Hydrogeological Tracer Techniques

for Groundwater,
Surface Water, and
Mine Water

Prof. Dr. habil. Christian Wolkersdorfer

South African Research Chair for Acid Mine Drainage Treatment

Contents

Why do we need tracer tests?

- Hydraulic connections (flow paths)
- Ground water flow direction
- Ground water velocity, retention time
- Hydrodynamic dispersion
- Flow rate, mass transport
- Variability of hydrogeological properties
- Transport properties of dissolved and particulate water contents and their interactions

Why do we need tracer tests in mines?

- Pollution of ground water
- Location and reliability of dams
- Mine water rebound after mine closure
- Flow of water within the flooded mine
- Drainage of contaminated mine water
- Duration of water treatment
- Pollution control by mine geometry
- Mass transport

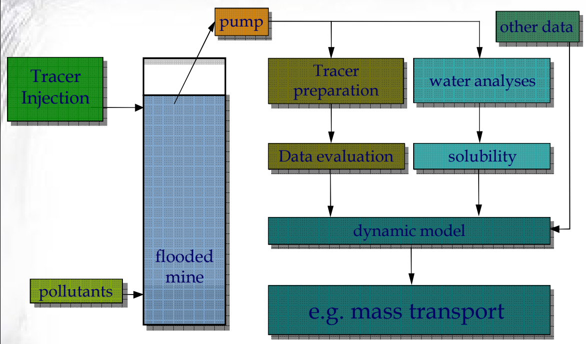
General demands on tracer tests

- Transport with velocity of transport medium
- No natural occurrence of the tracer used
- Good analytical detection (even in big dilution)
- Water soluble or used in suspension
- High resistance (chemical stability)
- No interaction between tracer and medium
- Economic (reasonably priced according to buying, handling and analytical procedures)
- Physiological safe (non toxic)
- No lasting negative effects on (ground) water quality

Demands on tracer tests in mines

- As deep as possible
- Injection without contamination
- More than one injection point
- Suitable tracer for mine water
- Tracer test must be repeatable
- Cheap and easy to handle

Scheme for a tracer test



Tracer types

- "Natural" Tracers
  - Environmental Isotopes
  - Environmental Chemicals
  - Organisms
  - Physical Effects
- Artificial Tracers 
  - Water Soluble
  - Water Insoluble

Natural Tracers

- Environmental Isotopes
  - Nuclides of substances, occurring in water
  - Usually without anthropogenetic influence
  - Low concentrations
    - Expensive measuring techniques
    - Complicated interpretation
  - Huge spatial and temporal interpretation possible
  - Age or temperature determination

Natural Tracers

- Environmental Isotopes (1/2)

Isotope	compound	half-life (years)	ratio
^{2}H	$^{2}H^{1}HO$	stable	$(9-17) \cdot 10^{-5}$
^{18}O	$H_2{}^{18}O$	stable	$(188-202) \cdot 10^{-5}$
^{3}H	$^{3}H^{1}HO$	12.34	$10^{-16}-10^{-17}$
^{3}He	dissolved	stable	$1.4 \cdot 10^{-6}$
^{4}He	dissolved	stable	–
^{39}Ar	dissolved	269	10^{-15}
^{85}Kr	dissolved	10.76	$6 \cdot 10^{-12}$

Natural Tracers

- Environmental Isotopes (2/2)

Isotope	compound	half-life (years)	Ratio
^{36}Cl	$^{36}Cl^-$	$3.01 \cdot 10^{5}$	$2 \cdot 10^{-12}$
^{13}C	$^{13}CO_2$, $H^{13}CO_3^-$	Stable	$1.1 \cdot 10^{-2}$
^{14}C	$^{14}CO_2$, $H^{14}CO_3^-$	5,730	$1.2 \cdot 10^{-12}$
^{34}S	$^{34}SO_4^{2-}$	Stable	$4.2 \cdot 10^{-2}$
^{15}N	$^{15}NO_3^-$	Stable	$3.7 \cdot 10^{-3}$
^{234}U	$^{234}U^{6+}$	$2.47 \cdot 10^{5}$	$5 \cdot 10^{-3}$

Environmental Isotopes

- Radioactive Decay (1/2)

$$n_t = n_0 \, e^{-\lambda t}$$

n_t: number of atoms after time t
n_0: number of atoms at $t = 0$
λ: decay constant
t: time

$$\lambda = \ln 2 \, (T_{1/2})^{-1} = 0.6931 \cdot (T_{1/2})^{-1}$$

$T_{1/2}$: half-life time

- Radioactive Decay (2/2)

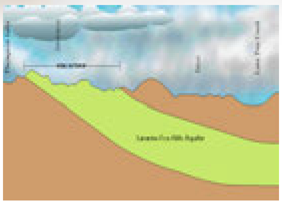
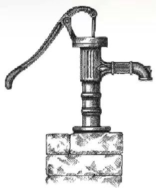
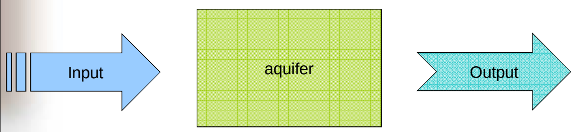
$$\tau_a = T_{½} (\ln 2)^{-1} \ln (n_0 \cdot n_t^{-1})$$

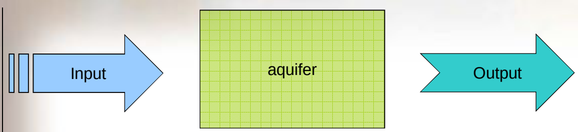
τ_a: time during radioactive decay
$T_{½}$: half-life time
n_0: number of atoms at $t = 0$
n_t: number of atoms after time t

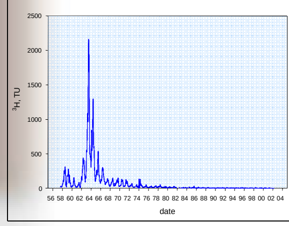
- Input – Output function

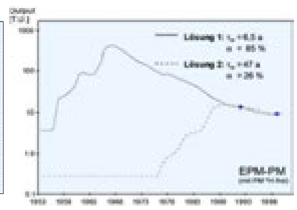
$$c_{out,\,t} = f(c_{in,\,t})$$

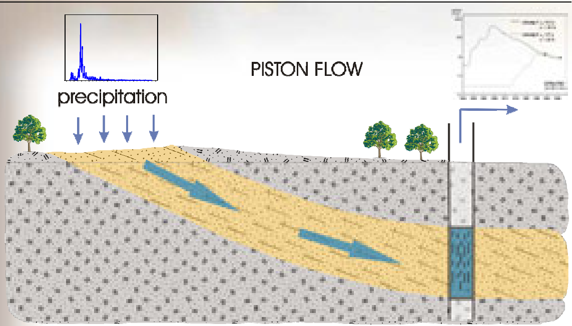
- PFM: Piston Flow Model
- EM: Exponential Model
- DM: Dispersion Model

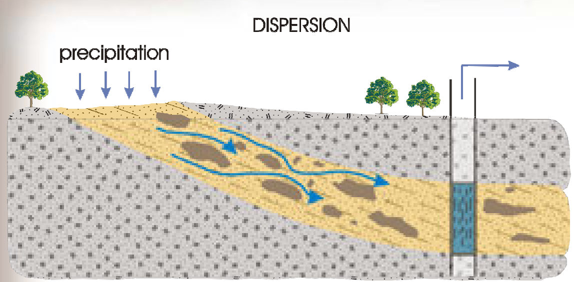





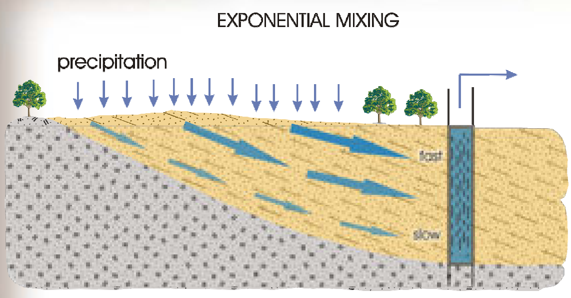








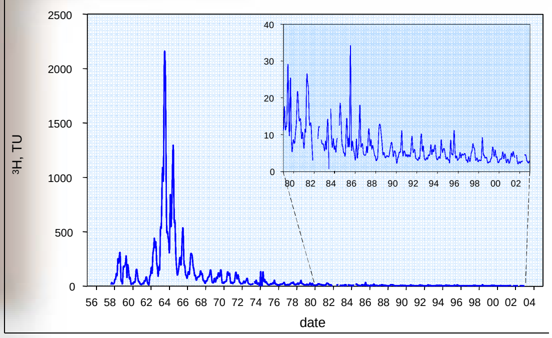




- Tritium (^3H)
  - Natural ^3H-content: < 10 TU
    - Stratospheric high energy protons (E > 100 MeV) react with nitrogen and oxygen
  - 1 TU ≙ 0.118 Bq kg^{-1}
  - Nuclear weapons' tests (1952 – 1963)
  - Input function with peak between 1963 and 1965 (up to 10,000 TU)
  - seasonal variations (winter: low; summer: high)

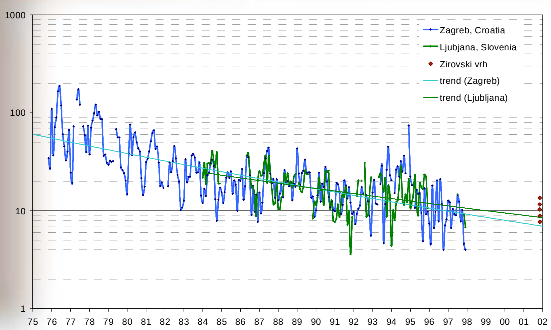
- Tritium
  - several models for result's interpretation
    - PFM: Piston Flow Model
    - EM: Exponential Model
    - DM: Dispersion Model
  - today: between 10 and 30 TU
  - more ^3H in northern than in southern hemisphere (mixing effect)
  - IAEA precipitation collection network

- Tritium



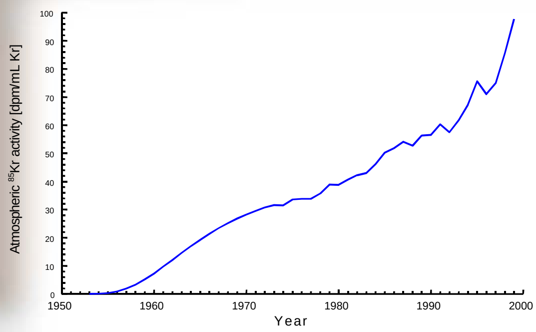
Valentia (IAEA)

