Chemistry for Civil Engineering 811.357

Teil: Sampling, Analyses

University of Natural Recources and Applied Life Sciences, Vienna
Department of Water, Atmosphere and Environment

Ao.Univ.Prof.DI.Dr. Maria Fürhacker
Institut für Siedlungswasserbau, Industriewasserwirtschaft und Gewässerschutz
maria.fuerhacker@boku.ac.at

Content

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- Sampling
- Analyses

Sampling

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Programm strategies

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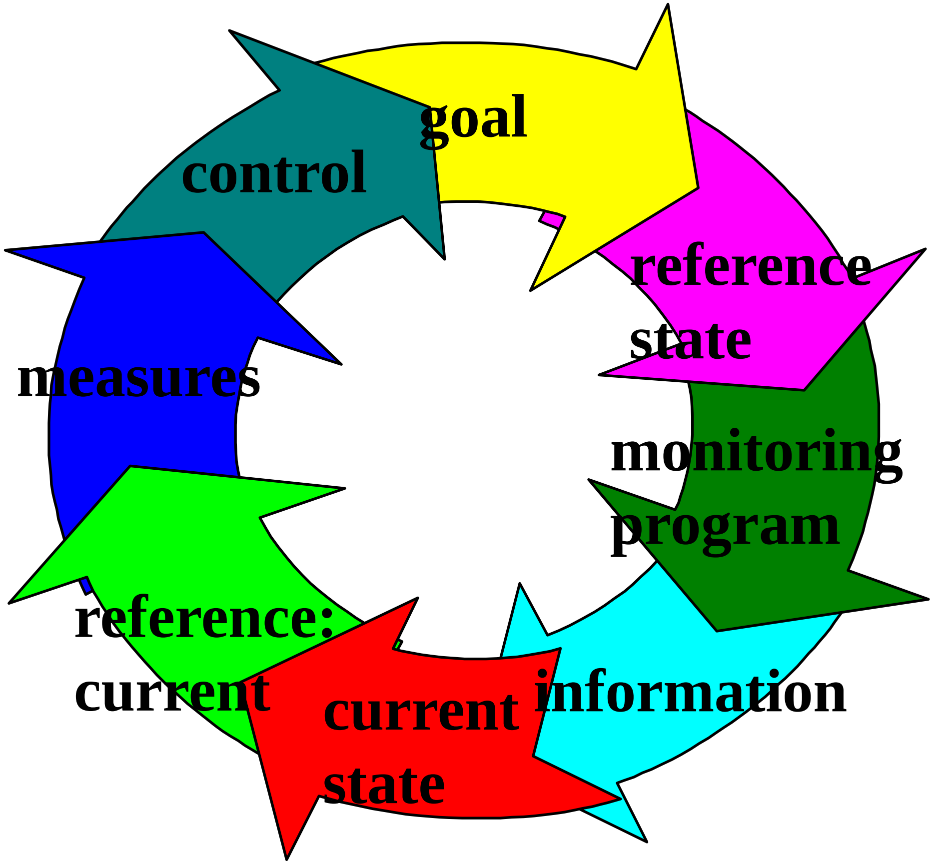

Type of sampling programs

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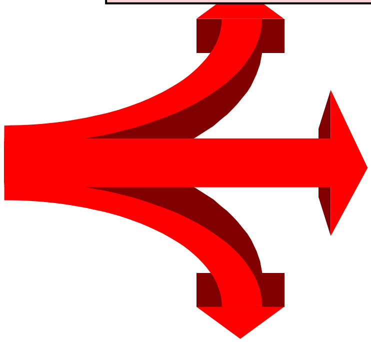
test for regulatory compliance
Short term corrections

Sampling



Quality characterization
Characterisation of trends

identify existing/emerging
water quality problems – source of contamination

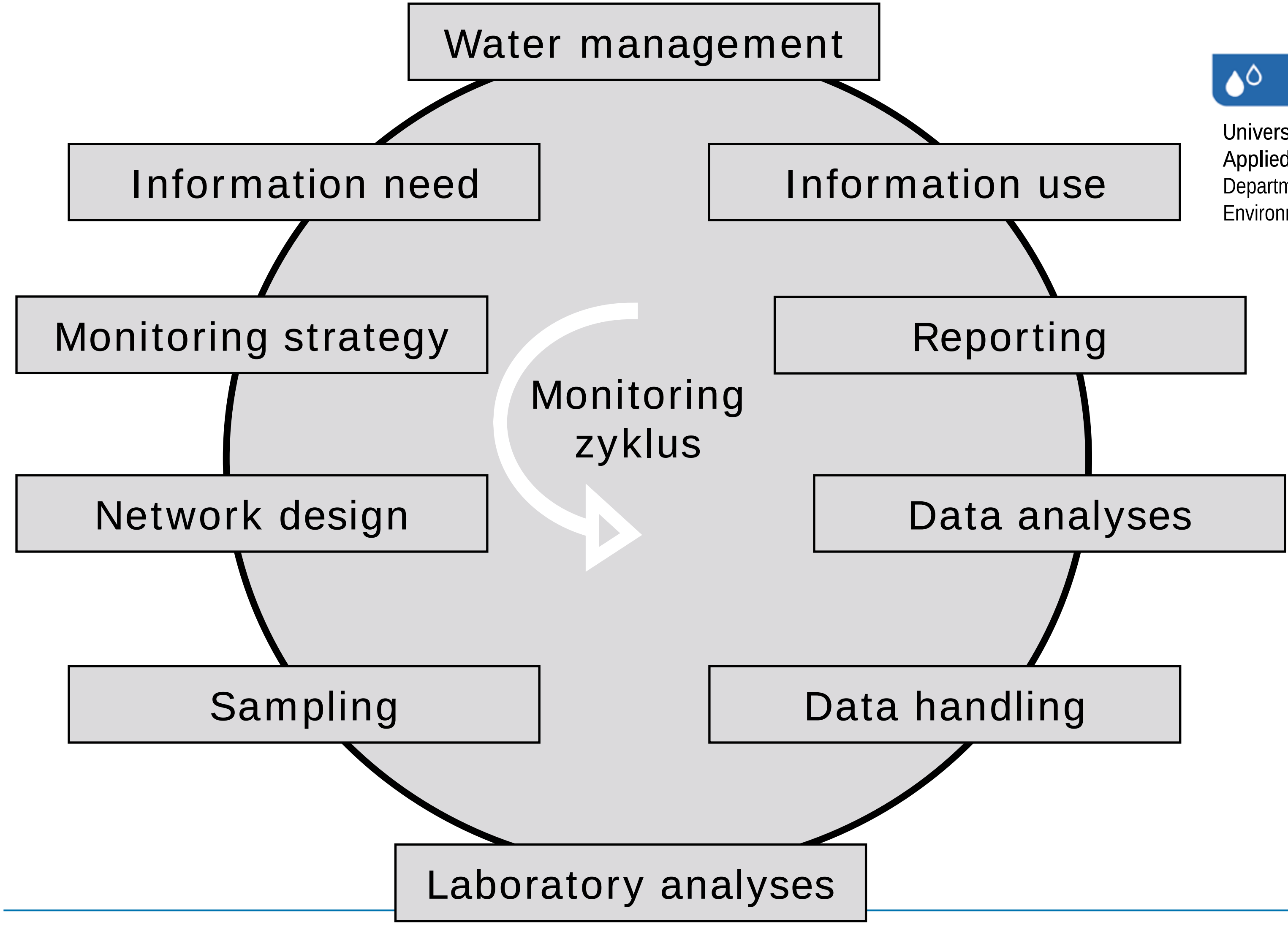
an appropriate sampling frequency is important
lab/personnel resources limit samples that can be collected and analyzed in acceptable time frame

