4. Hydrochemistry of water of hydrological cycle

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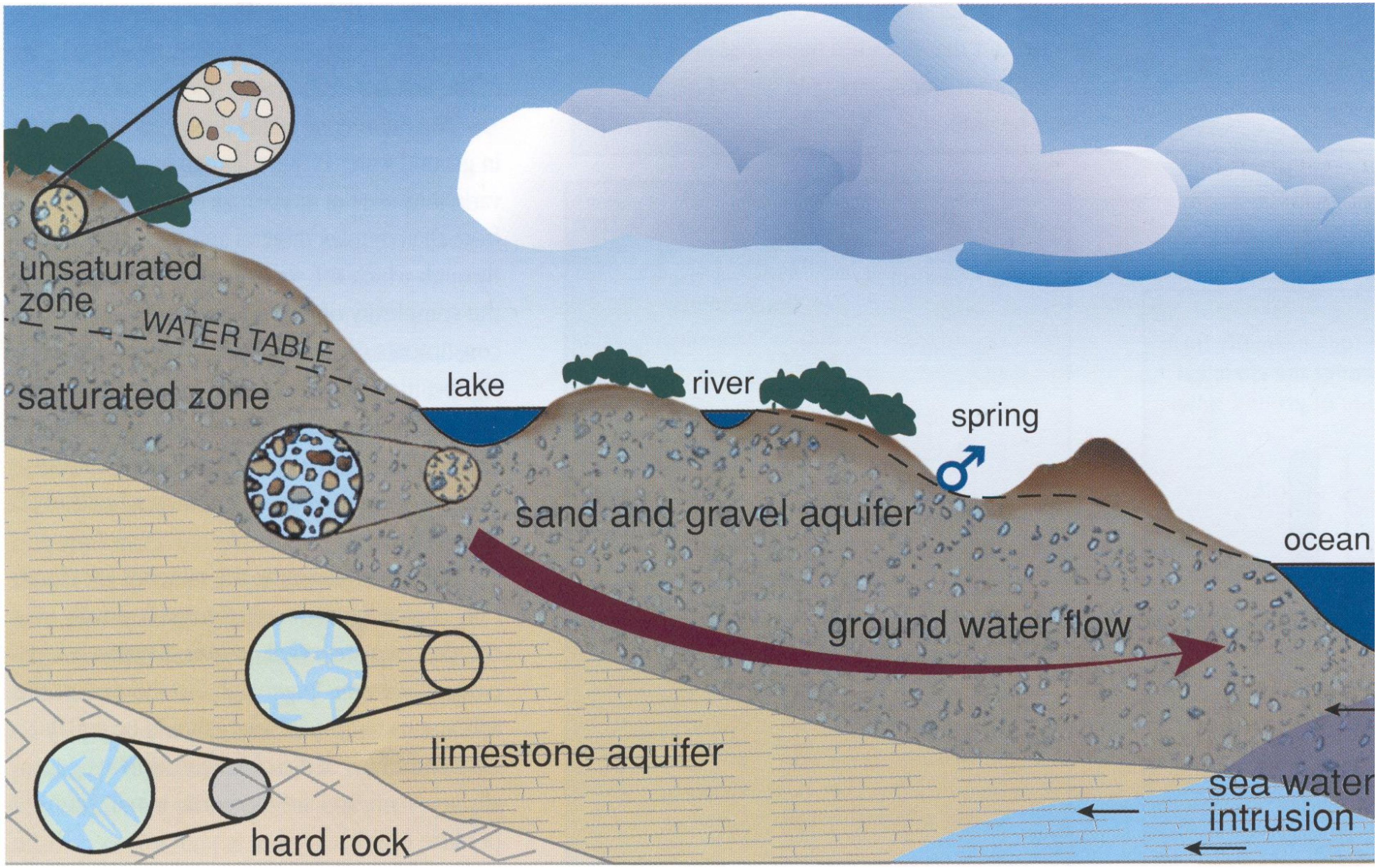
- Chemical evolution of natural waters
- Principles
- Constituents
- Composition of water (precipitation, surface, groundwater)

