ENV-200
Environmental Chemistry
Introduction

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How this course works

Instructors:

Meret Aeppli

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Lectures: Mon, 13-15h; Tue, 10-12h. We will do short exercises during lectures, in small groups.

Exercise session: Mon, 13-16h (bi-weekly) or Mon 15-16h (bi-weekly). See moodle for exact schedule. Solve the exercises at home. During the exercise sessions, teaching assistants are available to answer questions.

Teaching assistants: Josephine Meibom*, Bence Dienes*, Camila Morales, Louis Piguet, Alice Giorgetti, Lorenzo Prato

*email these TAs for questions

Midterm exams: 29. October, 26. November (each counts 15% of final grade)

Final exam: During exam session (70% of final grade)

You can bring a “cheat sheet” (3 pages) to all exams. No need to print tables!!

Goals of the course

1. Understand the chemistry of **natural aquatic systems**
   - pH: what influences the pH, and how do changes in pH affect the chemistry of the system?
   - Speciation: which species / solids are present and at which concentrations?
   - Etc.
2. Fate of organic **contaminants** in natural systems
   - Where do they go (water, air, sediment, ….) and why do they go there?
   - Etc.
3. Understand how environmental chemistry relates to environmental engineering

What is environmental chemistry

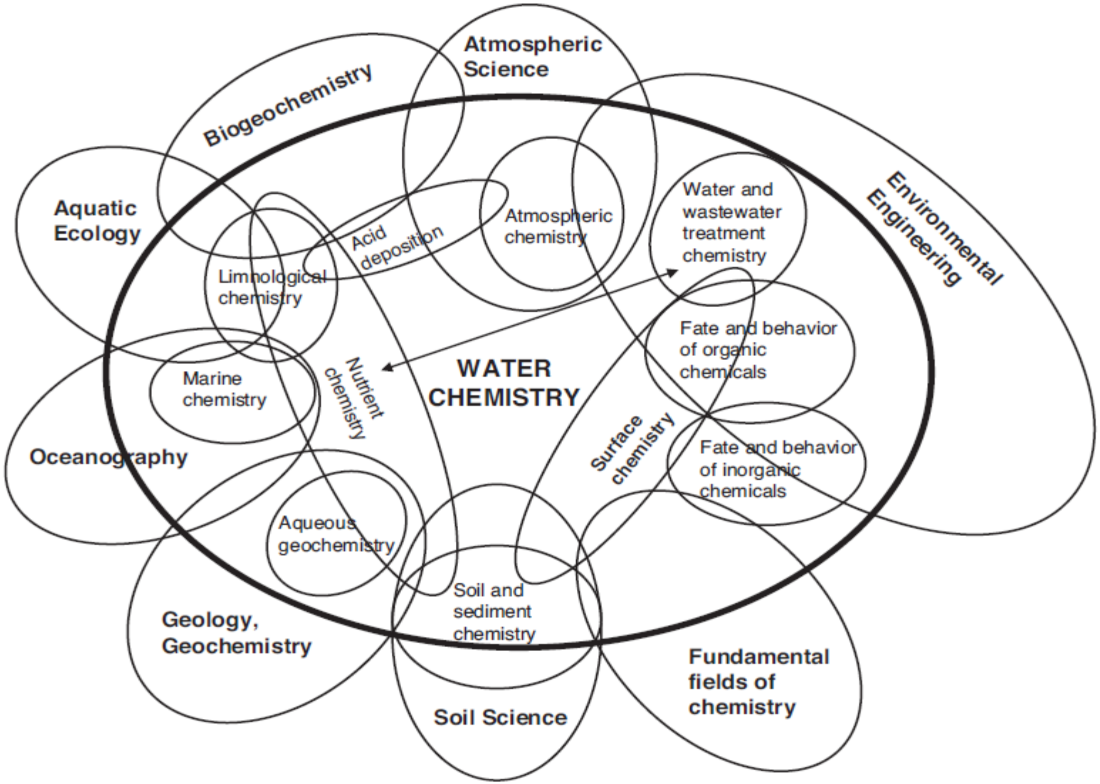
"What is environmental chemistry? This question is a little difficult to answer because environmental chemistry encompasses many different topics. It may involve a study of Freon reactions in the stratosphere or an analysis of toxic deposits in ocean sediments. It also covers the chemistry and biochemistry of volatile and soluble organometallic compounds biosynthesized by anaerobic bacteria.
Environmental chemistry is the study of the sources, reactions, transport, effects, and fates of chemical species in water, soil, and air environments."