Developing sampling strategies

Components and considerations

- Time- vs flow-weighted sampling
- Discrete and composite sampling
- Sampling goal
- Sampling and analysis resources
- Watershed characteristics

Water monitoring program



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Establishment of a monitoring program

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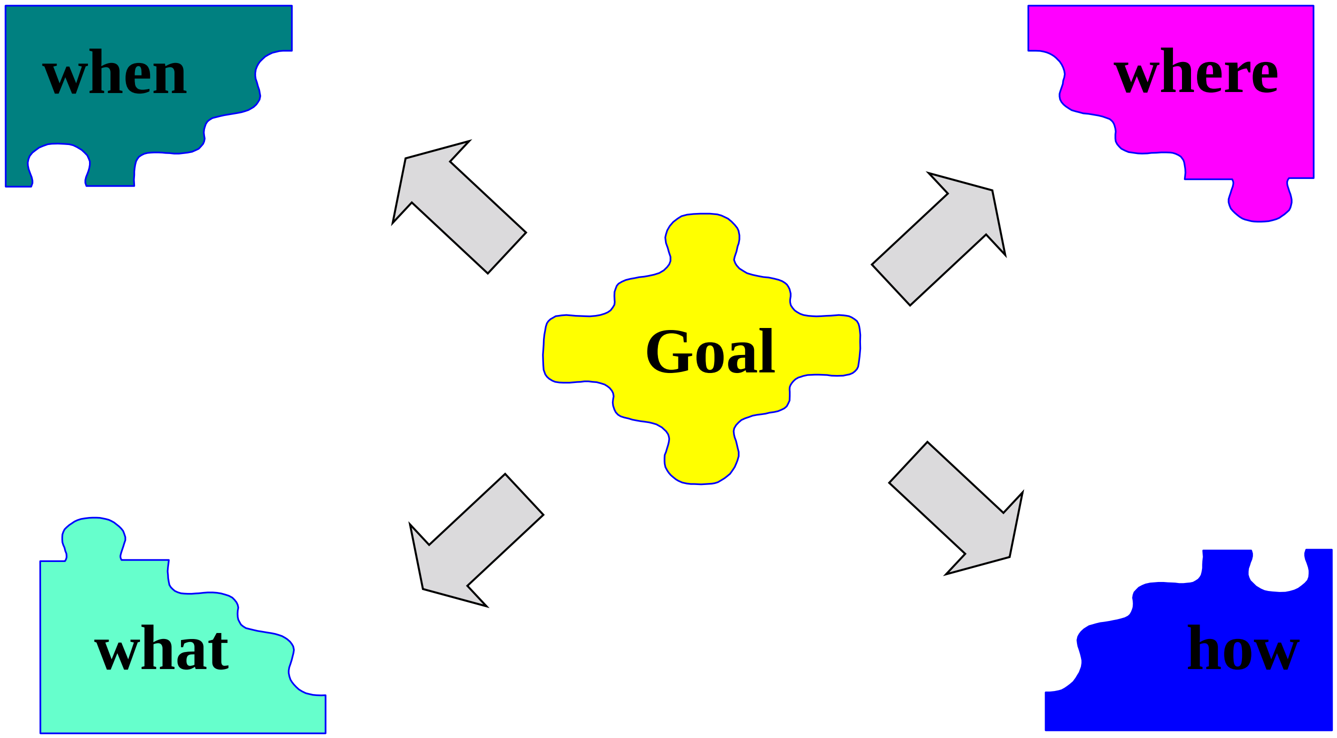

Parameter selection with consideration of the origin

	Waste water	Run-off	Agriculture	Deposition
Nutrient				
Ammonia	xxx	xx	xxx	
Nitrate/nitrite	xxx	xx	xxx	xxx
Norg	xxx	xx	xxx	
Phosphorus	xxx	xx	xxx	
Organic substances				
TOC	x	x	x	
DOC	xx	xx	x	
BOD	xxx	xx	xxx	

and
and

Parameter selection with consideration of the use

	Background monitoring	Aquatic biocoenoses	Drinking water	Bathing water	Agriculture
Nutrients					
Ammonia	x	xxx	x		
Nitrate/nitrite	xx		xxx		
Norg					
Phosphorus	xx	(xxx)			
Organic substances					
TOC	xx		x	x	
COD	xx	xx			
BOD	xxx	xxx	xx		x

Physical and chemical monitoring for drinking water (WHO, 2004)

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Physical parameters like:

- Temperature
- pH
- Conductivity
- ORP Potential (Eh)
- Turbidity
- Total suspended solids (filterable)
- Total dissolved substances

Chemical parameters like:

- free Chlorine
- Nitrate
- Fluoride
- Arsenic
- Aluminium
- Lead
- THMs
- some pesticides, etc..

Drinking water investigations (Austria)(BGBl.304/2001idgF 2008)

Routine monitoring

Parameter	Wert	
Geruch, Geschmack, Färbung		
Temperatur	25	C
Leitfähigkeit	2500	µS cm^{-1}
pH-Wert	>6,5 – <9,5	(-)
Trübung	annehmbar	
Gesamthärte		
Carbonathärte,Säurekapazität pH 4,3		
Oxidierbarkeit	5 (20)	mg/l O_2 ($KMnO_4$)
TOC	ohne anormale Veränderung	
Ammonium	0,5	mg/l
Nitrit	0,1	mg/l
Nitrat	50	mg/l
Chlorid	250	mg/l
Sulfat	250	mg/l
Eisen (Summe Fe)	0,2	mg/l
Mangan	0,05	mg/l
Aluminium	0,2	mg/l
Chlor, ClO_2, O_3, UV_{254}		

Water sampling, analysis, and interpretation

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- Step 1: Prepare sample containers for sampling.
- Step 2: The sampling procedure.
- Step 3: Transport to the laboratory for analysis.
- Step 4: Processing the water sample.
- Step 5: Analysis.