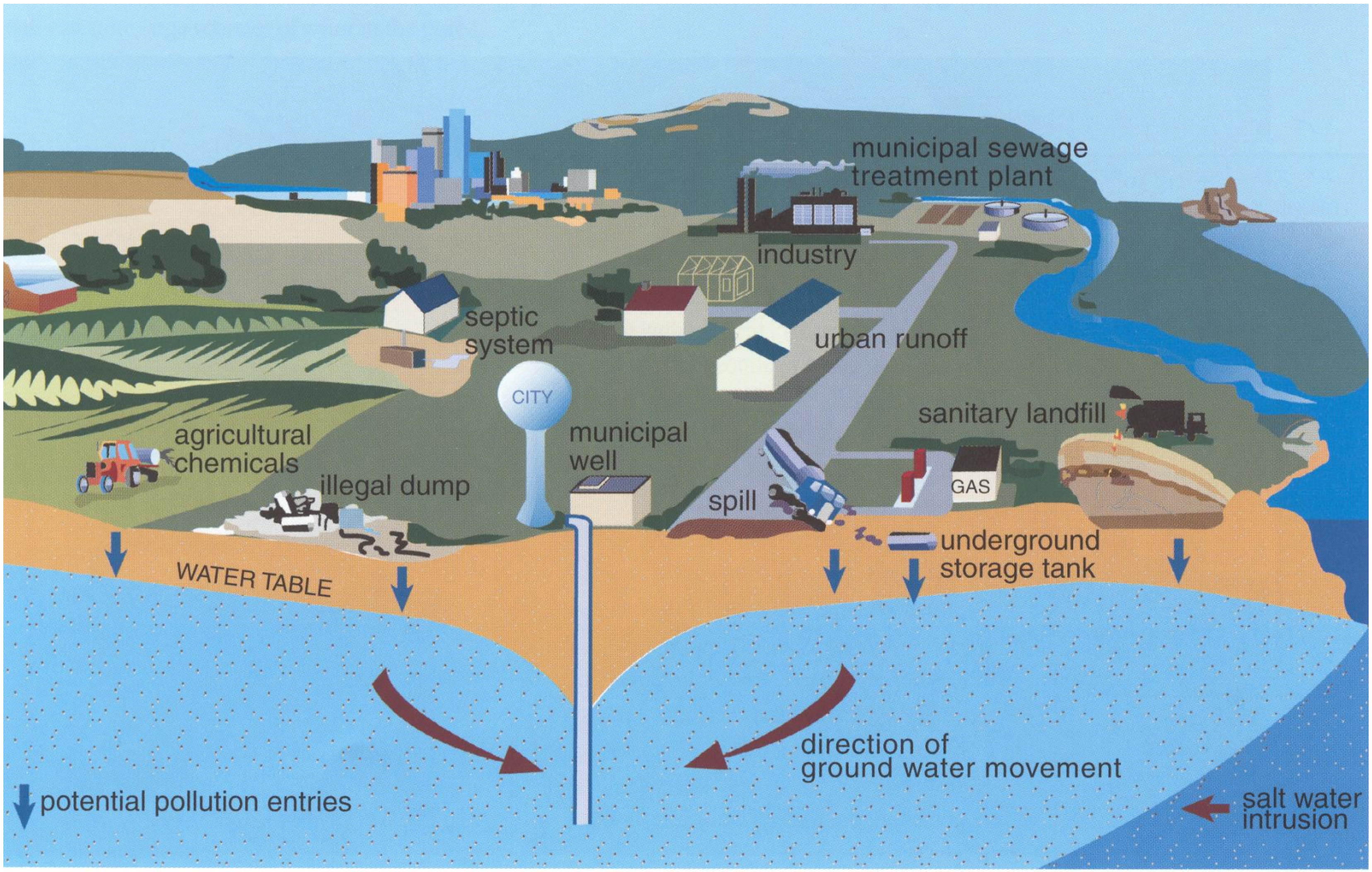
Introduction

A knowledge of the chemical composition of the groundwater and its areal (spatial) distribution and time (regime) variation is important both from the point of view of its suitability for water supply and for the information it can give about the direction of the water movement and extent of the groundwater flow-systems.

