Tracers in Hydrology

Experimental Design, Application in Water Research and Data Analysis

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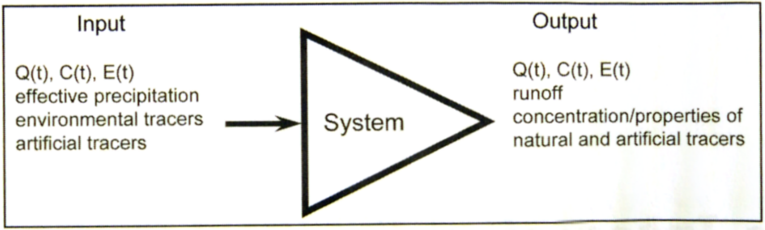
Introduction

This lecture is based on the accompagnying textbook Tracers in Hydrology (Leibundgut, Maloszewski, and Külls 2009). The lecture includes five major units:

1. The right choice of tracers, tracer properties, the tracer approach
2. Experimental Design for different hydrological compartments
3. Modelling of tracer experiments with different approaches and models
4. Data analysis and making use of data for applications in water systems research
5. Exercises (Group and online)

The Tracer Approach

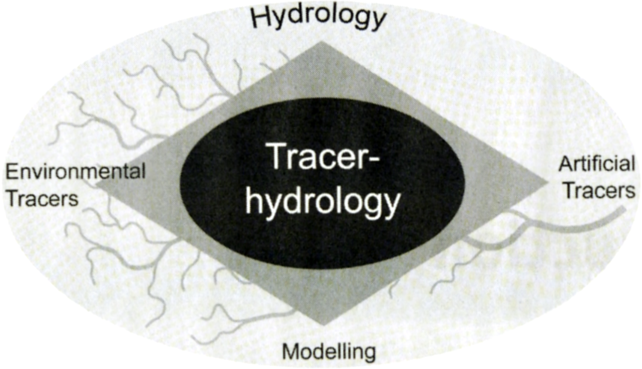
The information on the hydrological system **converges** in runoff and in the tracer properties of runoff (quality, artificial tracers, environmental isotopes.)



Convergence of information in Q(t), E(t) and C(t)

The Tracer Approach

Tracer hydrology is the scientific method of coding and decoding information contained in water properties and artificial or environmental substances transported by water.



Tracer hydrology as part of hydrological sciences and with its main tools and methods

Tracers

Classification

There are artificial, pollution and environmental tracers.

Environmental tracers	Artificial tracers
Utilization	*Application*
Environmental isotopes	Chemicals
Hydrochemical substances	Biological substances
Pollution tracers	Drift substances
Characteristics:	*Characteristics:*
Spatial input via precipitation, geogenic sources	punctual input (injection), defined by time, place, hydrological situation
Pollution tracers (e.g. Cl^- SF_6 CFCs)	

Current tracers

Environmental traces		Artificial traces	
Environmental isotopes		Solvents	
Stable		Radioactive	Salts
Deuterium	^{2}H	Tritium	$Na^{+}Cl^{-}$
Oxygen-18	^{18}O		$K^{+}Cl^{-}$
Carbon-13	^{13}C		$Li^{+}Cl^{-}$
	^{3}He		
Helium-3	^{15}N		HBO_2
Nitrogen-15			
Sulfur-34	^{34}S		
Radioactive		*Drifting particles*	*Fluorescence tracers*
Tritium	^{3}H		
Carbon-14	^{14}C		Uranine
Argon-39	^{39}Ar	Lycopodium spores	Eosine
Krypton-85	^{85}Kr	Fluorescent particles	Naphtionate
Silicium-32	^{32}Si	Bacteria	Pyranine
Chlorine-36	^{36}Cl	Viruses	Amidorhodamine
Geochemical compounds		Phages	Rhodamines
Elec. Conductivity	ec		
Sodium chloride	NaCl		
others	Si, B, DOC		
Pollution Tracers, for example CFCs, . . . heavy metals, phosphate, radioactive compounds			

Applications of artificial tracers

	Atmospheric water	Surface water	Soil and unsaturated zone	Ground-water	Glacier and Snow	Catchment hydrology	Special application
Global circulation	+					+	
Discharge measurement		+		+	+	+	
Delination of hydrological units and protection zones			+	+	+	+	
Hydrologic/hydraulic connections			+	+	+	+	
Evaluation of flow paths			+	+	+	+	
Altitude of source areas				+	+	+	
Age dating		+	+	+	+	+	
Experimental hydrograph separation				+	+	+	
Runoff generation processes			+	+	+	+	
Residence times		+	+	+	+	+	
Flow and transport parameters	+	+	+	+	+	+	
Dispersion and diffusion processes		+	+	+	+	+	+
Mixing processes	+	+		+		+	+
Permeabilities			+	+	+	+	
Infiltration processes			+			+	+
Infiltration/exfiltration processes		+	+	+	+	+	+
Groundwater recharge		+	+	+	+	+	
Interaction between surface and subsurface water		+	+	+		+	
Hyporheic exchange		+	+	+		+	+
Filtration processes		+	+	+			+
Stratification of lakes		+					
Circulation currents		+					
Contaminant transport	+	+	+	+		+	+
Engineering hydrology		+		+			+

Applications in water sciences

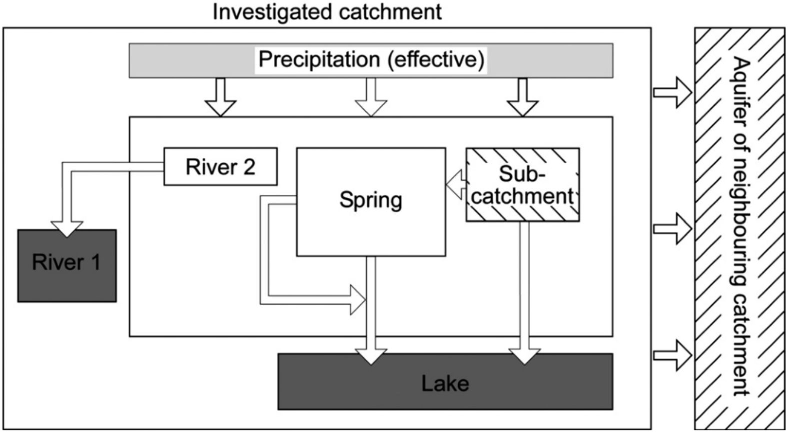
Tracer applications span of hydrological compartments and a wide range of purposes from basin delineation (groundwater, to residence time estimation or origin assigment). They can be subdivided according to:

- compartment type: rivers, lakes, glacers, groundwater, soil
- function and purpose: velocity estimation, discharge measurement, protection zones
- scale and circumstances of applications: micro- (cm to m), meso- (100m to 1000m), macro-scale ($>$ 1000 m)

In general, tracer applications are limited to durations of **less than 3 months max** and to **less than a km**.

Conceptualization

Tracer applications are closely linked to conceptualization of hydrological systems.



Tracer hydrology helps with the conceptualization of complex hydrogeological and hydrological basins

Case study

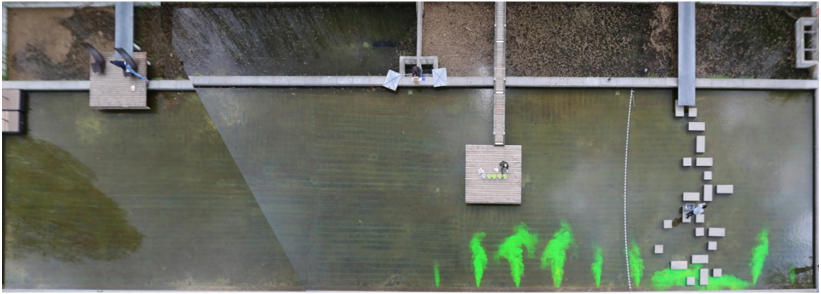
Study of a water treatment facility for a public bath: Initial condition t=0