- Stanley E. Manahan. 1991. Environmental Chemistry, 5th edition.

- Environmental chemistry acts on a local and a global scale.
- Not only catastrophic events are important, but also natural processes and chronic exposure to low pollutant concentrations.

EPFL

What is environmental chemistry



Source: Brezonik and Arnold, 2011

Some properties of natural waters

pH of sea water:
pH of surface water:
pH of ground water:
pH of rain:

Volume of oceans:
Volume of lakes:
Volume of groundwater:
Volume of ice:

Concentration of water in water:
Concentration of O_2 in water:

Anions:
[Cl-] in lake water:
[Cl-] in sea water:
[HCO_3-] in lake water:
[HCO_3-] in sea water:

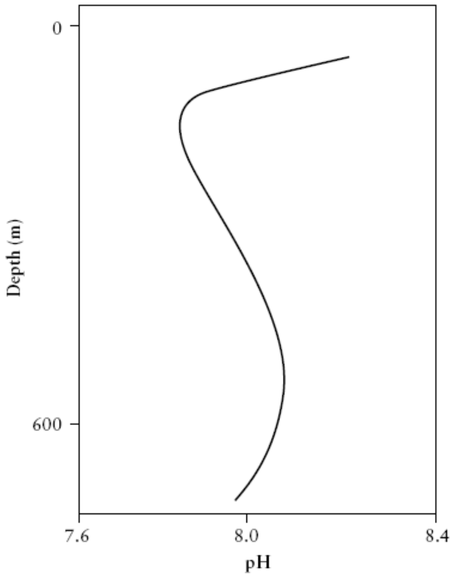
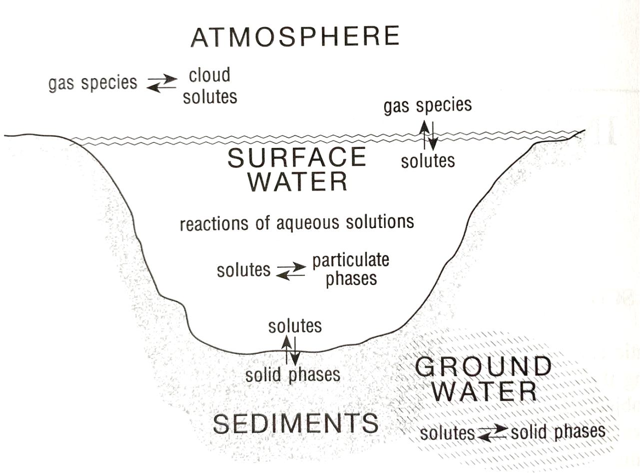


FIGURE 11-1 Variation of the ocean pH with depth.

Composition of natural waters

Waters acquire chemical characteristics by mineral dissolution and chemical reactions with **solids, liquids & gases**

Variation in water composition can be explained by the environmental history of the water and chemical reactions of the rock-water-air system

