Study of groundwater and soil moisture movement by applying nuclear, physical and chemical methods

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STUDY OF GROUNDWATER AND SOIL MOISTURE MOVEMENT BY APPLYING NUCLEAR, PHYSICAL AND CHEMICAL METHODS

by

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ABSTRACT

Groundwater and soil moisture movement can be studied with the help of nuclear, physical and chemical methods. This state-of-the-art report introduces the reader to the application of environmental isotopes, gravimetric, neutron and gamma-ray methods, the use of simulation models, and to the application of chemical tracers.

PREFACE

Although the total amount of water on Earth is generally assumed to have remained virtually constant during recorded history, periods of flood and drought have challenged the intellect of man to have the capacity to control the water resources available to him. Currently, the rapid growth of population, together with the extension of irrigated agriculture and industrial development, are stressing the quantity and quality aspects of the natural system. Because of the increasing problems, man has begun to realize that he can no longer follow a 'use and discard' philosophy -- either with water resources or any other natural resource. As a result, the need for a consistent policy of rational management of water resources has become evident.

Rational water management, however, should be founded upon a thorough understanding of water availability and movement. Thus, as a contribution to the solution of the world's water problems, Unesco, in 1965, began the first worldwide programme of studies of the hydrological cycle -- the International Hydrological Decade (IHD). The research programme was complemented by a major effort in the field of hydrological education and training. The activities undertaken during the Decade proved to be of great interest and value to Member States. By the end of that period a majority of Unesco's Member States had formed IHD National Committees to carry out the relevant national activities and to participate in regional and international co-operation within the IHD programme. The knowledge of the world's water resources as an independent professional option and facilities for the training of hydrologists had been developed.

Conscious of the need to expand upon the efforts initiated during the International Hydrological Decade, and, following the recommendations of Member States, Unesco, in 1975, launched a new long-term intergovernmental programme, the International Hydrological Programme (IHP), to follow the Decade.

Although the IHP is basically a scientific and educational programme, Unesco has been aware from the beginning of a need to direct its activities toward the practical solutions of the world's very real water resources problems. Accordingly, and in line with the recommendations of the 1977 United Nations Water Conference, the objectives of the International Hydrological Programme have been gradually expanded in order to cover not only hydrological processes considered in interrelationship with the environment and human activities, but also the scientific aspects of multi-purpose utilization and conservation of water resources to meet the needs of economic and social development. Thus, while maintaining IHP's scientific concept, the objectives have shifted perceptibly towards a multi- disciplinary approach to the assessment, planning, and rational management of water resources.

As part of Unesco's contribution to the objectives of the IHP, two publication series are issued: 'Studies and Reports in Hydrology' and 'Technical Papers in Hydrology'. In addition to these publications, and in order to expedite exchange of information, some works are issued in the form of Technical Documents.

FOREWORD

Project A.1.6 of the second phase of the International Hydrological Programme resulted in the compilation of a state-of-the-art report on the application of nuclear, physical and chemical (tracer) methods for the study of groundwater and soil moisture movement. The report is not intended as an exhaustive treatise but intends to provide an overview of the methods available and applicable. For more intensive studies, the reader is referred to the Bibliography.

For the execution of this IHP project the following experts agreed to write the present paper and Unesco is much indebted to the authors.

Professors H. Moser and W. Rauert from the Institute for Radiohydrometry (Neuherberg/München, Federal Republic of Germany, W. Morgenschweis of the Ruhrtalsperrenverein, Essen, Federal Republic of Germany, and H. Zojer, Unesco-sponsored Course on Groundwater Tracing Techniques, University of Technology, Graz, Austria.

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PART I PROGRESS IN APPLYING NUCLEAR TECHNIQUES FOR THE INVESTIGATION OF SOIL MOISTURE AND GROUNDWATER MOVEMENT

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INTRODUCTION

Application of nuclear techniques for the purpose of hydrological investigations is based mainly on the following facts:

a) Water naturally contains stable and often also radioactive isotopes by means of which it is labelled. Moreover, for some decades artificially radioactive isotopes such as waste products of military and industrial techniques enter the hydrological cycle as a result of which the water is marked unintentionally. These isotopic labels are covered by the term "environmental isotope". Table 1 outlines the main properties of the environmental isotopes routinely used today or potentially usable as hydrological tracers.

