

## **MEASUREMENT TOOLS: WATER SYSTEMS (INLAND WATERS)**

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### **Summary**

The article describes main items for the inquiry of the inland water quality. Based on the analytical cycle internationally accepted field techniques and instrumental methods for water analysis are presented in more detail. Important aspects for the successful and representative preparation of sampling, taking and storage of samples are listed and discussed. A tabulated overview on the kind of sampling boxes, sampling storage condition and maximum holding time for special parameters helps to get high quality data. Internationally accepted methods for physicochemical, chemical and microbiological water examinations are summarized and referred to standard literature. The use of these methods allows the comparison of the analytical data with international level data. Based on these results, international experience and help can be used to increase the inland water quality.

Finally, the fact should be remembered once more that true analytical results with a good judgement and assessment are the basis for correct description of inland water quality. High data quality as a base for the correct water quality characterization can be guaranteed only if the main and important aspects of an analytical cycle have been taken into consideration, beginning with the preparation of sampling, sample storage and analysis.

### **1. Introduction**

“The Earth is a water planet,” readable at the homepage of the Environmental Protection Agency (EPA) (<http://www.epa.gov/ow/>), means, that all life depends on water. Depending on its resource the inland water itself can be divided into groundwater and surface water.

Focusing on the use of the inland waters they are important:

- as habitat for fish and aquatic plants;
- as drinking water;
- for bathing purposes;
- for washing purposes;
- for swimming and water sports;
- as cooling agent; solvent; cleaning agent, building auxiliary material in the industry;
- for irrigation in agriculture;
- for cleaning purposes of animals and plants.

Water management is essential to guarantee all these different purposes of the inland waters also on a long-term basis. Substantial information (concluded in the analytical cycle Figure 1) must be processed correctly to be successful with the control measures and precautions.