Study of residence time in a water treatment facility

Study of a water treatment facility for a public bath: Initial condition t=1

t=2

t=3



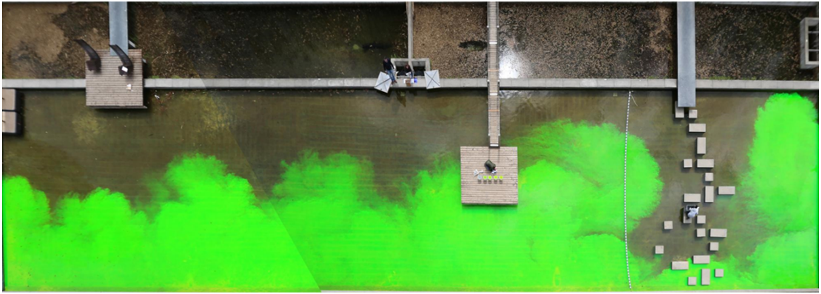
t=4

t=5

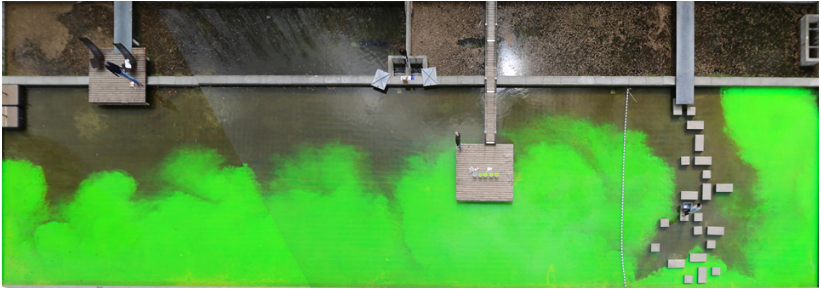
t=6

t=8

t=9



t=10



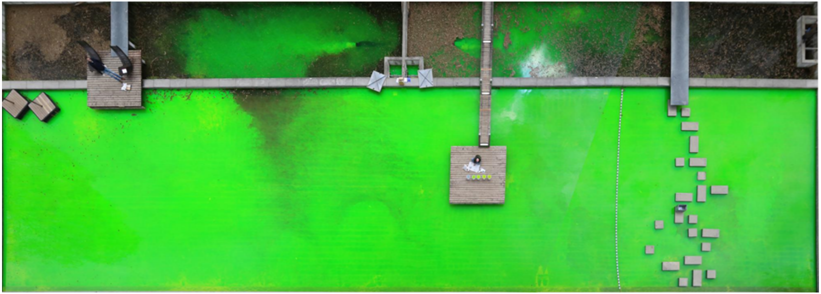
t=11

t=12

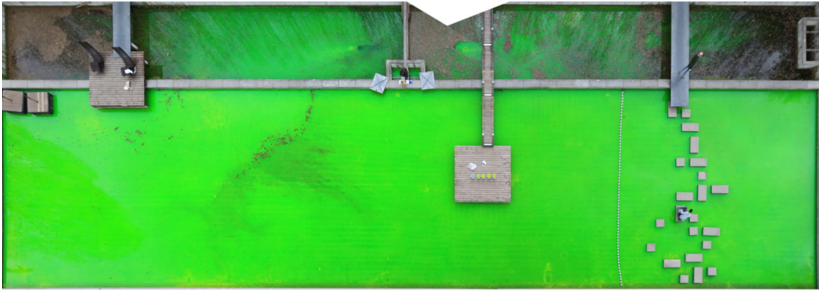
t=13

t=14

t=15

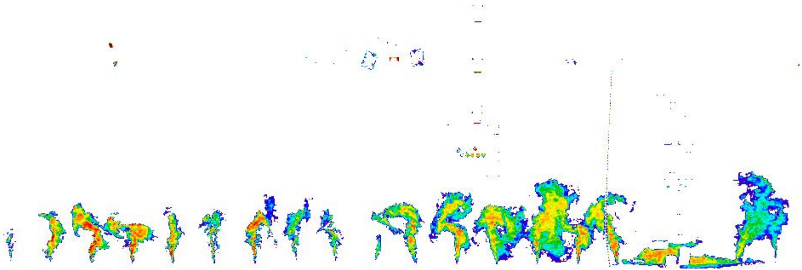


t=16



t=17

Calibration



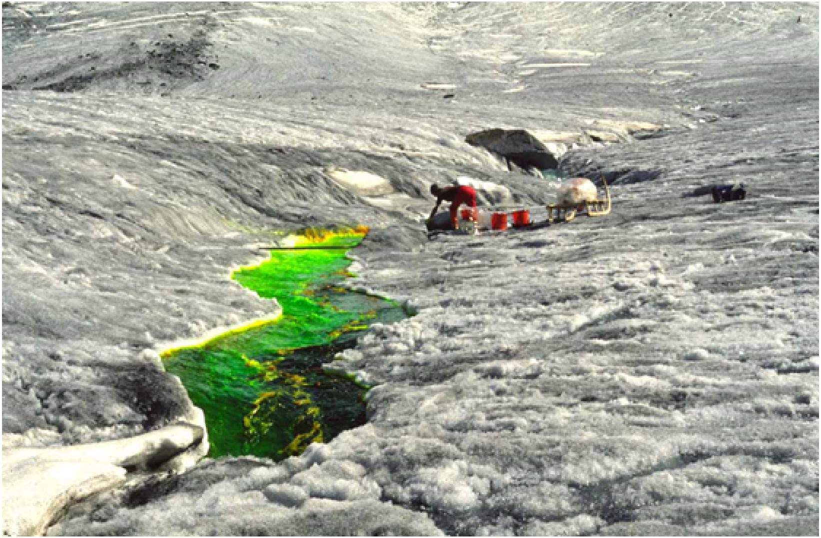
Calibration of picture with buckets containing tracer at different concentration

Results

Lakes

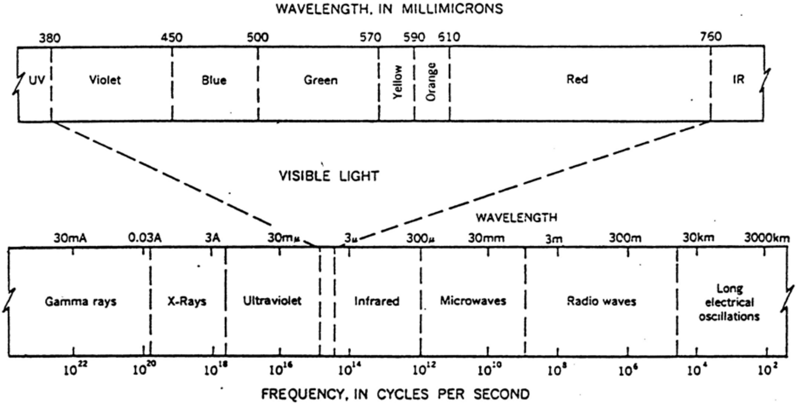
Rivers

Glacier



Tracer substances

Spectrum



aus: WILSON (1968)

Tracer substances

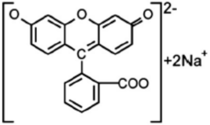
Artificial tracers

Artificial tracers					
Soluted or in aqueous solution					Solid
Fluorescence tracers	Salt tracers	Radioactive tracers	Activatable tracers (radioactive)	Advanced tracers	Drifting particles
Naphthionate	Chlorid (Na^+Cl^-, K^+Cl^-)	Tritium ^3H	Bromide (^{80}Br)	Gases (e.g. SF_6)	Lycopodium spores
Pyranine	Li^+Cl^-	Chrome (^{51}Cr)	Indium (^{116m}In)	'Heavy' water (^2H)	Fluorescent particles
Uranine	Bromid (K^+Br, Na^+Br^-)	Indium (^{114m}In, ^{114}In)	Manganese (^{56}Mn)	Fluorobenzoic acids	Bacteria/viruses
Eosine	Iodide (K^+I^-)	Cobalt (^{58}Co, ^{60}Co)	Lanthanum (^{140}La)	Nonfluorescence dyes	Phages
Amidorhodamine G		Bromide (^{82}Br)	Dysprosium (^{165}Dy)	Temperature	DNA
Rhodamines					