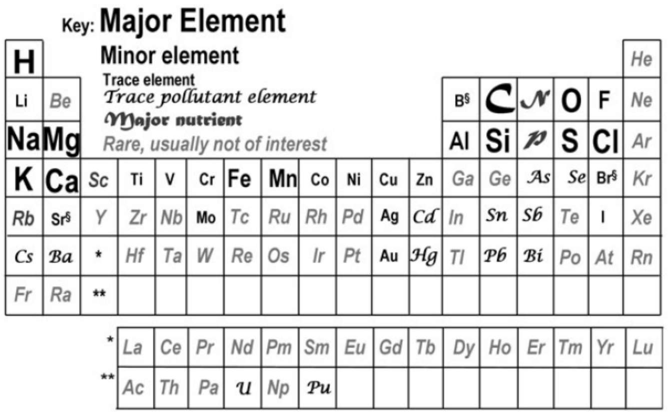


Source: Stumm and Morgan, 1996, Figure 1.1

First approximation:

- Seawater = acid-base titration of acid of volcanoes vs. bases of rocks
- Fresh water = CO_2 of the atmosphere vs. mineral rocks

Composition of natural waters



Source: Brezonik and Arnold, 2011

1. Water (H_2O): The primary constituent of lakes is water itself. It serves as the solvent for dissolved gases, minerals, and organic matter.

2. Dissolved Gases:

1. **Oxygen (O_2)**: Essential for aquatic organisms to respire.
2. **Carbon Dioxide (CO_2)**: Produced by aquatic organisms and other natural processes.
3. **Methane (CH_4)**: Produced in anaerobic conditions by microbial activity.

Composition of natural waters

3. Ions and Minerals:

1. **Cations**: Mainly calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}). These ions come from weathering of rocks and minerals in the watershed.
2. **Anions**: Mainly bicarbonate (HCO_3^{-}), sulfate (SO_4^{2-}), and chloride (Cl^{-}). They also originate from rock weathering, atmospheric input, and human activities.
3. **Neutral species**: Silicic acid ($Si(OH)_4$). Concentrations are highly dependent on local geochemistry; serves as nutrient for algae.

4. Nutrients: **Nitrogen (N)** and **Phosphorus (P)**: Typically present as nitrate (NO_3^{-}), ammonia (NH_4^{+}) and phosphate (PO_4^{3-}). These are essential nutrients for plant growth. Excessive levels, however, can lead to eutrophication, causing algal blooms and oxygen depletion. Can originate from weathering and atmospheric input, but also human activities (wastewater treatment plants, agricultural runoff, …)

5. Organic Matter:

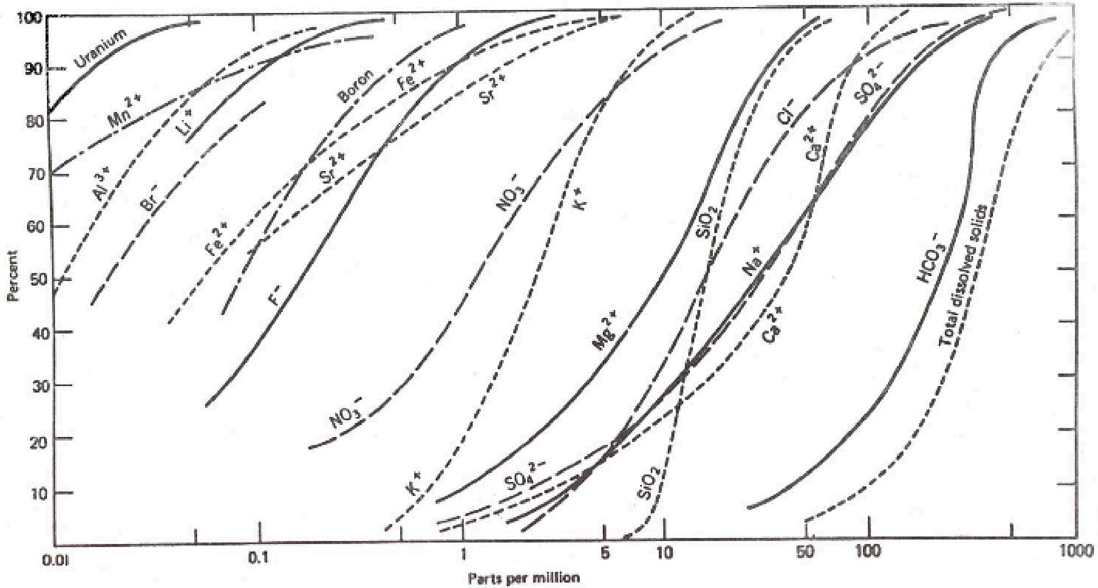
1. **Dissolved Organic Carbon (DOC)**: Consists of complex organic molecules derived from decaying plants, animals, and microorganisms.
2. **Particulate Organic Matter (POM)**: Suspended organic particles in the water column.