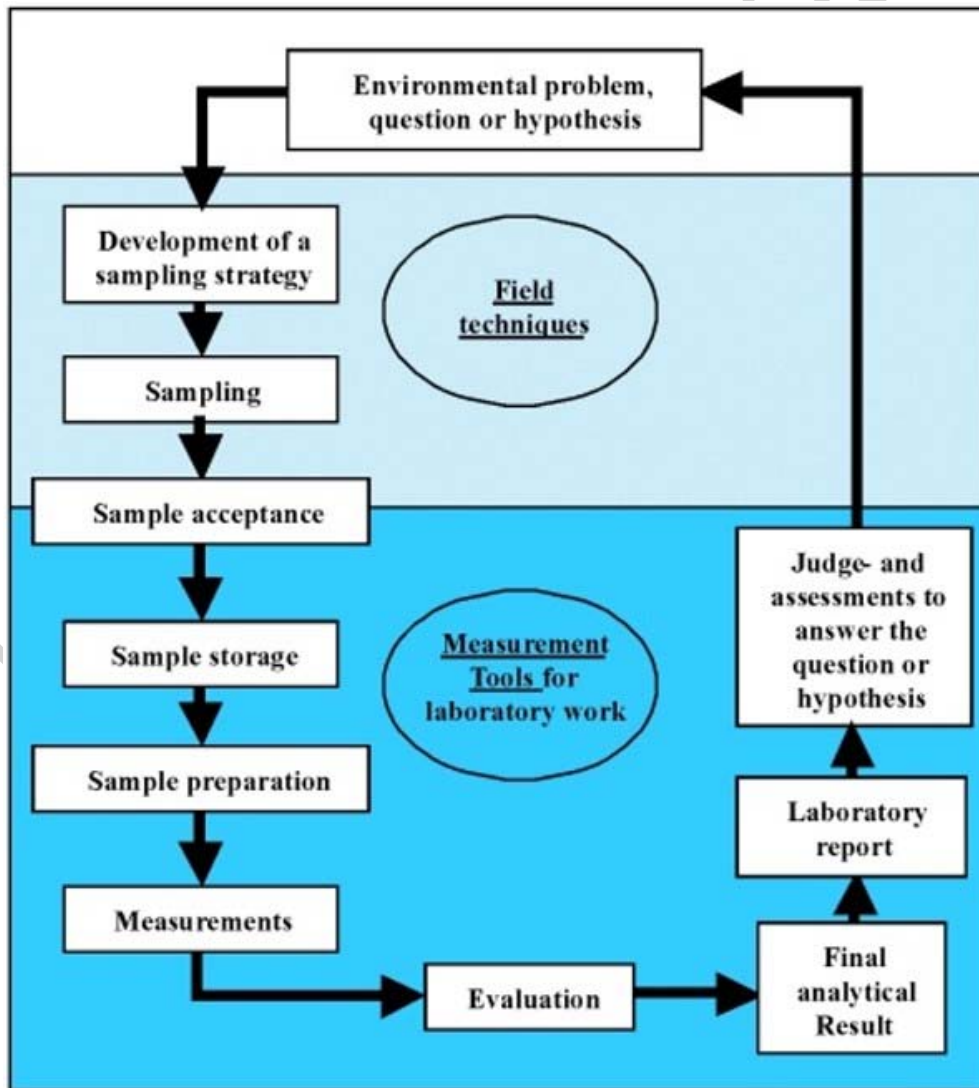


Figure 1. Analytical cycle with field techniques and measurement tools.

The cycle shown in Figure 1 already begins with the formulation of a valid question or hypothesis during planning the analyses. Only by this way the results of the investigations can supply the necessary information. After a well and correctly formulated question a meaningful, adequate sampling as well as optimal sample storage (in this paragraph summarized under “field techniques”) must take place. Closely connected with the field techniques are the sample preparation and sample analyses of the inland waters (measurement tools). Errors made within this area lead to false estimates and conclusions during the judgement and assessment. (See: Field techniques, measurement tools.)

## **2. Field Techniques**

The following main key points of the analytical cycle should be described in more detail to get the necessary information about the inland water quality.

### **What is important to know about the water in relation to the purpose and which parameters can optimally characterize the water quality?**

Reichert has given a good example for characteristic parameters depending on the special kind of an inland water:

Both the work expended and the costs increase from the first to the last group in the table. Often it will not be necessary to determine all parameters to answer the question or hypothesis. Group or sum parameters like BOD, COD, DOC, TOC, AOX give a first overview on the expected max. concentration of a single parameter detected in sum with other parameters. In comparison to the total concentration of the sum parameter the concentration of individual substances is often several times less.

A stepwise working with a pre-investigation of sum parameters can be helpful to answer the question and to find out if more tests are necessary or not.

### **Which laboratory can perform the requested tests and measures?**

Depending on the analytical question, the budget and the technical possibilities to investigate characteristic parameters should be mentioned for analyses. A corresponding laboratory for these analyses is to be selected. For a pre-selection a visit at the laboratories with the civil request for the analytical investigation of test water with substances in the estimated range for future analysis can be helpful. The kind of chain of custody and the analytical report including the quality assurance measures requested give a first impression about the importance of quality of laboratory. Accreditation for the requested parameters or the certification according to the ISO standard is often a good reference for high data quality. For a final selection only those laboratories should take part, the test results of which of the test waters were close to the true values.