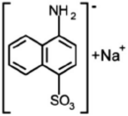
Overview of fluorescent dyes

Commercial name	Ex/Em max nm	Compound class	CI: generic name	CI number	Chemical name	Chemical formula	Molecular weight
Naphthionate *Naphtionate Sodium-salt*	325/420	Aminonaphtalensulfonic acid		—	4-Amino-1-naphtalensulfonic acid sodium salt	$C_{10}H_8NNaO_3S$	245.23
Pyranine *D&C Green 8*	Circa 460/510	Anthraquinone	Solvent Green	59040	1-Hydroxy-pyren-3,6,8-trisulfon-trisodium	$C_{16}H_7Na_3O_{10}S_3$	524.39
Uranine *Sodium-fluorescein, D&C Yellow 7*	491/516	Xanthene	Acid Yellow 73	45350	Hydroxy-6-oxo-9-(2-carboxyphenyl)-xanthene	$C_{20}H_{10}O_5Na_2$	332.31
Eosine *Eosine Yellow D&C Red 22*	515/540	Xanthene	Acid Red 87	45380	3-Hydroxy-6-oxo-2,4,5,7-tetrabromine-9(−2′-caboxyphenyl)-xanthene-disodium	$C_{20}H_6Br_4Na_2O_5$	691.88
Amidorhodamine G *Sulforhodamine G*	Circa 530/555	Xanthene	Acid Red 50	45220	3,6-Bis-ethylamino-2,7-dimethyl-9-2′,4′-disulfophenyl-sodium	$C_{25}H_{25}N_2NaO_7S_2$	552.59
Sulforhodamine B	Circa 560/585	Xanthene	Acid Red 52	45100	3,6-Bis-diethylamino-9-(2′,4′-disulfophenyl)-sodium	$C_{27}H_{29}N_2NaO_7S_2$	580.65
Rhodamine B	Circa 555/570	Xanthene	BasicViolet 10	45170	3,6-Bis-diethylamino-9-(2′carbophenyl)-xanthylium-chloride	$C_{28}H_{31}ClN_2O_3$	479.02
Rhodamine WT	Circa 560/585	Xanthene	Acid Red 388	—	3,6-Bis-diethylamino-9-(2′,4′-dicarboxylphenyl)-xanthylium-sodium	$C_{29}H_{29}N_2NaO_5$	480.55

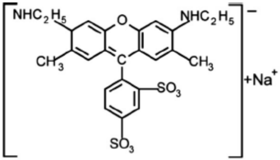
Dye tracer chemistry



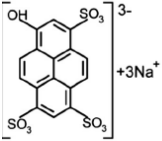
Uranine



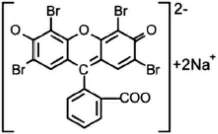
Naphtionate



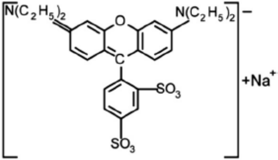
Amidorhodamine G



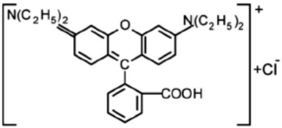
Pyranine



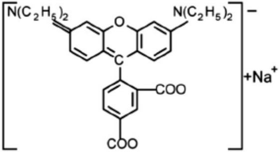
Eosin



Sulforhodamine B

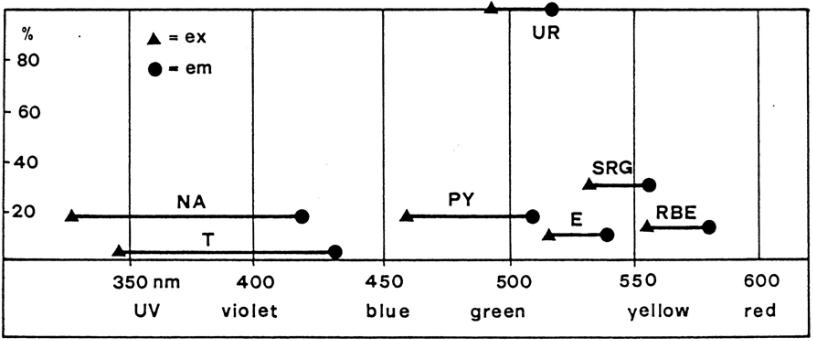


Rhodamine B



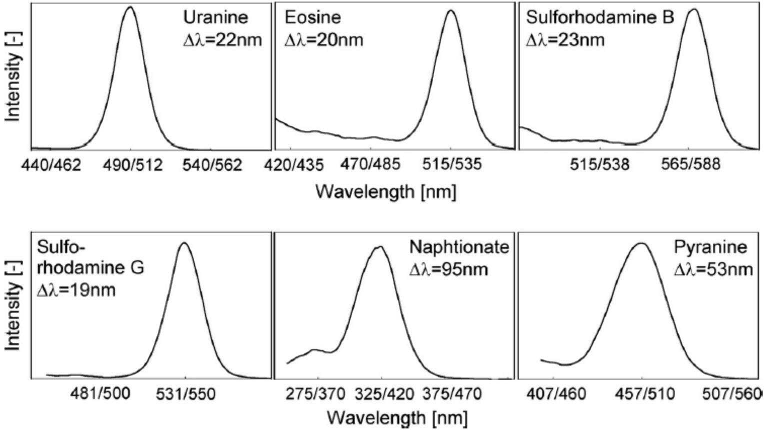
Rhodamine WT

Spectral ranges



NA = Naphthionat, T = Tinopal, PY = Pyranin, UR = Uranin, E = Eosin, SRG = Sulphorhodamin, RBE = Rhodamin B extra.

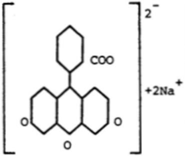
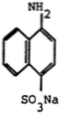
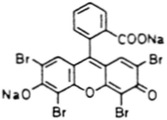
Tracer substances: Spectra and $\delta\lambda$



Excitation and emission spectra of common fluorescent dyes

Tracer substances

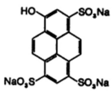
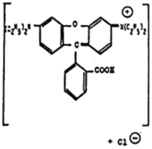
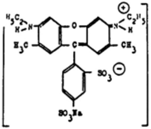
Fluorescent dyes

Handelsname	Uranin	Naphthionat	Eosin
Referenz-Farbindex	Acid Yellow 73 CI 45350		Acid Red 87 CI 45380
Chemische-Bezeichnung	Natrium-Fluoreszein	1-Naphthylamin-4-sulfonsäure Na - Salz;Naphthionsäure Natriumsalz	2',4',5',7',-Tetrabromfluorescein Dinatriumsalz
Summenformel	$C_{20}H_{10}O_5Na_2$	$C_{10}H_8NNaO_3S$	$C_{20}H_6Br_4Na_2O_5$
Strukturformel			
Molekulargewicht	376.15	245.23	691,88

Tracer substances: Naphthionate

Tracer substances

Fluorescent dyes

Handelsname	Pyranin	Rhodamin B	Sulphorhodamin G extra
Referenz-Farbindex	Solvent green CI 59040	Basic Violet 10 CI 45170	Acid Red 50 CI 45220
Chemische Bezeichnung	8-Hydroxy-1,3,6-pyrentrisulphonsaures Natrium	NNNN Tetraethylrhodamin-Chlorhydrat	Diethyldiamino-3,6-dimethyl-3,7-phenyl-9 xanthylium disulfonat-2,7-Natriumsalz
Summenformel	$C_{16} H_7 Na_3 O_{10} S_3$	$C_{28} H_{31} O_3 N_2 Cl$	$C_{25} H_{25} O_7 N_2 S_2 Na$
Strukturformel			
Molekulargewicht	524,38	479,02	631

Tracer substances: Rhodamines

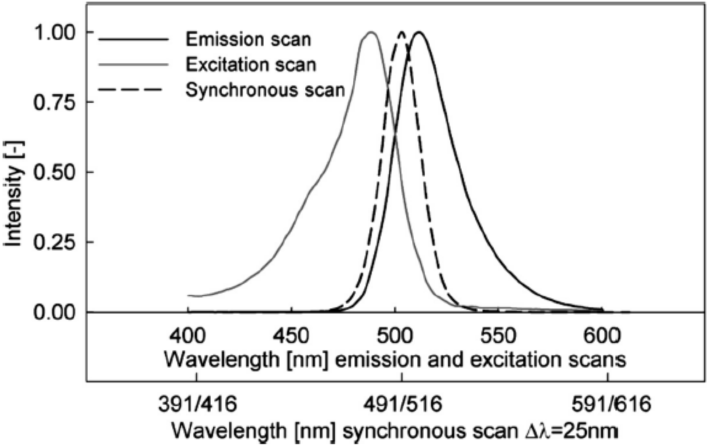
Tracer substances

Dectection limits

	Exitation/ Emission [nm]	Relative Fluorescene eff. [Uranin =100%]	Detection limit [mg/m³]
Uranin	491/516	100	0,002
Eosin	515/538	11,4	0,02
Amidorhodamin G extra	530/555	30	0,005
Rhodamin B extra	553/578	12,8	0,01
Rhodamin B	553/578	6,3	0,02
Tinopal	345/430	4	0,4
Pyranin	460/512	18	0,02
Naphtionat	325/420	18	0,3-0,5