- Tritium



- Krypton ^{85}Kr
  - Emitted from nuclear plants
  - Quasi-linear input function since 1958
    - 1950-1958: 0 dpm/ml ^{85}Kr
    - 1980: 40 dpm/ml ^{85}Kr
    - 2000: 80 dpm/ml ^{85}Kr
  - Quick mixing in atmosphere
  - Low seasonal and local variations
  - water marked by ^{85}Kr dissolved in air
  - No disturbing ^{85}Kr in the underground

- Krypton ^{85}Kr



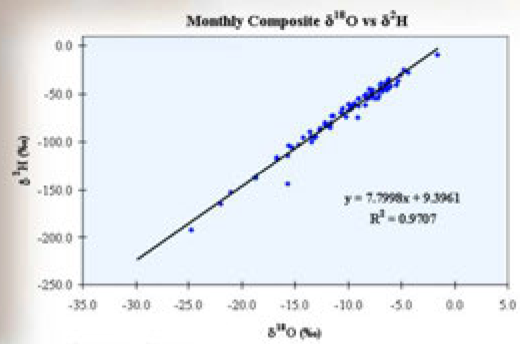
- Deuterium ^{2}H – Oxygen ^{18}O

$$\delta^{18}O/^{2}H = \frac{R_{sample} - R_{standard}}{R_{standard}} \cdot 1000‰$$

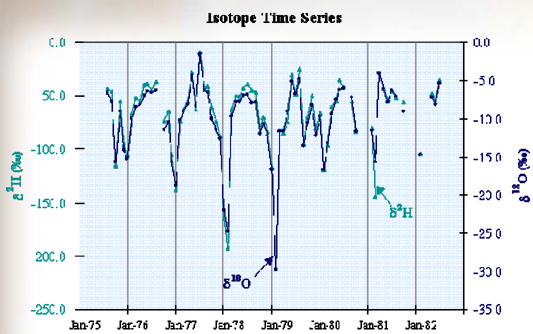
$$R = \frac{^{18}O}{^{16}O}; \quad R = \frac{^{2}H}{^{1}H}$$

$$\delta^{2}H = (8.2 \pm 0.07) \cdot \delta^{18}O + (11.27 \pm 0.65)‰$$

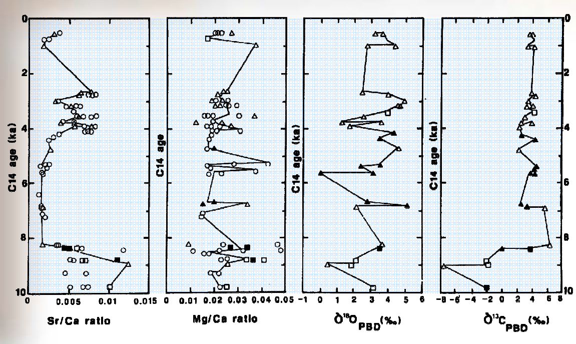
$$r^2 = 0.98; n = 205$$



Simcoe, Ontario, Canada

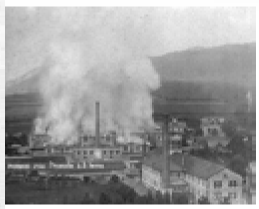


Simcoe, Ontario, Canada



Lake Keilambete

.cals

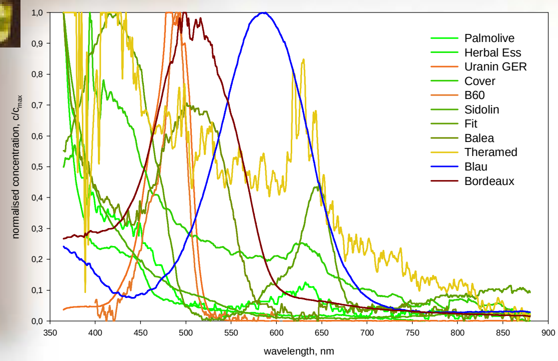


bons

- Uranine (2.5 – 2,400 mgL^{-1})
  - Bath Products
  - Cosmetics
  - Cleaning Products

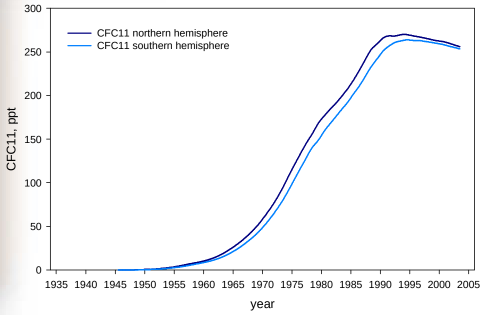
Badedas	2,400 mg L^{-1}
Benny	410 mg L^{-1}
Dressin Pine needle	1,350 mg L^{-1}
General	15.5 mg L^{-1}
Wundi	2.5 mg L^{-1}

Käss 1998

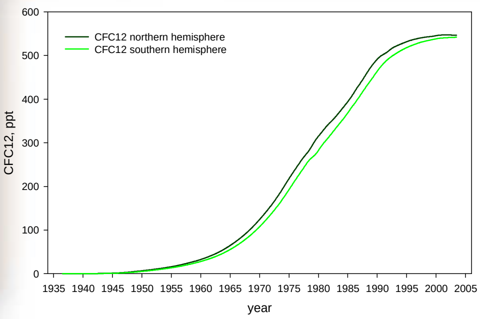


- Borate
  - Sewage
  - Waste Deposits
  - Laundry Detergents
  - up to 83 mg L^{-1} HBO_2

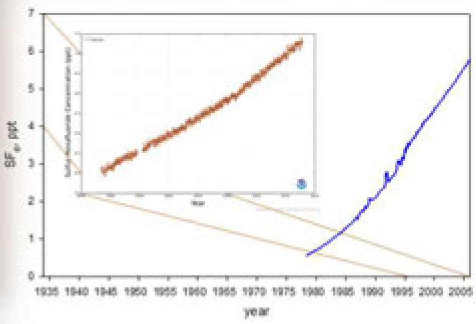
- Chlorinated Hydrocarbons / SF_6



- Chlorinated Hydrocarbons / SF_6



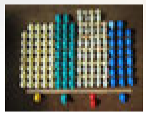
- Chlorinated Hydrocarbons / SF_6



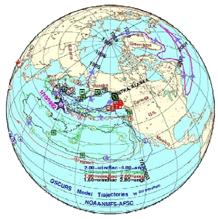
Natural Tracers

- Organisms
  - Bacteria
  - Pollen
  - Eels
  - Ducks

Rubber Duckies

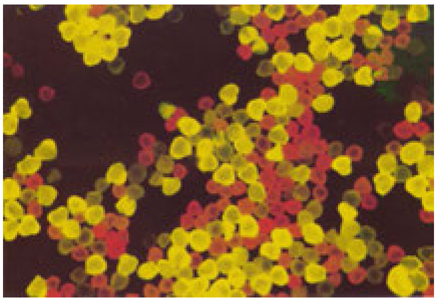


- Spill over: 10 January 1992
- 44.7°N, 178.1°E
  - North American west coast
- 29,000 bathtub toys (including rubber ducks)
- Ten months later the toys began washing ashore near Sitka, Alaska
- Ocean Surface Current Simulations (OSCURS)



Organisms

- Pollen (*Lycopodium clavatum*)



Käss 1998

Natural Tracers

- Physical Effects
  - Temperature
    - Altitude effect
  - Salinity
    - Waste deposits
    - Salt lakes
    - Ocean influence

Artificial Tracers

- Artificial Tracers
  - Water soluble
    - e.g. dyes
    - salts
  - Water insoluble
    - e.g. spores
    - microspheres

Artificial Tracers: Water Soluble

- Dyes
  - Fluorescent dyes
  - Non-fluorescent dyes
- Salts
- Radioactive Tracers
- Activation analytical tracers

- filtering of white light
  - dyes are coloured
- absorption can be measured
  - dye intensity
- fluorescent dyes
  - light energy is emitted
    - Fluorescence
  - detection limit 10^4 times lower than for non-fluorescent dyes

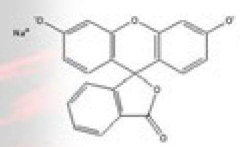
- Characteristic wave lengths for each dye
  - Absorption spectra
  - Stimulation wave length
  - Emission spectra
- Important: wave length maxima
- Detection limit for dyes with two maxima is lower than with one maximum

- Chemical composition and structure
  - Organic molecules
    - C, H, O, N, S, Na, Cl, Br
  - Chemical structure, Arrangement of atoms results in colour and fluorescence
  - chemical structures must not be destroyed during the tracer test
  - fluorescence is a result of double bindings in the aromatic molecules
  - Xanthene-structure of most fluorescent dyes

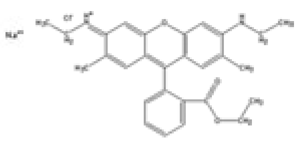
- Chemical composition and structure
  - Trivial names instead of exact chemical name
    - Fluorescein: 9-(2-carboxyphenyle)-3-hydroxy-6-fluoron
  - Be exact when using trivial names!
  - Use full trivial name (e.g. there are many rhodamins)
  - Use CAS number
    - Na-Fluorescein: 518-47-8
  - Fluorescein ≠ Uranine

- Chemical composition and structure
  - Many names for one substance might be in use e.g.
    - uranine
    - c.i. acid yellow 73
    - fluorescein sodium; Na-fluorescein
    - spiro(isobenzofuran-1(3h),9'-(9h) xanthen)-3-one,3',6'-dihydroxy-, disodium salt (9ci)
    - Fluorescein (often used in Anglo-Saxon)
    - disodium salt
    - yellow 73, c.i. acid

- Chemical composition and structure



Uranine (Na-fluoresceine)



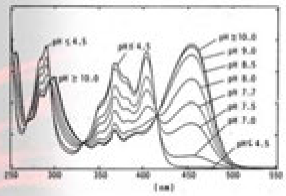
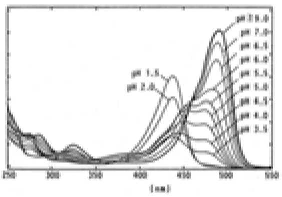
Rhodamine 6G

