Groundwater sampling

Applied Hydrogeology

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Why GW Sampling?

- To monitor the long term sustainability of an aquifer as a safe and stable water supply and adjust appropriate policies accordingly.
- To identify subsurface contaminants, estimate the speed and direction of the contamination flow and narrow down the contamination sources.
- To manage groundwater levels and prevent damage by salt water intrusion.
- To monitor network provides the data on which measures can be designed and provides the information when to change the settings of your water management system.
- The groundwater monitoring network will enable water boards and municipalities to timely issue drought or flood warnings and take appropriate mitigation measures.

Pre-sampling and planning

- What is the research question, can it be addressed through sampling of water?
- What are the minimum and optimum sets of parameters that you should include in the sample analyses?
- What is the optimum number of samples to be collected in time and space to solve your research question?

- Discuss your work plan with your supervisor: number of samples and selection of water quality parameters.
- Make an agreement with the lab analysts about when the samples can be analyzed.
- Bring with you into the field
  - Sufficient sample bottles. Per sampling point:

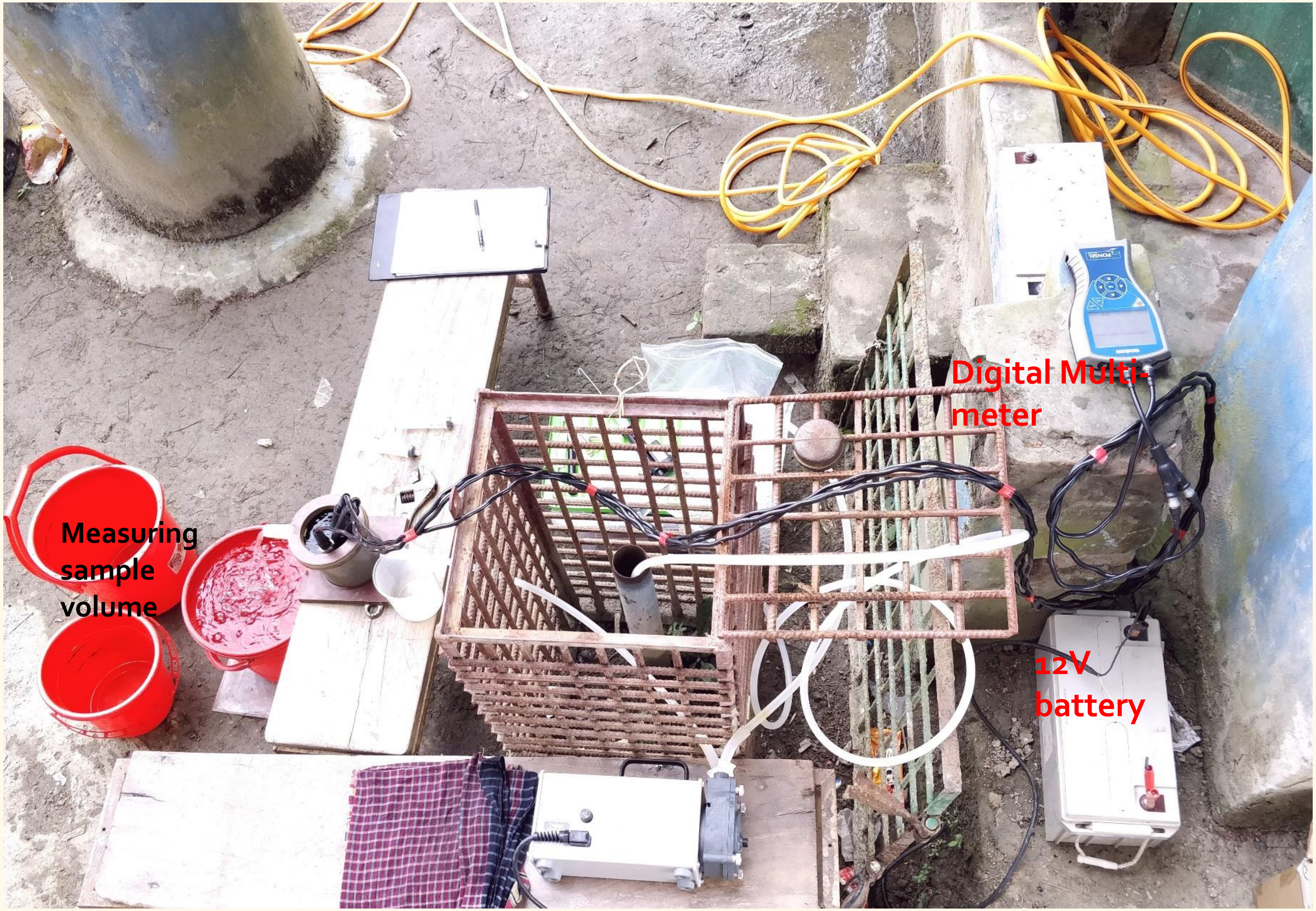
    filtered sample for cation and metal analysis: IPC-MS