Measurement

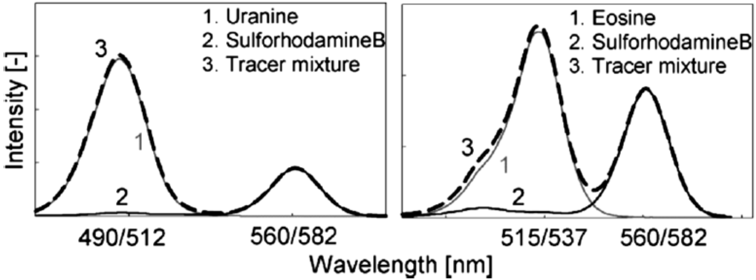
Synchronous scan of excitation and emission, $\delta\lambda = 25nm$



Excitation-spectrum (peak $\Delta\lambda = 491\,\text{nm}$), emission-spectrum (peak $\Delta\lambda = 516\,\text{nm}$)

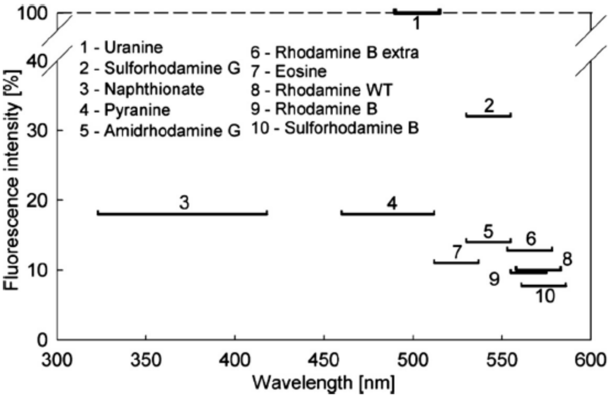
Results of synchro-scan with spectral fluorometer

Measurement of dye tracers



Separating tracers with different $\delta\lambda$

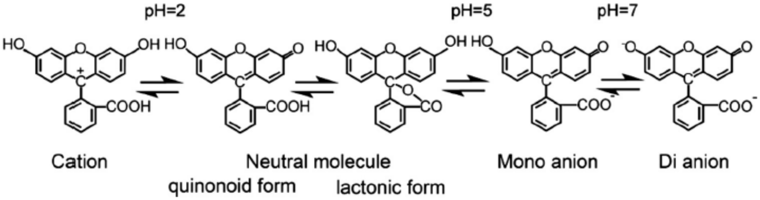
Measurement of dye tracers



Fluorescent tracers: Stokes shifts (nm) and intensities (%) of different tracers.

Wavelengths of excitation and emission of common dyes

pH dependency (Uranine)



Chemical causes of pH dependency for Uranine, Behrens (1986)

Tracer properties

Criteria for the choice of tracers

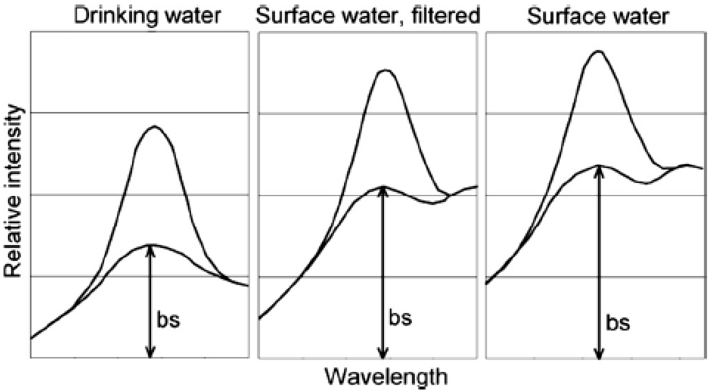
Properties to be considered	Requirements of an ideal (conservative) tracer
1. Solubility in water	High
2. Fluorescence intensity	High
3. Detection limit	Low
4. ***pH dependence***	Low
5. ***Temperature dependence***	Low
6. ***Photolytic stability***	High
7. ***Sorption processes***	Negligible
8. ***Chemical and biological stability***	High
9. Toxicity and related environmental effects	None or minimal
10. Costs and other practical aspects	Low or moderate

Tracer properties

Detection limits of dye tracers

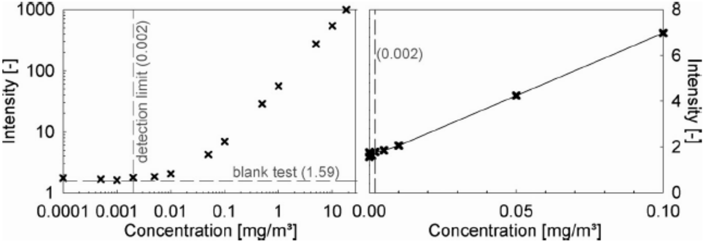
Dye	Relative fluorescence intensity [Uranine = 100%]	Detection limit [mg/m^3]	Excitation/ emission [nm]
Naphthionate	18	0.2	325/420
Pyranine	18	0.06	455/510
Uranine	100	0.001	491/516
Eosine	11.4	0.01	515/540
Amidorhodamine G	32	0.005	530/555
Rhodamine B	9.5	0.02	555/575
Rhodamine WT	10	0.02	560/585
Sulforhodamine B	7	0.03	561/586

Detection limits



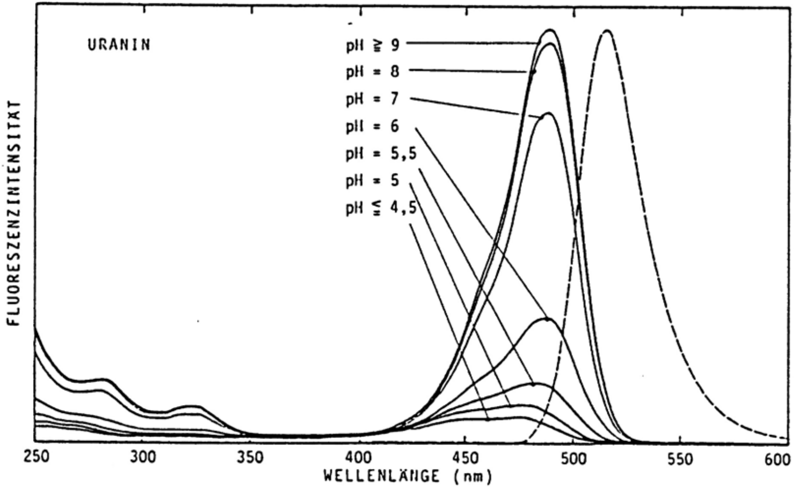
Spectral curves and background signals (bs) of Naphthionate (1 mg/cm) in different waters, excitation and emission peaks at 325 and 420 nm.

Calibration

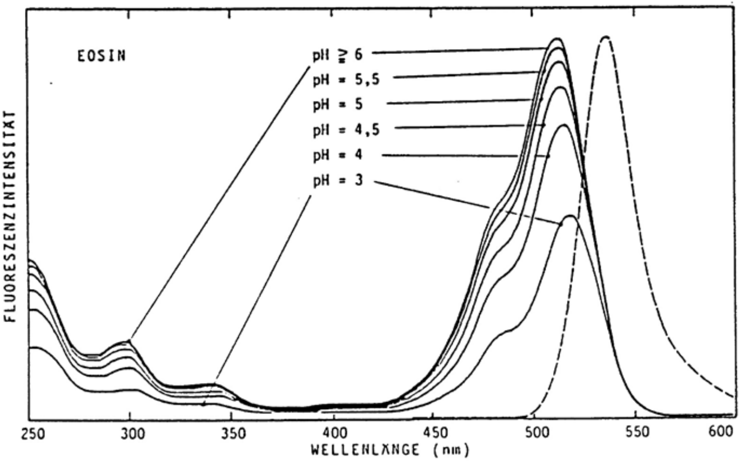


Calibration curve of Uranine in the range of linearity up to a fluorescence intensity of approximately 20mg/cm ($y = 54.553x + 2.26213$; $R^2 = 0.99$) *(for concentration* $>0.002\ mg/m^3$*)*