US National Toxicology Program

Tracer Types

Chemical composition and structure

- pH-dependency of fluorescence

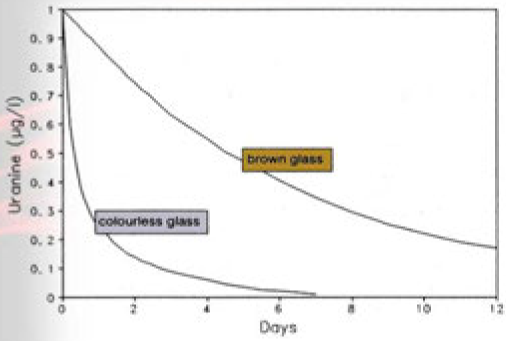
pyranine uranine (Na-fluoresceine)

Käss 1998

Tracer Types

Chemical composition and structure

- Decomposition of fluorescent tracers

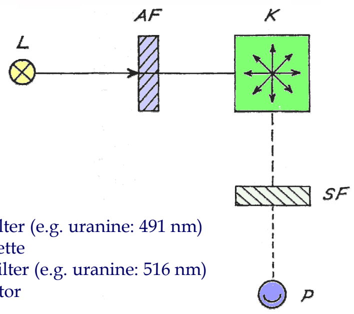


Käss 1998

Tracer Types

Chemical composition and structure

- Detection of fluorescent tracers



L lamp
AF excitation filter (e.g. uranine: 491 nm)
K sample cuvette
SF secondary filter (e.g. uranine: 516 nm)
P photo detector

Käss 1998

Tracer Types

Chemical composition and structure

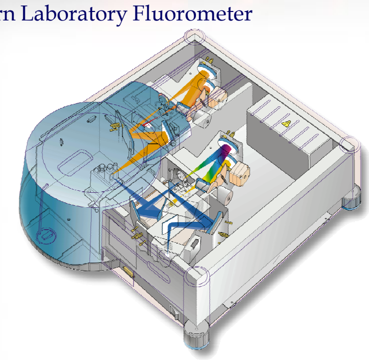
- Modern Laboratory Fluorometer


Varian Cary Eclipse

Tracer Types

Chemical composition and structure

- Modern Laboratory Fluorometer

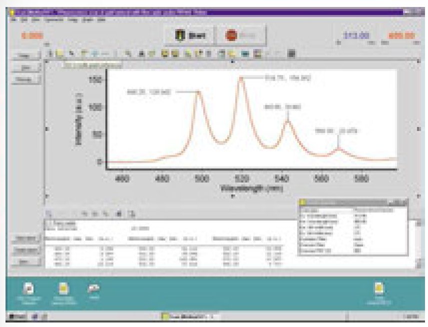


Varian Cary Eclipse

Tracer Types

Chemical composition and structure

- Modern Laboratory Fluorometer



Varian Cary Eclipse

Fluorescent Dyes

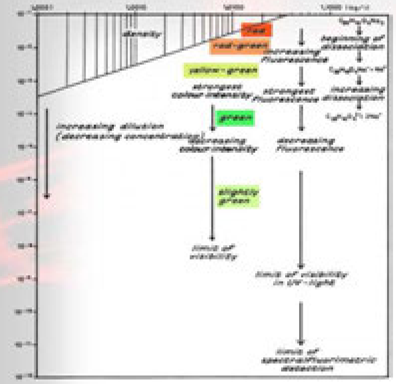
Tracer	CAS number	Detection limit, µg/L	Sorptivity
Uranine, Na-fluoresceine	518-47-8	0.002	very low
Eosin Y	17372-87-1	0.01	low
Pyranin	6358-69-6	0.008	very low
Sulforhodamine G	5873-16-5	0.005	weak
Sulforhodamine B	3520-42-1	0.007	weak
Rhodamine B	81-88-9	0.006	strong
Rhodamine WT	37299-86-8	0.006	medium
Lissamine FF	2391-30-2	0.03	medium
Tinopal CBS-X	38775-22-3	0.07	medium
Naphthionate	130-13-2	0.01	low

Fluorescent Dyes

Tracer	CAS-Number	Toxicological assessment	Assessment basis
Uranine (sodium fluoresceïn)	518-47-8	Safe	Tox, Lit
Eosin yellow (Eosin Y)	17372-87-1	Safe	Lit, Work
Sulforhodamine B	3520-42-1	Ecotoxicologically unsafe	Tox
Amidorhodamine G	5873-16-5	Safe	Tox
Rhodamine WT	37299-86-8	Not recommended	Tox
Rhodamine B	81-88-9	Not recommended	Tox, Lit
Rhodamine 6G	989-38-8	Not recommended	Tox, Lit
Sodium naphthionate	130-13-2	Safe	Tox
Pyranine	6358-69-6	Safe	Tox
Tinopal CBS-X	38775-22-3	Safe	Tox
Tinopal ABP liquid	68155-70-4	Safe	Tox
Lithium salts		Safe with restrictions	Lit, Work
Strontium salts		Safe with restrictions	Lit, Work
Bromides		Safe with restrictions	Lit, Work
Activatable isotopes		Safe with restrictions	Lit, Work
microspheres	9003-53-6	Safe	Lit, Work
Club moss spores	–	Safe	Tox, Work

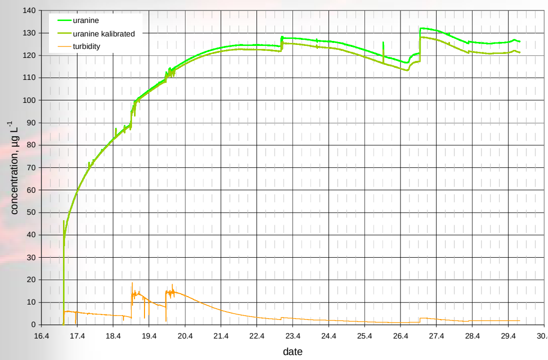
Modified from Behrens *et al.* 2001, CAS numbers added

Uranine (Na-fluoresceine)

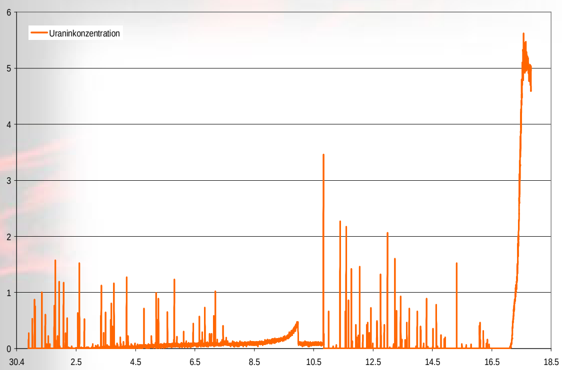


Käss 1998

Na-fluoresceine stability



Reiche Zeche Shaft Freiberg



Na-fluoresceine

Georgi Unterbau, Brixlegg

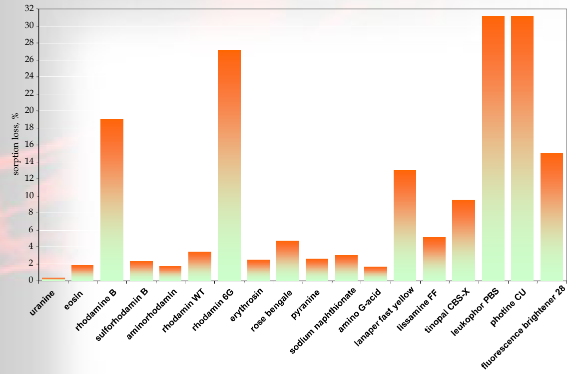
Tracer Types

Na-fluoresceine

Stöckelgraben Speyer 15.11.2002

Tracer Types

Sorption Loss



after Käss 1998

Tracer Types

Non-fluorescent Dyes

☹
- poor detection limits
- only small surface of water body
- short travel distances
- water of good quality

☺
- good light and pH stability
- modern spectral photo-meters can be used

Tracer Types

Non-fluorescent Dyes

- Indigo (Riba Reka, Slovenia 1864)
- Aniline red (Danube 1869)
- Fuchsine (Lur cave system 1928)
- Congo red, malachite green (Mendip Hills 1968)
- Brilliant blue (1994, 1995)
- Aniline violet
- Auramine
- Methyl blue

Tracer Types

Salts

- NaCl
- LiCl
- KCl
- Borax ($Na_2B_4O_7.10H_2O$)
- SrCl
- CsCl
- Br^-
- I^-
- Ammonium
- Dichromate
- $ZnCl_2$

Tracer Types

Salts: Introduction

- first test 1872 (900 kg near Lausen, Switzerland)
- first important use of salts in 1877
  - Danube Immendingen
  - NaCl: 10,000 kg (+ 10 kg Na-Fluorescein)
  - recovery 92.6 %
- in natural or mine waters often high background of "Salts"
  - Gernrode/Harz: 1,700 mgL^{-1} Cl^-
  - Niederschlema/Alberoda: 5.6 mgL^{-1} Li^+
- always measure background concentrations
- also: sewage water; landfill drainage water; polluted rivers

Salts: Introduction

- high salt concentrations might be harmful for biology and microbiology
  - trees and/or worms might die
- increase in electrical conductivity can be used to determine salt concentration
  - used in surface flow investigations
  - high amounts of salt necessary
  - in practice for NaCl only
- salts: cation + anion
- usually, only one ion is tracer
- high density of salts can result in density flows

Salts: Introduction

- cations and anions show different flow characteristics
  - example: LiBr
  - either use LiCl, KBr, or NaBr
- adsorption or cation exchange might cause loss of ions
  - higher in pore than in karst water
  - ion exchange capacity falls with increasing ion potential
  - Li: ionic potential 1.28 ⇒ low exchange capacity
  - Cs: ionic potential 0.61 ⇒ high exchange capacity