Water circulation natural



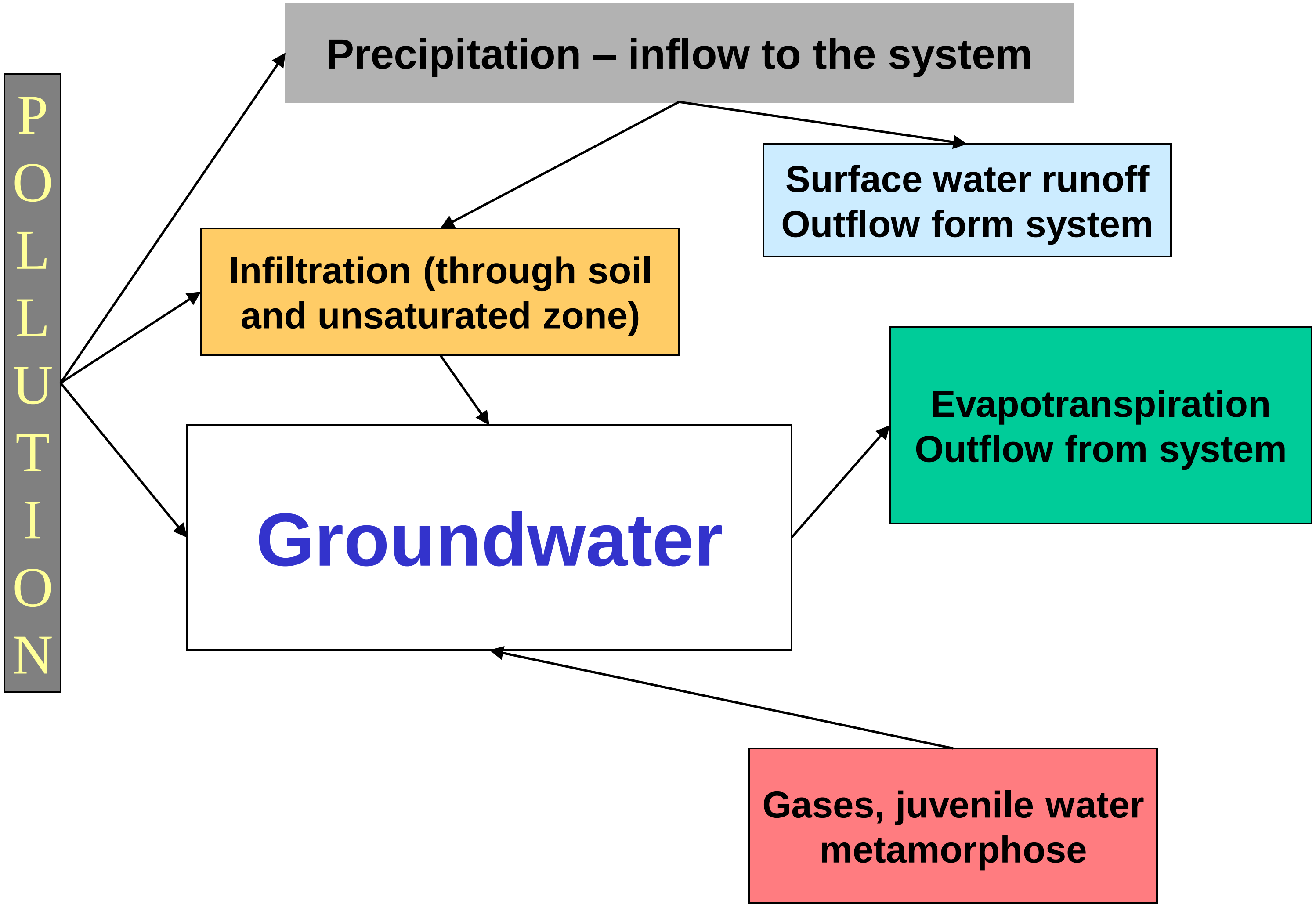
Water circulation and Men



GROUNDWATER

„The groundwater moves within geological environment as the blood circulates in living organisms. Hydrochemist by analyzing chemical composition of groundwater thus can as hematologist diagnose not only sickening the groundwater but even the illness of the environment as a whole” - Zdenek Herrmann

Nature and Men complex composition



Principles 1

Most of the geochemical principles are based on solution of minerals and equilibrium concepts

(silicate weathering and direct dissolutions of minerals – rock salt)

Ion exchange and sorption by clay minerals and organic matter

Redox processes (O_2,Fe^2,H_2S,CH_4)

Mixing processes (water, gass, pollution)

Principles 2

Degree of mineral content is proportional to matrix and residence time (under normal condition)

Groundwater chemistry is result of chemical and biochemical interactions in (ground)water - soil - rock system through which it flows, and to a lesser extent on contributions from atmosphere, and surface water bodies

Infiltration

infiltration into aquifers through soil in pedological sense of meaning
capability to generate acid and to consume available dissolved oxygen
the most important acid is H_2CO_3, (reaction of CO_2 and H_2O)
CO_2 generated by decay of organic matter, respiration of plant roots – principle of karstification
reaction of oxygen with pyrite is another sources of acidity
many organic acids produced biochemical processes.

Soil profile = acid pump

pump is playing major role in:

- development of soil profile
- weathering of mother rock
- transport of dissolved solids downward towards groundwater table

Constituents

- major constituents (grater than 5 mg/l)
- minor constituents (0.01 – 5.0 mg/l) and
- trace constituents (less than 0.01 mg/l)

The total concentration of six major ions (Na^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO^- SO^{2-}) 90% of TDS

The major inorganic constituents occur mainly in ionic form.

Hydrochemical study includes also isotope analyses

Sodium and Potassium

Weathering (45% of DTS – Na and K feldspar, zeolite, mica – rhyolite, basalt) +dissolution of evaporates

Cation exchange processes by clay minerals (Ca^{2+}, Mg^{2+}) for (Na^{+}, K^{+})

Sodium accompanied by potassium

No important precipitation reaction

Average concentration in CR 13. 4 mg/l Shalla 1060 mg/l

Chloride

Weathering (rhyolite, basalt), direct dissolution of evaporates and direct evaporation in arid regions (Somali region) and rainwater in coastal areas (soil 10 – 500 mg/kg)

Pollution (human urine 9 g of Cl daily)

Average concentration in CR 24 mg/l (Korahe Formation 114 g/l Dolo area)

Taste of water affected above 200 mg/l

Calcium and Magnesium

Weathering (plagioclase, olivine, pyroxene, amphibole, mica - granite, mica shists, basalt), dissolution of carbonates and gypsum

Long residence times of water in carbonate aquifers produce [Mg]:[Ca] ratio above 1.0 and higher pH

Average in CR Ca = 50 and Mg = 10 mg/l

Increased if juvenile CO_2 is mixed with water

Bicarbonate and Carbonate

The HCO_3 is from soil and weathering zone (plagioclase, pyroxene, amphibole,) and from dissolution of carbonates.