Table 1: Environmental isotopes used or potentially usable as hydrological tracers (MOSER & RAUERT 1983)

(1) Isotope	(2) Half-life	(3) Chem.composition in natural water	(4) Pro-duction	(5) Isotope ratio abundance in recent groundwater	(6) Max.decay rate (dpm) per m^3 water in natural water	(7) Detection limit[a)] (%),related to (5)	(8) Detection limit[a)] with sample size
^{2}H	stable	$^{2}H^{1}HO$	N	$(90-170)\cdot10^{-6}$ $^{2}H/^{1}H$	-	0.2	50 ml H_2O
^{3}H	12.43 a	$^{3}H^{1}HO$	N,A	$\approx 10^{-16}$ $^{3}H/H$	10^{6} b)	0.2	1.5 l H_2O
^{14}C	5730 a	$^{14}CO_2$, $H^{14}CO^{-}$	N,A	$1.2\cdot10^{-12}$ $^{14}C/^{12}C$	$\approx 10^{3}$ b)	0.5	4-5 g C d) (50-200 l H_2O)
^{18}O	stable	$H_2{}^{18}O$	N	$(1880-2018)\cdot10^{-6}$ $^{18}O/^{16}O$	-	0,03	5 ml H_2O
^{32}Si	108 a c)	$^{32}SiO_2$	N	$\approx 2\cdot10^{-16}$ $^{32}Si/Si$	1 b) <0.2-0.6	1	50-200 g Si (1-10 m^3 H_2O)
^{39}Ar	269 a	dissolved gas	N	$\approx 10^{-15}$ $^{39}Ar/Ar$	0.04	4	2 l Ar ($\approx$10 m^3 H_2O)
^{81}Kr	$2.1\cdot10^{5}$ a	dissolved gas	N	$6\cdot10^{-13}$ $^{81}Kr/Kr$	$8\cdot10^{-6}$	?	50 ml Kr e) ($\approx 10^3$ m^3 H_2O)
^{85}Kr	10.76 a	dissolved gas	A	$6\cdot10^{-12}$ $^{85}Kr/Kr$	2.8	3	10 µl Kr ($\approx$200 l H_2O)
^{36}Cl	$3\cdot10^{5}$ a	$^{36}Cl^{-}$	N,A	$2\cdot10^{-12}$ $^{36}Cl/Cl$	0.2 b)	0.1	10 mg Cl (1-5 l H_2O)

a) 2 σ criterion for the measured isotope ratio in a water sample
b) influenced by nuclear weapon tests
c) published values vary between 101 a and 701 a
d) using accelerator measurement $\approx$10 mg C
e) using resonance ionisation spectroscopy: 10^{-5} ml Kr ($\approx$1 l H_2O)

N = natural; A = man made; a = years; dpm = disintegrations per minute

b) Groundwater and surface water can be marked by the intentional addition of radioactive or activable substances ("tracers"). Table 2 lists the most commonly used hydrological tracers.

Table 2: Possible radioactive tracers for groundwater field experiments (IAEA 1983b)

(1) Isotope	(2) Half-life	(3) Chem. compound
^{3}H	12.4 a	H_2O
^{46}Sc	84 d	EDTA-complex
^{51}Cr	27.7 d	EDTA-complex
$^{57/58/60}Co$	270 d/70.8 d/5.27 a	$Co(CN)_6^{3-}$ EDTA-complex
^{82}Br	35.34 h	Br^-
$^{114}In^m$	50 d	EDTA-complex
$^{125/131}I$	60/8.04 d	I^-

c) Where an interaction occurs between the radiation of a radioactive substance and the aquifer, the extent of that interaction may characterize parameters of the aquifer concerned, in particular density and water content. The development of density and moisture probes based on this principle was, to a large extent, completed by the early seventies (see, e.g., IAEA 1970, 1971, 1983a).

The progress made in the course of the last few years in the application of nuclear techniques has been described in detail by Moser & Reuert (1980) as well as in the Guidebook on Nuclear Techniques in Hydrology (IAEA 1983a). In the present report an attempt is made to give a brief survey of the main results; for details reference is made to the literature quoted.

1. INVESTIGATIONS IN THE UNSATURATED ZONE

Apart from the use of density and moisture probes mentioned above the application of nuclear techniques in the unsaturated zone is limited mainly to investigations using tracers such as ^{3}H, ^{2}H and ^{18}O.