- Interpretation of the data

Water sampling, analysis, and interpretation

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Step 1: Prepare sample containers for sampling.

- These containers mustn't contain any of the compounds that samples are to be analyzed for.
- Sampling bottle material must be suitable for sampling the water without affecting the compound.
- glass for organic or colloidal dissolved inorganic substances
  - special treatment for trace elements and micro-pollutants
  - AOX, POX-samples- brown glass bottles with air tight glass stoppers
- plastics
  - Na, B in plastic bottles
- aluminium
  - e.g. nonylphenols

Sample composition

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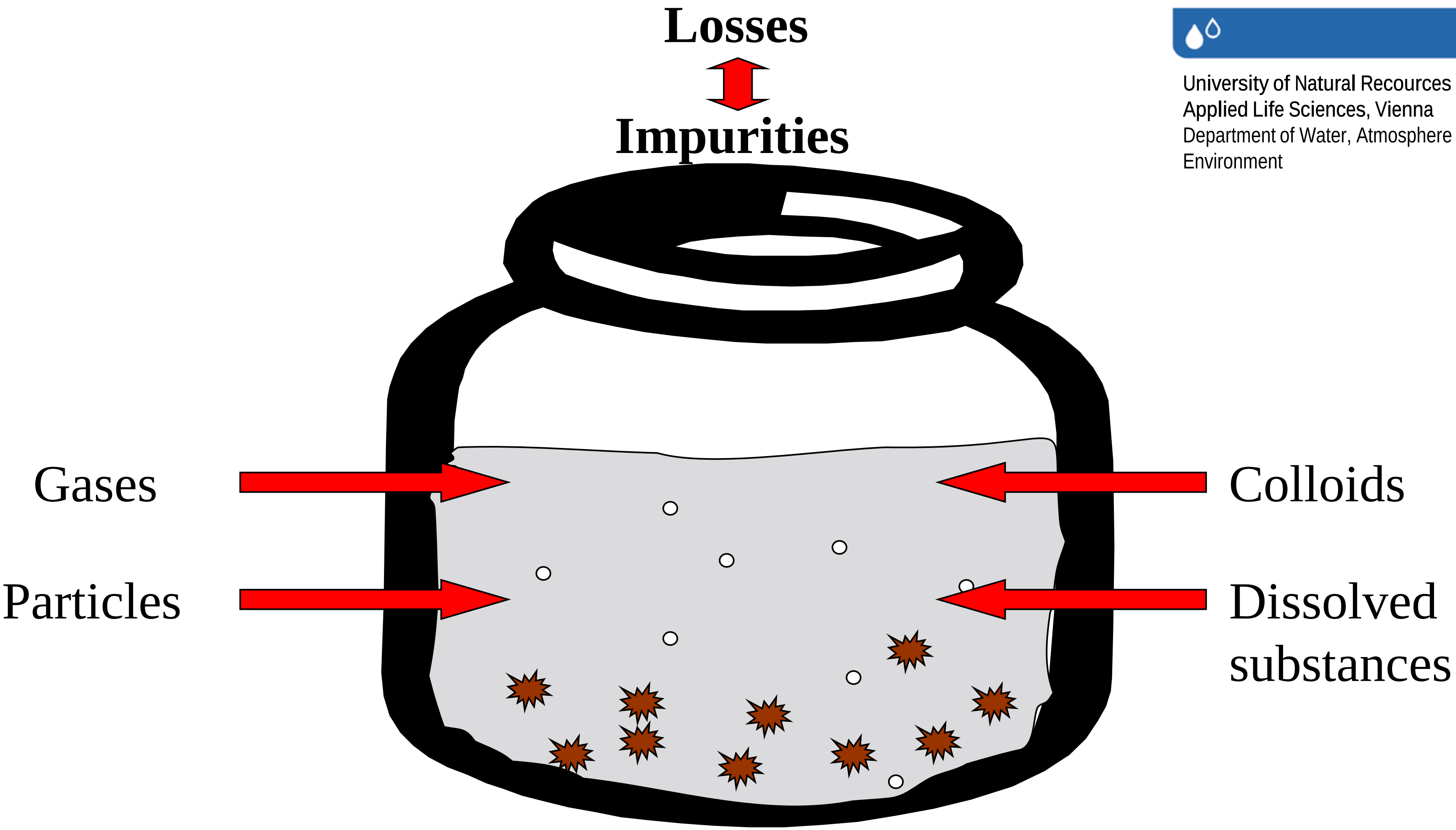

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Step 2: The sampling procedure.

- This must be rigorous, ensuring that a representative sample is collected and at no time is the sample or sample bottle contaminated by the collector.
- This is no trivial task when it comes to collecting samples with low levels of compounds such as phosphorus.
- Depending on the compounds to be analyzed, a preservative may be necessary.

Balance between goals and resources

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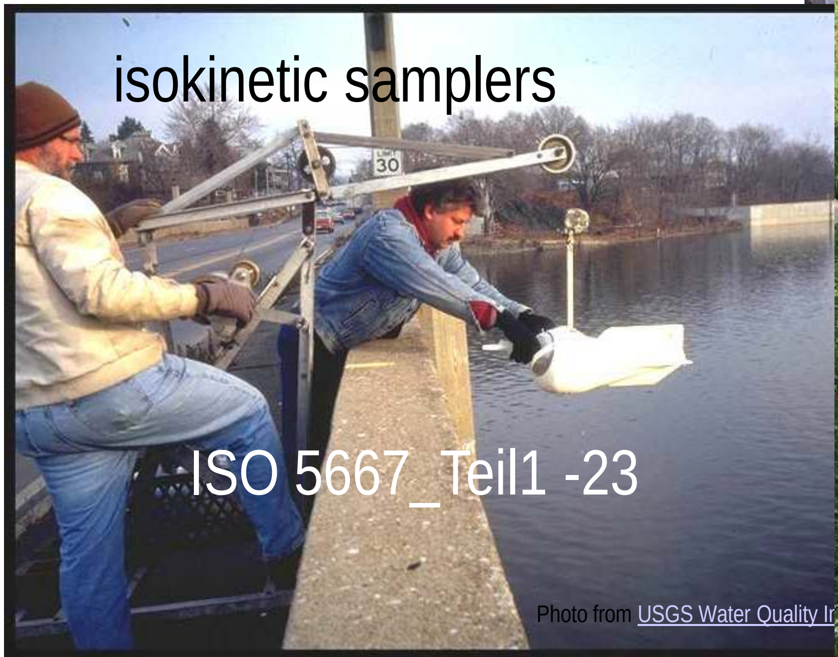
- Attempt to adequately sample water quality within project resources
- Sampling components affect this balance between:
  - **Uncertainty and sample numbers**
- Discussion based on this balance