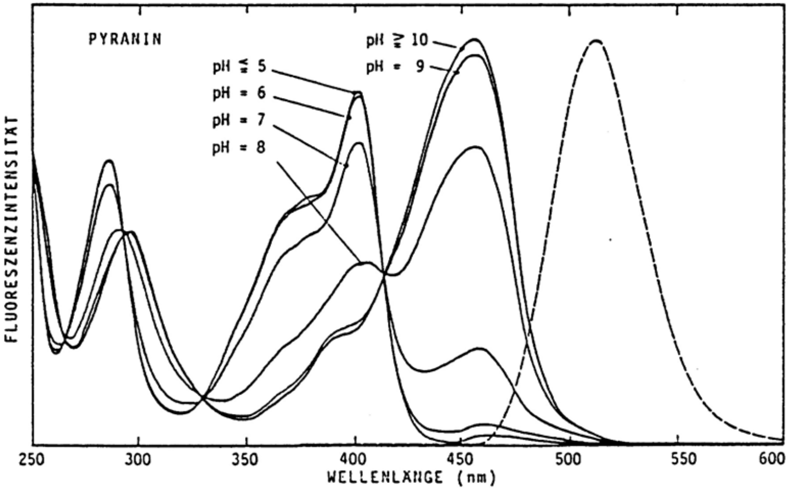
pH dependency



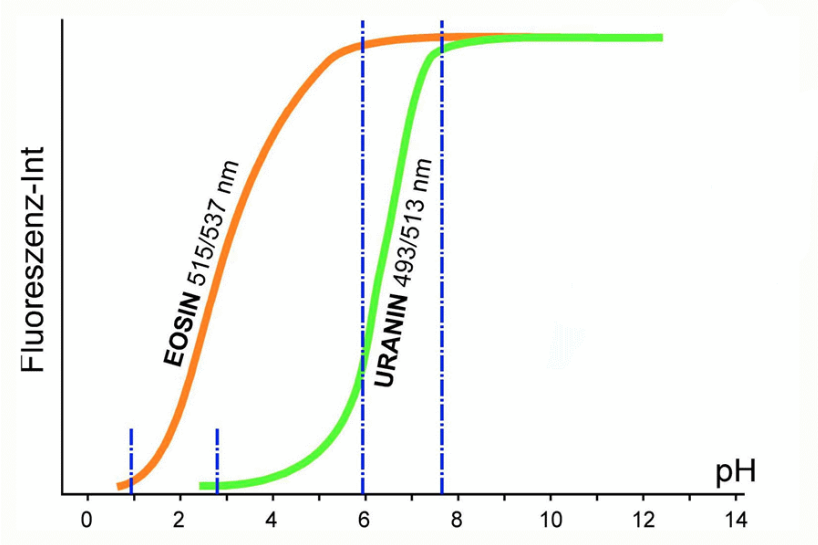
pH dependency



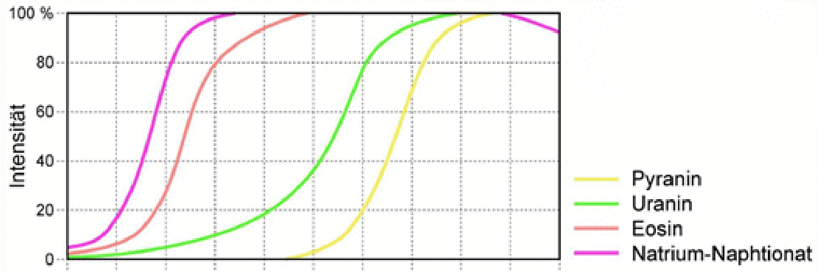
pH dependency



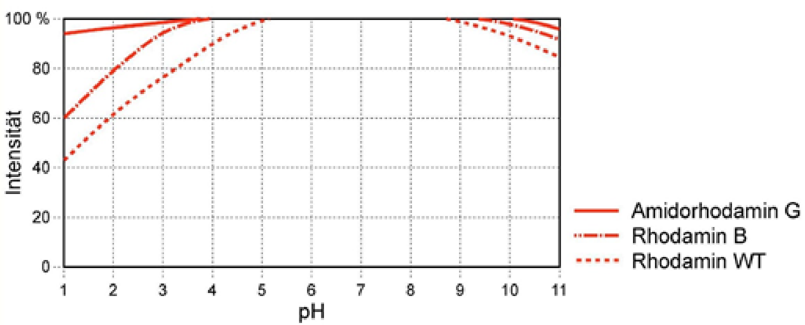
pH dependency



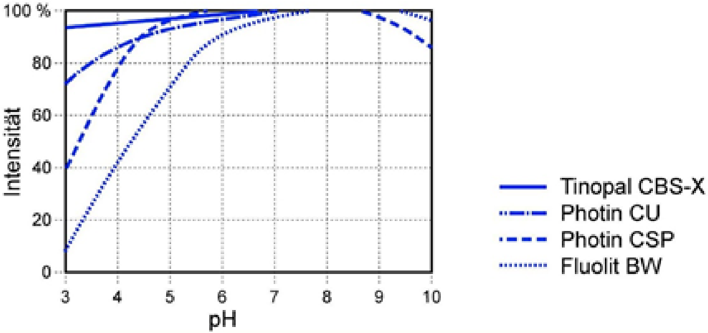
pH dependency of other dye tracers



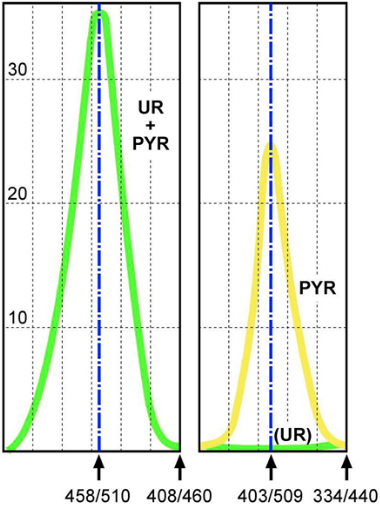
pH dependency of other dye tracers



pH dependency



Making use of pH dependeny



Suppressing fluorescence when measuring two tracers

Temperature dependency

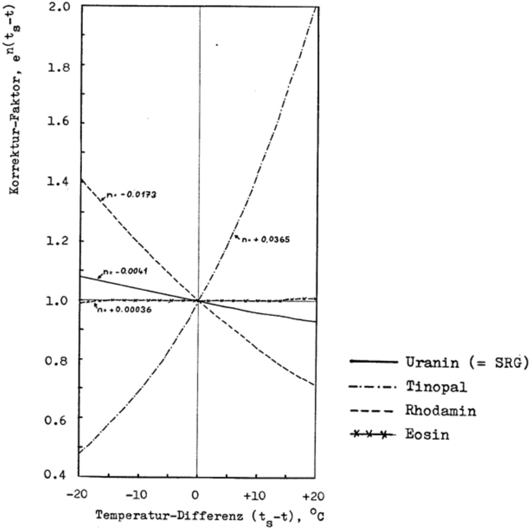
General formula for Temperature dependency of fluorescence

$$F_s = F * \exp(h(T_s - T))$$

F_s – fluorescence at temperature T_s
F – fluorescence at temperature T
h – tracer dependent coefficient (1/°C)
T_s – standard temperature (°C)
T – measurement temperature (°C)

Temperature dependency

Temperature dependency of fluorescence of common dye tracers



$F_s = F\, e^{n(t_s-t)}$

F_s = Fluoreszenz bei Standard-Temp. t_s

F = Fluoreszenz bei Proben-Temp. t

$t_s = 20^{\circ}$ C

STAMPFLI aus LEIBUNDGUT 1978

Temperature coefficients

Temperature coefficients of common dye tracers

Tracer	Coefficient (h)
Naphthionate[a]	−0.0056
Pyranine[b]	−0.0019
Eosine[c]	0.00036
Uranine[c]	−0.0041
Rhodamine B[c]	−0.0172
Amidorhodamine G[c]	−0.0041

[a] Analyzed at the tracer laboratory of the institute of hydrology, Freiburg, in 2008.
[b] Smart and Smith (1976).
[c] Leibundgut (1978).

