Part 2: Common Water Quality Parameters

Importance of water quality for health:

- Drinking
- Irrigation and recreational purposes
- Flora and fauna

Parameters: Water temperature pH value Electrical conductivity Dissolved oxygen



Part 2: Common Water Quality Parameters

Growth of autotrophic organisms (plants):

Nutrition elements for plants: carbon (C), nitrogen (N), phosphorus (P), oxygen (O), hydrogen (H), sulphur (S), magnesium (Mg), potassium (K), calcium (Ca), iron (Fe)

and other trace elements

Nutrients and trace elements are only available in finite quantities

LIEBIG's minimum law: The nutrition element that is available in smallest quantity, limits the growth of organisms

Hydrom. Pract. Training: Common Water Quality Parameters

Metabolism reactions:

Assimilation (photosynthesis, chemosynthesis) Catabolism (respiration) Biological decomposition (primary decomposition, final decomposition)

Cycles of matter e.g. for everlasting renewed conversion of:

- Carbon, oxygen, hydrogen,
- > Nitrogen,
- > Phosphorus,
- > Sulphur



Usual range in running waters (Germany): 0 to 25° Celsius

An increase of water temperature commonly causes:

physically:

- Above 4° C a reduction of <u>density</u> and <u>viscosity</u>: sedimentation is forwarded
- Increase of gas replacement between water and atmosphere
- > Decrease of <u>solubility</u> of gases in water (O_2 , CO_2 , NH_3 , N_2)

physically/chemically:

- Increase of the free ammonia (NH₃), toxic for fish, compared with chemically bound ammonium (NH₄)
- Escape of <u>lightly volatile</u> compounds
- Increase in the velocity of <u>chemical reactions</u>

biologically:

Increase of the velocity of reactions of aerobic and anaerobic biochemical processes (e.g. degradation of carbon, nitrification, degradation of surfactants)



Dependency of NH₃/NH₄⁺-N balance on pH-value and water temperature (WOKER, H., 1949)



Influence of temperature on activity of metabolism of poikilotherm organisms

Ratios of carbon degradation at various temperatures referred to five-day biochemical oxygen demand at 20 °C (BOD₅) (Fair, quoted in Imhoff, K., K. R. Imhoff, 1990)

dovo	Temperature (°C)						
days	5	10	15	20	25	30	
1	0,11	0,16	0,22	0,30	0,40	0,54	
5	0,45	0,60	0,79	1,00	1,23	1,47	
10	0,70	0,90	1,10	1,32	1,52	1,71	

<u>Salmonid waters</u>: Running waters, in which life of fish species such as salmon (Salmo salar), trout (Salmo trutta), greyling (Thymallus thymallus) and vendace (Coregonus) is protected or could be protected



Salmon

<u>Cyprinid waters</u>: Running waters, in which life of fish species such as cyprinids (Cyprinidae) or other species such as pikes (Esox lucius), perches (Perca fluviatilis) and eels (Anguilla anguilla) is protected or could be protected



Cyprinid

Council Directive 78/659/EEC of 18.07.1978	Salmonid waters : 21,5 $\Delta T = 1,5^{2}$ (I) ¹⁾
on the quality of fresh waters needing	Cyprinid waters : 28 $\Delta T = 3,0^{2}$ (I)
protection or improvement in order to support	The 10°C temperature limit applies only to
fish life (directive for fish waters)	breeding periods of species which need cold
	water for reproduction and only to waters
	which may contain such species. (I, O) 1)

Limiting (mandatory) and reference (guide) values for water temperatures (°C)

- 1) (I) Limiting (imperative, mandatory) value;
 - (G) Guide (reference value);
 - (O) Derogations are possible in accordance with Article 11 (exceptional weather or special geographical conditions)
- 2) ΔT Upstream/downstream of thermal discharge (at the edge of the mixing zone)

Council Directive 75/440/EEC of 16 June 1975	
concerning the quality required of surface water in the	Category A1, A2, A3 (degree of treatment) ³⁾ : 22 (G) ¹⁾ . 25 (I, O)
Member States	

Limiting (mandatory) and reference (guide) values for water temperatures (°C)

3) Definition of the standard methods of treatment for transforming surface water of categories A1, A2 and A3 into drinking water

Category A1:

Simple physical treatment and disinfection, e.g. rapid filtration and disinfection.