The partial pressure of CO_3 and solubility of carbonate results in HCO_3 concentration of 100 – 600 mg/l in shallow groundwater.

Increased if juvenile CO_2 is mixed with water

Sulfate

Gypsum or anhydride, sulfides.

Gypsum and anhydrite if dissolved in water at 25^{O}C, water will become brackish, with TDS about 2 100 and 2 400 mg/l

Average concentration in CR 70 mg/l

Adola – sulphidic mineralization 2.5 g/l

Minor constituents

Fluoride – fluorite CaF_2

Acid volcanic rocks (mineral water – granite 6.69 mg/l) – evaporation

Average concentration in CR 0.37 mg/l
Rift valley – Shalla 300 mg/l

Concentration related to temperature

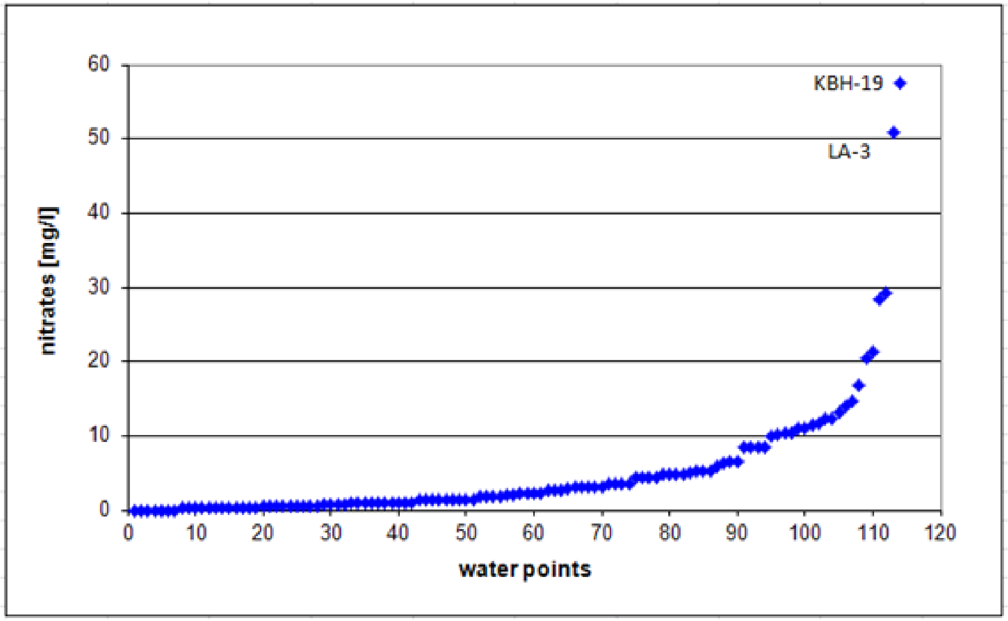
Recommended 0.8 – 1.0 mg/l

Fluoride

It is considered that chemical weathering of the volcanic strata is the most likely source of fluoride. The interacting matrixes are mainly rhyolites consisting of volcanic glass and its weathering products, which is extremely reactive. The interaction of these weathered and or reworked volcanic materials with percolating groundwater and carbon dioxide at high pH causes the release of fluoride into the groundwater.

Nitrates

The background content of nitrates in groundwater is about 5 to 10 mg/l depending on the relevant land cover (forest higher).



Concentration >50 mg/l indicates pollution of groundwater by human and/or animal waste

Trace constituents

EPA priority list of pollutants:

arsenic, cadmium, chromium, cooper, lead, mercury, nickel, and zinc

Arsenic

The surface water is usually contaminated by industrial waste water (mining, chemical, municipal – detergents). The river was contaminated also through geothermal activity in New Zealand (0.08 mg/l river water and 550 mg/kg sediments).

Cadmium

Cadmium associated with zinc in carbonate and sulfide ores.

Used for electroplating (finishes in automobile and aircraft industries), pigments (yellow – orange - red) for plastic and ceramic industry traffic pints (Coca-Cola bottles), plastic stabilizers, batteries, TV tubes, fire detection, telephone wires, solar cells.

The content of Cadmium ranged from 0.00029 to 0.00055 mg/l for Yarra River, Australia.

Chromium

Cromite and phosphate (Colemmanit) form fertilizers rich in Cr

(pigments, dyes in textile industry, tanning agents in leather industry)

Dissolved concentration in unpolluted lakes and rivers vary from 0.001 to 0.002 mg/l.

Cooper

Sulfides, arsenides, chlorides and carbonates

Use is universal in the electrical, construction, plumbing and automotive industries

Soluble cooper levels in uncontaminated freshwater usually range from 0.0001 to 0.0002 mg/l in urban areas

Lead

Sulfide - solder and ammunition, casting materials and sheet lead, pigments and chemicals – tetraethyl lead – antiknock agent in gasoline

Concentration of soluble lead is usually less than 0.003 mg/l

Mercury

Elemental mercury only liquid metal at $25^{O}C$

Mercury is enzyme and protein inhibitor, whereas zinc and cadmium play active role in protein, lipid and carbohydrate metabolism of variety of organisms

Concentration of dissolved mercury in unpolluted fresh water varies between 0.00002 and 0.0001 mg/l

Nickel

Sulphide - nickel is used for alloys (3000 different types), railway car manufacturers, food processing machinery, petroleum refining and in architectural applications.