1.1 Methodology

The tracer distribution in the water of the unsaturated zone measured at a specified time first depends on the distribution in time and space of the tracer input from precipitation and the water vapour of the air or from some intentional tracer input. In the surface soil layers the tracers distribution may then undergo variations as a result of evaporation and evapotranspiration.

1.1.1 Tracer Input

In using ^{3}H, ^{2}H and ^{18}O as environmental isotopes the distribution in time and space of the isotope content in the precipitation forms the input function for infiltration into the unsaturated zone. Depending on climatic conditions, type of soil and vegetation, part of the water derived from precipitation is returned to the atmosphere. This normally seasonal effect changes the mean isotope content of the infiltrated water, particular ^{2}H and ^{18}O (see, e.g., Mönnich et al. 1967, 1980 and Münnich 1983). These variations depend on the area under investigation and must therefore be taken into consideration in each individual case.

Tracing precipitation by means of ^{3}H mainly originates from the concentration peak of the years 1962-1963. Since 1970 the ^{3}H content of precipitation no longer shows significant variations (see Fig. 9) and can, for that reason, be used only to a limited extent, as a "natural" tracing of seepage waters infiltrating at present. For this reason, today soil water is intentionally marked in order to be able to follow the water movement in the unsaturated zone. When applying this method, a tracer solution of water containing ^{3}H, is injected by means of a special device into the soil at points in linear or areal order at a distance of about 10-20 cm from one another at a depth of 0.1-1 m (see, e.g., Mönnich 1983). In using ^{3}H about $2x10^{3}$ Bq ^{3}H in the form of tritiated water is used per injection. In this case overall activity in the area under investigation normally does not exceed 10^{4} - 10^{5} Bq and therefore avoids any problems of radiation protection.

1.1.2 Tracer Detection

The method of measurement of the tracer distribution in the vertical profile of the unsaturated zone depends on the tracer used. It is undertaken either in the laboratory by means of soil or water vapour samples which are collected at specified times in the course of the tracer experiment or directly in the field in boreholes drilled at the beginning of the experiment. Should a soil moisture profile be required for evaluation, this may be obtained either by neutron moisture test probes (see, e.g., IAEA 1970) or by gravity methods using soil samples.

1.1.3 Tracer Dispersion of Seepage Water

The water marked by a tracer is normally distributed in the unsaturated zone in horizontal layers which move in a vertical direction ("piston-flow"). The fact that the movement of the seepage water occurs in layers in spite of natural inhomogeneities (root channels, holes) has been proved to exist by means of tracer experiments (e.g. Matthess et all. 1979) is due to the generally relatively low seepage velocity of water in the range of 1-10 m/year as compared to the lateral velocity of molecular diffusion (Münnich, e.g., 1977, 1983): taking a diffusion constant of about 1.5×10^{-5} cm^{2}/s and overall porosity of 20% as a basis, extensive homogenisation of the tracer concentration over 20 cm already takes place after four weeks (Fig. 1). This diffusion effect is intensified by the fact that the water movement in the unsaturated zone preferably follows the narrow channels of the grain structure binding the water rather than large openings owing to capillary forces. The resultant "diffusion effect" is larger by at least two orders of magnitude than that of molecular diffusion. The result is that water is absorbed from a root pipe into the surrounding unsaturated zone in less than a minute.