    filtered sample for anion analysis: IC

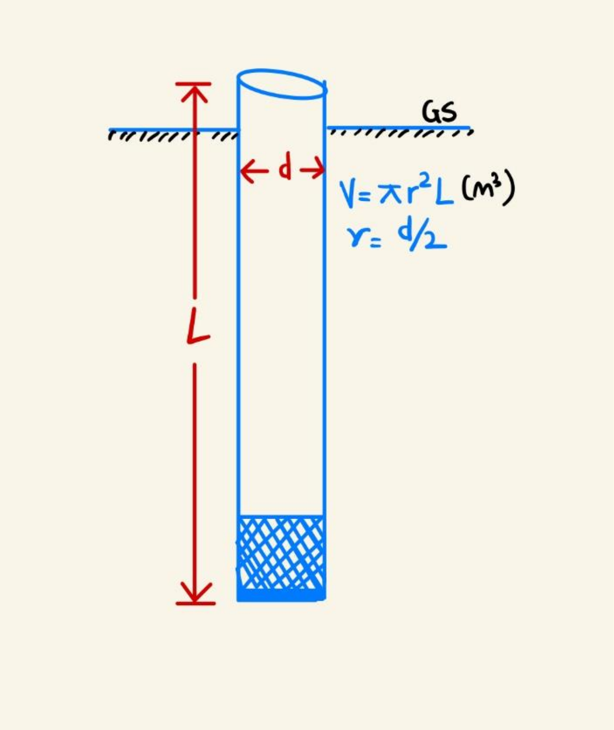
    Other bottles like for microbial analysis; organic micro-pollutants; etc
  - A few syringes (20-50 mL); filters (0.45 µm pore size), ≥ per sampling point
  - Sensors (EC, pH (+T), and optionally O_2)
  - A flow through cell or similar to place the field electrodes into (optional)
  - A (manual) pump and (sufficiently long) tubing for groundwater sampling
  - A field kit for alkalinity determination (and optionally Cl, Ca, Ca+Mg)
  - Test strips for nitrate (optional; always determine pH with a pH electrode!)
  - A field book, pencil, and watertight markers to code the sample bottles
  - A cool box to cool the water samples (optional)