Concentration of dissolved nickel in unpolluted fresh water varies between 0.001 and 0.003 mg/l

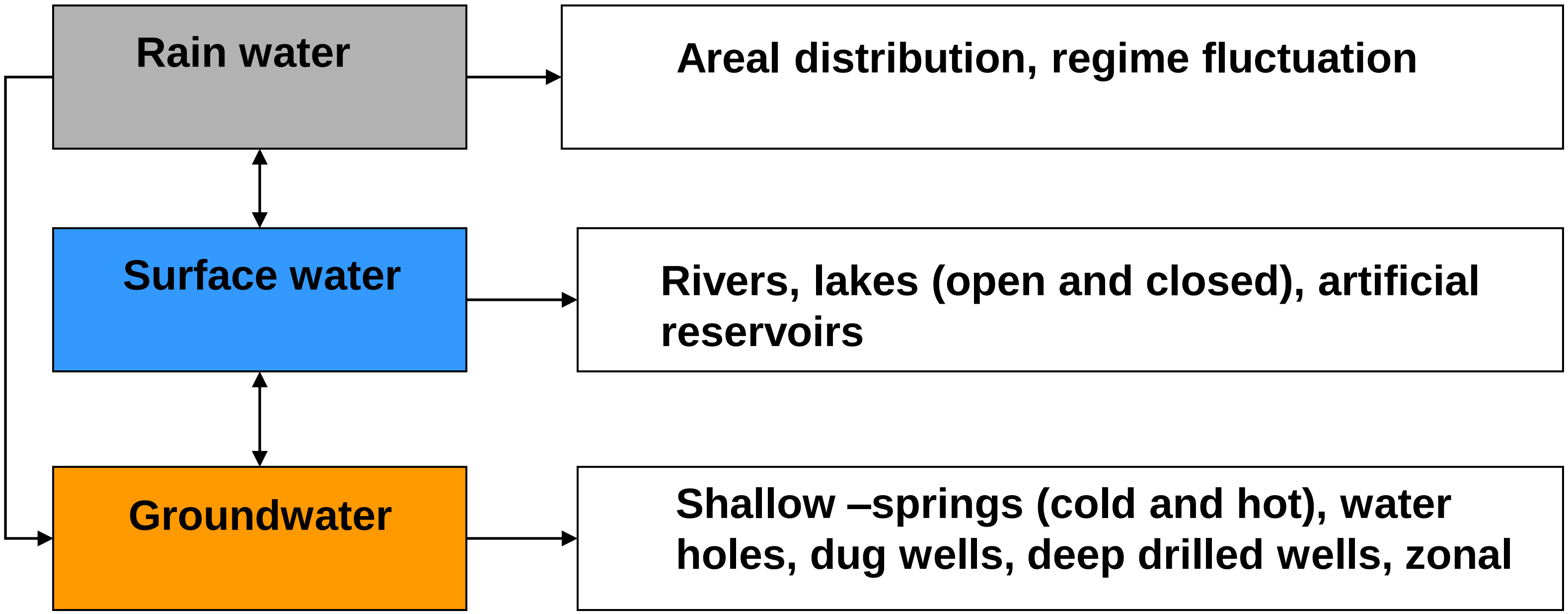
Zinc

Zinc is relative rare in nature, however, it occurs in a number of minerals

Uses of zinc are: pigments, rayon fiber manufacture and wood preservative waste incineration, rubber tire wear, phosphate fertilizers

Concentration of dissolved zinc in unpolluted fresh water varies between 0.0005 and 0.015 mg/l

Water circulation flow chart – followed by samplig program



Sampling

Circulation system

- Rainwater
- Surface water
- Groundwater
- (Wastewater)

Basin system

- Aquifers

(infiltration, transport, discharge)

- Aquitards /aquicludes

Hydrogeological cycle

- rain water (climatic stations, roofs – cumulative, one episode, dry deposit)
- surface water (upper, middle and lower reaches, before confluence and after confluence of the main river with tributaries,lakes, ponds)
- groundwater (each aquifer, aquicludes, aquitards)

Precipitation

Analyses of rainwater indicates that the dissolved solids in rain water range from several milligrams per liter in continental to several tens of milligrams per liter in coastal area and in industrial areas

Rain water examples out ETH

	Nevada	Northern Carolina	Australia	California	Ontario	Northern Europe	Maryland	Dehli	Prague
pH	5.6			5.9	5.3	5.5	4.1		4.41
Na	0.6	0.4	2.46	2.24	0.35	2.05	0.26	4.44	0.2
K	0.6	0.2	0.37	0.35	0.14	0.35	0.13	0.23	0.11
Ca	0	0.9	1.2	0.77	0.53	1.42	0.42	0.92	0.69
Mg	0.2	0	0.5	0.43	0.15	0.39	0.09	0.46	0.06
Cl	0.2	0.2	4.43	3.75	0.22	3.47	0.38	8.12	0.43
HCO_3	3	2		1.95					
SO_4	1.6	2		1.76	0.45	2.19	3.74	0.67	4.23
NO_3	0.1			0.15	0.41	0.27	1.96		2.9
SiO_2	0	0.1		0.29	0.6	0	0.9		
TDS	4.8	5.1		12.4	2.85	10.14	7.88		9.83