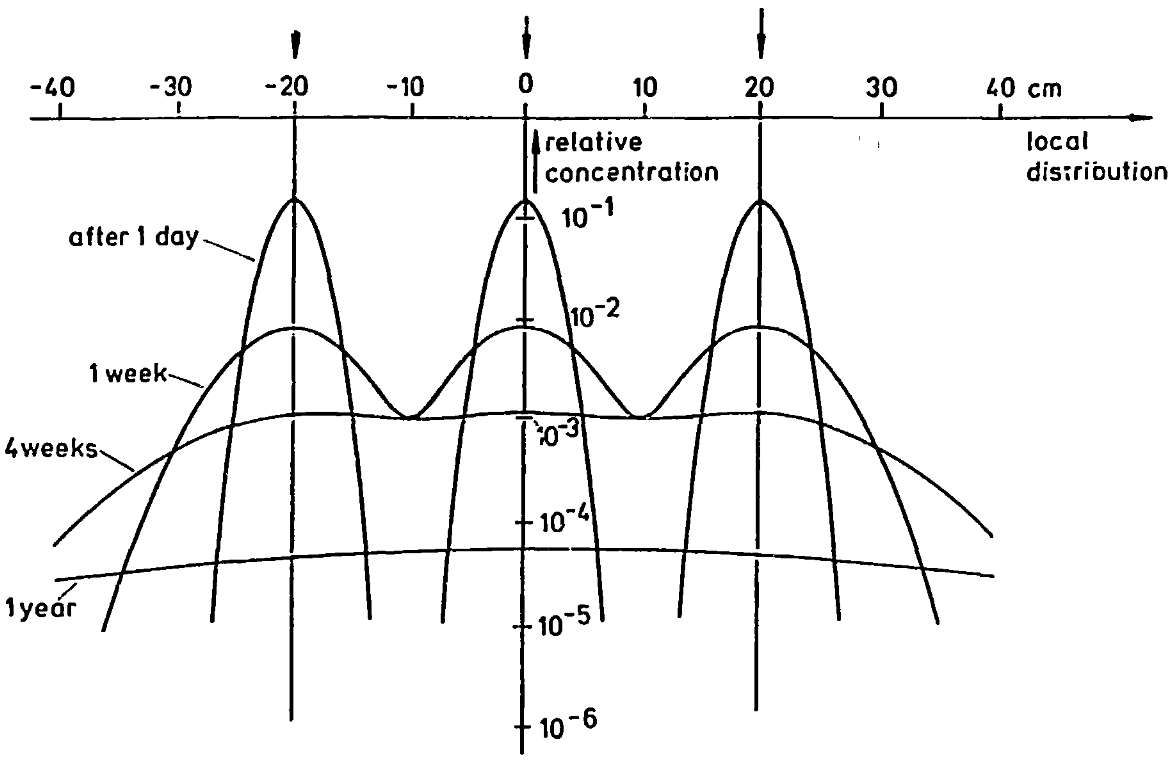


Figure 1: Homogenization and decrease of tracer concentration by molecular diffusion in the unsaturated zone (diffusion coefficient about 1.5 10-5 cm2/s (according to Munnich, 1977). It is assumed tht the tracer (e.g. tritiated water) is injected at three points into the unsaturated zone.

The horizontally stratified seepage movement is interrupted only where the differences between individual seepage paths exceed diffusion length. In these cases local distortions of the flow field occur which may lead to hydrodynamic dispersion processes. Such effects occur in the case of local, e.g. morphology-dependent, variations of the infiltration rate and substantial inhomogeneities in the horizontal profile of the rock.

Lateral diffusion in general entails only a relatively slight lateral extension of the labelled water in the course of the infiltration movement (some dm) which, however, renders sampling difficult in the case of linear tracer injection. On the other hand, a substantial decrease of downward permeability (via clay lenses) can have a backwater effect which may entail considerable lateral movement of the labelled water.

The molecular diffusion which is effective also in a vertical direction increases the thickness of the labelled water layer in the course of infiltration. If inhomogeneities of the infiltration movement entail hydrodynamic dispersion, the tracer peak is, as a consequence, additionally flattened and enlarged.

1.1.4 Determination of Groundwater Recharge

Measurements of the variation in time of the vertical distribution of a marked water layer in the unsaturated zone supply not only knowledge about the movement of water (e.g. with a view to the dispersion of pollutants) but make it, moreover, possible to determine groundwater recharge directly. In this context, it is not necessary to know the percentage of evaporation which normally is required for balances and which is difficult to determine; however, it is necessary to determine the water content profile of the unsaturated zone (see Section 1.1.2).

If the "peak method" is applied, the water content W (mm) is determined in that part of the vertical profile of the unsaturated zone which is above the marked water layer in the course of the period under investigation. In this case the peak, or better the centre of gravity of the tracer distribution in the vertical profile should be used as the site parameter. The groundwater recharge rate r, i.e., the share of the precipitation P (mm) contribution to groundwater recharge may than be computed for the period under investigation from $r = W/P$. For infiltration velocities of about 1 m/year, which are typical for field capacities of about 20 vol-% and precipitation quantities of more than 200 mm/year, r may be determined with an accuracy of $\pm$ 10%.

In the case of the "total tritium method" a balance is established between the total ^3H quantity in the precipitation and of the ^3H share infiltrating into the unsaturated zone and on this basis r is computed. This method is accordingly restricted to the evaluation of the measurements of the environmental ^3H content. The uncertainty of the ^3H input function governs accuracy.

1.2 Measuring Examples

Examples of measurements of the water movement in the unsaturated zone and the derived value for groundwater recharge have been summarized by Moser & Rauert (1980) and IAEA (1983a). For the mathematical models underlying these values reference must be made to the literature.