Category A2:

Normal physical treatment, chemical treatment and disinfection, e.g. pre-chlorination, coagulation, flocculation, decantation, filtration, disinfection (final chlorination).

Category A3:

Intensive physical and chemical treatment, extended treatment and disinfection e.g. chlorination to break-point, coagulation, flocculation, decantation, filtration, adsorption (activated carbon), disinfection (ozone, final chlorination).

pH is applied for naming the acid, neutral or alcaline chemical behaviour of a solution.

<u>Definition</u>: pH is minus the decimal logarithm of the numerical value of hydrogen ion activity in mol/I (H_3O^+ = Oxonium ion) (\approx hydrogen concentration) of a solution.



Ranges of pH-values

pH-values of fluids of human / animal organisms or solutions of everyday use:

Stomach hydrochloric acid	0,9 - 2,3
Vinegar (normal)	3,1
sour milk	4,4
With air carbonic acid saturated fresh water	5,5 - 5,8
Urine	4,8 - 7,4
Blood liquid	7,4
Ocean water	7,8 - 8,3
Soapy water	8,2 - 8,7
Lime water, saturated	12,3
Rainwater	2,9 - 7,8

pH-values of pure water can differ from the neutral value (pH = 7) by:

- Carbonic acid, humic acid from the underground
- Seepage water from the underground (acid or alcaline)
- > Mineral salts (e.g. buffering effect of calcium hydrogen carbonate) (Ca(HCO₃)₂)
- Waste water intake
- Acid rain
- > Temperature

Fluctuation of natural waters between pH 6,5 and 8,5 Continuous tolerance for most organisms from pH 6 to 9 Damage or killing of small creatures by pH < 5,5 Lethal for all native fish species are values < 4 or > 10,8

Impact of pH on chemical and physical processes:

- > Part of free NH_3 (ammonia) compared with NH_4 (ammonium)
- Water solubility of metallic salts
- Progression of processes of water purification (neutralisation, flocculation, disinfection)

Ecological impacts of pH:

- Inhibition of metabolism processes
- Decrease of biodiversity
- Decrease of natural self-purification
- (Re)mobilisation of heavy metals and other trace elements. They can be highly effective toxic substances even in traces (secondary effects)

Council Directive 78/659/EEC of 18.07.1978 on the quality of fresh waters needing protection or improvement in order to support fish life (directive for fish waters)	Salmonid waters: $6 - 9$ (I, O) Cyprinid waters: $6 - 9$ (I, O) Changes not more than $\pm 0,5$ pH- units
Council Directive 75/440/EEC of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States	Category A1: 6,5 – 8,5 (G) Category A2: 5,5 – 9 (G) Category A3: 5,5 – 9 (G)
Verordnung über die Qualität von Wasser für den mensch- lichen Gebrauch (Trinkwasserverordnung vom 21.05.2001) (German directive for drinking water)	6,5 – 9,5 (I)

Limiting (mandatory) and reference (guide) values for pH (-)

Electrical conductivity gives information on total concentration of dissolved salts Units of measurement: μS/cm (microsiemens per centimeter), mS/m

1000 μ S·cm⁻¹ \cong ca. 1000 mg·l⁻¹ of dissolved solids (evaporation residue)

Possible **sources of natural or anthropogenic salts** in running waters:

- Salt from geogenic background (weathering)
- Industrial discharge of salt
- Consumption of salt by households and industry
- Excretion of urine of humans and animals
- Gritting salt for iced roads in winter

Ecological importance of salt content in waters:

- Vital functions for the organism of creatures, harmful effects in case of lack and overdose
- Different effects depending on substantial composition of salts
- Plants commonly act more sensitive than animals
- aquatic biocenosis comprise physiologically different organisms according to salt content

lons in salt pollution of waters:

- Cations (+): sodium, calcium, magnesium, potassium, ammonium
- Anions (-): chloride, sulphate, hydrogen carbonate, nitrate

High salt pollutions in running waters commonly have disadvantages for water use only:

- > Drinking water purification: Limiting value 1000 μ S·cm⁻¹
- Water for irrigation: depending on salt tolerance of plant species, mean salt tolerance about 300 to 800 μS·cm⁻¹
- ➢ Ocean water: 50 000 µS·cm⁻¹
- Spring water from gneiss, granite, Buntsandstein (german word for coloured sandstone): 10 100 μS·cm⁻¹
- > Spring water from lime stone: often > 1000 μ S·cm⁻¹
- Running waters with tolerable salt content: below 1000 µS·cm⁻¹, rich in minerals: from 700 µS·cm⁻¹

Council Directive 75/440/EEC of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States	Category A1, A2, A3: 1000 (G)	
Verordnung über die Qualität von Wasser für den mensch- lichen Gebrauch (Trinkwasserverordnung vom 21.05.2001) (German directive for drinking water)	2500 (I)	

Limiting (mandatory) and reference (guide) values for electrical conductivity (μ S·cm⁻¹ at 20 °C)

Oxygen is the most often occurring chemical element on earth

- about 50 % by weight in the earth's crust
- 20.9 % in the air

In water: bound (H_2O) and dissolved (O_2)

Classification of creatures after their behaviour on oxygen:

- > Obligate aerobes: can only exist in presence of oxygen
- Microaerophile organisms: have their optimum of growth in the area of low concentrations of oxygen
- Facultative anaerobes or aerotolerant organisms: grow as well in presence as in absence of oxygen too
- Obligate anaerobes: can only exist in fully absence of oxygen, may even die in its presence

Actual concentration of dissolved oxygen c (mg/l): Easily interacted by internal or external processes of waters with daily and annual variations

Dissolved oxygen saturation (maximum) **c**_s (mg/l): Equilibrium of saturation concentration, dependent on temperature and normal pressure of 1013 hPa

Relative oxygen saturation c_{s.r} (%): Ratio of both:

$$c_{s,r} = \frac{c}{c_{s'}} \cdot 100$$
 (%) $c_{s'} = c_{s} \cdot \frac{p}{p_{0}}$ (mg/l)

- c_s' Concentration of oxygen saturation after correction of pressure of air and water (mg/l) p Actual pressure of air and water (hPa)
- p Actual pressure of air and water (h p_0 Normal air pressure (= 1013 hPa)

	Water	0,0	0,2	0,4	0,6	0,8
	temperature (°C)	c _s (mg/l)				
	6	12,42	12,36	12,29	12,23	12,17
	7	12,11	12,05	11,99	11,93	11,87
	8	11,81	11,75	11,69	11,64	11,58
	9	11,52	11,47	11,42	11,36	11,31
	10	(11,25)	11,20	11,15	11,10	11,05
-2,17	11	10,99	10,94	10,89	10,84	10,79
	12	10,75	10,70	10,65	10,60	10,55
	13	10,51	10,46	10,41	10,37	10,32
	14	10,28	10,23	10,19	10,15	10,10
	15	10,06	10,02	9,97	9,93	9,89
	16	9,85	9,81	9,76	9,72	9,68
	17	9,64	9,60	9,56	9,53	9,49
	18	9,45	9,41	9,37	9,33	9,30
	19	9,26	9,22	9,19	9,15	9,11
	20	9,08	9,04	9,01	8,97	8,94

Concentration of dissolved oxygen c_s of water at saturation and normal pressure 1013 hPa



Concentration of dissolved oxygen with air saturated water in dependence of temperature at normal air pressure (1013 hPa)

Concentrations of dissolved oxygen in waters are results of oxygen supplying and consuming processes

Oxygen supplying processes:

- Photosynthesis
- Entry of oxygen over water surface in case of undersaturation
- Entry by discharge from tributaries

Oxygen consuming processes:

- Consumption by respiration of organisms
- Microbial degradation and mineralisation of organic material by decomposers
- Withdrawal (loss) from water surface in case of oversaturation



oxygen supplying (+) oxygen consuming (-)

- 1 Photosynthetic O₂-production
- 2 O₂-consumtion by dissimilation processes
- 3 O₂-exchange between water and atmosphere
- 4 Resultant of O_2 -production (crosswise hatched) and O_2 -consumption (simple hatched)
- 5 Real graph of O_2 in mg/l and % of saturation

Oxygen budget of a river section during a cloudless day

(Schwoerbel, J., Brendelberger, H., 2005, changed)