6. Trace Elements: Lakes can contain trace amounts of various elements, including metals like iron (Fe), manganese (Mn), and trace metals like copper (Cu) and zinc (Zn). The presence of these elements can be influenced by geology and human activities.

7.Anthropogenic Contaminants: These can include pollutants like pesticides, industrial chemicals, pharmaceuticals, heavy metals, and other contaminants from human activities.

Composition of natural waters

Frequency distribution of constituents in terrestrial waters



Source: Stumm and Morgan, 1996, Figure 15.1

Many aquatic constituents show little variation
- dissolved silica: $10^{-3.8}$ to $10^{-3.2}$ M (80%)
- H^+: $10^{-6.5}$ to $10^{-8.5}$ M

Some examples of water compositions

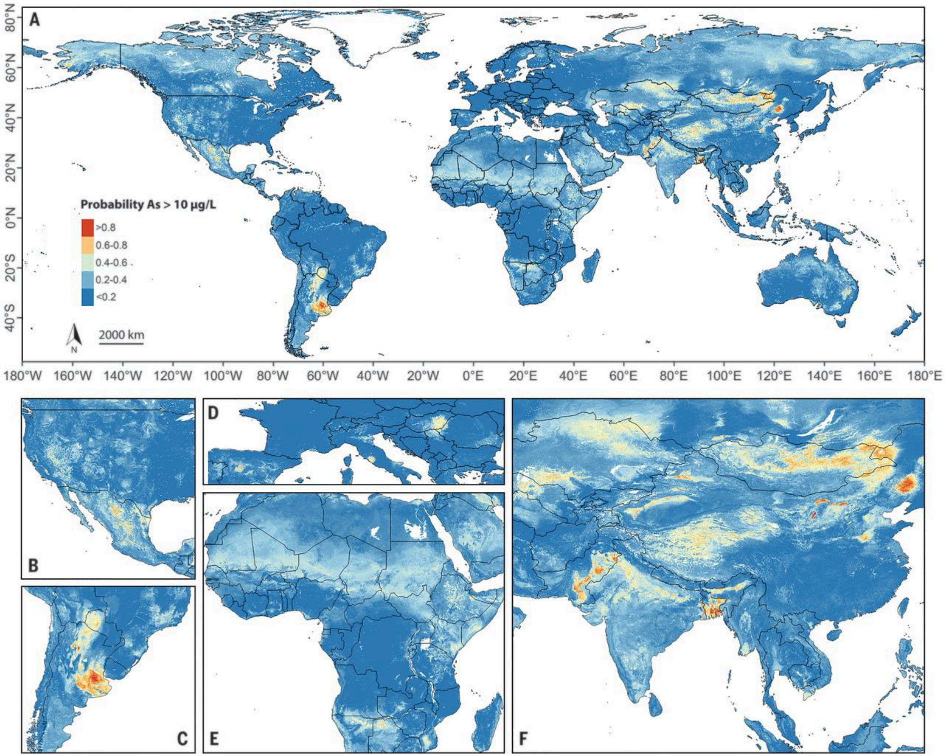
Type of water Rock Location	Wet deposition (Rain) Dübendorf	River water Limestones kleine Emme	**River water** **Molasses** **Rhine (Basel)**	Spring water Silicates Verzasca	Groundwater Molasses Glattfelden	**Lake water** **Molasses** **Lake Zürich**	Ocean
Parameter /Unit	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/kg
Calcium	0,39	56	53	5,2	80	45,6	410
Magnesium	0,055	4,2	6,6	0,85	18	6,0	1300
Sodium	0,14	3,3	6,2	0,40	22		11 000
Potassium	0,060	1,3	1,4	0,16	4,0		400
Bicarbonat		172	129	15,4	284	126	140
Sulfate	1,5	12	27	7,9	27	15	2700
Chloride	0,71	4,3	8,6	0,53	36	2.5	19 300
Silicic acid	<0,2	5,6	3,6	18,8	10		7,6
Ammonium	0,71	0,06	0,09	0,005	0,01	< 0,1	0,07
Nitrate	2,3	5,7	1,3	2,1	22	0.77	2,6
Phosphate	0,003	0,15	0,09	0,030	1,8	0.08	0,2
Unit	µg/l	µg/l		µg/l	µg/l		µg/kg
Lead	7,6	2,2		<1	0,2		0,2
Cadmium	0,13			<0,1	0,05		0,07
Zinc	18	24		<5	1,8		0,1
Copper	1,6	3,8		<1	3,6		0,3