1.2.1 Investigations with the Aid of Added Tracers

The use of intentionally added water with ^3H tracer for the investigation of infiltration processes in the unsaturated zone was for the first time proposed by Zimmermann et al. (1966) and realized on several test fields in the Federal Republic of Germany. In the meantime the method was applied in particular in India for the purpose of determining regional groundwater recharge. In this case, ^{60}Co was also used as a tracer (e.g. Gupta & Sharma 1979, RAO 1983). Fig. 2 shows as an example the vertical profile of the ^3H content and of the water content determined by weighing for a field experiment with loess loam near Heidelberg (Federal Republic of Germany) from which the process of groundwater recharge could be ascertained (Jakubick 1972). Relying on such measured ^3H profiles the concepts descripted in Section 1.1.3 about seepage water movement and tracer diffusion could be confirmed with the aid of a simple multibox model taken from chromotography. Simultaneously, the rates of groundwater recharge determined by comparison with daily climate observations and the resultant precipitation - evaporation relationship were verified (Thoma et al. 1979). The tracer distributions determined on the basis of these computation models agree well with the ^3H profiles measured (see, e.g., Fig. 3).

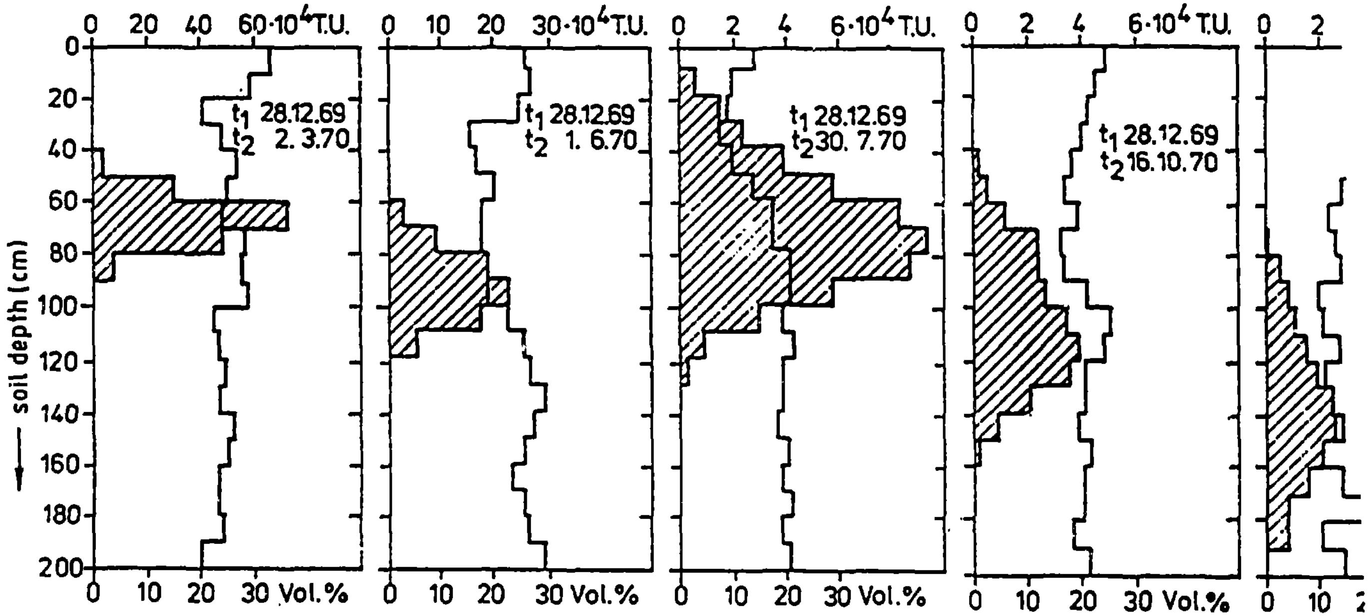


Figure 2: Field experiment Bammental near Heidelberg (Federal Republic of Germany. Measured 3H content (hatched) and soil moisture content (vol-%) for different sampling dates t2, t1 is the date of 3H injection (according to Jakubick, 1972)