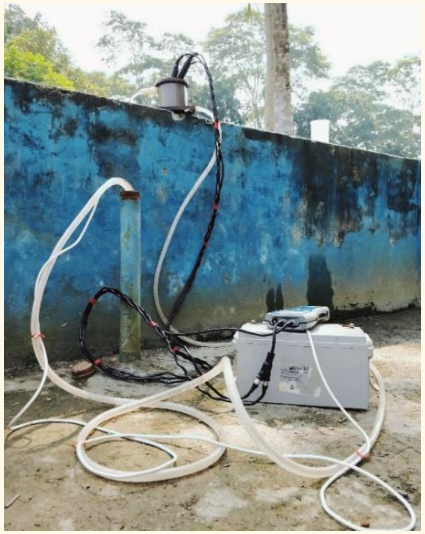
Sampling points

Sampling with submersible pump



Well volume and purging

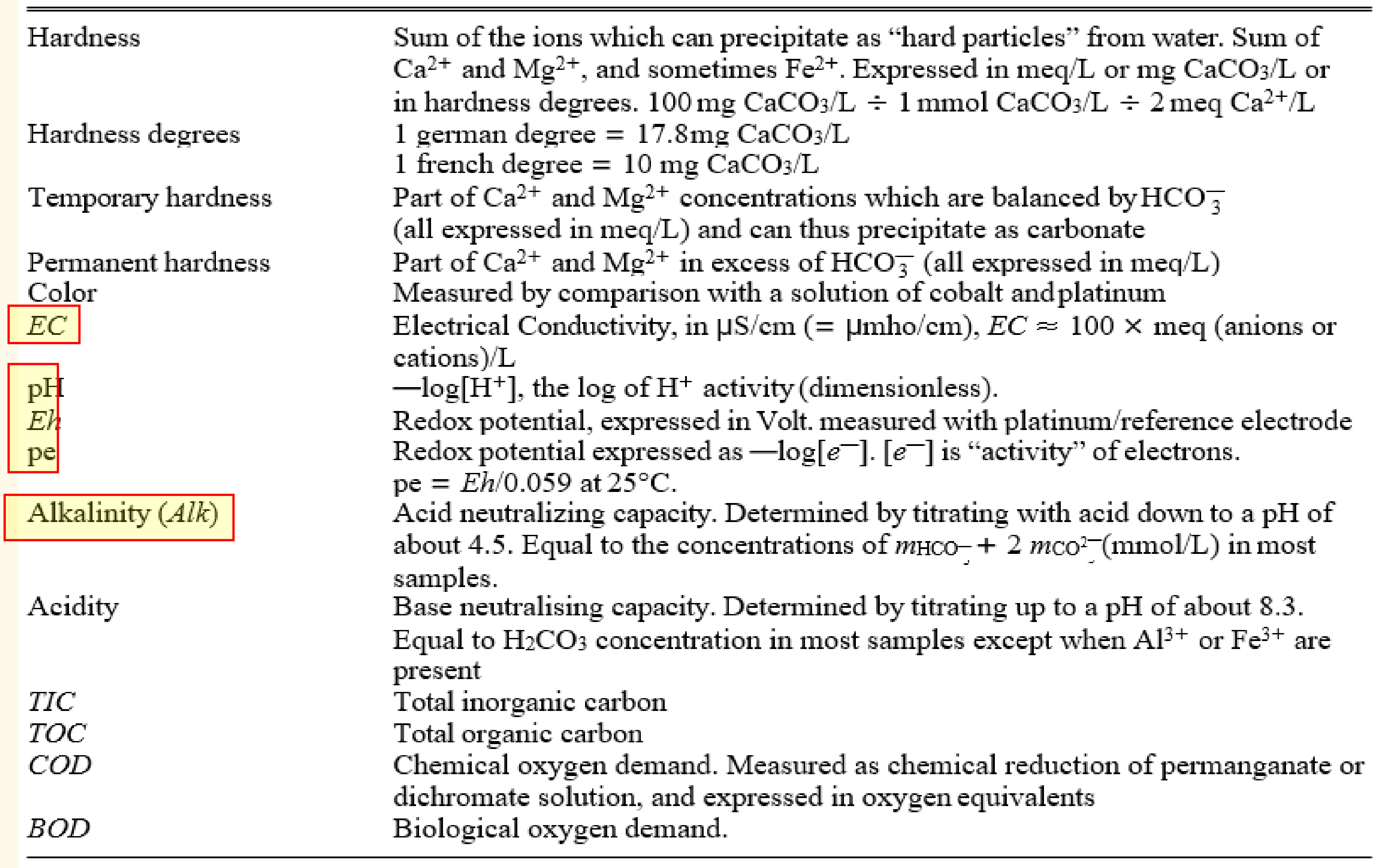




Onsite parameters

(cf. Standard Methods, 1985; Hem, 1985)