Parameter	Ground water	Seepage water	Surface water	Table water	waste water	International Norms
<b>Aggregate properties</b>						
Taste	x			x		EN 27887
Odour	x	x	x	x	x	EN 27027
Turbidity	x	x	x	x	x	ISO 7027
Colouring	x	x	x	x	x	ISO 7887
<b>Physico - chemical parameter</b>						
Temperature	x	x	x	x	x	DIN 38405 T4
pH Wert	x	x	x	x	x	ISO 10523
Conductivity	x	x	x	x	x	ISO 7888
Redox potential	x	x	x	x		DIN 38407T6
Absorption at 254 nm	x					DIN 38404 T3
<b>Microbes</b>						
Total coliforms	x	x	x	x	x	ISO 9308/1/2
Faecal coliforms	x	x	x	x	x	ISO 9308/1/2
Chlorophyll A			x			ISO 10260
Faecal streptococci	x	x	x	x	x	ISO 9308/1/2
<b>Group- and sum parameters</b>						
Total solids residue		x	x			ISO CD11923
Residue on ignition		x	x			ISO CD11923
Settable matter		x	x		x	DIN 38409 T9
Chemical Oxygen Demand COD	x	x	x		x	ISO 6060
Biological Oxygen DemandBOD	x	x	x		x	ISO 5815
Dissolved Organic Carbon DOC	x	x	x		x	ISO 7827
Total Organic CarbonTOC	x	x	x		x	ISO 8245
Phenol Index	x	x	x	x	x	ISO 6439
Hardness	x		x	x		DIN 38409 T 6
<b>Cations and Anions</b>						
Sodium	x	x	x	x		ISO 9964-1 ISO 9964-3
Potassium	x	x	x	x		ISO DIS 9964-2 ISO 9964-3
Ammonia	x	x	x	x		ISO 5664 ISO 7150/1
Nitrite	x		x	x	x	ISO 6777 ISO 10304/1+2 ISO DIS11732
Nitrate	x		x	x	x	ISO 7890/1+2 ISO 10304/1+2
Calcium	x	x	x	x		ISO 6058
Magnesium	x	x	x	x		ISO 6058
Iron	x	x	x	x		ISO 6332
Manganese	x	x	x	x		ISO 6333
Chloride	x	x	x	x	x	ISO 9297 ISO 10304/1+2
Fluoride	x	x	x	x	x	ISO 10359/1/2 ISO 10304/1+2
Sulphate	x	x	x	x	x	ISO 9280 ISO 10304/1+2
Sulfide		x			x	ISO 10530 ISO DIS13358
Cyanide	x	x	x	x	x	ISO 6703/1-3
Phosphate	x	x	x	x	x	ISO 6878/1 ISO 10304/1+2
Oxygen	x		x	x		ISO 5813 ISO 5814

Parameter	Ground water	Seepage water	Surface water	Table water	waste water	International Norms
Oxygen	x		x	x		ISO 5813 ISO 5814
<b>Heavy metals</b>						
Arsenic	x	x	x	x		ISO 6595 ISO DIS11885
Antimony			x	x		ISO DIS11885
Selen			x	x		ISO 9965 ISO DIS11885
Lead	x	x	x	x		ISO DIS11885
Barium			x	x		ISO DIS11885
Bor		x	x	x		ISO 9390 ISO DIS11885
Cadmium	x	x	x	x		ISO 5961 ISO DIS11885
Chromium	x	x	x	x		ISO 9174 ISO 11083 ISO DIS11885
Mercury	x	x	x	x		
Copper	x	x	x	x		ISO DIS11885
Nickel	x	x	x	x		ISO DIS11885
Zinc	x	x	x	x		ISO DIS11885
<b>Organic contaminants</b>						
AOX		x	x	x	x	ISO 9562
Easily volatile halogenated hydrocarbon	x	x	x	x	x	ISO DIS10301
Low volatile hydrocarbons	x	x	x	x	x	ISO DIS6468 ISO DIS10301
PCB	x	x	x	x	x	ISO DIS 11369
PAH	x	x	x	x	x	ISO DIS 7981-2 ISO DIS 7981/1
<b>Radionuclides</b>						
alpha activity	x		x	x	x	ISO 9696
beta activity	x		x	x	x	ISO 9697

Table 1. Characteristic parameters for water examinations with their international norms.

According to the facilities of the laboratories three categories for bacteriological and chemical investigations can be differentiated:

- **Basic laboratories.** This is the lowest level of a laboratory, which could also be described as peripheral. Often they are located in smaller provincial towns and at small water works. They are designed to carry out bacteriological routine analyses for natural waters, drinking water, treated wastewater and other effluents. It is equipped to perform the following tests:
  - total coliforms
  - fecal coliforms.
- **Intermediate laboratories.** These are located in provincial capitals or other major municipalities. The purpose of these intermediate laboratories is to carry out physical and chemical analyses of natural waters and drinking waters in a more

complete way than a basic water laboratory. Additionally to the basic parameters these laboratories should have the capability to determine the following parameters:

- chemical oxygen demand (COD)
  - biological oxygen demand (BOD)
  - sodium, potassium, calcium, magnesium, manganese, iron
  - ammonia
  - sulfide
  - nitrite, nitrate, phosphate, fluoride, chloride, sulfate
  - sulfide, cyanide, dissolved oxygen
  - heavy metals like As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn
  - AOX.
- **Central laboratories.** These Laboratories are at the highest level. Often they are located in the capitals. They should be in a position to analyse water and wastewater samples for nearly all parameters listed in the table 1 above.