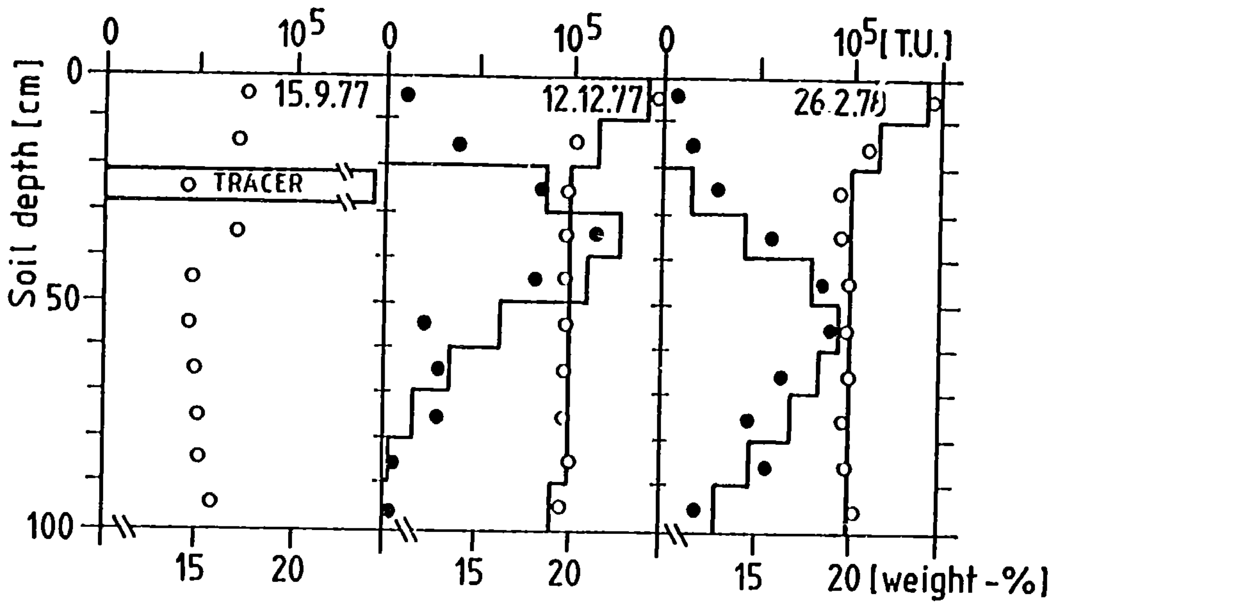
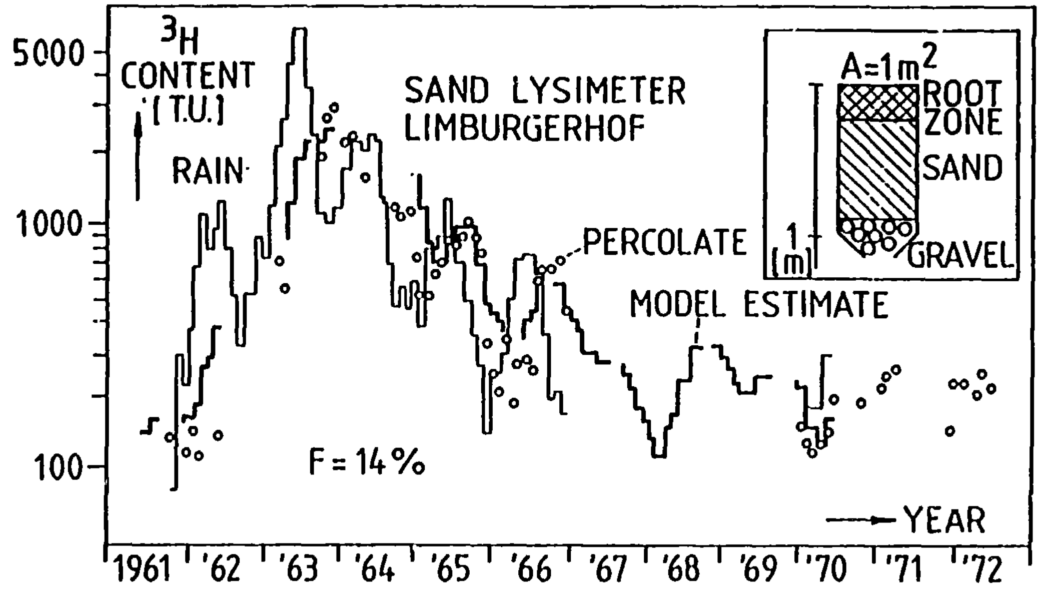


Figure 3: Field experiment Bammental near Heidelbeg (Federal Republic of Germany): Measured 3H content (●) and soil moisture content (o) profiles and an estimate due to the multibox HETP model (solid lines), as calculated from daily data of precipitation, air temperature and saturation deficit in atmospheric moisture (Thoma et al. 1979).