EC, pH/Eh/Redox, Temperature, DO, Turbidity, Alkalinity



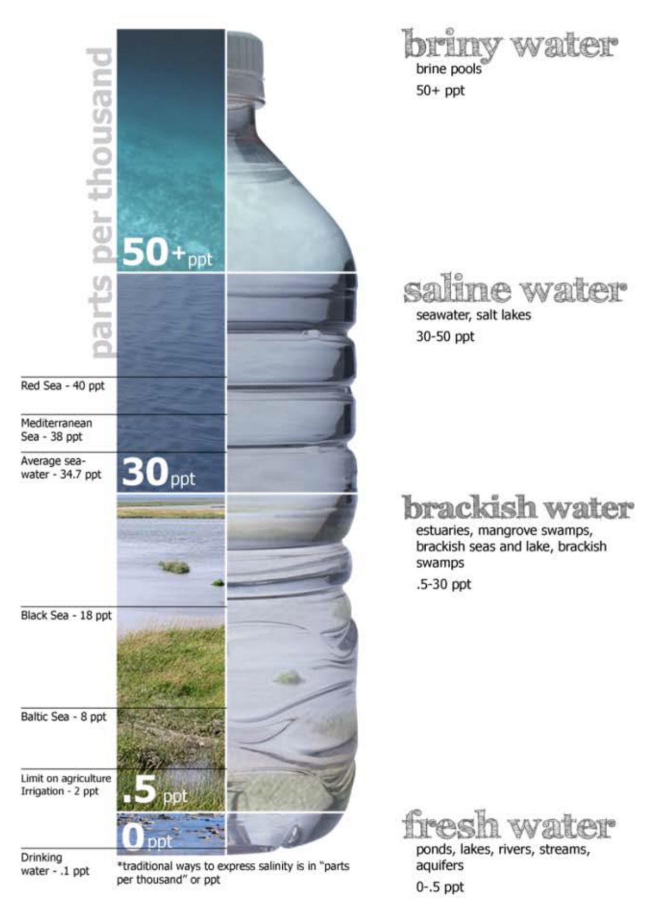
Hardness	Sum of the ions which can precipitate as "hard particles" from water. Sum of Ca^{2+} and Mg^{2+}, and sometimes Fe^{2+}. Expressed in meq/L or mg $CaCO_3$/L or in hardness degrees. 100 mg $CaCO_3$/L ÷ 1 mmol $CaCO_3$/L ÷ 2 meq Ca^{2+}/L
Hardness degrees	1 german degree = 17.8mg $CaCO_3$/L 1 french degree = 10 mg $CaCO_3$/L
Temporary hardness	Part of Ca^{2+} and Mg^{2+} concentrations which are balanced by HCO_3^- (all expressed in meq/L) and can thus precipitate as carbonate
Permanent hardness	Part of Ca^{2+} and Mg^{2+} in excess of HCO_3^- (all expressed in meq/L)
Color	Measured by comparison with a solution of cobalt and platinum
EC	Electrical Conductivity, in μS/cm (= μmho/cm), $EC \approx 100 \times$ meq (anions or cations)/L
pH	$-\log[H^+]$, the log of H^+ activity (dimensionless).
Eh	Redox potential, expressed in Volt. measured with platinum/reference electrode
pe	Redox potential expressed as $-\log[e^-]$. $[e^-]$ is "activity" of electrons. $pe = Eh/0.059$ at 25°C.
Alkalinity (*Alk*)	Acid neutralizing capacity. Determined by titrating with acid down to a pH of about 4.5. Equal to the concentrations of $m_{HCO_3^-} + 2\, m_{CO_3^{2-}}$ (mmol/L) in most samples.
Acidity	Base neutralising capacity. Determined by titrating up to a pH of about 8.3. Equal to H_2CO_3 concentration in most samples except when Al^{3+} or Fe^{3+} are present
TIC	Total inorganic carbon
TOC	Total organic carbon
COD	Chemical oxygen demand. Measured as chemical reduction of permanganate or dichromate solution, and expressed in oxygen equivalents
BOD	Biological oxygen demand.

Recording onsite parameters

Alkalinity

Collection and preservation

Sample at 25° C	EC (µS/cm)
Distilled water	0.5-3
Precipitation	5-50
Streams running through silicate rock (granite)	10 - 50
Streams running through limestone formations	500 - 700
Fresh water streams (general)	100-2,000
Potable waters	50-1,000
Brackish waters	2,000-20,000
Ocean water	55,000 (40,000-60,000)
Reject brines	65,000-85,000



*traditional ways to express salinity is in "parts per thousand" or ppt

Salinity vs TDS vs EC

Indicative!	Fresh	Brackish	Saline	Brine
Salinity (ppt)	<0.05	0.05-3	3-5	>5
EC (µS/cm)	<2000	2000-20,000	40,000-60,000	> 60,000
TDS (mg/L)	<500	500-30,000	30,000-40,000	> 40,000

- Salinity = mass of salts in water
  - Units: ppt | % | ppm
  - Mostly used for brackish-saline waters