Dissolved oxygen of waters polluted and unpolluted with nutrients (Vereinigung Deutscher Gewässerschutz, 2003, changed)



Hydrometric Practical Training: Measuring Instruments



Handheld instruments for measurements of pH, electrical conductivity, oxygen

Hydrometric Practical Training: Nutrients

Nitrogen compounds in running waters

Ammonium (NH₄⁺)

- Liquid manure and ammonium fertilizer
- Biochemical degradation of substances containing nitrogen (natural substances and waste water)
- By air and rain into waters

Ammonia (NH₃)

- Dissociation balance with ammonium: at rising pH (>7) and temperature in favour of NH₃
- Toxic for fishes

Nitrite (NO₂⁻)

- Oxidation of Ammonia (bacteria nitrosomonas)
- Toxic for fishes at high concentrations

Nitrate (NO₃⁻)

- Oxidation of nitrite (bacteria nitrobacter)
- Even at high concentrations not harmful for water organisms
- Limiting value for drinking water 50 mg/l (danger of disease for infants)

Hydrometric Practical Training: Nutrients

Phosphorous compounds in running waters

- Necessary nutrient: Part of cell structures, important for numerous vital metabolisms (P : N

 1 : 7 optimal for development of herbal biomass)
- > Minimum factor, because usually it is only available in small concentrations

Anthropogenic sources:

- Point sources: Domestic, industrial and agricultural wastewater
- Nonpoint sources: By erosion from agricultural areas (fertilizers, pesticides), in case of large discharges by raising sediments in waters
- Entry by rain (because of high adsorption direct entry by groundwater and drain water is very small)
- Existence as inorganic and organic, undissolved and dissolved fractions
- Ortho-Phosphate(PO₄³⁻): Inorganic dissolved compounds available for herbal organisms
- Main factor for eutrophication in case of anthropogenic entry of nutrients: Excessive growth of plants with periodic variation of oxygen content: Oversaturation during the day (photosynthesis), deficits in the night (no photosynthesis)

Hydrometric Practical Training: Nutrients

Substance	Unit	Chemical Water Quality Class						
Oubstance		I	I - II	II	-		III - IV	IV
Total Nitrogen	mg/l	≤ 1	≤ 1,5	≤ 3	≤6	≤ 12	≤ 24	> 24
Nitrate Nitrogen	mg/l	≤ 1	≤ 1,5	≤ 2,5	≤ 5	≤ 10	≤ 20	> 20
Nitrite Nitrogen	mg/l	≤ 0,01	≤ 0,05	≤ 0,1	≤ 0,2	≤ 0,4	≤ 0,8	> 0,8
Ammonium Nitrogen	mg/l	≤ 0,04	≤ 0,1	≤ 0,3	≤ 0,6	≤ 1,2	≤ 2,4	> 2,4
Total Phosphate	mg/l	≤ 0,05	≤ 0,08	≤ 0,15	≤ 0,3	≤ 0,6	≤ 1,2	> 1,2
Ortho-Phosphate Phosphorus	mg/l	≤ 0,02	≤ 0,04	≤ 0,1	≤ 0,2	≤ 0,4	≤ 0,8	> 0,8
Chloride	mg/l	≤ 25	≤ 50	≤ 100	≤ 200	≤ 400	≤ 800	> 800
Sulphate	mg/l	≤ 25	≤ 50	≤ 100	≤ 200	≤ 400	≤ 800	> 800
TOC (Total organic carbon)	mg/l	≤ 2	≤ 3	≤ 5	≤ 10	≤ 20	≤ 40	> 40
AOX (adsorbable organic halogen compounds)	µg/l	"0"	≤ 10	≤ 25	≤ 50	≤ 100	≤ 200	> 200

Classification of water quality for nutrients, salts and parameters; reference value: 90th percentile (LAWA, 1998)

Hydrometric Practical Training: Measuring Instruments for Nutrients



Portable Photometers

Cuvette tests for on-site analysis of nutrients e.g. NH_4 , NO_3 , PO_4

Hydrometric Practical Training: Other Measuring Instruments

243,12 °C



Measurement of temperatures at two thermometers: Dry air temperature $T_{I}(T)$ (°C) Wet bulb temperature T₁ (F) (°C) relative humidity U (%) $U = 100 \cdot \frac{e_a(T_L(T), T_L(F))}{e_s(T_I(T))}$ Magnus formula: $e_{s}(T_{L}(T)) = C_{1} \cdot exp^{\frac{C_{2} \cdot T_{L}(T)}{C_{3} + T_{L}(T)}}$ For ice For water C_1 6,11 hPa 6.11 hPa C_2 22,46 17,62