Selection of sample typ

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fluctuation in quality

fluctuation in quantity

low

high

low

qualified grab samples

high

time weighted composite samples

volume or flow weighted composite samples

ÖNORM EN ISO 5667-1 - 22 Wasserbeschaffenheit — Probenahme

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- Part 1: *Guidance on the design of sampling programmes*
- Part 3: *Guidance on the preservation and handling of water samples*
- Part 4: *Guidance on sampling from lakes natural and man-made*
- Part 5: *Guidance on sampling of drinking water and water used for food and beverage processing*
- Part 6: *Guidance on sampling of rivers and streams*
- Part 7: *Guidance on sampling of water and steam in boiler plants*
- Part 8: *Guidance on sampling of wet deposition*
- Part 9: *Guidance of sampling from marine waters*
- Part 10: *Guidance of sampling of waste waters*
- Part 11: *Guidance of sampling of groundwaters*
- Part 12: *Guidance on sampling of bottom sediments*

ÖNORM EN ISO 5667-1 - 22 Wasserbeschaffenheit — Probenahme

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- Part 13: *Guidance on sampling of sludges from sewage and water-treatment works*
- Part 14: *Guidance on quality assurance of environmental water sampling and handling*
- Part 15: *Guidance on preservation and handling of sludge and sediment samples*
- Part 16: *Guidance on biotesting of samples*
- Part 17: *Guidance on sampling of suspended sediments1*)
- Part 18: *Guidance on sampling of groundwater at contaminated sites*
- Part 19: *Guidance on sampling in marine areas*
- Part 20: *Guidance on the use of sampling data for decision making – Compliance with limits and classification systems*
- Part 21: *Guidance on sampling of drinking water distributed by tankers or means other than distribution pipes*
- Part 22: *Guidance on design and installation of groundwater sample points2*)
- *Part 23: Determination of priority pollutants in surface water using passive sampling*

Water sampling, analysis, and interpretation

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Step 3: Transport to the laboratory for analysis.

- This needs to be done under appropriate conditions, often in a dark cooler with ice packs.

Parameter – changes during transportation

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- Typ 1: do not change
  - Arsenic, chloride, fluoride, total hardness, sodium, pesticides, salt content
- Typ 2: changes are likely
  - Aluminium, chloroform, iron, manganese, pH, chlorine, oxygen
  - Substances as contamination from the pipes: benzo(a)pyren, copper, zinc, lead

Modification of the sample

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- Chemicals could react with each other for instance:
  - Iron or manganese with dissolved oxygen or phosphate to precipitated iron and manganese oxidhydrates and phosphates, respectively.
  - pH- value can change through loss of dissolved CO_2

Preservation

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Please discuss with the laboratory!!

- Cooling (4°C)
- Acidification pH < 2
- Freezing
- Filtration
- Special conservation

Sampling protocol

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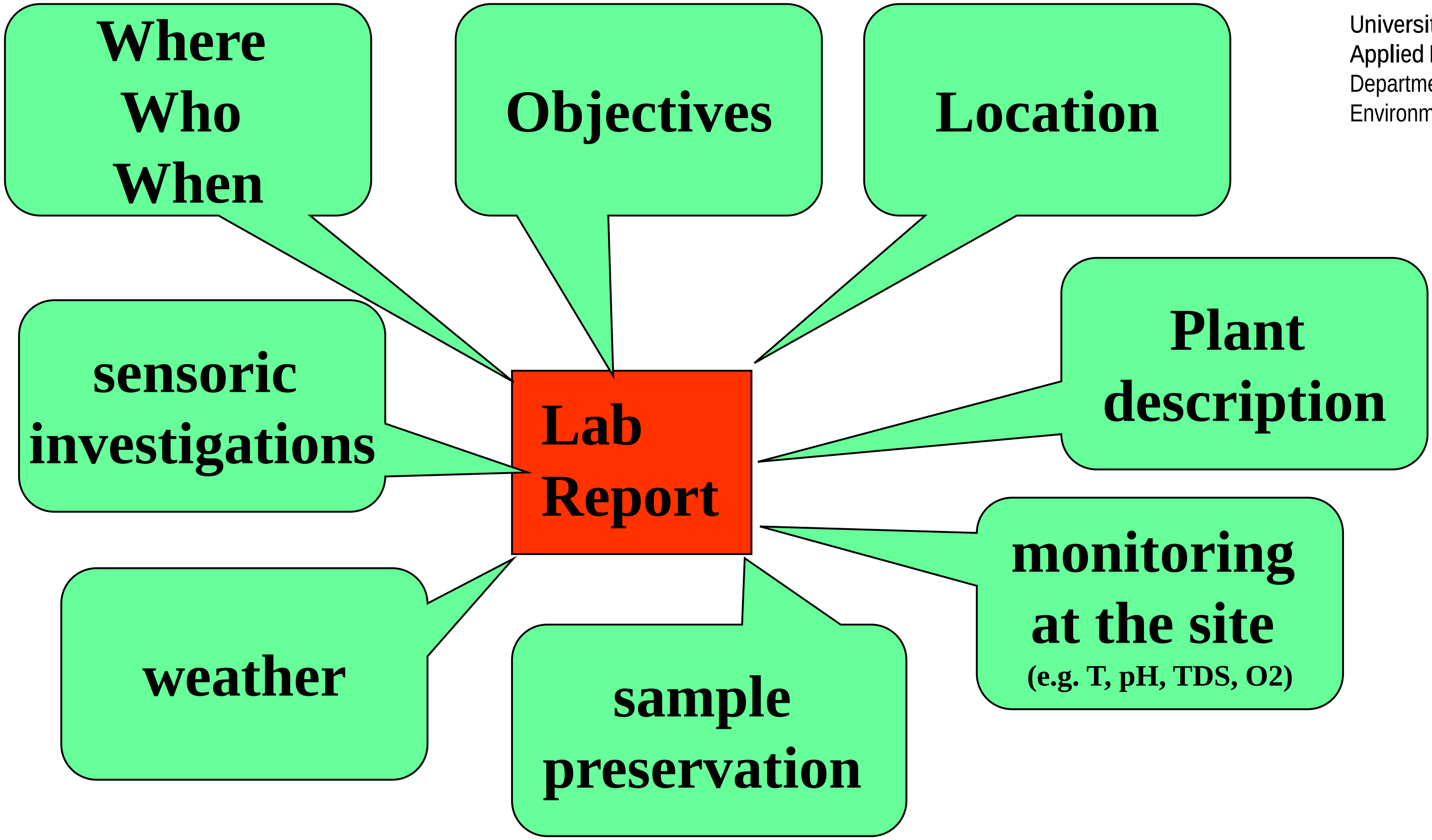