- Total dissolved solids (TDS) = mass of salts <u>plus organic solutes</u>
  - Units: mg/L
  - Mostly used for (polluted) fresh waters

- Electrical conductivity (EC) widely used as qualitative & quantitative indicator of salinity and TDS
  - Units: µS/cm | at higher salinity: mS/cm or mS/m

Composition & quality indicator

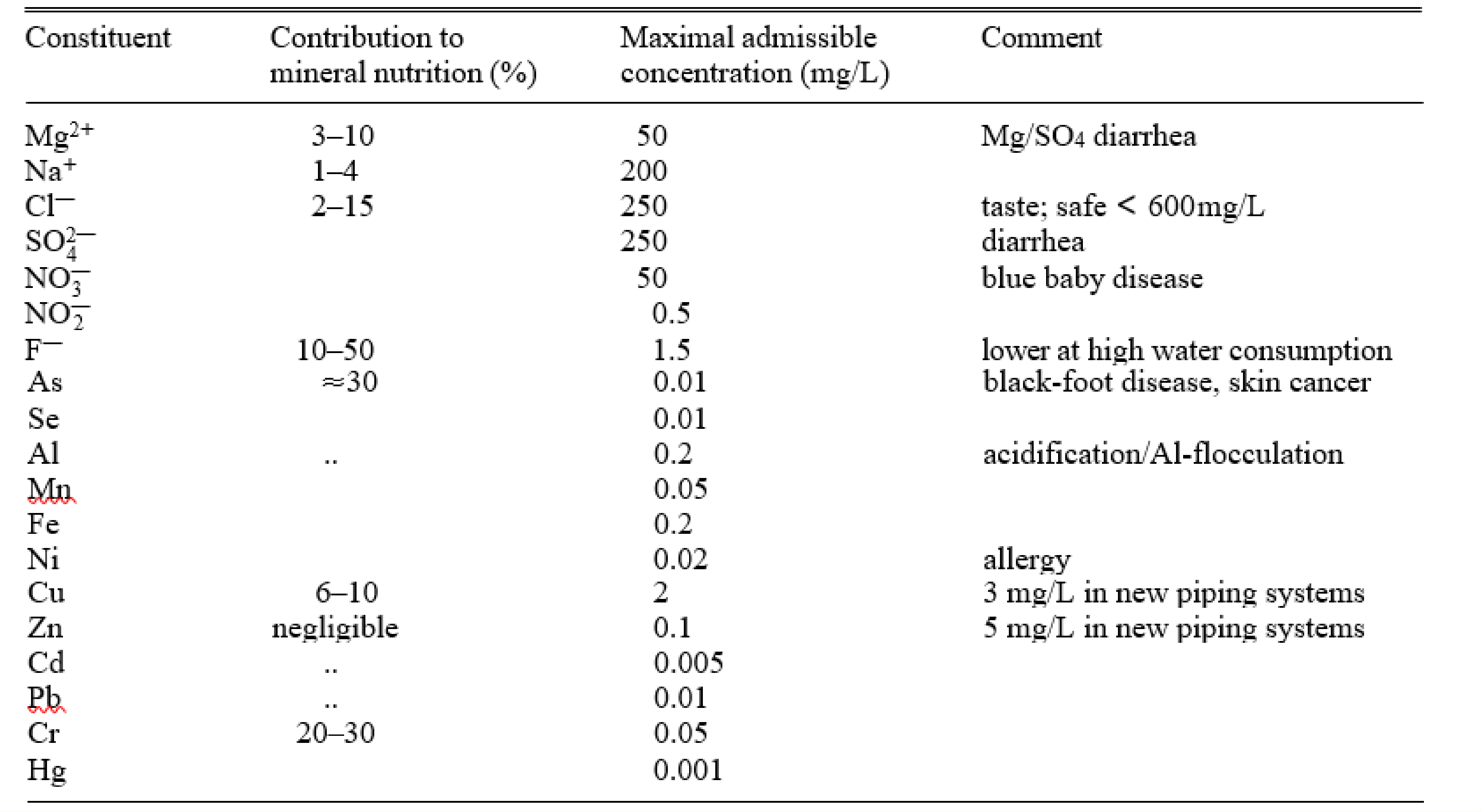
- Major ions
  - Cations: **Ca^{2+}, Mg^{2+},** Na^{+}, K^{+}
  - Anions: Cl^{-}, SO_4^{2-}, NO_3^{-}, and **HCO_3^{-}**
  - Trace metals: Fe, Mn, As
  - Nutrients: PO_4^{3-}, **$NO3^{-}$,NH_4^{+}, org-N**
  - Silica: H_4SiO_4
  - Dissolved matter (Organic/carbon)
    - Organic micro pollutants
  - Dissolved gasses:
  - pH
  - Pathogens: bacteria, viruses
  - Total suspended solids