Naturally occurring contaminants: Arsenic

Some facts on Arsenic:

- Arsenite, As(III), and arsenate, As(V) are natural components of groundwater
- As(III) is more toxic than As(V), but both are problematic in drinking water
- As(III) is mobile, As(V) is immobile and therefore easier to remove by filtration or adsorption
- Ground water in regions of India, Bangladesh, Mexico, etc. are heavily contaminated by As.
- Chronic exposure leads to hyperkeratosis, cancer, hyperpigmentation, etc.

Naturally occurring contaminants: Arsenic

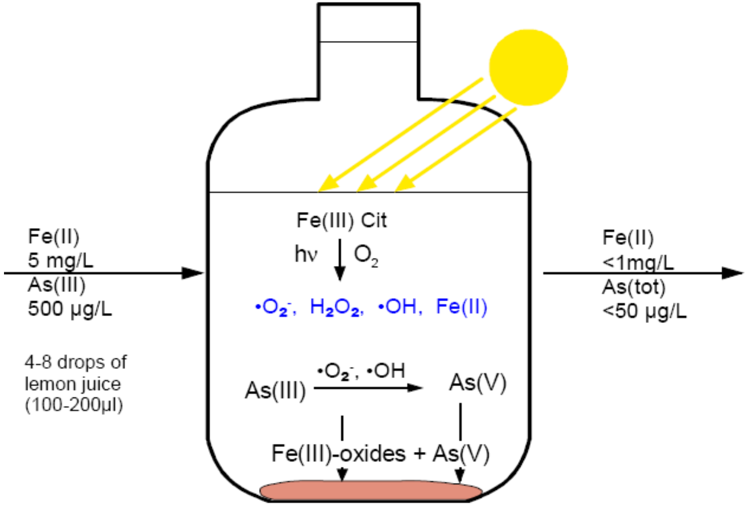


Probability of arsenic concentration in groundwater exceeding 10 µg/liter

Source: Podgorski and Berg, Science, 2020

Naturally occurring contaminants: Arsenic

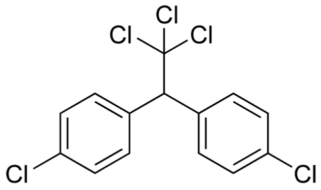
Solar removal of Arsenic (SORAS):



In the presence of dissovled Fe(III), citrate and oxygen, oxygen-based radicals can oxidize As(III) to As(V), which then adsorbs onto the precipitating Fe(III)-oxides.