Sensitivity to light - photo-decay

Experiment to study photochemical decay

Formula for photolytic decay

$$I_{(t)} = I_{(t=0)} * exp^{(-k*t)}$$

with:

- $I_{(t)}$: Fluorescence at time t
- $I_{(0)}$: Initial fluorescence
- k: Fluorescence decay constant
- t: time

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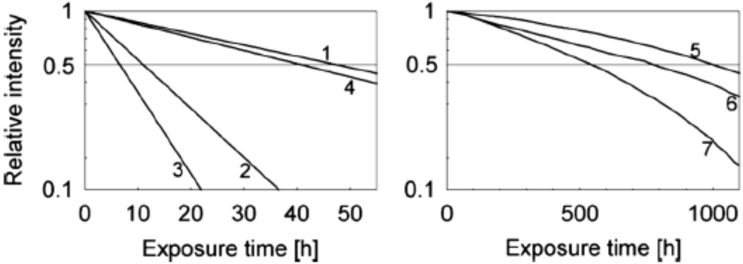
Photolytic decay

Half-life of common tracers

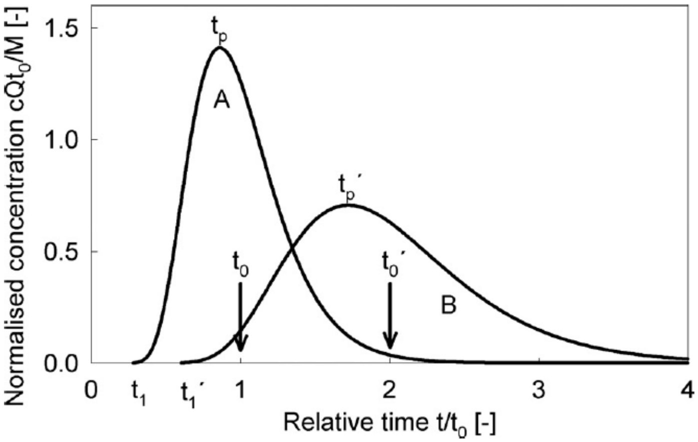
Fluorescence tracer	Measured half-life $T_{1/2}$ (h)	$T_{1/2}$ tracer/$T_{1/2}$ Uranine
Naphthionate	41	3.7
Pyranine	47	4.3
Uranine	11	1
Eosine	6	0.5
Amidorhodamine G	550	50
Rhodamine B	790	71
Rhodamine WT	1300	118
Sulforhodamine B	820	75

Photolytic decay



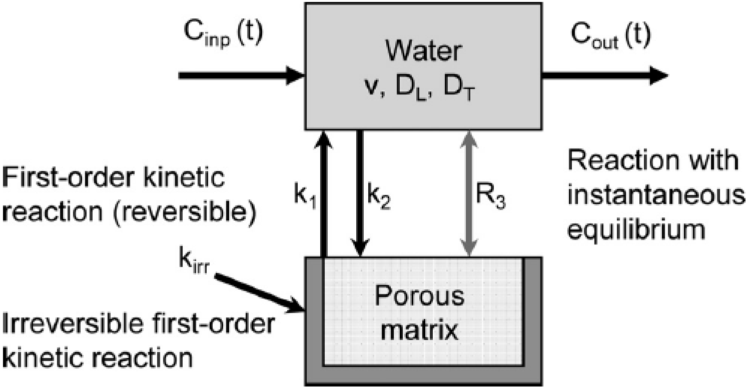
Photolytic decay of various fluorescence tracers caused by exposure to light. Left: tracer group with an excitation maximum below circa 520 nm (1: Pyranine, 2: Uranine, 3: Eosine, 4: naphthionate). Right: tracer group with an excitation maximum above 520 nm (5: Rhodamine WT, 6: Sulforhodamine B, 7: Amidorhodamine G), source: Behrens and Teichmann, 1982; Wernli, 1986.

Sorption of fluorescent dyes



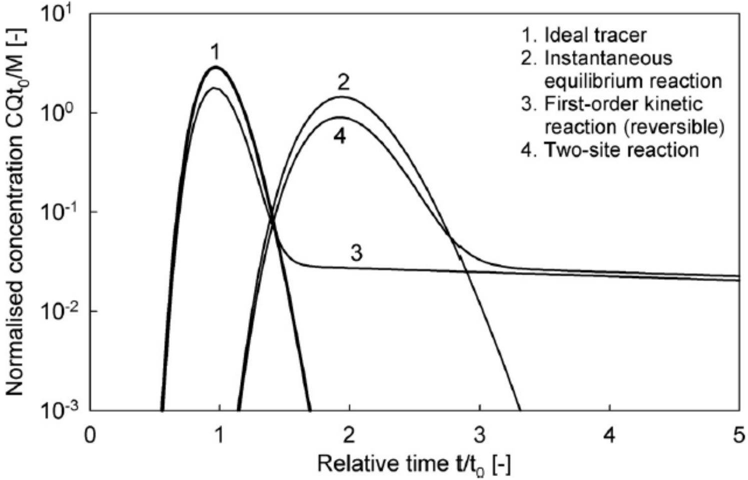
Effect of chromatography caused by reversible adsorption depicted in a tracer breakthrough curve. Curve A: ideal tracer; Curve B: reactive tracer.

Sorption of fluorescent dyes



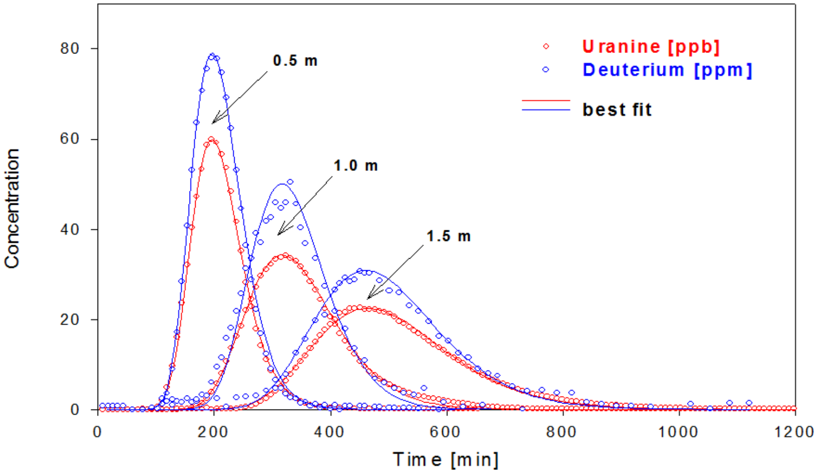
Conceptual model of sorption processes in a hydrogeological system.

Sorption of fluorescent dyes



Breakthrough curves (log-scale) of ideal and non-ideal tracers with sorption.

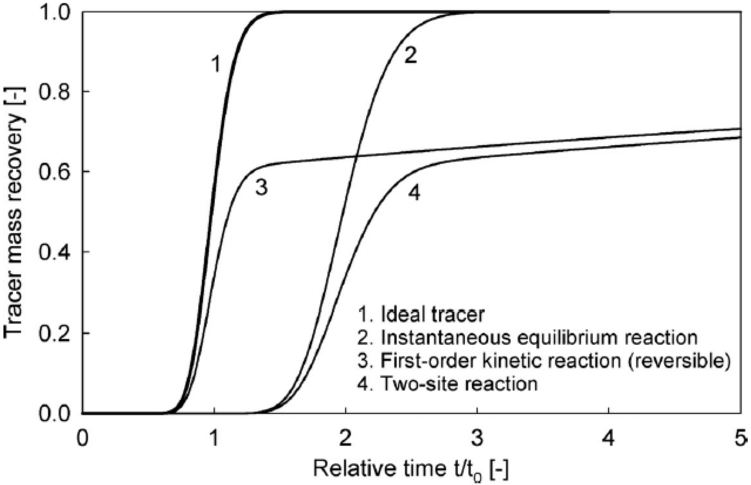
Sorption of fluorescent dyes



Ideal tracers deuterium and uranine.

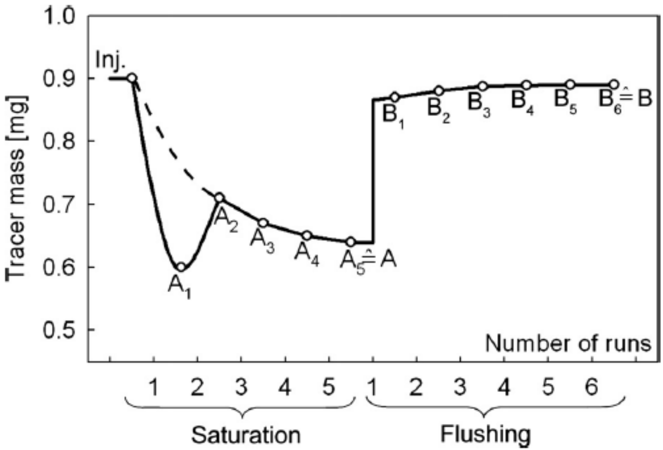
Sorption of fluorescent dyes - batch experiment

Sorption of fluorescent dyes - recovery curves



Recovery curves indicating sorption (reversible and irreversible).

Sorption of fluorescent dyes - flushing effects



Tracer breakthrough curve of Uranine in a sandy substrate showing complete tracer recovery. A saturation of the column water, B flushing effect.

Distribution coefficient K_d

The distribution coefficient K_d is determined by means of a batch test as follows:

Add 250 ml tracer solution (volume V with a concentration c_i) to a glass bottle containing 100 g of substrate (m) dried at a temperature of 105 °C. Shake for 24 h at a rate of 140 shakes per minute. After 24 h the tracer concentration in the equilibrium solution (c_s) is measured. K_d is calculated according to Equation ( ).

$$K_d = V/m * \frac{c_i - c_s}{c_s} [\mathrm{cm}^3/\mathrm{g}]$$

where

V = volume of the solution,
m = mass of the dry substrate,
c_i = initial tracer concentration and
c_s = dissolved tracer concentration (equilibrium solution).
K_d = depends on the ionic composition of the exchanger and the solution.