Laboratory analysis

Result #	Value	Unit	Correction Factor	Remark
#1	0.0103	mol/kgw (**k**ilo**g**ram **w**ater) = M (*molality*: molal concentration: moles per kg solution)		
#2	10.3	mmol/kgw	#1 × 1000	Moles to millimoles
#3	10.56	mmol/L = mol/m^3 (SI unit: *molarity*)	#2 × 1.025	Density seawater (kg/L)
#4	412.8	mg/kgw = ppm	#2 × 40.078	Atom weight Ca
#5	423.1	mg/L	#4 × 1.025	Density seawater
#6	20.6	meq/L	#2 × 2	Charge Ca^{2+}

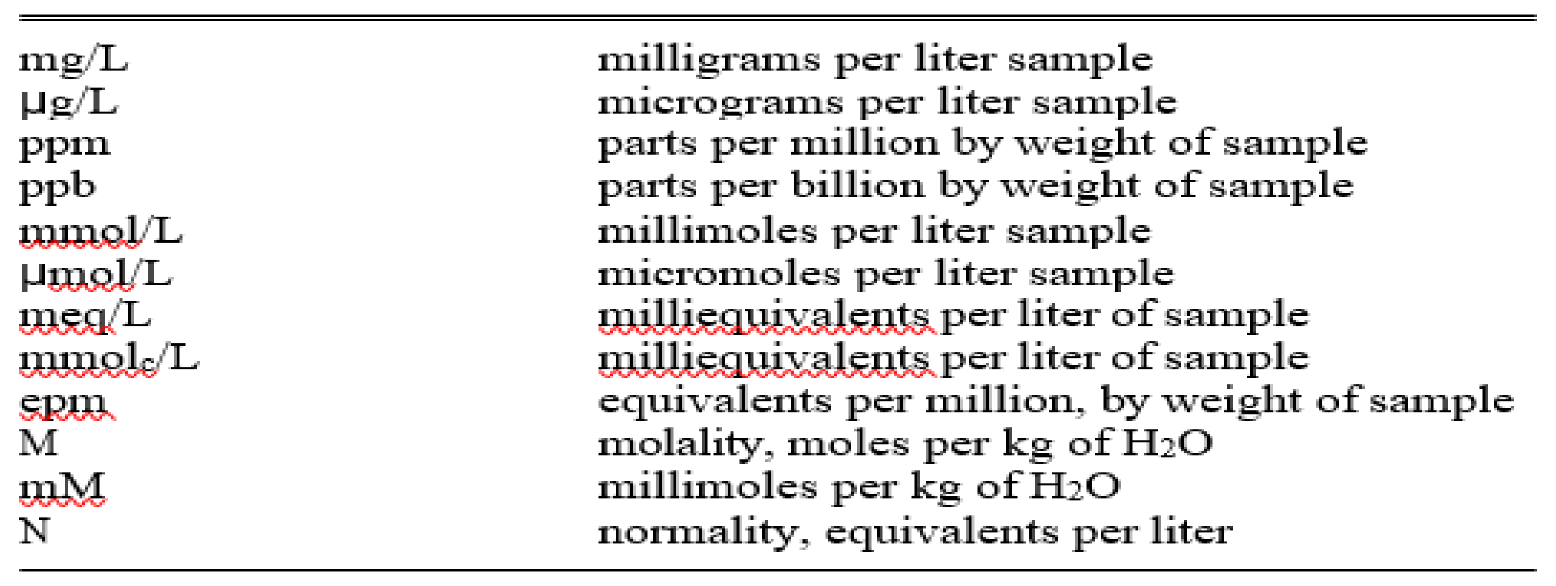
ppm = parts per million; eq = equivalents