### **Where, how and how often must the sampling take place?**

Only in close co-operation with the selected laboratory, local and regional authorities, non-governmental organizations, the local population and sometimes also with the military, the monitoring concept can be adequately worked out.

By talking with these people often main and important socioeconomic, hydrogeological and hydrochemical information can be collected. The following main items should be mentioned:

- information about possible purchase of good maps (may be also of satellite data);
- mean and extreme water levels;
- information about unusual hydrological features like shallows, whirlpools, stratification and sedimentation areas;
- possible contamination caused by settlements, industry and agriculture;
- observations of temporarily occurring turbidity, smells, coloring;
- main and important socioeconomic changes in the last years.

According to the analytical question, the financial budget and analytical possibilities as well as the sampling frequency and the sampling locations must be defined with the help of the pre-information.

A more detailed description about the monitoring concept is in chapter Field Techniques: Inland Waters

### **Which kind of sample containers, what minimum sample sizes are necessary from the analytical point of view, and how to preserve and store the samples?**

Sampling experiences of many years about necessary minimum sample size, kinds of sample containers and storage conditions are concluded in the “standard methods” (Table 2) and should be considered.

Determination	Container	Minimum Sample Size mL	Preservation	Maximum Storage Recommended/Regulatory
Acidity	P, G(B)	100	Refrigerate	24 h/14 d
Alkalinity	P,G	200	Refrigerate	24 h/14 d
BOD	P,G	1000	Refrigerate	6 h/48 h
Boron	P	100	None required	28 d/6 months
Bromide	P,G	-	None required	28 d/28 d
Carbon, organic, total	G	100	Analyze immediately; or refrigerate and add HCl to pH<2	
Carbon dioxide	P,G	100	Analyze immediately	stat/N.S.
COD	P,G	100	Analyze as soon possible, or add H <sub>2</sub> SO <sub>4</sub> to pH<2;refrigerate	
Chlorine, residual	P,G	500	Analyze immediately	0.5 h/stat
Chlorine dioxide	P,G	500	Analyze immediately	0.5 h/N.S.
Chlorophyll	P,G	500	30 d in dark	30 d/N.S.
Color	P,G	500	Refrigerate	48 h/48 h
Conductivity	P,G	500	Refrigerate	28 d/28 d
Cyanide: Total	P,G	500	Add NaOH to pH>12, refrigerate in dark	24 h/14 d; 24 h if sulfide present
Amenable to chlorination	P,G	500	Add 100 mg Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /L	stat/14 d; 24 h if sulfide present
Fluoride	P	300	None required	28 d/28 d
Hardness	P,G	100	Add HNO <sub>3</sub> to pH<2	6 months/6 months
Iodine	P,G	500	Analyze immediately	0.5 h/N.S.
Metals, general	P(A), G(A)	-	For dissolved metals filter immediately, add HNO <sub>3</sub> to pH<2	6 months/6 months
Chromium VI	P(A), G(A)	300	Refrigerate	24 h/24 h
Copper by colorimetry*				
Mercury	P(A), G(A)	500	Add HNO <sub>3</sub> to pH<2, 4°C, refrigerate	28 d/28 d
Nitrogen:				
Ammonia	P,G	500	Analyze as soon possible, or add H <sub>2</sub> SO <sub>4</sub> to pH<2;refrigerate	7 d/28 d
Nitrate	P,G	100	Analyze as soon possible or refrigerate	48 h/48 h (28 d for chlorinated samples)
Nitrate + nitrite	P,G	200	Add H <sub>2</sub> SO <sub>4</sub> to pH<2, refrigerate	none/48 d
Nitrite	P,G	100	Analyze as soon as possible or refrigerate	none/48 d
Organic, Kjeldahl	P,G	500	Refrigerate, add H <sub>2</sub> SO <sub>4</sub> to pH<2	7 d/28 d
Odor	G	500	Analyze as soon as possible;	6 h/N.S.
Oil and grease	G, wide-mouth calibrated	1000	Add H <sub>2</sub> SO <sub>4</sub> to pH<2, refrigerate	28 d/28 d

Table 2. Main information about the minimum sample size, kind of sample containers and storage conditions.