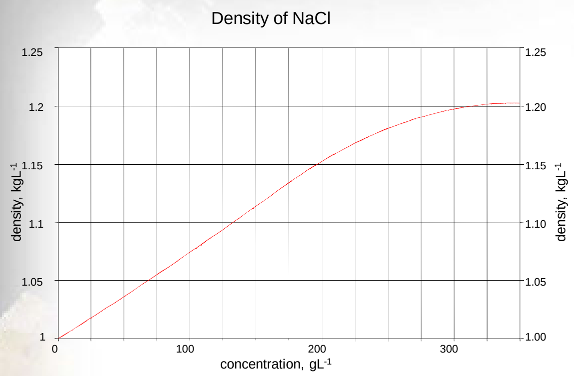
Salts: Detection

- electrical conductivity
  - mainly NaCl
- titration of Cl^- anion
- flame emission photometry
- atom absorption spectrophotometry
- photometry
  - e.g. permanganate
- HPLC + ion chromatography
  - Br^-, I^-
- ICP-MS
  - Inductively Coupled Plasma - Mass Spectrometry

Rock Salt (NaCl)

- first and most widely used salt tracer
- dissociation into Na^+ and Cl^-
- samples should always be analysed for both ions
- normally, the Cl^- is the tracer
- saturation: 0 °C 356 gL^{-1}; 30 °C 361.5 gL^{-1}
- to avoid sinking of the solution:
  - warm water
  - max concentration 0.5 % NaCl (3 gL^{-1})
- sample volume at least 250 mL when using titration of Cl^-

Rock Salt (NaCl)

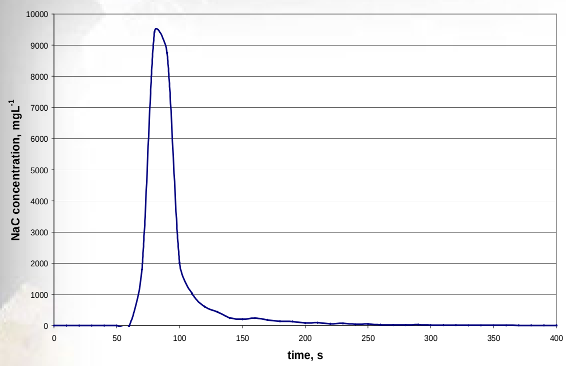


Rock Salt (NaCl)

- detection methods
  - gravimetrical (AgCl)
  - titrimetrical ($NaCr_2$ + AgCl)
  - flame emission at 589.3 nm
  - ion sensitive electrode (not known for chloride determination on site)
  - electrical conductivity (high precision)
  - ion chromatography (only with low concentrations)
- toxicology (LD_{50}):
  - warm blooded animals: 3,000 mg kg^{-1}
  - fish and fish fry: 10,000 mgL^{-1}

Tracer Types

Rock Salt (NaCl)



Tracer Types

Lithium-salts

- first use in 1907
  - 50 kg in Notranjska Reka near St. Kanzian, Slovenia
- Li has a small ionic radius, therefore least subjected to ion exchange
- possible use in porous aquifers with flow distances below ca. 200 m
- cheapest Li-Salt is LiCl (approx. € 10 kg^{-1})
- technical purity grade (99 %) is sufficient
- solubility: 20 °C 832 g L^{-1}; 60 °C 984 g L^{-1}
- exothermic reaction during solution ⇒ avoid plastic containers

Tracer Types

Lithium-salts

- background Li and variation must be known
- detection methods
  - Ca has to be removed prior to analyses to increase Li detection limits (ammonium oxalate)
  - flame photometry
  - ICP-MS
  - bad: atomic absorption spectrometry (AAS)
- toxicology (LD_{50}):
  - warm blooded animals: 526 mg kg^{-1}
  - fish and fish fry: 2,000 – 3,500 mgL^{-1}
  - no more than 0.5 mg L^{-1} at public water supplies during a tracer test

Tracer Types

KCl

- Only used when K should be the tracer
  - K concentrations are lower than Na concentrations (0.1 – 8 mgL^{-1})
  - Na and K have approx. same abundance in crust
  - K is bound in rock building minerals (e.g. feldspar)
- If Cl is meant to be the tracer the cheaper NaCl should be used (cost KCl = 4 × cost NaCl)
- K is more sorptive and subject to ionic exchange than Na
- In tracer tests, exchanged Ca often arrives before K

Tracer Types

KCl

- solubility
  - 10 °C: 313 gL^{-1}
- detection methods
  - flame emission
  - ionic chromatography
  - not advisable: AAS (766.5 nm)
- toxicology:
  - Humans (†): 2,430 mg kg^{-1}
  - fish (†): 700 – 5,200 mgL^{-1}
  - water organisms (†): 400 – 5,000 mgL^{-1}

Tracer Types

Borax ($Na_2B_4O_7.10H_2O$)

- first used in 1948/49 (Oilfields in Kansas and Oklahoma)
- transported as undissociated form
  - ⇒ low adsorption
  - ⇒ ion exchange
  - Only clay minerals can adsorb small amounts of B
- natural B concentration of water must be known (0.02 – 121 mgL^{-1} observed)
- don't warm water to dissolve Borax (recristallisation)
- adding up to 30 % of boric acid increases the dissolution
- Unimportant in artificial tracer tests but as natural tracer (sewage water, waste deposits)

Borax ($Na_2B_4O_7.10H_2O$)

- solubility
  - 10 °C: 16.2 gL^{-1}; 20 °C: 25.2 gL^{-1}
- detection methods
  - colorimetrical
    - B + Azomethin H ⇒ yellow dye
  - ICP-MS
  - fluorimetrical boric acid determination
- toxicology (LD_{50}):
  - rats: 4,500 – 5,000 mg kg^{-1}
  - Humans (†): 500 – 5,000 mg kg^{-1}
  - fish (†): 3,000 – 7,000 mgL^{-1}
  - water organisms (†): 540 – 9,900 mgL^{-1}

$SrCl_4.6H_2O$

- Sr, not Cl is the tracer
- natural Sr concentration ("background") must be known (0.005 – 14 mgL^{-1})
- compared to Na-fluoresceine, a retardation factor of 10 must be expected
- Amounts used so far: 50 kg; 2 kg
- detection methods
  - analyse within 48 hours to avoid Sr precipitation!
  - Flame emission
  - AAS
  - ICP-MS
- toxicology:
  - trout (†): 10,000 mgL^{-1}

CsCl

- used in Notranjska Reka (Slovenia) and Upper Rhine Valley
- highly sorptive!

Bromide (1/2)

- only present in traces in natural waters
- no sorption
- stable towards microbiological activities: but uptake by plants
- but: high costs and complicated analytical procedures
- good water solubility of NaBr
  - 10 °C: 850 gL^{-1}
- detection methods
  - ion sensitive electrodes
    - high detection limit: 50 μgL^{-1}
  - ion chromatography
  - isotope dilution analyses (change of isotope ratios)

Bromide (2/2)

- not to be used near drinking water supplies, if water is chlorinated or ozonated
  - bromate and Br-organics will be formed
- toxicology (LD_{50})
  - Rat: 3,500 mg/kg
  - Trout, bluegill, sunfish (96 h): > 1000 mgL^{-1}
  - Water flea (48 h): > 1000 mgL^{-1}

Iodide

- smaller natural concentrations than Br^-
- iodite can be chemically or microbiologically affected
- only suitable for
  - short flow distances
  - short residence times
  - low organic pollution
- detection methods
  - ion sensitive electrodes
  - ion chromatography
  - isotope dilution analyses (change of isotope ratios)

Tracer Types

Ammonium

- first use 1942 (Warsteiner Massenkalk)
- sensitive to sorption and oxidation
- too much amounts must be used
  - e.g. 72 kg Warstein tracer test
  - ⇒ restricted use
- toxicology
  - in alkaline waters, ammonium is strongly toxic to fish
  - in strong sunshine pH can increase to 8, even 10
  - trout (†): 1.25 – 5 mgL^{-1}

Tracer Types

Dichromate ($Cr_2O_7^{2-}$)

- discharge measurements in channels and rivers (up to 50 $m^3 s^{-1}$)
- 2 kg per $m^3 s^{-1}$ of flow needed
- solubility
  - $K_2Cr_2O_7$: 77 gL^{-1} (10 °C)
  - $Na_2Cr_2O_7.2H_2O$): 1,700 gL^{-1} (10 °C)
- detection methods
  - photometric
  - colorimetric with diphenylcarbazide
- toxicology
  - very toxic!
  - trout (†): 0.2 – 0.35 mgL^{-1}
  - drinking water: 0.05 mgL^{-1}

Tracer Types

Radioactive Tracers

^{3}H	12.3 a	$^{3}H^{2}HO$	β
^{24}Na	15.0 h	Na^{+}-cation	β
^{51}Cr	27.7 d	EDTA-complex	γ
^{58}Co	70.8 d	$[Co(CN)_6]^{3-}$	γ
^{82}Br	36 h	Br^{-}-anion	γ
^{85}Kr	10.76 a	gas	
^{114}In	49.5 d	EDTA-complex	γ
^{131}I	8.05 d	I^{-}-anion	γ
^{198}Au	2.7 d	Au^{3+}-cation	β

Tracer Types

Radioactive Tracers

- Radioactive Decay (1/2)

$$n_t = n_0\, e^{-\lambda t}$$

n_t: number of atoms after time t
n_0: number of atoms at $t = 0$
λ: decay constant
t: time

$$\lambda = \ln 2\, (T_{½})^{-1} = 0.6931 \cdot (T_{½})^{-1}$$

$T_{½}$: half-life time

Tracer Types

Radioactive Tracers

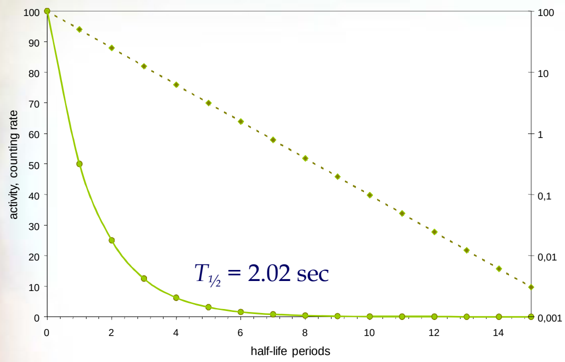
- Radioactive Decay (2/2)

$$\tau_a = T_{½}\, (\ln 2)^{-1} \ln (n_0 \cdot n_t^{-1})$$

τ_a: time during radioactive decay
$T_{½}$: half-life time
n_0: number of atoms at $t = 0$
n_t: number of atoms after time t