Interactions between waters

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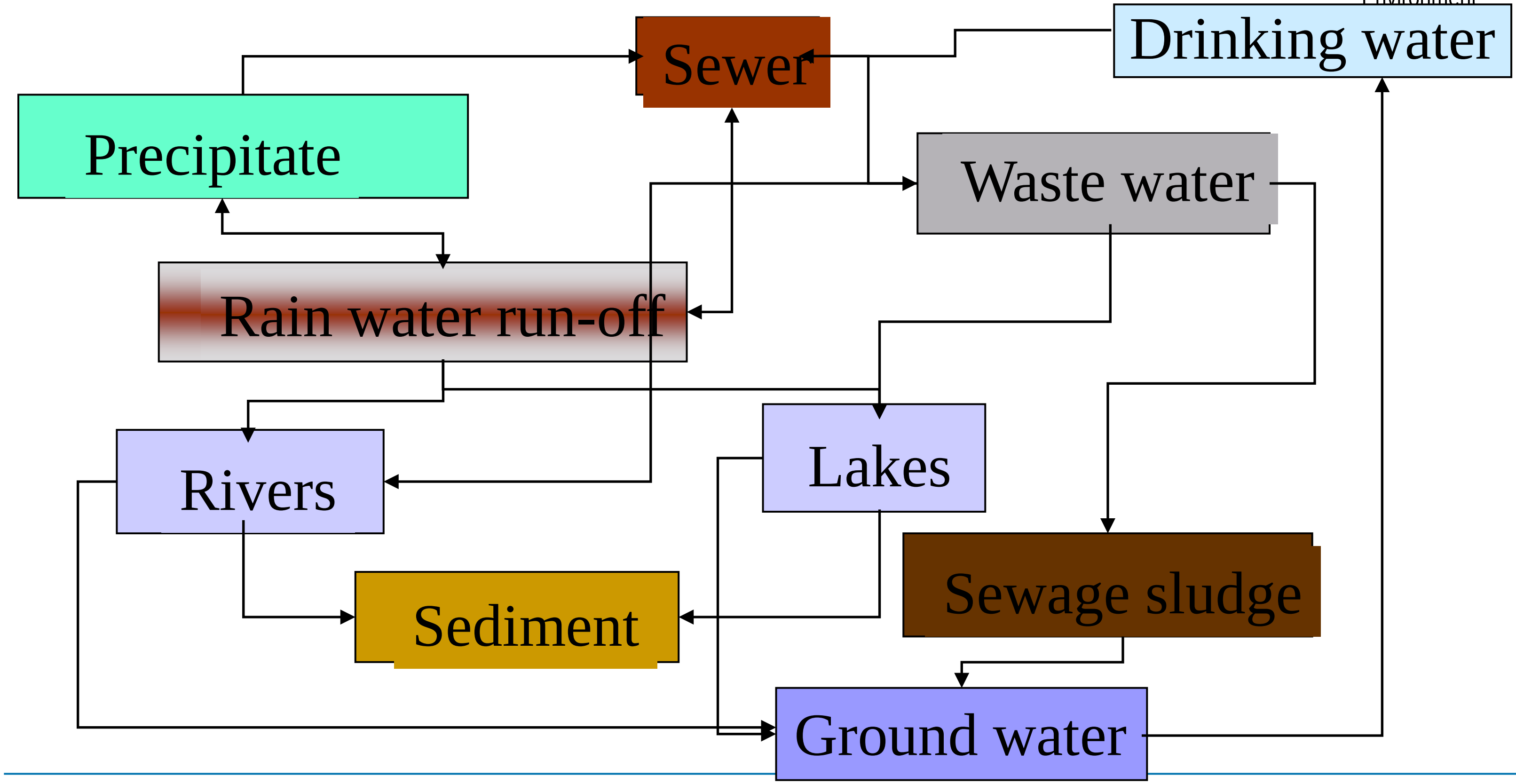

River water sampling

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Fluctuation of the quality

Statistical reasons

importance of the parameter

Trend

Frequency
Period
Moment

source control

Complexity

Events

Risk for utilisation

Effluent dilution

Hot spot analysis – for micropollutants

ISO 5667 Part 6: Guidance on sampling of rivers and streams

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- Generally, sampling at or near the surface, bottom, bank, stagnant areas and pools should be avoided.
- It has been suggested that samples should, whenever possible, be collected from positions at least 30 cm above the bottom of a stream, and a similar distance below the surface will usually be satisfactory.
- Bucket ---- containers or containers directly filled

- It should be noted that different determinands may show different degrees of heterogeneity.
- It is suggested that the following determinands (provided they are required for the routine programme) should be checked at each sampling location to be tested: pH, conductivity, chloride, ammonia, suspended solids, dissolved oxygen, colour, iron, chlorophyll, total organic carbon and biochemical oxygen demand.