## Which parameters should be determined on the sampling site?

The best way to get true analytical results is to measure the parameters directly after sampling. The following parameters can be determined directly after sampling, without preservation and storage:

- pH
- dissolved oxygen
- turbidity
- water temperature
- conductivity
- Redox potential
- odors
- color
- taste.

See: Group parameters, sum parameters, BOD, COD, DOC, TOC, AOX, pH, turbidity, conductivity, redox potential.

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### Biographical Sketches

**Wolf von Tümpling** was born at Erfurt, Germany, on 21 December 1964. After school in Erfurt, and military service, 1986–1991, he studied chemistry at the Friedrich-Schiller-University, Jena, finishing with a Diploma examination in chemistry (master of science). 1995, finishing doctoral thesis at Friedrich-Schiller-University, Jena with PhD (magna cum laude). Work at the Max-Planck-Institute for Limnology, Plön, 1991 to 1994, with activities of planning and installation of a modern environmental analytical laboratory for mercury analyses according to the requirements of ISO Guide 25 in Cuiabá, Brazil. Assistance with project management of the German Brazilian cooperative project with independent responsibility for the 'mercury' subproject. Expert activity for the Ecuadorian project "Mineria sin contaminación" sponsored by the Swiss department of aid to developing countries CORTESU. Work at the GKSS Research Centre Geesthacht, 1994 to 1997, as assistant to the head, finally as the head, of the German-Czech cooperative project 'Patterns of Elements in the Elbe River and its Tributaries'. During this time teaching at the University of Lüneburg with lectures on 'Chemical environmental loads' and 'Statistical Methods in Environmental Analysis'. Work for the Pollution Control Department of the Thai government, Bangkok, 1997 to 1999, as Senior Advisor, supported by the German government, for the planning and installation of a new environmental analytical laboratory, especially for water analyses for heavy metal and organic contaminant monitoring programs. Expert activity for implementing main and important quality assurance procedures according to ISO Guide 25, including adaptation, validation and troubleshooting of analytical procedures for GCECD, GCMS and IC, and implementation of a LIMS system. Since 2000, work at the UFZ Center for Environmental Research Leipzig-Halle, Magdeburg, as the head of the department for aquatic chemistry.

**Walter Geller** was born on 11 December 1944. He studied biology at the universities of FU Berlin, Kiel and Freiburg, finished in 1970 with a thesis on hydrography and fauna of a running water system in the Upper-Rhine valley. Ph.D. in 1975 with a dissertation (Profs. Elster, Lampert) about an experimental ecophysiological study on the feeding rate of *Daphnia*. In his first professional position, he became deputy head of the research laboratory of 'Bodensee-Wasserversorgung', the largest drinking water plant of Germany, where he worked on all kinds of drinking-water problems. He developed a computerized biological early-warning system using *Daphnia* and a weakly electric fish. Then he changed to the Limnological Institute of Constance University working on the zooplankton community of Lake Constance. He reached the habilitation degree in 1986. As one of the principal researchers of the 'Sonderforschungsbereich' (SFB 248) of the German Research Foundation on 'Cycling of Matter in the Ecosystem of Lake Constance' he worked on 'zooplankton in the pelagic zone', and on the assessment of general characteristics on the ecosystem's level. In a Chilean-German project, the preandine lakes of Patagonia were investigated. In 1992 he became head of the department of inland water research in Magdeburg, belonging to the national research centers GKSS/Geesthacht (until 1994), and UFZ-Center for Environmental Research/Leipzig-Halle Ltd. (since 1995). Research fields are environmental problems and limnology of the river Elbe, of natural lakes and of opencast lignite-mining lakes in the area of the former G.D.R., including many geogenically acidic lakes. Professor of limnology of the Martin-Luther-University Halle-Wittenberg since 1994. About 70 publications in scientific journals and books.