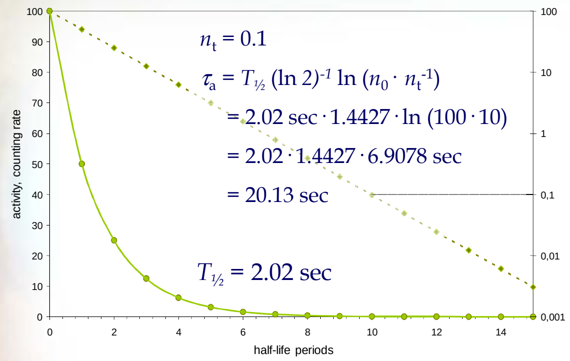
Tracer Types

Radioactive Tracers



Tracer Types

Radioactive Tracers



Tracer Types

Activable Isotope Tracers

- substances must be under detection limit in the water to be tested
- representative tracer properties
- most important activation process: neutron activation
- nuclides formed mostly unstable
- sensitivity increases with increasing radioactivity
- atomic reactors have to be used (e.g. Karlsruhe, Munich)
- low detection limits
- expensive method

Tracer Types

Activable Isotope Tracers

- *n,γ*-process
  - ^{115}In (stable) → ^{116}In ($T_{½}$ = 54 min)
- *n,p*-process
  - ^{32}S (stable) → ^{32}P ($T_{½}$ = 14.2 d)
- *n,α*-process
  - ^{6}Li (stable) → ^{3}H ($T_{½}$ = 12.3 a)
- detection limit increases with irradiation period
- e.g. detection limit In: 0.0005 ppb

Tracer Types

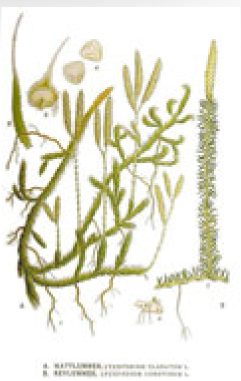
Artificial Tracers: Water Insoluble

- drift particles
  - club moss spores (*Lycopodium clavatum*)
  - microparticles (microspheres)
  - bacteria
  - phages
  - geobombe
  - saw dust
  - tennis balls
  - yeast
  - eels

Tracer Types

Club Moss Spores

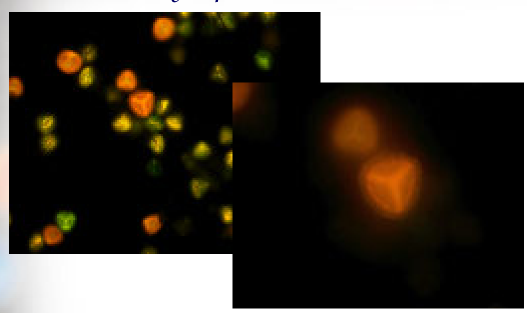
- *Lycopodium clavatum*
- 50 µm diameter
- first used in karst tracing
- natural and artificial colours possible



Tracer Types

Club Moss Spores

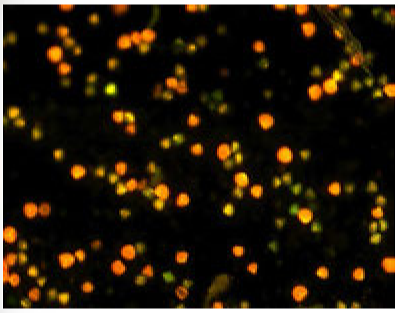
- Canadian *Lycopodium clavatum*



Tracer Types

Club Moss Spores

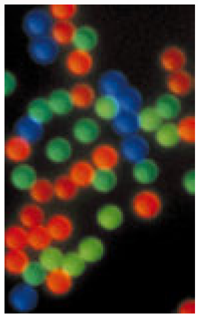
- Canadian *Lycopodium clavatum*



Tracer Types

Microparticles (Microspheres)

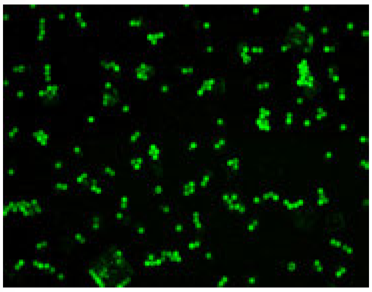
- microparticles (microspheres)
- 0.2 – 100 µm diameter
- density 1.006 g cm^{-3}
- polystyrene
- latex
- positively, negatively, neutrally charged surfaces



Tracer Types

Microparticles (Microspheres)

- microparticles (microspheres)



Tracer Types

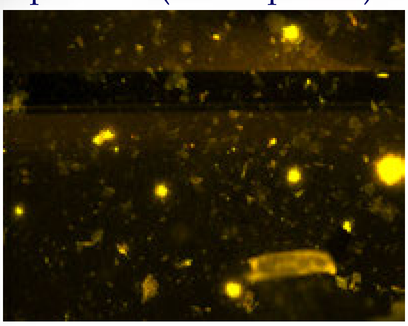
Microparticles (Microspheres)

- microparticles (microspheres)

Tracer Types

Microparticles (Microspheres)

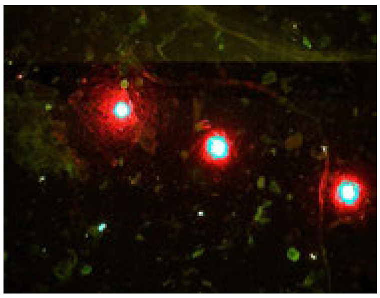
- microparticles (microspheres)



Tracer Types

Microparticles (Microspheres)

- microparticles (microspheres)

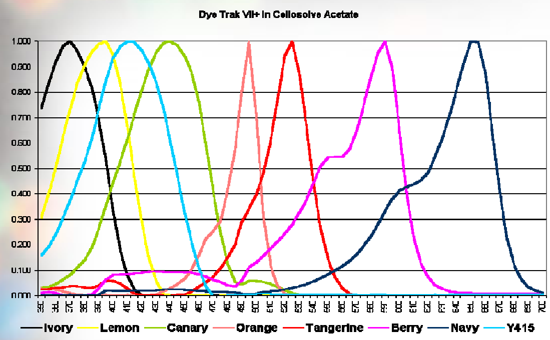


Microparticles (Microspheres)

- microparticles (microspheres)

Triton Technologies

Microparticles (Microspheres)



composite absorbance spectra

Triton Technologies

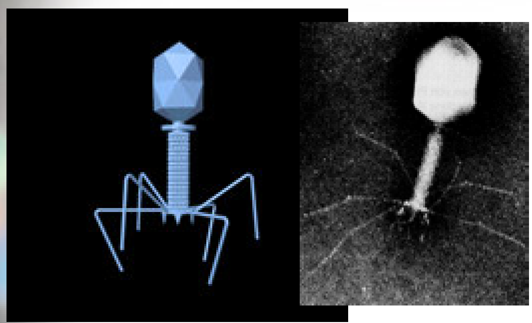
Bacteria

- bacteria (*Escherichia coli*)

Woods Hole Biological Laboratory

Phages

- phages (T4)



"Rarities"

- geobombe
- sawdust
- tennis balls
- yeast
- eels

Preparation of Tracer tests

- What data is necessary?
- Where shall the tracer be injected and sampled?
- Which tracer to be used?
- What amount to be injected?
- Who is responsible for what?

⇓

- Plan of the Tracer Test
- Documentation of Tracer Test

Necessary Data

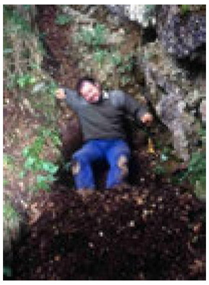
- always start with a
  - geological (e.g. rock types; sediments)
  - hydrogeological (e.g. type of aquifer, isolines: ground water contour lines)
  - hydrological (e.g. discharge; precipitation)
  - geochemical (e.g. anomalies)
  - hydrogeochemical (e.g. background values)
  - biological (e.g. bacteria, micro-organism)
- Investigation

Necessary Data

- hydrogeological investigation
  - (ground) water flow direction
  - Isolines (ground water contour maps)
  - (ground) water velocity
  - dissolution of tracer
  - water usage
  - physico-chemical parameters
  - hydrogeochemistry

Necessary Data

- Preparation of tracer tests needs time
- Go Out!
- Don't sit at your desk!



Necessary Data

- Costs (direct)
  - Tracer
  - Sampling containers
  - Preliminary investigations
  - Preliminary expert reports
  - Site visits
  - Man power
  - Tracer analyses
  - Final report

Necessary Data

- Costs (indirect)
  - Authorization (permits)
  - Sampling
  - Storage, transport of samples
  - Preparation of observation sites
  - Possible damages

Tracer Injection

- one or more injection sites
- based on preliminary investigations
- keep in mind:
  - you have to carry the injection equipment and tracers
  - situation could change between site visit and final test
- injections sites should be hydraulically connected to sampling sites
  - exception: unsaturated zone

Preparation of Tracer Tests

Tracer Injection

Preparation of Tracer Tests

Tracer Sampling

- one or more sampling/observation sites
- better too much than too few of them
- you must be able to reach your sampling points in due time
- nearby sites could be hydraulically separated from each other
- worst thing that could happen:
  - negative result due to incorrect selection of injection and sampling sites!
- be open to any surprise!