Lake water sampling

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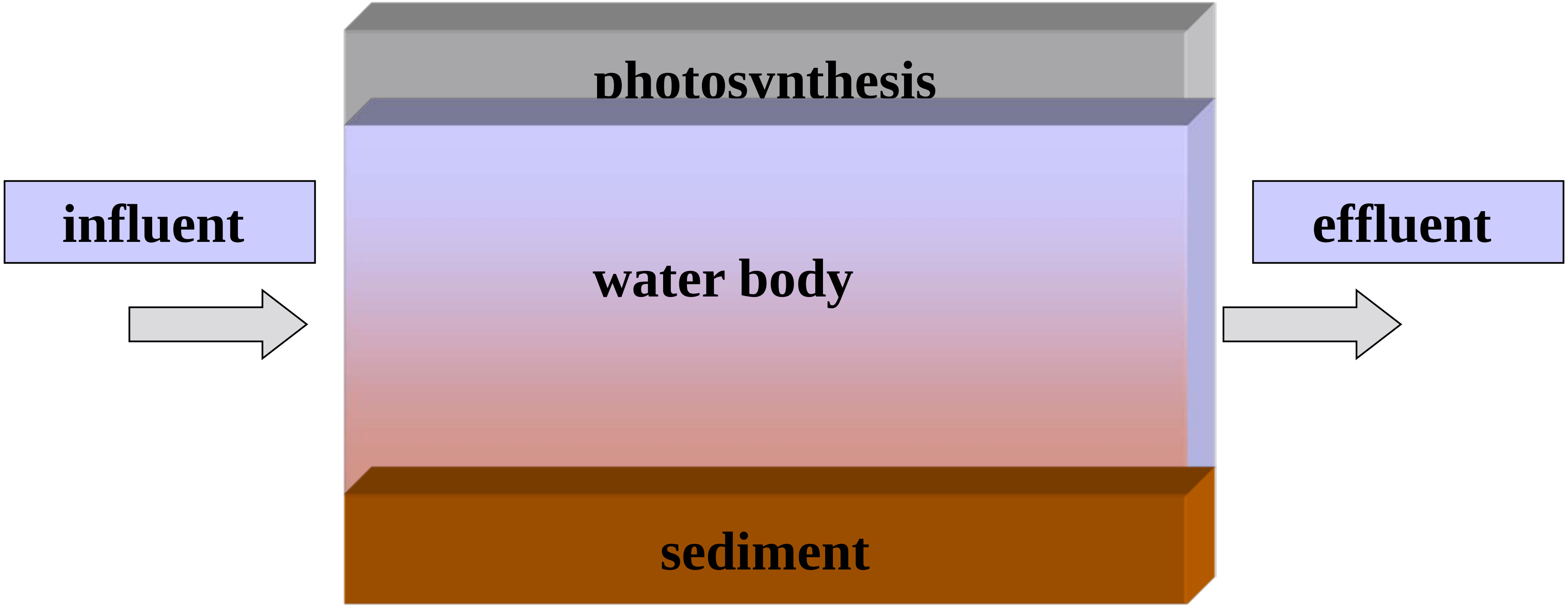

Surface water sampling

For non or semi-volatile: Slowly submerge an amber glass-capped bottle completely into the water. Open and fill bottle from below the water surface. If wading is required, approach the sample site from downstream and do not enter the actual sample area. Do not disturb bottom sediments. Open-end of the bottle should be pointed at approximately 90° to the upstream direction, in undisturbed gently flowing water. This procedure will be performed to minimize the effects due to high turbulence and aeration, or if surface scum is prevalent.

-

For metals, slowly pour surface water sample into pre-preserved plastic container to sufficiently fill the container. Surface water samples may be collected as totals (unfiltered) or dissolved (filtered).

Ground water sampling

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- Identification or description of the sampling location (position, state)
  - when possible sampling from special depth (with packers)
  - pumping until pH, T, (O_2) and conductivity are constant

- groundwater with low ORP - take care to exclude air
- gaseous or volatile compounds (CO_2, O_2) - fill with a tube under water

Drinking water sampling

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- For official sampling: sample sites are defined
- Sampling dependent on problem/question :
  - intensive flushing or immediate sampling
  - the position either defined at the tap or
  - directly at the tap after the water meter
- Sample containers filled directly at the tap
- use a funnel or a hose to protect volatile substances or gases (CO_2, O_2)

Problems occuring when sampling in sewers

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- Inhomogenicity
- Transformation processes
- Low water depth
- Sedimentation
- Health hazards
- Change of flow by measurement devices
- Infiltrations, leakage
- High fluctuating flows

Never without permit // never without appropriate safety equipment

Waste water sampling

ISO 5667_13

Purpose of sampling	Sample location	Sample type	Sample parameter
Raw influent monitoring	Influent	Composite	NH_3-N; BOD; TSS; COD, metals, organics
		Grab	pH
Process control	Primary sedimentation	Composite	BOD; COD; TSS
		Grab	pH
	Aeration tank	Grab	Return sludge flow; waste sludge flow, DO uptake rate; microscopic exam; settleability
		On-line monitoring	DO; Temperature
		Composite	Return sludge TSS; Mixed liquor TSS; pH
	Secondary sedimentation	Composite	pH; TSS; BOD; COD; DO; NH_3-N
Quality control monitoring	Final effluent	Composite	TSS; pH; NO_3-N; H_2PO_4; metals; microbial activity; organics

Waste water sampling

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- mainly collected after the screen
- representative samples for suspended solids – use lines with turbulent currents
- sampling below the surface
- no representative samples for oil and fat - very difficult
- volatile substances – grab samples

Mistakes during waste water sampling

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- Take care of internal cycles !!
- too low frequency
- periodical changes - day – week
- wrong period (Summer - Winter)
- wrong sample location

Analytical - methods

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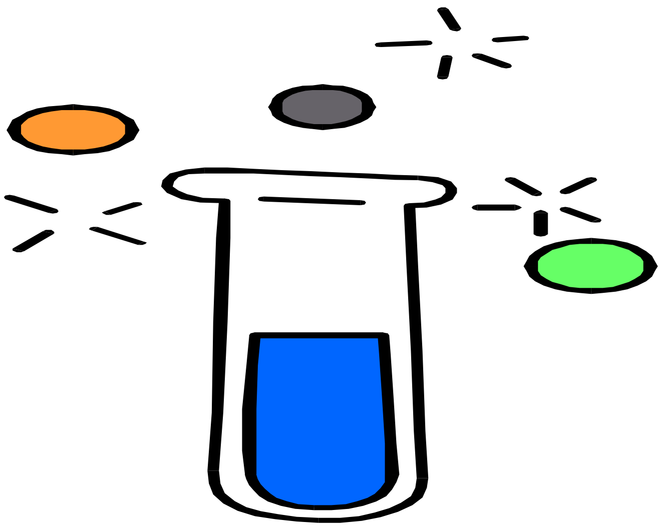

Water sampling, analysis, and interpretation

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Step 4: Processing the water sample.

- Many samples need to be filtered before testing. In some cases, the filtering step must be done in the field as soon as the sample has been collected.
- The sample analysis needs to be carried out according to a protocol that doesn't introduce contaminants or otherwise compromise the sample. After suitable processing, the sample is ready to be analyzed.