Concentration in mg/l

Surface Water

- Rivers (upper, middle, lower, important tributary, effluents)
- Lakes (open, closed, different environment – Awasa, Abyiata, Tana)
- Dam reservoirs, ponds

Surface water composition

Chemical composition of surface water is highly variable through both time and space

surface water consists part of:

base-flow (groundwater)

direct runoff

Other processes:

mixing of river water with stream sediments

discharge of waste water

effects of water living biota

Surface water CR and ETH

	Amazon	Mississipi	World mean	Upper vltava	Lowr Vltava	Bilina	Jizera	Lower Elbe	Hoha
pH	6.5	7.4		7.1	7.6	7.7	6.9	7.6	7.36
Na	1.8	20	6.3	3.4	15.9	108	4.8	24.1	5.2
K		2.9	2.3	1.86	5.87	17.75	1.02	6.17	2.4
Ca	4.3	38	15	8.7	38.3	95.6	12.1	52.2	12
Mg	1.1	10	4.1	1.7	10	28.3	1.67	10.5	5
Cl	1.9	24	7.8	7.3	24.9	151	3.7	31.4	0
HCO_3	19	113	58	17.7	73.2	391	22	104	66
SO_4	3	51	11	11.7	85.6	301	18.5	94.2	1
NO_3	0.1	2.4	1	2.4	17	34.3	5.1	21.2	0.04
SiO_2	7	7.9	13						21
TDS	38.2	269.2	118.5	54.76	270.77	1126.95	68.89	343.77	112.64

Concentration in mg/l

Groundwater

Concentration of dissolved solids increases along its flow paths and shallow groundwater in recharge areas is lower in TDS that the water from greater depth of the same hydrogeological system

Groundwater tends chemically towards the composition of seawater with increasing time and travel distance

Anion evolution sequence can be explained in terms of two main variables, mineral availability and mineral solubility