Preparation of Tracer Tests

Tracer Sampling

- some tracers are light sensitive
- avoid sampling in polluted water
- don't sample treated water
- if necessary drill a borehole
- water with suspended matter should be filtered

Preparation of Tracer Tests

Tracer Sampling

Preparation of Tracer Tests

Tracer Selection

- type of aquifer and lithology
- toxicology
- sorption and ion exchange
- pore sizes of aquifer
- water quality
- light impact
- water usage (e.g. fishing water)
- analytical criteria
- cost aspects
- injection site
- sampling site

Preparation of Tracer Tests

Tracer Amount

- most tracer test guides: experience necessary
- EHTD 2003 (Efficient Hydrologic Tracer-Test Design): calculation is possible
- several equations used (EHTD lists 33 equations):
  - Dienert (1913): Na-fluoresceine (different aquifers)
  - Martel (1921): Na-fluoresceine (karst)
  - Timeus (1926): Na-fluoresceine (karst)
  - Aley & Fletcher (1976): Na-fluoresceine (karst, fissured)
  - UNESCO 1, 2 (1973/1983): Na-fluor. (porous/fissured)
  - Leibundgut & Wernli (1982): Na-fluoresceine (karst)
  - Käss (1992): general equation

Tracer Amount: different equations $^1/_4$

- Käss (1992):
  - $M = L \cdot k \cdot B$
  - L = 2.4 km; k = 1; B = 3 → Na-fluoresceine; porous aquifer
  - $M \approx$ 7 kg Na-fluoresceine
- UNESCO 1:
  - $M = L \cdot K$
  - L = 2.4 km; K = 1.5 → Na-fluoresceine; porous aquifer
  - $M \approx$ 3 kg Na-fluoresceine

Tracer Amount : different equations $^2/_4$

- e.g. Na-fluoresceine; porous aquifer

Q = 20 L s^{-1}; v = 10 m d^{-1}; t = 3600 h; L, s = 0.5 km; s_1 = 100 m; V = 100,000 m³; h = 10 m; C_{max} = 10 µg L^{-1}; $A = A_m$ = 1; K = 0.25 – 1

equation	M, kg	variables
UNESCO 1	0.25 – 1	K, L
UNESCO 2	3	K, Q, L, v, V
BENDEL 1949	2.5	K, Q, L
LEIBUNDGUT 1974	1.3	Q, t, C_{max}, A, „S“
LEIBUNDGUT & WERNLI 1974	2.92	t, h, s, C_{max}, A_m

Tracer Amount : different equations $^3/_4$

- e.g. WOLKERSDORFER et al. (2002): spores, closed space (flooded mine)

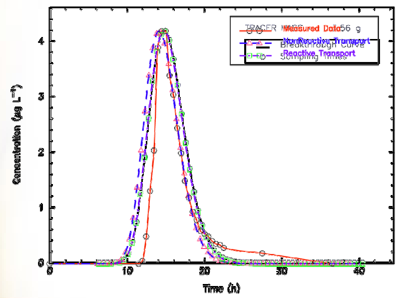
$$m = \frac{1}{55,000} \times \frac{V_m}{r_r \times q} \times f$$

m: mass/volume of tracer, g/mL; V_m: volume of enclosed fluid, m³; r_r: expected recovery rate (0.02 – 1); q: pumping capacity, L min^{-1} ; f: factor (spores 1; microspheres 0.25), g L m^{-3} min^{-1}

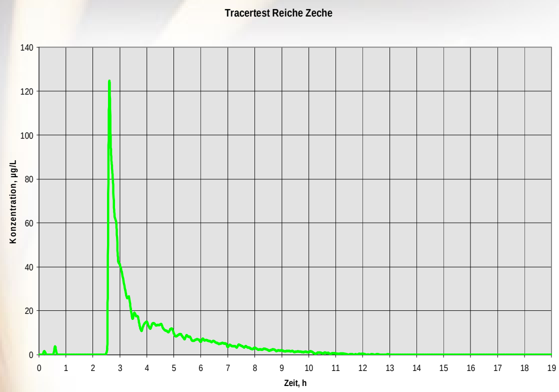
Tracer Amount : different equations $^4/_4$

- EHTD: Efficient Hydrologic Tracer-Test Design

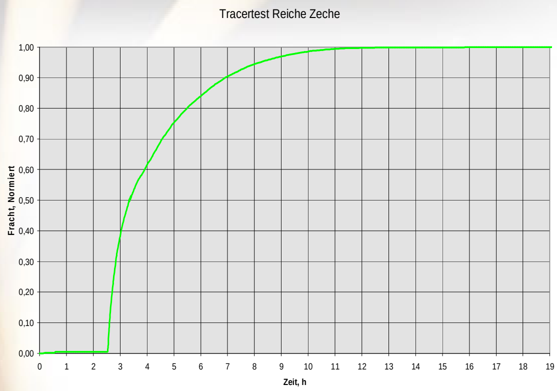
flowing stream; solution conduit (similar to "mine aquifer")



Tracer Test Reiche Zeche



Tracer Test Reiche Zeche



Responsibilities

- company
  - contract, money, site
- authorities
  - permits, public information
- you
  - everything – especially a good mood
- your employees
  - injection, sampling
- laboratory
  - analytical procedures

Preparation of Tracer Tests

Tracer Test Plan

- all relevant data must be given
- hand out tracer plan as early as possible
- public should be informed
- tracer test plan can be used to ask for permission from authorities
- tracer test plan should be ready at time of proposal to company

Preparation of Tracer Tests

Tracer Test Plan

- district, local community
- exact description of injection sites
- Home, work, and mobile telephone numbers of participants and substitutes
- relevant authorities
- goal/aim of tracer test
- type and quantity of tracers
- injection time
- quantity of priming and flushing water needed
- list of sampling sites and times

Preparation of Tracer Tests

Tracer Test Plan

Preparation of Tracer Tests

Documentation 1/4

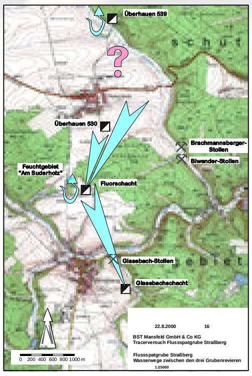
- time of injection
- type of injection
- time of sampling
- sampling procedure
- sampling interval
- sample numbers
  - think about that prior to the start of test
  - Project – Date – Sampling Site – Number
  - BRX-1902-BS1
  - SBG-0708-GS2

Preparation of Tracer Tests

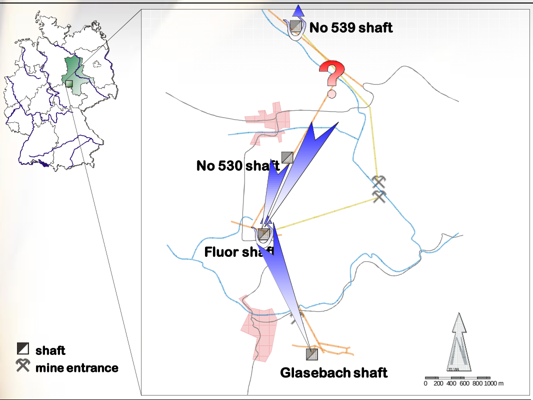
Documentation 2/4

- administrative district
- number of topographical map(s)
- detailed description of the investigation area
- name of project head
- type and quantity of tracer
- injection site(s) with co-ordinates
- start and finish times of injection
- priming and flushing water amounts
- data about every sampling site
- data presentation (e.g. breakthrough curves)

Documentation $^{3}/_{4}$



Documentation $^{4}/_{4}$



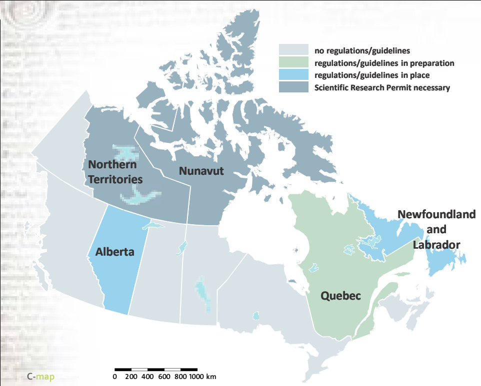
Legal Questions/Permission

- a tracer test is utilization of water
- utilization of water needs permission
  - ⇒ artificial tracer tests have to be permitted
  - ⇒ natural tracer tests need no permission
- permitting authorities
  - water authorities, mining authorities
  - contact authorities before applying for a permit
  - take into account guidelines for use of tracers
    - Germany: UBA-list
- permission takes 4–6 weeks (sometimes even longer)

Legal Questions/Permission

- no *special* legislation for tracer tests exists
- nevertheless:
  - national or regional water laws
  - in Germany: „Wasserhaushaltsgesetz“
    - § 1a: General Introduction
    - § 2: Need for Permissions
    - § 3: Utilization
    - § 4: Conditions for Utilization
    - § 7: Permission
- necessary data for permission
  - kind of tracer, duration, start, place, responsible persons

Legal Questions/Permission



Responsibilities in Canada

- In Canada, inform the following authorities
  - Fisheries and Oceans Canada (DFO)
  - Environment Canada
  - Provincial environment department.
- Guidelines exist in
  - Alberta
- Draft Version of Guidelines
  - Quebec
- Case by Case Decision
  - Newfoundland and Labrador
  - Northwest Territories
  - Nunavut

Legislation

Provide the following information

- District and place name including map and map references
- Person responsible for conducting tracer test and contact phone numbers
- Customer with full address
- Purpose of the tracer test
- Type of tracer with its exact name, CAS number (Chemical Abstracts Service Registry Number), expected dilution, LD_{50} (50% lethal dose) data and MSDS sheets
- Description of injection sites including map
- A list of sampling sites including map and sampling intervals
- Water quantities to flush the injection site and the tracer including where water will be drawn from
- Start of tracer test including start and end of tracer injection
- Work schedule for continuous sampling
- Necessary measurements on site
- Work schedule for analytical laboratory
- Emergency plan including contact phone numbers

Implementation

Implementation

- Injection Time and Injection Procedure
  - when to inject the tracer
  - how to inject the tracer
- Sampling procedure
  - kind of sampling procedure
- Tracer Preparation, Analyses
  - storage, preparation
  - analytical procedures
- Documentation and Presentation
  - report
  - graphical presentation

Implementation

Injection: Time and Procedure

- injection time
  - results from hydrogeological investigation
  - leave enough time for preliminary preparations on site
  - all personnel and material should have enough time to get to the site
  - start at the beginning of a week to avoid the usual „Friday-late-afternoon“ hurry
  - take into account holidays and working hours in factories or mines
  - inject most effective tracers first (long flow distances)

Implementation

Injection: Time and Procedure

- procedure
  - flush containers several times to inject tracer fully
  - flush tracer into aquifer or unsaturated zone by using excess water
  - tracer has to flow through unsaturated zone first before reaching the aquifer
  - avoid any contamination
  - avoid cross-contamination (e.g. pH-meters)
  - dissolve fluorescent tracer dyes in the laboratory
  - it might be necessary to use boreholes for tracer injection
  - keep in mind: tracer injection changes the groundwater's flow properties

Implementation

Injection: Time and Procedure

- procedure
  - avoid slow tracer injection
    - „smearing“ could sham non existing dispersion
  - inject tracer as quick as possible (DIRAC-function)

$$\delta(t) = \begin{cases} 0 & t \neq 0 \\ \infty & t = 0 \end{cases}$$

$$\int_{t_1}^{t_2} dt\,\delta(t) = 1$$

Implementation

Sampling procedure

- people taking the samples have great responsibility – choose them carefully
- correct labelling is essential
- you must stay to the predefined sampling plan
- inform head of project immediately if any changes occur (e.g. no more tracer visible or vice versa)
- if possible, use automatic sampling devices
- pumps can help