Sample processing

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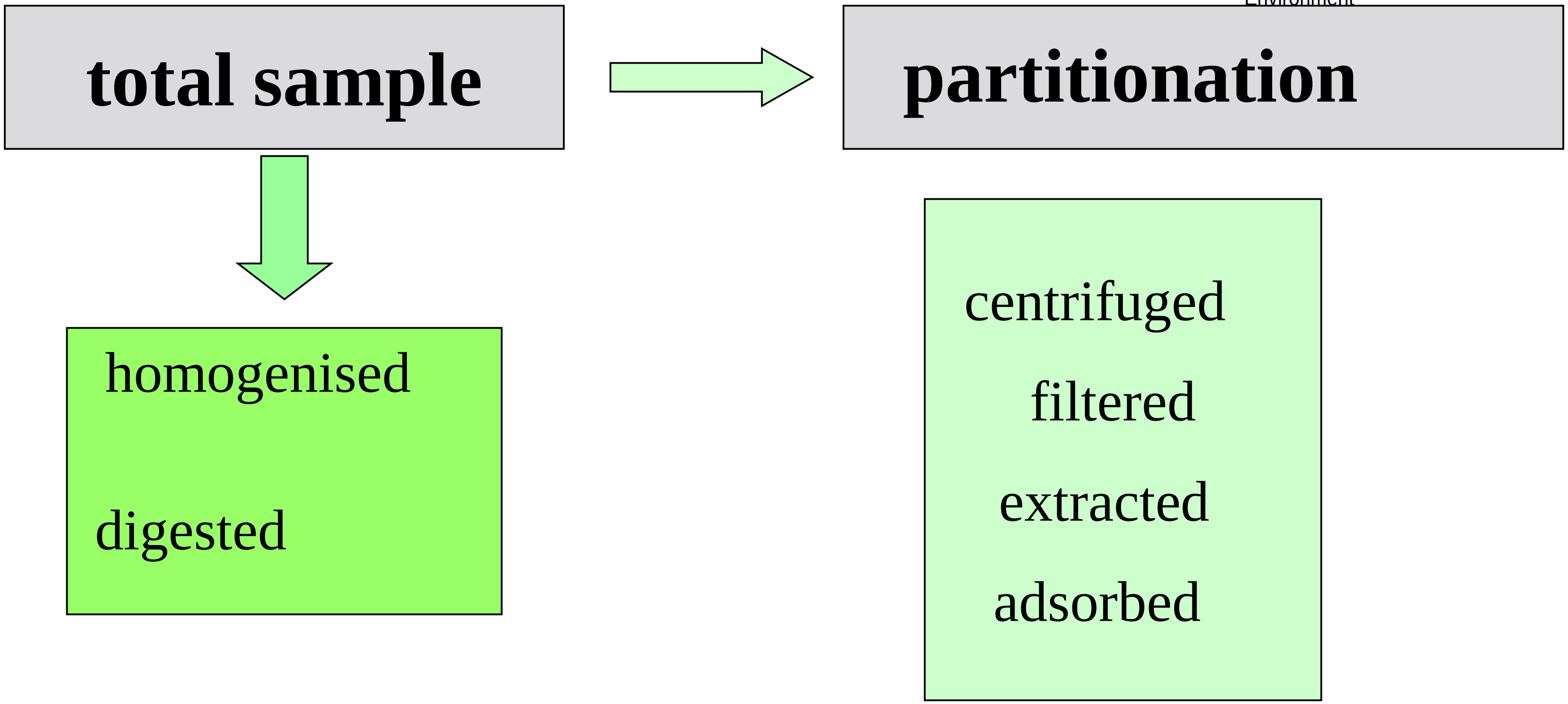

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Step 5: Analysis.

- This fifth step can also introduce problems.
- The laboratory needs to have quality control/assurance procedures in place so analytical values aren't compromised.

Criteria for the selection of analytical procedures

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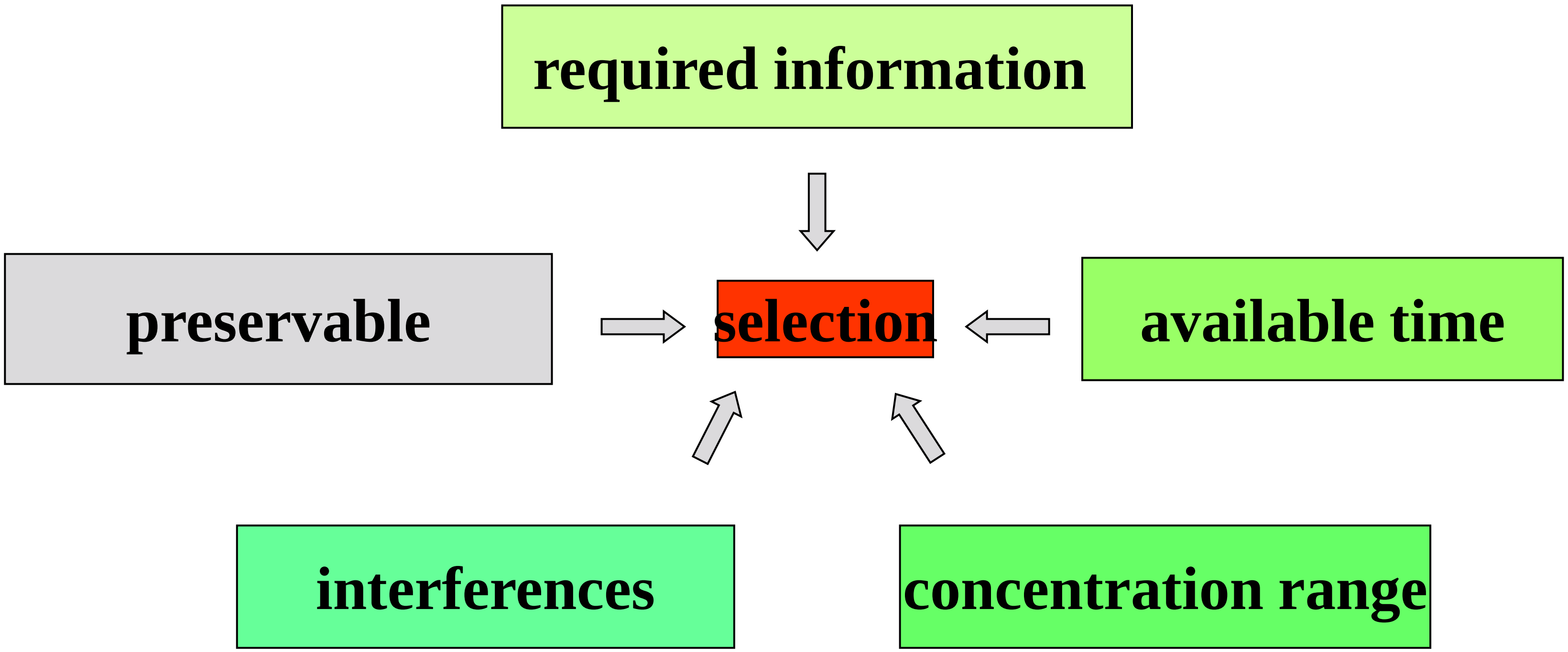

Selection of the analytical procedures

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Question/Problem	**Requirements for the analytical procedure**
Substance presence? Yes/no	Sensitive orientation tests
Concentration range	Orientation test with quantification
Concentration satisfactory far from the limit value?	Orientation test with quantification Field methode
Investigation of a guideline value	Precise standardized or equivalent procedure
Concentration (+/- SD) of a substance	