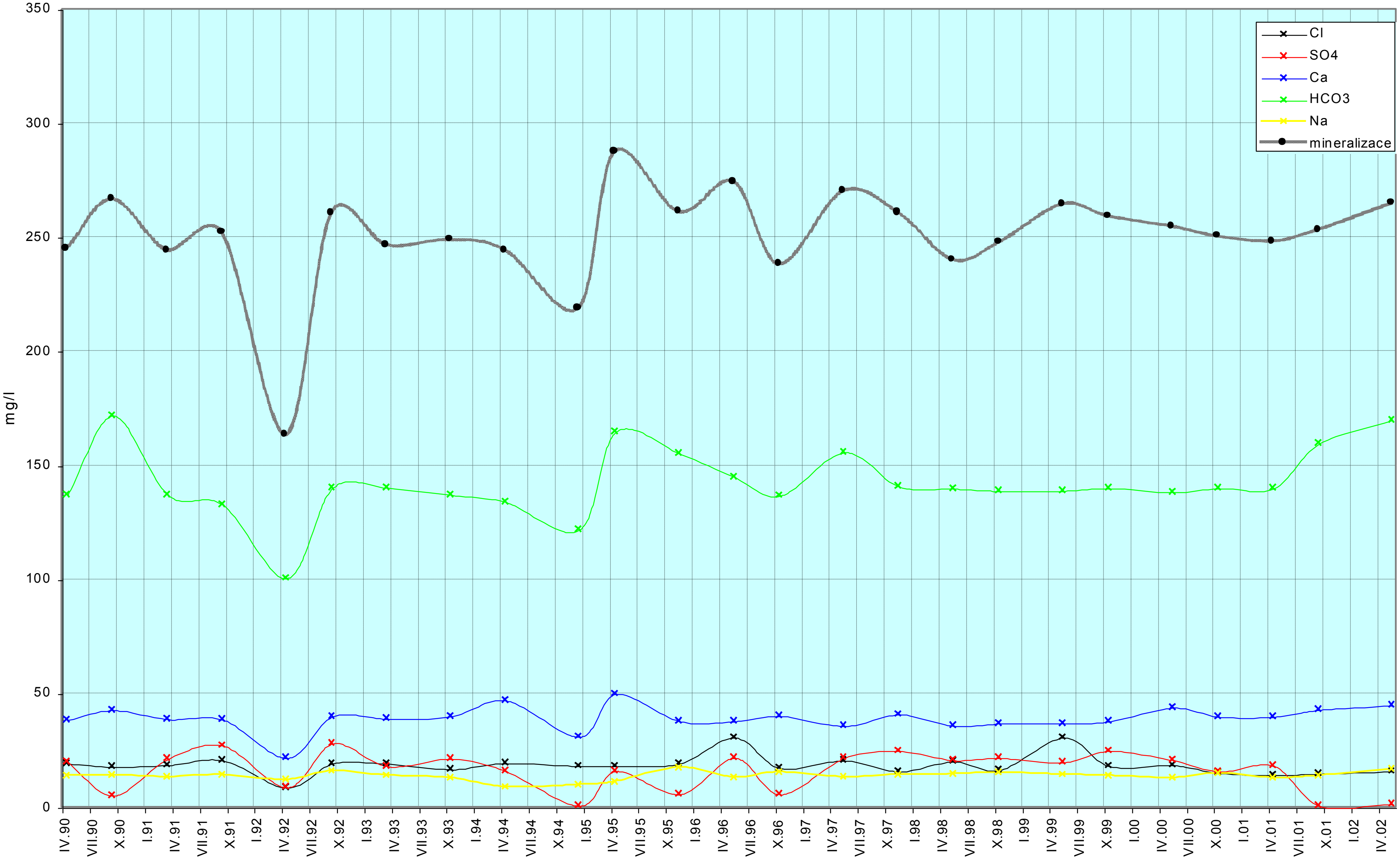
Groundwater CR and ETH

	granit	basalt	lim.	snads.	Glauber	Mlynsky	Magnezia	Asosa granite	Asosa basalt
pH	5	7.5	7.2	7	6.25	6.95	6.15	7.12	6.18
Na	7.5	2	1.5	35.6	2677	1713	4.34	3.4	1
K	4.5	0.5	1	11	52.4	98.04	2.5	1.1	2
Ca	25.7	19.9	52.7	105	130	135.9	39.8	18	3
Mg	11.3	41.3	28.9	27	39.3	37.33	341.11	6.2	1.1
Cl	4.6	5.1	3.8	25.6	1133	607.7	3.03	0	0
HCO_3	4.9	229	294	363	1629	2163	1818	96	17
SO_4	119	15.2	20.2	137	3250	1639	16.9	1	3
NO_3				14.1	0.188		0.195	0.41	0.04
SiO_2	7.8	11.68		3.69	31.66	25.23	33.8	43	13
TDS	185.3	324.68	402.1	721.99	8962	6432	2264	176.54	46.42

Interpreting chemistry

- **Areal, vertical, regime**
- **Graphs (Piper, Stiff, barr, circular, spider, etc.)**
- **Statistical (average, mean, correlation, deviation, etc.)**
- **Maps (parametric, types, categories)**