1.2.2 Investigations with Environmental Isotopes

The field experiments, e.g. summarized in Moser & Rauert 1980, were carried out mostly in loose rocks and under humid or semi-arid climatic conditions. A comparison of the two time curves of the ^3H input from precipitation and of the ^3H content of two lysimeter outflows (lysimeter Sindorf: 40 cm loess on 110 cm loam and 150 cm gravel; lysimeter Limburgerhof: 100 cm fine sand on a gravel layer) shows that the ^3H peaks of the input appear in the outflow of the sand lysimeter with a five-month lag (corresponding to a seepage velocity of 2.4 m/year) whereas they are not identified in the outflow of the loess loam lysimeter. Here, merely a broad maximum with a 2.5-year lag as compared to the ^3H input peak of 1963 can be registered. The application of the chromotopographic model mentioned in Section 1.2.1 confirmed these processes on the basis of the field capacities F (Thoma et al. 1979) indicated in Fig. 4. But Fig. 4 also shows that the tracer marking of the seepage water with the ^3H peak in 1963 can now be found only in areas with little groundwater recharge, i.e., in seepage water at depths greater than 20 m. Thus, for instance, a downward movement of the ^3H peak between 1972 and 1978 (Fig. 5) could be found in the course of investigations in the Ad Dahna sand dunes (Saudi Arabia) and, on that basis, a groundwater recharge of 23 mm/year was calculated which appears realistic and in agreement with a simple infiltration - evaporation model using precipitation and ^3H input data (Sonntag et al. 1980). Measurements of the ^3H and ^{18}O contents (Fig. 5) supplied additional insights into the relationship between evaporation and infiltration which were confirmed by laboratory experiments (Munnich et al. 1980).



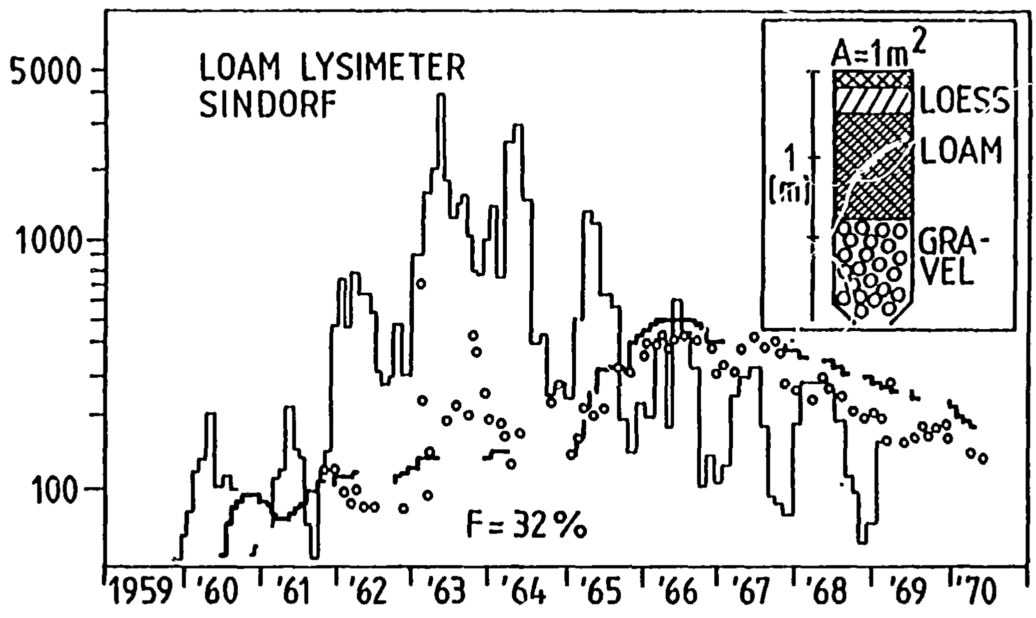


Figure 4: Environmental 3H response of grass covered lysimeters of Limmburgerhof (1 m of sand) near Ludwigshafen and of Sindorf (1.5 m of loess loam) near Cologne (Federal Republic of Germany): Circles = measured 3H contents of monthly percolate samples, thin line histograms = 3H content of local precipitation, thick line histograms = HETP-model estimate of lysimeter 3H response based on a mean soil water content of F = 14 vol-% for Limburgerhof and 32 vol-% for Sindorf, respectively (according to Thoma et al., 1979).