Implementation

Sampling procedure

- sample time must be recorded accurately (not as in the sampling plan!)
- sample containers must be clean
- try to use brown glass containers
- store samples in a dark cool place
- take enough sample volume (at least 250 mL)
- samples should be brought to the laboratory as soon as possible

Implementation

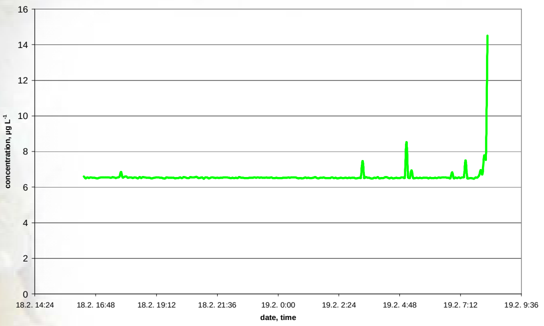
Tracer Preparation, Analyses

- some minerals have spectral bands similar to the tracers you use
- sort the samples in the order of their extraction to recognize sampling errors
- include background analyses
  - lithium in karst water: 1 – 2 µg L^{-1}
  - fluorescein-Na in karst water: 0.003 µg L^{-1}
- only if background is know accurately enough, tracer test can be evaluated
- series determination is easier than single determination – but keep in mind tracer decomposition

Implementation

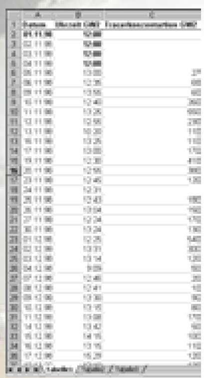
Tracer Preparation, Analyses

- background signals



Implementation

Documentation and Presentation



- date
- time
- sampling circumstances
- person in charge of sampling
- weather conditions
- tracer concentration
- physico-chemical parameters

Implementation

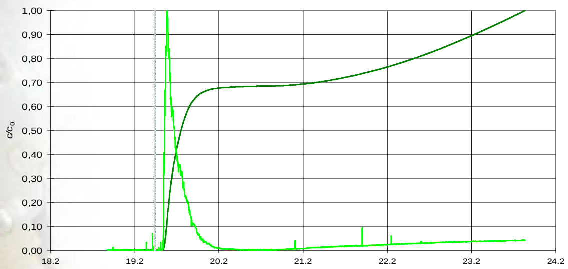
Documentation and Presentation

- municipal and administrative district
- number of topographical map
- designation of investigation area
- name of project head
- type and quantity of tracer
- injection sites with name, co-ordinates, altitude, geological formation
- start and finish times of tracer injections, priming and flushing water, flow volume
- sampling sites
  - name, co-ordinates, discharge or pump rate, tracer concentration, start and finish of observation

Implementation

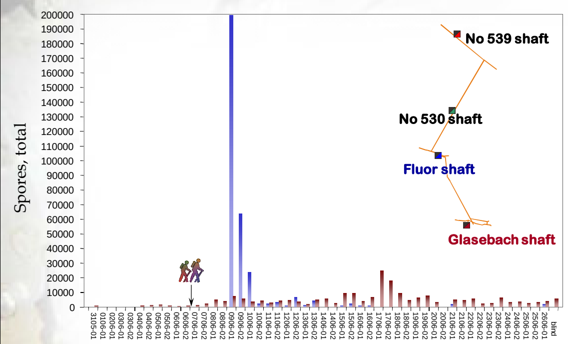
Documentation and Presentation

- use breakthrough curves
- normed curves should be used
- summation curves ease understanding



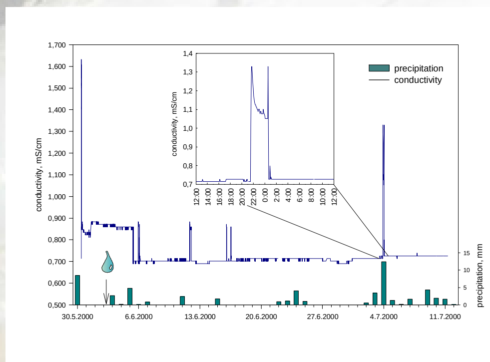
Implementation

Documentation and Presentation



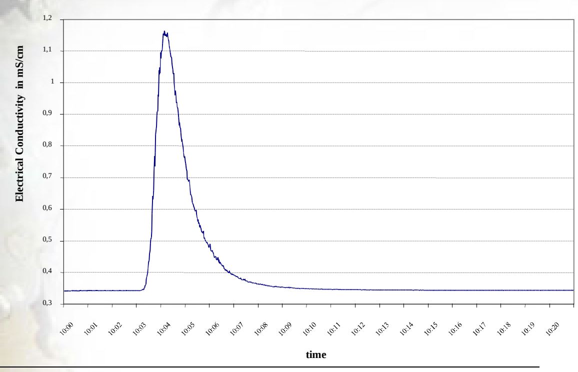
Implementation

Documentation and Presentation



Implementation

Documentation and Presentation



Meister 2002

Evaluation

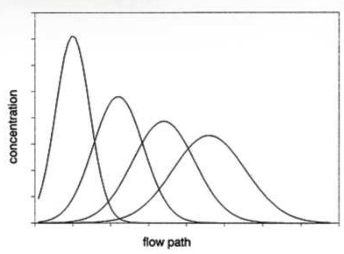
Types of Aquifers and Methods

- Porous Aquifers
- Fracture Aquifers
- Karst Aquifers
- Evaluation of Break Through Curves

Evaluation

Porous Aquifers

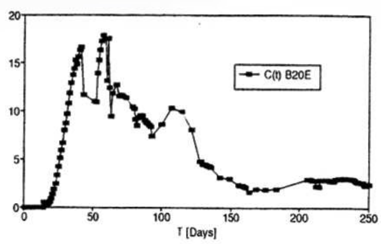
- DARCY flow
- GAUSS distribution
- Relatively high recovery rates
- Low effective velocities
- Analytical solution is possible



Evaluation

Fracture Aquifers

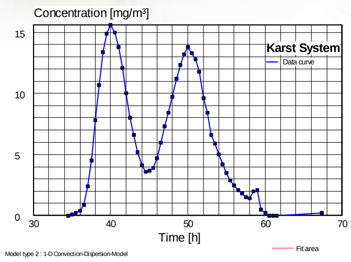
- No DARCY flow
- No GAUSS distribution
- Relatively low recovery rates
- Mean effective velocities
- SFDM model commonly used (single fissure dispersion model)



Evaluation

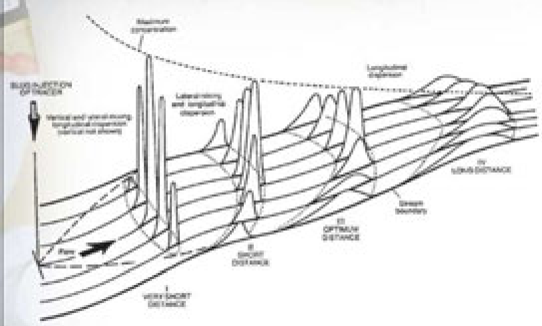
Karst Aquifers

- DARCY flow can be used
- GAUSS distribution
- Relatively high recovery rates
- High to extreme effective velocities
- MDM model (multi dispersion model)



Evaluation

Evaluation of Tracer Tests



Kilpatrick & Wilson 1989,

Evaluation

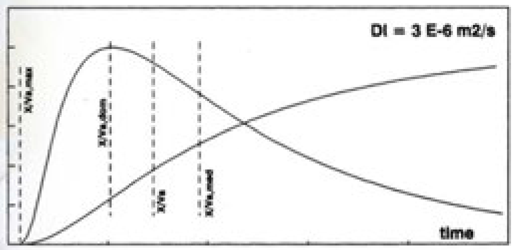
Evaluation of Tracer Tests

- Different Methods have been developed
  - Cumulative curve method
  - Method of moments
  - Analytical Methods

Evaluation

Evaluation of Break Through Curves

- Break through curve
- Sum curve



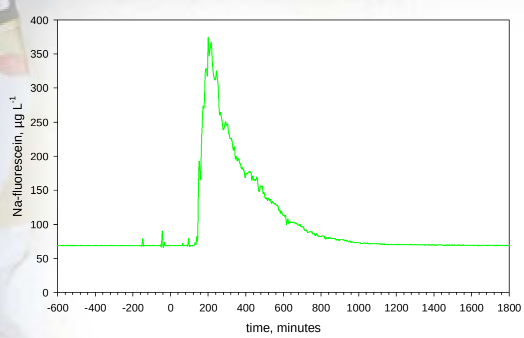
Evaluation

Evaluation of Break Through Curves

- t_0: start of tracer test
- t_1: first tracer arrival
  - Maximal effective velocity
- t_{dom}: maximal tracer concentration
  - Dominating effective velocity
- $t_{med} = t_{50}$: median tracer concentration
  - Mean effective velocity
- t_w: mean tracer concentration
  - Real effective velocity