Analytical methods

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- Gravimetry
- Photometry
- Titration
- Chromatography
- ICP/AAS
- Effect analyses

Inhibition tests – toxicity tests

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- Degradation tests
  - Final degradation – Measurement of CO_2
  - Elimination of DOC
- Respirometer measurements
  - Inhibition of carbon degradation, nitrification
- Nitrification inhibition test

- Fish test, daphnia test, algae test

Analytical protocol

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amount

sample volume

dilution

sample pretreatment

Protocol

analytical device

problems

method

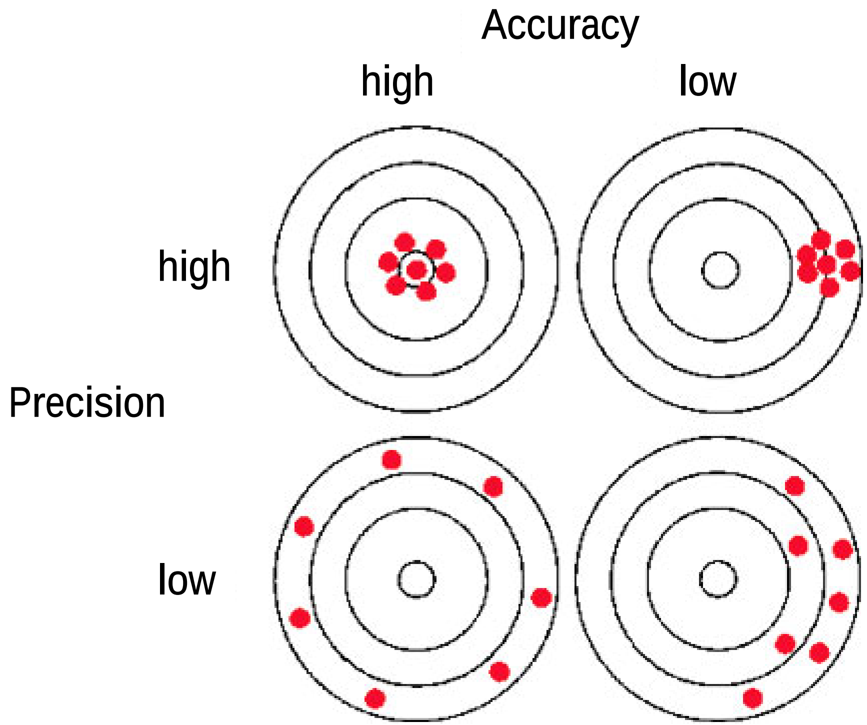
calculation steps

Analytical results

Expression of uncertainty

Limit of detection (LOD) ⟷ **Limit of quantification (LOQ)**

Accuracy ⟷ **Precision**



Analytical quality managment

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- Blank controls

- Measurement of standard solution, reference material
- Internal standards
- Standard addition

- Control chart with limits
- Validation of the procedure

- Participation at interlaboratory comparison programmes

Plausibility examination

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Ion balance

- Anion equivalents = Cation equivalents

Water-chemical correlations

- groundwater with low ORP
- ratios: COD/TOC/BOD, P_{tot}/PO_4-P, N_{tot}/N

Checks of time series

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Ion balance						
CATIONS		Mol mas	Conc.	Mol conc.	Equivalents	Equival.%
			mg/l	mmol/l	m equ./l	equ. - %
	Na+	22,99	4,17	0,18	0,18	3,02
	K+	39,10	0,67	0,02	0,02	0,29
	Mg++	24,31	7,29	0,30	0,60	9,99
	Ca++	40,08	104	2,59	5,19	86,41
	Sr++	87,62		0,00	0,00	0,00
	Fe++	55,85	0,5	0,01	0,02	0,30
	Mn++	54,94		0,00	0,00	0,00
	NH4+	18,04		0,00	0,00	0,00
	Al+++	26,98		0,00	0,00	0,00
	Sum cations		116,63	3,10	6,01	100,00
ANIONEN		Mol mas	Conc.	Mol conc.	Equivalents	Equival.%
			mg/l	mmol/l	m equ./l	equ. - %
	Cl -	35,45	4	0,11	0,11	1,83
	NO3 -	62,00	5,68	0,09	0,09	1,49
	HCO3 -	61,02	4	0,07	0,07	1,06
	SO4 - -	96,06	270	2,81	5,62	91,30
	F -	19,00	5	0,26	0,26	4,27
	Br -	79,90		0,00	0,00	0,00
	I -	126,91		0,00	0,00	0,00
	NO2 -	46,01		0,00	0,00	0,00
	HPO4 - -	95,98	0,11	0,00	0,002	0,04
	HS -	33,07		0,00	0,00	0,00
	Sum anions		288,79	3,35	6,16	100,00
Max. admissible deviation						
	up to 2 mmol(eq)/l anions- and cations				5%	
	more than 2 mmol(eq)/l anions- and cations				2%	
Deviation of the average of sum of anions- and cations					1,24	%

Ion balance						
CATIONS		Mol mass	Conc.	Mol conc.	Equivalents	Equival.%
			mg/l	mmol/l	m equ./l	equ. - %
	Na+	22,99	3	0,13	0,13	2,65
	K+	39,10	12	0,31	0,31	6,24
	Mg++	24,31	12	0,49	0,99	20,08
	Ca++	40,08	70	1,75	3,49	71,03
	Sr++	87,62		0,00	0,00	0,00
	Fe++	55,85		0,00	0,00	0,00
	Mn++	54,94		0,00	0,00	0,00
	NH4+	18,04		0,00	0,00	0,00
	Al+++	26,98		0,00	0,00	0,00
	Sum cations		97,00	2,68	4,92	100,00
ANIONEN		Mol mass	Conc.	Mol conc.	Equivalents	Equival.%
			mg/l	mmol/l	m equ./l	equ. - %
	Cl -	35,45	10	0,28	0,28	5,63
	NO3 -	62,00	55	0,89	0,89	17,72
	HCO3 -	61,02	180	2,95	2,95	58,92
	SO4 - -	96,06	30	0,31	0,62	12,48
	F -	19,00	5	0,26	0,26	5,26
	Br -	79,90		0,00	0,00	0,00
	I -	126,91		0,00	0,00	0,00
	NO2 -	46,01		0,00	0,00	0,00
	HPO4 - -	95,98		0,00	0,000	0,00
	HS -	33,07		0,00	0,00	0,00
	Sum anions		280,00	4,69	5,01	100,00
Max. admissible deviation						
	up to 2 mmol(eq)/l anions- and cations				5%	
	more than 2 mmol(eq)/l anions- and cations				2%	
Deviation of the average of sum of anions- and cations					0,90	%

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