Regime variation



Piper

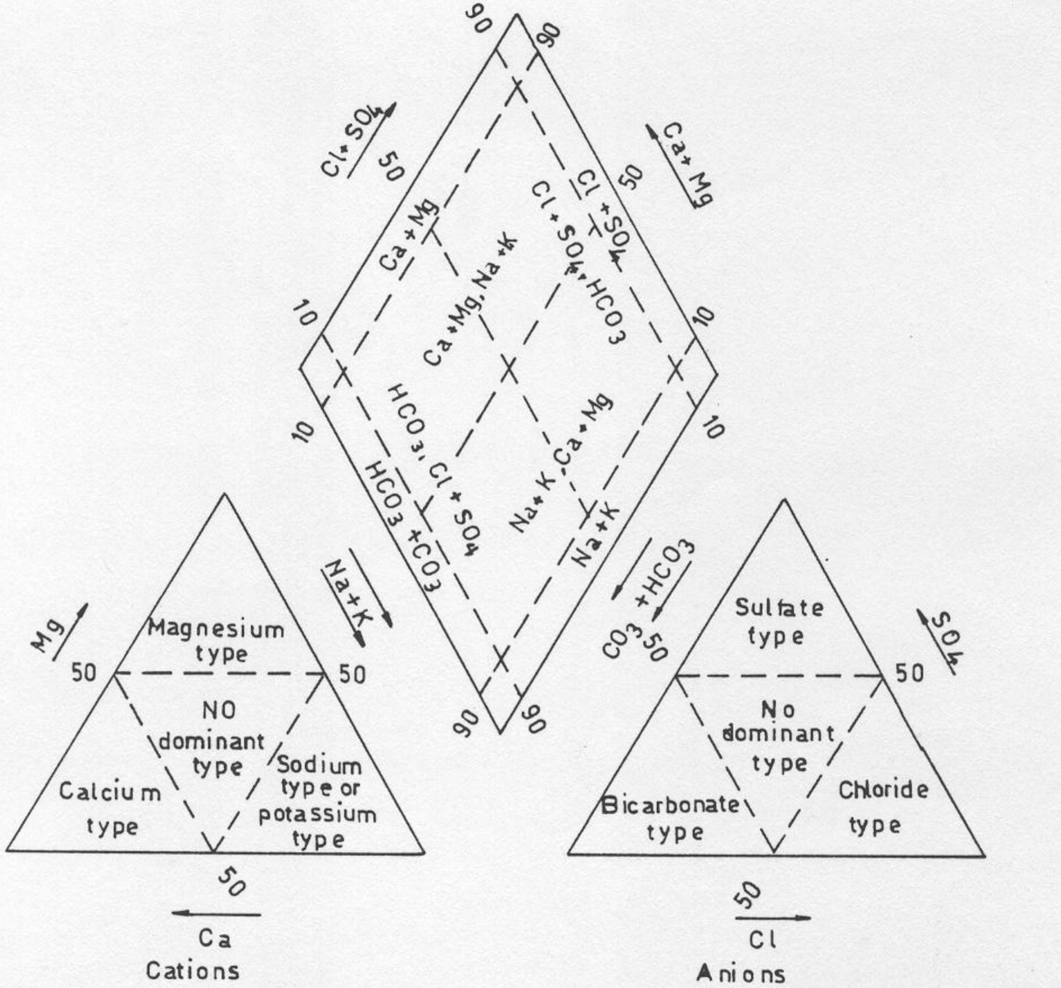
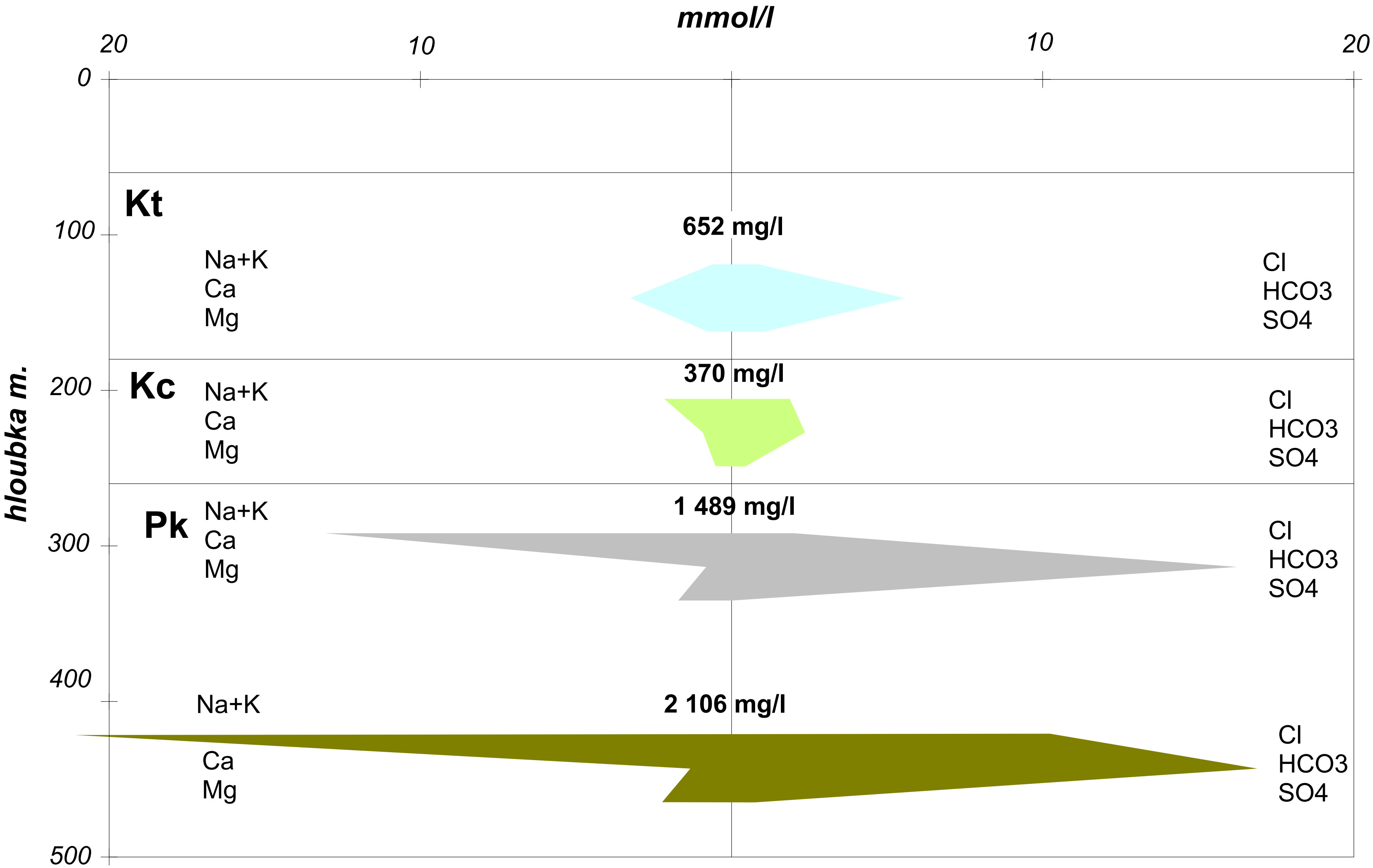


FIG C.3.7 Piper's Trilinear Diagram Showing Analyses Represented by Three-point Plotting Method (after Freeze & Cherry, 1978)

Vertical zonality CR



Transport of chemicals

Numerical modeling of transport – behavior of componets (precipitation of calcite – function of pH and HCO_3) along flow line

PHREEQ – carbonate problem

EQ3 – mineral equilibrium

MINTEQ – cation exchange

GEOCHEM, WATEQP, CHARON, etc.