
A lot of effort has been made to identify the sources of major discharges. Several techniques have been developed, such as gas chromatography, IR spectrophotometry, and atomic absorption, in order to 'fingerprint' oil samples.

Herbicides and pesticides have been demonstrated as potential carcinogens and there is a relevant concern that they are entering the human food chains and water supplies.
Very **sensitive techniques are usually required for this work due to the relatively low concentration of these compounds**. Gas chromatographs integrated with mass spectrometers, or high-pressure liquid chromatographs coupled to fluorescence detectors are usually employed to provide definite identification of specific chemicals.