272,62 °C

Sprung's formula:

 $\mathbf{e}_{a}(\mathsf{T}_{\mathsf{L}}(\mathsf{T}),\mathsf{T}_{\mathsf{L}}(\mathsf{F})) = \mathbf{e}_{s}(\mathsf{T}_{\mathsf{L}}(\mathsf{F})) - \gamma \cdot (\mathsf{T}_{\mathsf{L}}(\mathsf{T}) - \mathsf{T}_{\mathsf{L}}(\mathsf{F})) \cdot \frac{\mathsf{p}}{\mathsf{p}_{100}}$

 $e_s(T_L(T))$ Saturated vapour pressure (hPa)

- $e_a(T_L(T), T_L(F))$ Actual vapour pressure (hPa)
- γ Psychrometer coefficient (for water $\gamma = 0,65$ hP/°C, for ice at the wet bulb termometer

γ = 0,58 hPa/°C)

- p Air pressure at the station (hPa)
- p100 mean air pressure at level NN+100 m \approx 1000 hPa (up to station heights of NN + 800 m correction of height p/p₁₀₀ can be neglected)

 $T_L(T) - T_L(F)$ psychrometric difference (°C)

Assmann-Psychrometer

 C_3

<u>Gravimetric method</u>: Soil sample ring method, weighing wet soil, drying wet soil, weighing dry soil

m...

Gravimetric water content:

Volumetric water content:

$$w_{m} = \frac{m_{W}}{m_{t}} \cdot 100 \quad (\% \text{ by mass})$$
$$w_{V} = \frac{V_{w}}{V} \cdot 100 = w_{m} \cdot \frac{\rho_{t}}{\rho_{w}} \quad (\% \text{ by volume})$$
$$S = \frac{V_{w}}{V_{H}} \cdot 100 \quad (\% \text{ of voids})$$

Water saturation:

 w_m Gravimetric water content (%) w_V Volumetric water content (%) S Water saturation (%) m_w Mass of water of soil sample (M)

- S Water saturation (%) m_w Mass of water of soil sample (M)
- m_t Mass of soil sample (solid matter), dried at 105 °C (M)
- V Volume of soil sample (solid matter and voids) (L³)

$$V_{H}$$
 Volume of voids of soil sample (L³)

- V_w Volume of water of soil sample (L³)
- ρ_t Bulk density (M·L⁻³)

Newer method:

Time-Domain-Reflectometry-method (TDR)

From about 1980 developed further for measuring moisture in building materials, method for investigation and analysis of runtime and reflection characteristics of electromagnetic impulses and signals:

- Runtime of a electromagnetic signal along two or more parallel wave guides (probe rods) is measured
- From runtime of an impulse the dielectric constant (DC, extent for attenuation of electrical fields by nonconductors) can be determined
- > Soils mainly contain mineral compounds and water, DC of water ($\epsilon_r \approx 81$) and of dry porous material ($\epsilon_r < 5$) differ strongly
- > So DC of soils can be expressed as a function of water content in % by volume

Basis for an application of TDR-method is the equation

- Speed of an electromagnetic wave signal
- $\mathbf{c} = \frac{\mathbf{c_0}}{\sqrt{\mathbf{\epsilon_r} \cdot \boldsymbol{\mu_r}}}$

- Speed of light $(3,0.10^8 \text{ m}\cdot\text{s}^{-1})$
- c_0 Speed of light (3,0.10³) ϵ_r Dielectric constant (-)
 - Magnetic permeability of the material, in which the wave signal spreads (-)

In nonmagnetic matters $\mu_r = 1$

Electromagnetic wave signals run along the probe rods, are reflected at the tip of the rods and run back the same way.

Runtime t is measured.