Retardation factor

The retardation factor can be calculated with:

$$R_d = \frac{v}{v_t}$$

where

v = mean flow velocity of water and ideal tracer respectively,
v_t = mean transport velocity of the tracer

or

$$R_d = 1 + \rho^* \frac{(1 - n_e)}{n_e} {}^* K_d$$

Retardation factor

Retardation factors determined by batch experiments:

Tracer	c_i [mg/m^3]	K_d [cm^3/g][a]	K_d [cm^3/g][b]	K_d [cm^3/g][c1]	K_d [cm^3/g][c2]	K_d [cm^3/g][c3]
Naphthionate	10	0	0.38	—	—	—
	100	0	0.28			
Pyranine	10	0.03		—	—	—
	100	0.24				
Uranine	10	0	0.4	0	—	—
	100	0	0.28	0	0	0
Eosine	10	0	5.51	0	—	—
	100	0.03	4.37	0.025	0.09	0.24
Amidorhodamine G	10	1.23	—	1.23	—	—
	100	0.92		0.92	0.19	0.75
Rhodamine B	10	5.56	—	5.61	—	—
	100	4.75		4.75	1.25	9.18
Rhodamine WT		—	—	—	—	—
Sulforhodamine B	10	—	36.6	—	—	—
	100		29.4			

Measured Retardation coefficients

Retardation coefficients determined by batch experiments:

Tracer	c_i [μg/l]	R_d^{a1}	R_d^{a2}	R_d^{a3}	c_i [μg/l]	R_d^{b1}	c_i [μg/l]	R_d^{b2}	c_i [μg/l]	R_d^{b3}
Pyranine	20	1.18	1.22	1.04						
Uranine	10	1.18	1.22	0.99	10	1	10	1	10	1
Eosine	20	1.69	1.55	1.12	90	1	90	1.9	90	1.1
Amidorhodamine G					30	2.7	30000	22.1	30	1.3
					80	2.3	80000	9.9		
Rhodamin B	50	>6	>5	>8	10	8.8	80000	40.3	80	2.4
					100	5.9				

[a] Klotz (1982a, b), substrate: (1) fluvio-glacial gravel; (2) drift and valley sand; (3) tertiary gravel sand.
[b] Dervey (1985), substrate: (1) mica gneiss; (2) molasse sandstone; (3) limestone.

Summary of tracer properties

A summary of tracer toxicity was given by Behrens (2001).

Tracer	Toxicological assessment	Assessment basis
Uranine	Safe	T, L
Eosin yellow	Safe	L, W
Sulforhodamine B	Ecotoxicologically unsafe	T
Amidorhodamine G	Safe	T
Rhodamine WT	Not recommended	T
Rhodamine B	Not recommended	T, L
Rhodamine 6G	Not recommended	T, L
Sodium naphthionate	Safe	T
Pyranine	Safe	T
Tinopal CBS-X	Safe	T
Tinopal ABP liquid	Safe	T
Lithium salts	Safe with restrictions	L, W
Strontium salts	Safe with restrictions	L, W
Bromides	Safe with restrictions	L, W
Activatable isotopes	Safe with restrictions	L, W
Fluorescent polystyrene microspheres	Safe	T, W
Spores of club moss dyed with acridine orange	Safe	T, W

Summary of tracer properties

Tracer	Ex/Em [nm]	Relative fluorescence yield	Detection limit [mg/m^3]	Toxicity	Solubility [g/l]	Light sensitivity	Absorption behaviour
Naphthionate	325/420	18	0.2	Harmless	240	High	very good
Pyranine	455/510	18	0.06	Harmless	350	High	Good
Uranine	**491/516**	**100**	**0.001**	**Harmless**	**300**	**High**	**Very good**
Eosine	515/540	11,4	0.01	Harmless	300	Very high	Good
Amidorhodamine G	530/555	32	0.005	Sufficient	3	Low	Sufficient
Rhodamine B	555/575	9.5	0.02	Toxic	3–20	Low	Insufficient
Rhodamine WT	561/586	10	0.02	Toxic	3–20	Very low	Insufficient
Sulforhodamine B	564/583	7	0.03	Sufficient	10 (10 °C)	Low	Insufficient

A summary of tracer properties indicates the most suitable fields of application.

Hydrological compartment	Suitable tracer based on the sorption criteria
Porous groundwater	Uranine, Pyranine, Eosine, Naphthionate
Karst groundwater	Uranine, Pyranine, Naphthionate, Eosine, Rhodamines
Fissured rock groundwater	Uranine, Pyranine, Naphthionate, Eosine
Unsaturated (vadose) zone	Uranine, Eosine
Surface water	All fluorescent tracers
Glaciated areas	All fluorescent tracers, except Pyranine

Measurement

type	method	result
visual	Colorimetric	qualitative/ half-quantitative
Fluoroscope	Colorimetric	Half-quantitative
optical fluorometer	electric	quantitative reproducible

Measurement

$$I_e = A^* I_0{}^* \varepsilon(\lambda_{ex})^* \Phi(\lambda_{em})^* c^* d$$

I_e = fluorescence intensity
A = instrumental constant
I_0 = incident light intensity
$\varepsilon((\lambda_{ex})$ = molecular extinction coefficient at wavelength λ_{ex}
c = tracer concentration
$\Phi(\lambda_{em})$ = quantum yield
d = sample layer thickness

Devices

Filtre fluorometer

fixed lamps + filtre

↓

1 Fluorescence tracer

Spectral fluorometer

monochromator

Fibre optics

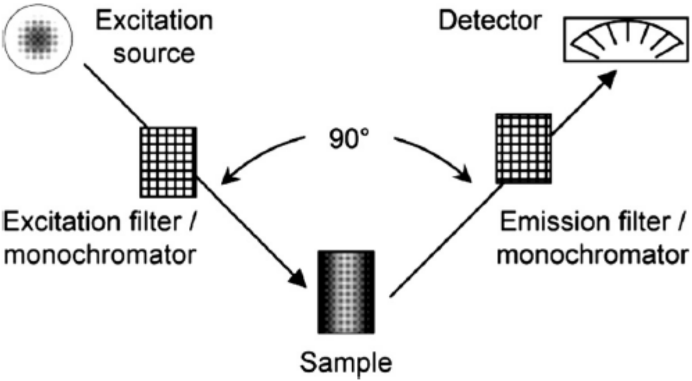
like Filter fluorometer
But more channels

→ several fluorescence tracers

Spectral fluorometer

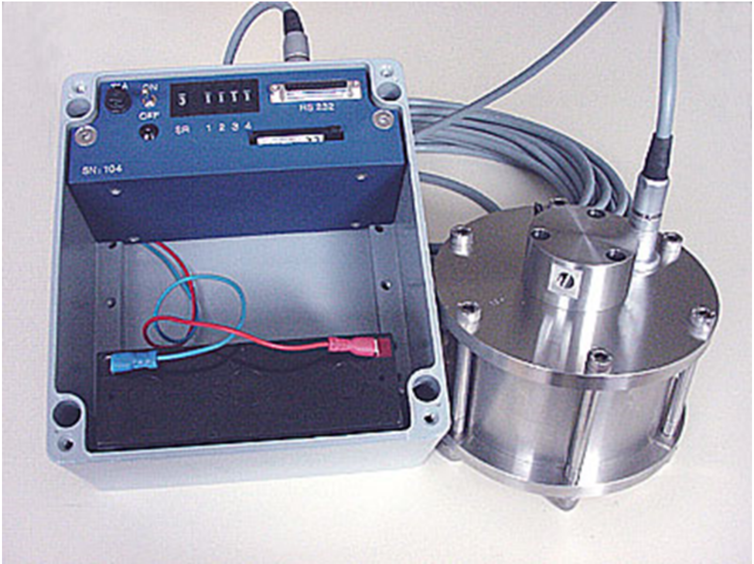
Perkin Elmer Spectral fluorometer

Spectral fluorometer



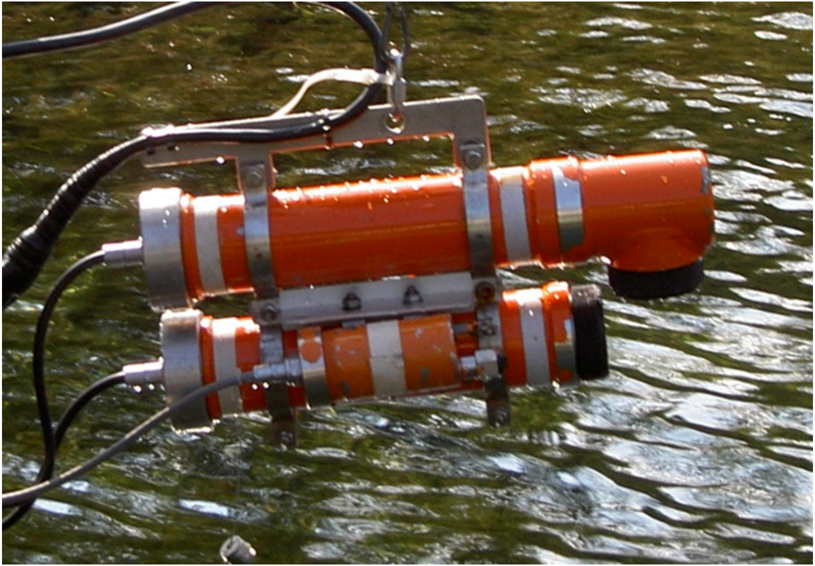
Principle of measuring fluorescence with a spectral fluorometer