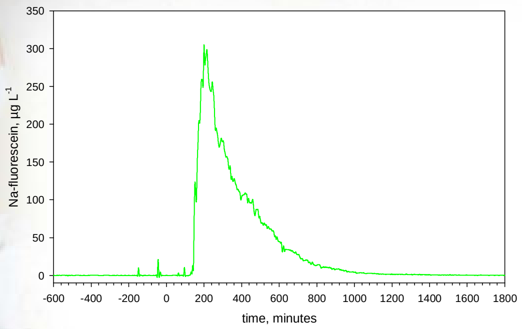
Evaluation

Original Break Through Curve



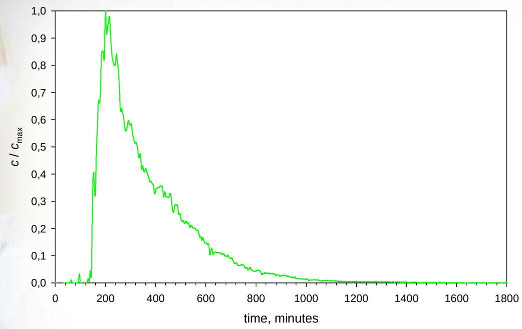
Evaluation

Break Through Curve without background



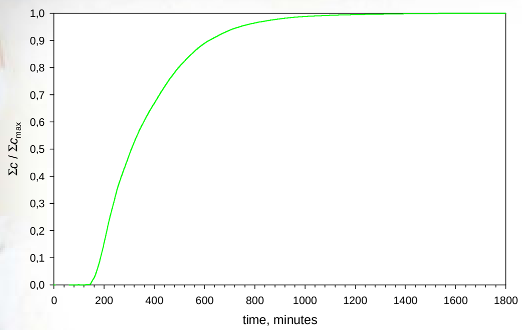
Evaluation

Break Through Curve Normalised



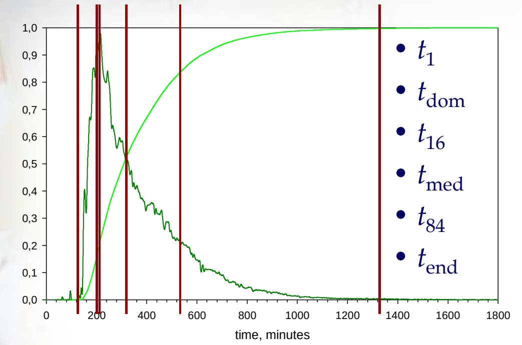
Evaluation

Sum Curve Normalised



Evaluation

Sum Curve Normalised



- t_1
- t_{dom}
- t_{16}
- t_{med}
- t_{84}
- t_{end}

Evaluation

Velocities

$$v = \frac{x}{t} \qquad D_L = \frac{v_{50}^2 \cdot (t_{84} - t_{16})^2}{8 \cdot t_{50}} \qquad D_L = v \cdot \lambda$$

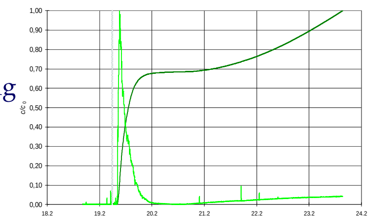
- t_1 150 min: v = 6,67 cm min^{-1}
- t_{dom} 200 min: v = 5,00 cm min^{-1}
- t_{16} 201 min: v = 4,98 cm min^{-1}
- t_{med} 309 min: v = 3,24 cm min^{-1}
- t_{84} 538 min: v = 1,86 cm min^{-1}
- t_{end} 1500 min: v = 0,67 cm min^{-1}
- D_L = 1,5 m² min^{-1} (λ = 0,005 m)
- $D_T \approx 0{,}1\ D_L$ = 0,15 m² min^{-1}

Evaluation

Recovery Rate

$$r = \frac{\int_{t_1=0}^{t_n} c \cdot \delta t \cdot Q}{M}$$

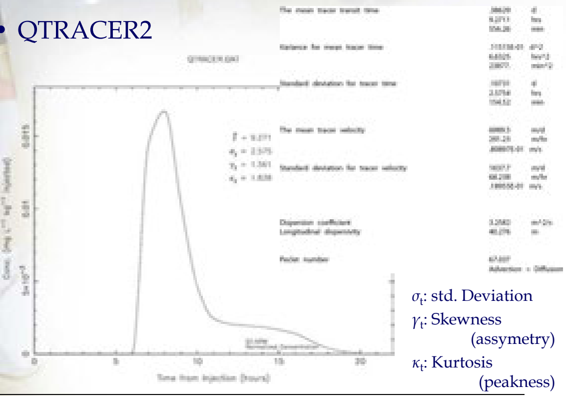
- Q = 23 L min^{-1}
- M = 50 g
- *Integral* = 485,3 mg
- r = 1 %



Evaluation

Method of Moments

- QTRACER2



σ_t: std. Deviation
γ_t: Skewness (assymetry)
κ_t: Kurtosis (peakness)

Examples

Examples

- Surface/Ground Water
  - Surface flow measurements
  - hydraulic connection (Taucherfriedhof Bautzen)
- Mine Water
  - Multiple shafts (Straßberg/Harz)
  - Single shaft (Brixlegg/Tirol)

Examples

Surface Flow Measurements

- Standing (lakes) and flowing (rivers) water bodies
- Detection of flow connections
- Flow Velocities
- Mixing conditions
- Dispersion
- Flow Measurements
- Evaluation of physical parameters
  - Oxygen depletion (degasing measurements)
  - Light input (decomposing tracer)

Examples

Surface Flow Measurements

- Flow velocities
- Known tracer amount injected
- Mixing of tracer
- DIRAC impulse

$$Q = \frac{M}{\int_{t=0}^{t=\infty} c_t \, dt}$$

M = injected tracer amount
C_t = concentration of tracer at time t
t = time of tracer sampling

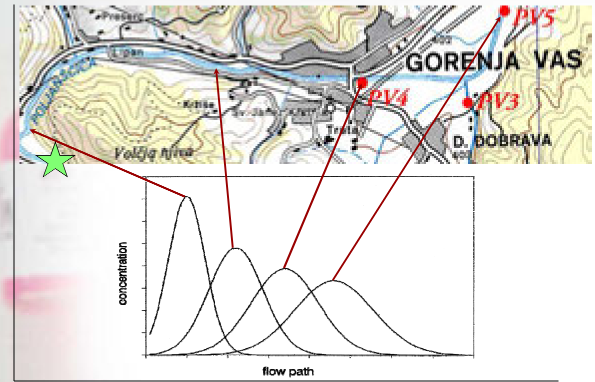
Examples

Surface Flow Measurements

- Measurement in middle of river
- Possible Tracers
  - NaCl
  - Na-fluorescein (Uranine)
  - Rhodamine WT
- Fluorimeter (fibre optics)
- Electrical Conductivity

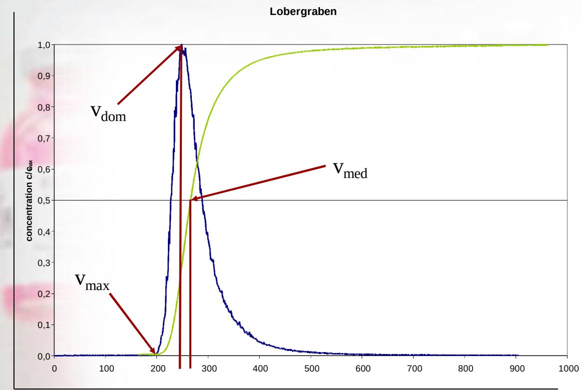
Examples

Surface Flow Measurements



Examples

Surface Flow Measurements



Examples

Surface Flow Measurements

- Results

$$Q = \frac{M}{\int_{t=0}^{t=\infty} c_t\,dt} = \frac{10{,}000\ \text{g}}{65.9\ \frac{\text{g}\cdot\text{s}}{\text{L}}} = 0.15\ \text{L}\cdot\text{s}^{-1} = 9.1\ \text{L}\cdot\text{min}^{-1}$$

M = injected tracer amount

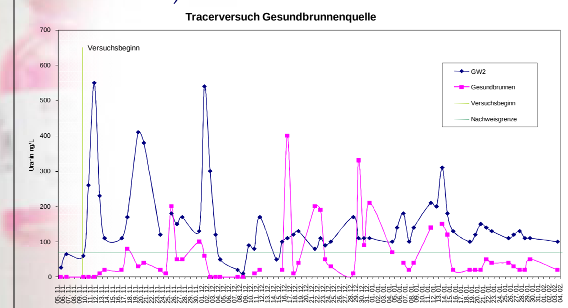
c_t = concentration of tracer at time t

t = time of tracer sampling

Examples

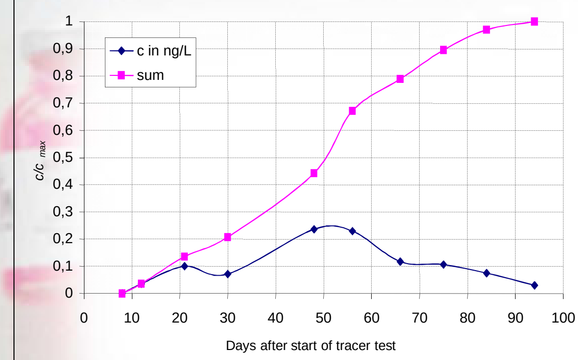
Ground Water

- Taucherfriedhof Bautzen (hydraulic connection)



Examples

Ground Water



Examples

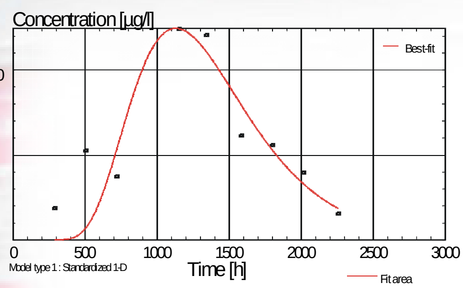
Ground Water

- $t_1 = 12$ d $\Rightarrow$ $v_1 = 2.7 \cdot 10^{-4}\ \text{m}\cdot\text{s}^{-1}$
- $t_{dom} = 49.5$ d $\Rightarrow$ $v_{dom} = 6.5 \cdot 10^{-5}\ \text{m}\cdot\text{s}^{-1}$
- $t_{16} = 25.6$ d $\Rightarrow$ $v_{16} = 1.3 \cdot 10^{-4}\ \text{m}\cdot\text{s}^{-1}$
- $t_{50} = 49.7$ d $\Rightarrow$ $v_{50} = 6.5 \cdot 10^{-5}\ \text{m}\cdot\text{s}^{-1}$
- $t_{84} = 68.5$ d $\Rightarrow$ $v_{84} = 4.7 \cdot 10^{-5}\ \text{m}\cdot\text{s}^{-1}$

$$v_a = \frac{v_f}{n_e} = \frac{2.1\cdot 10^{-6}}{0.025} = 8.4\cdot 10^{-5}\ \text{m}\cdot\text{s}^{-1}$$

Examples

Ground Water



$t_{50} = 56.9$ d $\Rightarrow v_{50} = 5.7 \cdot 10^{-5}$ m/s

$D_L = 5 \cdot 10^{-3}$ m²/s

$\lambda = 91$ m

- Brixlegg/Tirol
  - historical silver-barite mine
  - 100 m deep shaft
    - 20, 40, 70, 100 m levels
  - Flooded since 1990
  - Outflow 20—50 $L \cdot min^{-1}$