Standards for drinking water

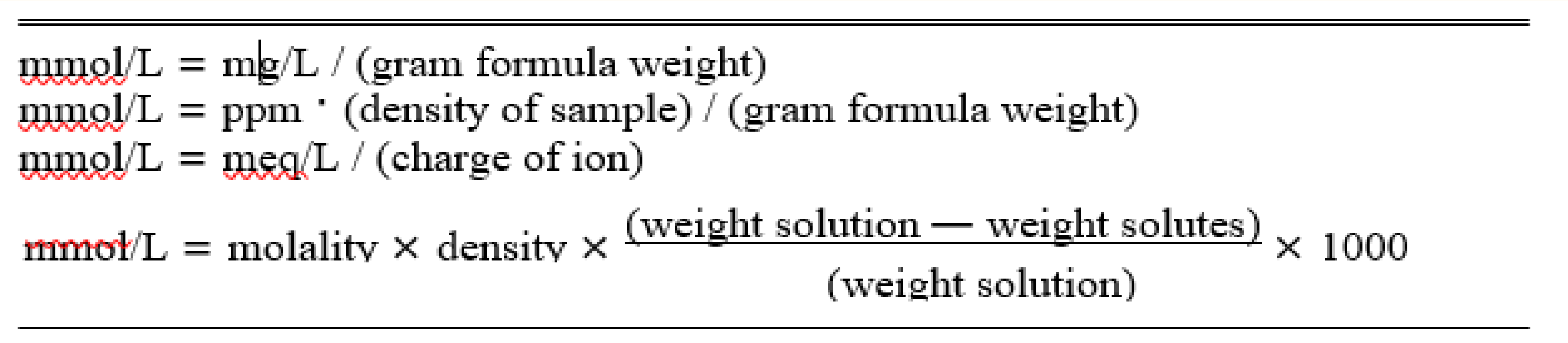


Constituent	Contribution to mineral nutrition (%)	Maximal admissible concentration (mg/L)	Comment
Mg^{2+}	3–10	50	Mg/SO_4 diarrhea
Na^+	1–4	200	
Cl^-	2–15	250	taste; safe < 600mg/L
SO_4^{2-}		250	diarrhea
NO_3^-		50	blue baby disease
NO_2^-		0.5	
F^-	10–50	1.5	lower at high water consumption
As	≈30	0.01	black-foot disease, skin cancer
Se		0.01	
Al	..	0.2	acidification/Al-flocculation
Mn		0.05	
Fe		0.2	
Ni		0.02	allergy
Cu	6–10	2	3 mg/L in new piping systems
Zn	negligible	0.1	5 mg/L in new piping systems
Cd	..	0.005	
Pb	..	0.01	
Cr	20–30	0.05	
Hg		0.001	

Concentration units



mg/L	milligrams per liter sample
µg/L	micrograms per liter sample
ppm	parts per million by weight of sample
ppb	parts per billion by weight of sample
mmol/L	millimoles per liter sample
µmol/L	micromoles per liter sample
meq/L	milliequivalents per liter of sample
$mmol_c/L$	milliequivalents per liter of sample
epm	equivalents per million, by weight of sample
M	molality, moles per kg of H_2O
mM	millimoles per kg of H_2O
N	normality, equivalents per liter