Anthropogenic contaminants: DDT

- First synthesized in 1874
- Insecticidal action discovered by the Swiss chemist Paul Hermann Müller in 1939
- Highly effective pesticide, used to protect crop and prevent disease (malaria, typhus louse, etc.)
- Eliminated typhus epidemic in Naples under wartime conditions
- Estimated to have saved 5 Mio lives over the world through destruction of malarial mosquitoes
- Millions saved from starvation because of increased crop yield
- Dr. P.H. Müller (Geigy, CH) was awarded the 1948 Medicine Nobel Prize for DDT
- Most widely and heavily used chemical pesticide until the late 50s
- But then….

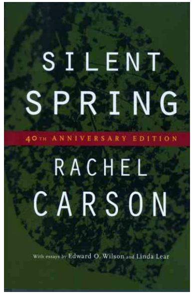


DDT (Dichlorodiphenyltrichloroethane)

Time magazine, 1940s

Anthropogenic contaminants: DDT

- Quite persistent, hydrophobic, accumulates in sediments
- Transported by wind and aqueous particles, found in fat of antarctic wildlife
- Bioaccumulates to toxic degrees in the upper level of the food chain (fish, birds, otters)
- Resistant organisms emerged, requiring ever higher DDT doses
- Effects on wildlife: development of <u>resistant</u> insect strains, reproductive failure in birds, otters
- Effects on humans: damages nervous system, liver, kidneys, immune system; potential carcinogen, endocrin disruptor
- Awareness about ecotoxicological problems raised in book «Silent Spring»
- Banned (mostly) in the US, EU and Switzerland for > 20 years
- WHO and the Food and Agricultural Organization strongly oppose prohibition of DDT

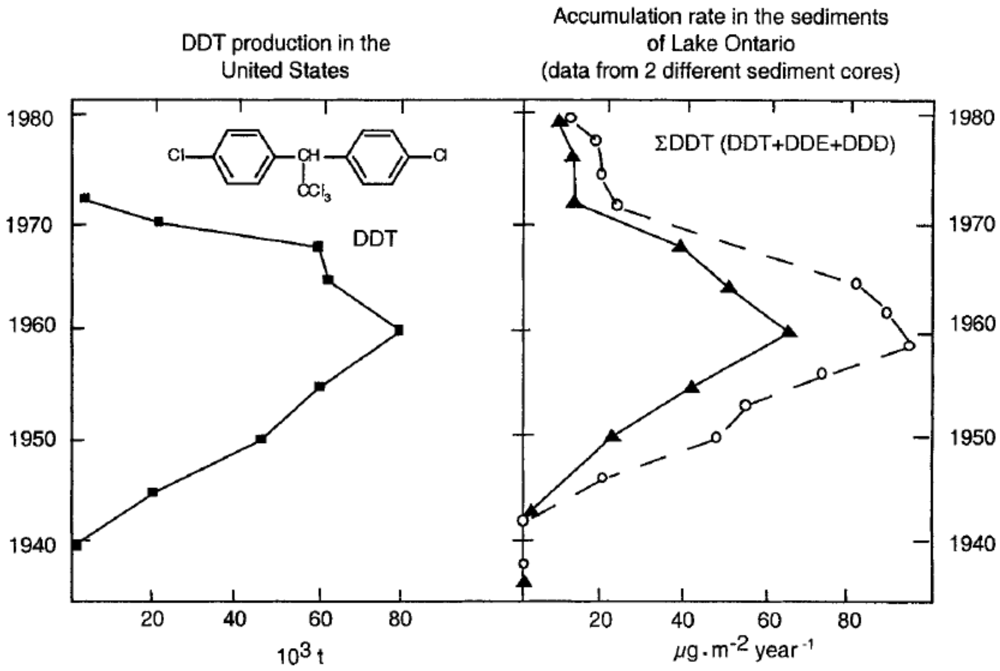


A robin *(source: Wikipedia)*

Bald eagle *(source: Wikipedia)*

Anthropogenic contaminants: DDT

Historic record of DDT sales and sediment accumulation



Eisenreich et al., 1989

Anthropogenic contaminants: DDT

Bioaccumulation through the food chain