By means of the known length of the probe rods I a calculation of the velocity

$$\mathbf{c} = \frac{2\mathbf{I}}{\mathbf{t}}$$
 and so of DC $\varepsilon_r = \left(\frac{\mathbf{c_0} \cdot \mathbf{t}}{2\mathbf{I}}\right)^2$ is possible.

Because of very short runtimes time measurements are difficult and require steep edged very short electromagnetic signals (<10⁻⁹ s)

Further development of TDR-method:

TRIME-methods (Time Domain Reflectometry with Intelligent MicroElements):

- Water contents up to 100 % by volume can be measured
- Dependency of electric conductivity of soil water is widely eliminated (up to 2 mS/cm)
- Measurements of runtime of electromagnetic signals are performed by direct time measurements instead of indirect measurements of voltage in case of other TDRmethods



Topsoil probe TRIME-EZ



	Power supply	7 V 15 V-DC	
ng on tube tion	Supply current	8mA standby, 200mA during 4 s of measuring time	
device HD	Measuring range	0 100 % by volume water content	
5 m 5 m 5 m 63 mm 190 mm ods 40 mm 6 mm 160 mm	Measuring accuracy Range 0 40 % by volume Range 40 60 % by volume	± 1 % by volume ± 2 % by volume	
	Repeating accuracy	± 0.3 Vol%	
	Bulk electrical conductivity	0 2 dS/cm	
	Pore water electrical cond.	010 dS/cm	
	Temperature range	-15 °C 50 °C	
	Temperature caused drift	max. ± 0.4 %	

TRIME-IPH and T3-tube probe for greater depths of measuring

Cable in a protective hosepipe

Probe head TRIME-IPH



Power supply	7 V 15 V-DC		
Supply current	8mA standby, 200mA during 4 s of measuring time		
Measuring range	0 60 % by volume water content		
Measuring accuracy Range 0 40 % by volume Range 40 60 % by volume	\pm 2 % by volume \pm 3 % by volume		
Repeating accuracy	± 0.3 Vol%		
Bulk electrical conductivity	0 2 dS/cm		
Pore water electrical cond.	010 dS/cm		
Temperature range	-15 ⁰C 50 ⁰C		
Temperature caused drift	max. ± 0.5 %		



Measurement of soil profiles in 18 cm (T3) increments to a depth of 3 meters in any number of tubes (e.g. root zone to about 1.0 m)

TECANAT-plastic tubes must be installed prior to taking the measurements by using a specially developed drilling set.

- > Measuring probe has to be imported to the requested depth of the tube.
- The electric lines of the T3-Tube relevant for measuring reach out about 15 cm into the soil.

Because of the elliptic form of the measuring volume, it is sensible to turn the probe in the tube and to average the values of water content.



TRIME-HD handheld display device





Left side: Battery charger, analogue output cable interface







Top side: Probe interface (TRIME-EZ/-EZC/-IT/-ITC/-IPH)

Hydrometric Practical Training: Literature

Council Directive 78/659/EEC of 18.07.1978 on the quality of fresh waters needing protection or improvement in order to support fish life (directive for fish waters).

Council Directive 75/440/EEC of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States.

DVWK- Merkblätter zur Wasserwirtschaft, H. 227: Aussagekraft von Gewässergüteparametern in Fließgewässern, Teil 1: Allgemeine Kenngrößen, Nährstoffe, Spurenstoffe und anorganische Schadstoffe, Biologische Kenngrößen. Hamburg und Berlin: Paul Parey, 1993.

Schwoerbel, J., Brendelberger, H.: Einführung in die Limnologie. 1. Aufl., München: Spektrum Akademischer Verlag, 2005.

Vereinigung Deutscher Gewässerschutz e.V. (VDG) (Hrsg.): Ökologische Bewertung von Fließgewässern. Schriftenreihe, Band 64, 2. Aufl., Bonn, Eigenverlag, 2003.

Verordnung über die Qualität von Wasser für den menschlichen Gebrauch – TrinkwV 2001

– Trinkwasserverordnung vom 21.05.2001. BGBI. I S. 959.

Weiner, E. R.: Applications of environmental aquatic chemistry – a practical guide. Boca Raton: 2008.

Woker, H: Die Temperaturabhängigkeit der Giftwirkung von Ammoniak auf Fische. Internat. Ver. f. theoret. u. angew. Limnologie 10 (1949), S. 575 – 579.