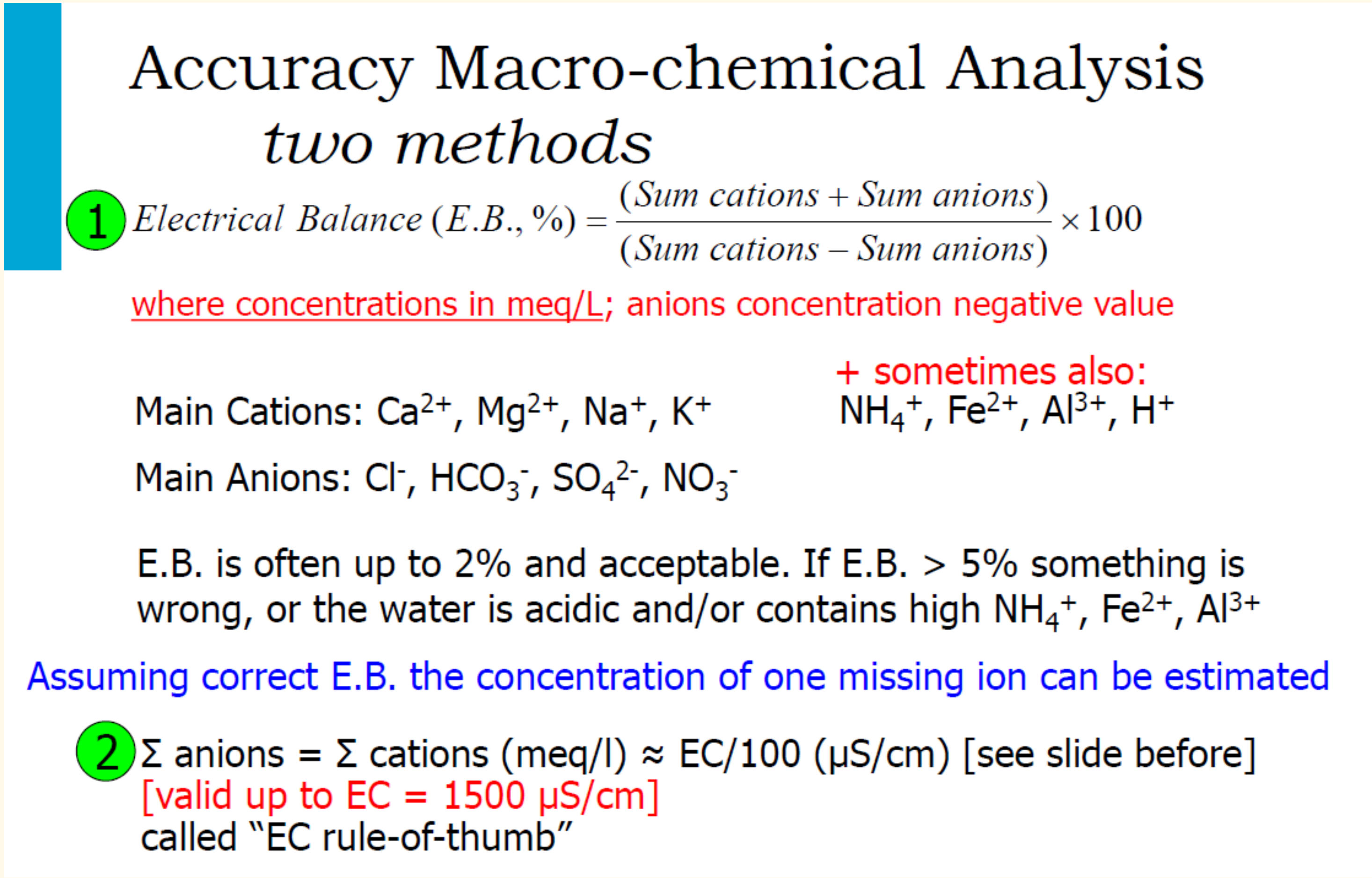
mmol/L = mg/L / (gram formula weight)

mmol/L = ppm · (density of sample) / (gram formula weight)

mmol/L = meq/L / (charge of ion)

$$\text{mmol/L} = \text{molality} \times \text{density} \times \frac{(\text{weight solution} - \text{weight solutes})}{(\text{weight solution})} \times 1000$$

Accuracy of analysis



Accuracy Macro-chemical Analysis

two methods

① $$\text{Electrical Balance (E.B., \%)} = \frac{(\text{Sum cations} + \text{Sum anions})}{(\text{Sum cations} - \text{Sum anions})} \times 100$$

where concentrations in meq/L; anions concentration negative value

Main Cations: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}

+ sometimes also: NH_4^{+}, Fe^{2+}, Al^{3+}, H^{+}

Main Anions: Cl^{-}, HCO_3^{-}, SO_4^{2-}, NO_3^{-}

E.B. is often up to 2% and acceptable. If E.B. > 5% something is wrong, or the water is acidic and/or contains high NH_4^{+}, Fe^{2+}, Al^{3+}

Assuming correct E.B. the concentration of one missing ion can be estimated

② Σ anions = Σ cations (meq/l) ≈ EC/100 (µS/cm) [see slide before]
[valid up to EC = 1500 µS/cm]
called "EC rule-of-thumb"

Sampling all about