Filtre fluorometer



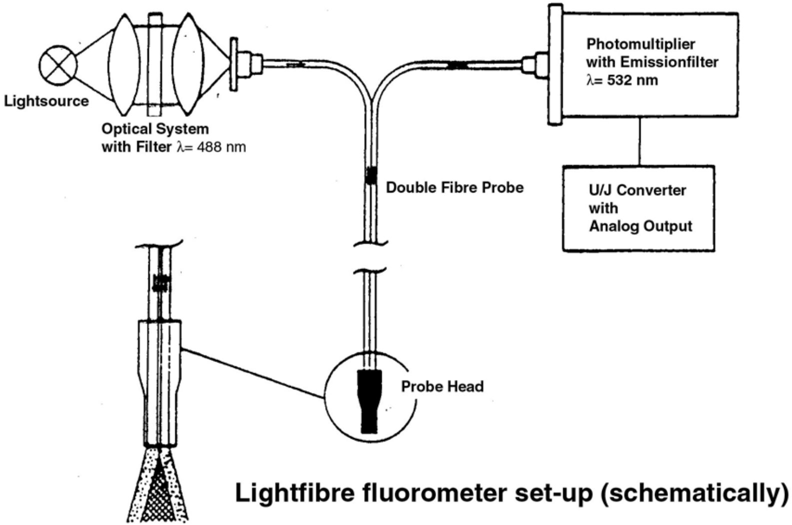
Filtre fluorometer GGUN for rivers

Fibre optic fluorometer



Fibre optic fluorometer

Fibre optic fluorometer

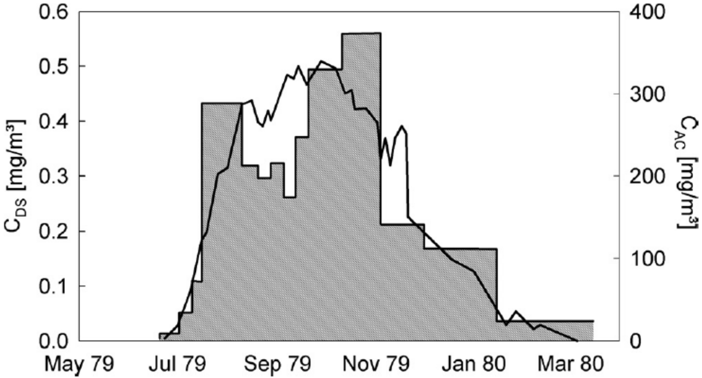


Principle of measuring fluorescence with a fibre optics fluorometer

Measurement

Technique	Principle	Result	Detection limit for Uranin (ppb)	Detection limit for Uranin (mg/m^3)
Visual	-	qualitativ	ca. 50 ppb	ca. 20
Quarz lamp/ UV-Lamp	colorimetric	qualitative	ca. 5 ppb	ca. 2
Fluoroscope	colorimetric	half-Quantitative	ca. 1 ppb	ca. 0,5
Spectralphotometer	photometric	Quantitative	0,5 ppb	0,2
Optical Fluorometer	fluorometric	Quantitative	0,005 ppb	0,002
Fibre optics	optical	Quantitative	0,005 ppb	0,002

Fluoro-capteurs

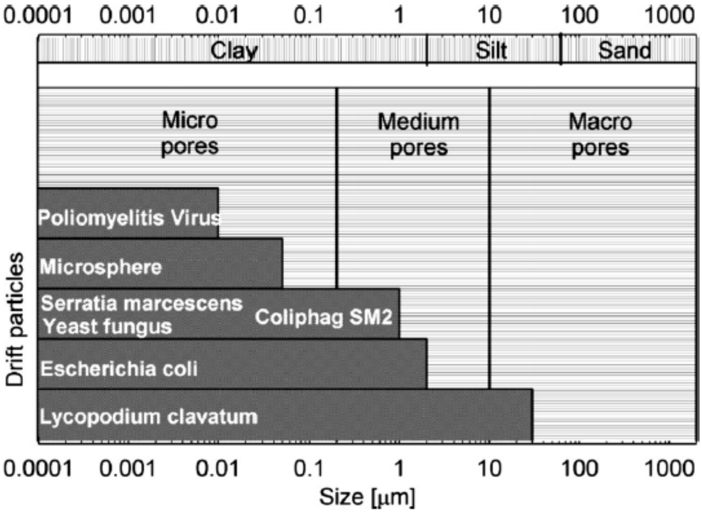


Salt tracers

Salt	Molecular formula	Water solubility at 10 °C [g/l]	Ionic radius [Å]	Ionic potential (charge/radius)	Molecular weight [g/mol]	ion	Analysis method
Sodium chloride (mine salt)	NaCl	357	Na^+: 1.02	Na^+ 1.0	58.44	Cl^-	EC, ISE, flame photometry
			Cl^-: 1.81	Cl^- −0.6		Na^+	
Potassium chloride	KCl	313	K^+: 1.38	K^+ 0.7	74.55	Cl^-	EC, ISE
			Cl^-: 1.81	Cl^- −0.6		K^+	ISE, flame photometry
Bromide	NaBr	850	Br^-: 1.96	Br^- −0.5	102.89	Br^-	IC, ISE
Lithium	LiCl	820 (20 °C) 672 (0 °C)	Li^+ 0.76	Li^+ 1.3	42.39	Li^+	Spectroscopy, flame photometry
	$LiCl\ 3H_2O$				96.38		
Borax (sodium borat)	$Na_2B_4O_7{*}10H_2O$	16.2	—	—			
Iodide	NaI	184 (25 °C)	I^- 2.2	I^- −0.5	149.89	I^-	IC, ISE

EC: Electrical conductivity, ISE: Ion sensitive electrode.

Pollen and micro-spheres



Relative size of pollen and micro-spheres to pores

Radioactive substances

Radioactive nuclide	$T_{1/2}$	Chemical compound	Radiation	Characteristics
^{3}H	12.35 a	^{3}HHO (Water)	β	Chemically identical to the labelled water
^{51}Cr	27.7 d	EDTE - chelat	γ	Low sorption
^{114m}In	50 d	EDTE - chelat	γ	Low sorption
^{114}In	72 s	EDTE - chelat	β	Low sorption
^{58}Co	70.8 d	$[Co(CN)_6]^3$- chelat	γ	Low sorption
^{60}Co	5.3 a	$[Co(CN)_6]^3$ – chelat	γ	Low sorption
^{82}Br	36 h	Br^- – Anion	β	Very low sorption, chemically very stable
^{131}I	8.05 d	I^- – Anion	β	Chemically unstable, sorption by oxidation
^{24}Na	15.0 h	Na^+ - Kation	β	Sorption, can be used in channels
Activation product				
^{80}Br	17.6 min	Br^- - Anion	γ	Low sorption
^{116m}In	54 min	EDTE - chelat	γ	Low sorption
Rare earth elements		EDTE - chelat	γ	Low sorption

Radioactive substances as artificial tracers

Rules for tracer hydrologists

- study basin, system first: chemistry, pH
- minimize mass
- use several approaches
- use most sensitive fluorometers
- avoid rhodamine
- use only when knowledge can be gained
- combine with other methods (stable isotopes, chemistry)
- it is a time snap-shot

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References

Leibundgut, C., P. Maloszewski, and C. Külls. 2009. *Tracers in Hydrology*. 1st edition. Wiley & Sons.