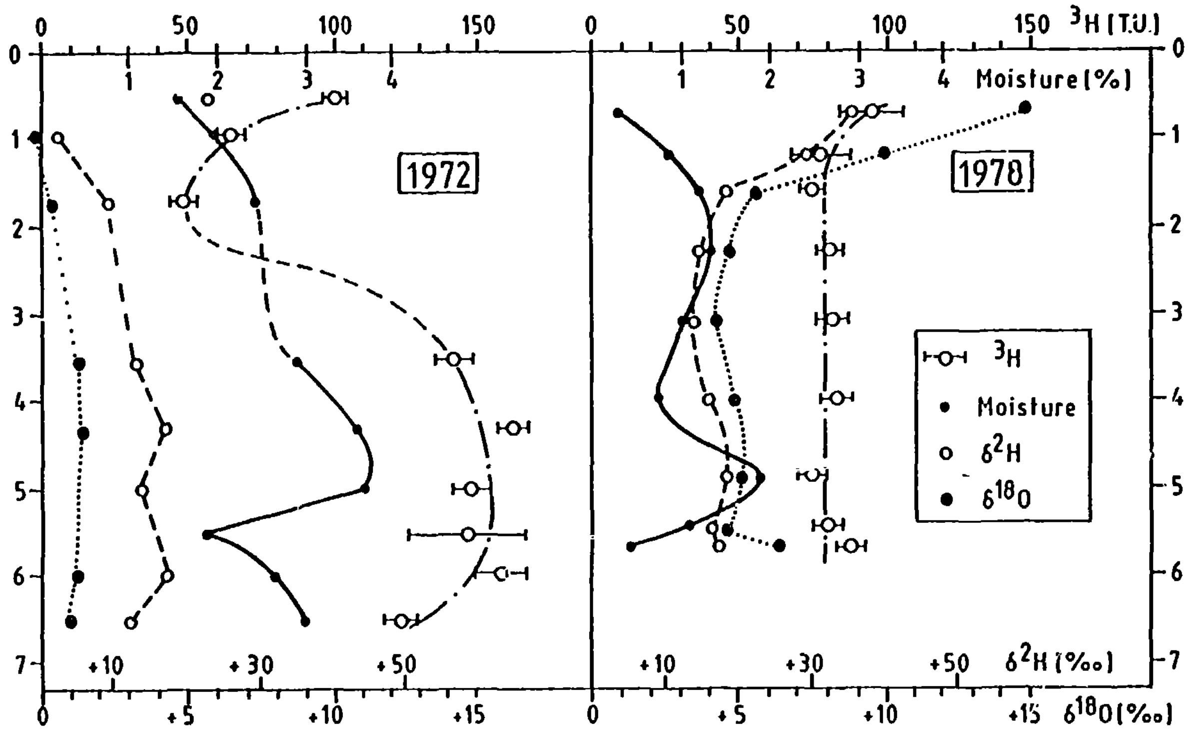


Figure 6: Soil moisture, 3H, 2H and 18O profiles in the Dahna sand dune (Saudi Arabia), 1972 and 1978 (Sonntag et al. 1980).

2. INVESTIGATIONS IN THE SATURATED ZONE

The parameters of the groundwater movement determinable with the aid of environmental isotopes and intenionally added tracers are provided by time differentiation as well as by means of direct measurement of the filtration and distance velocities and the flow direction of the groundwater.

2.1 Determination of Parameters of Groundwater Movement from Measurements of the Environmental Isotope Content.

The ^{2}H, ^{18}O, ^{3}H and ^{14}C contents (together with ^{13}C of groundwater have, in the last few years, been extensively used for the investigation of water movement. The use of other isotope contents (such as, for instance, ^{85}Kr, ^{39}Ar, ^{32}Si, ^{81}Kr and ^{36}Cl) have been discussed, technologically prepared, and practically applied in individual cases.

2.1.1. Time Differentiation of Groundwaters

Fig. 6 shows schematically the dating periods of groundwaters for individual environmental isotopes. From such measurements, distance, velocity, moisture ratios of groundwater bodies as well as their interconnections and relation to surface water may be deduced with the aid of hydraulic models.

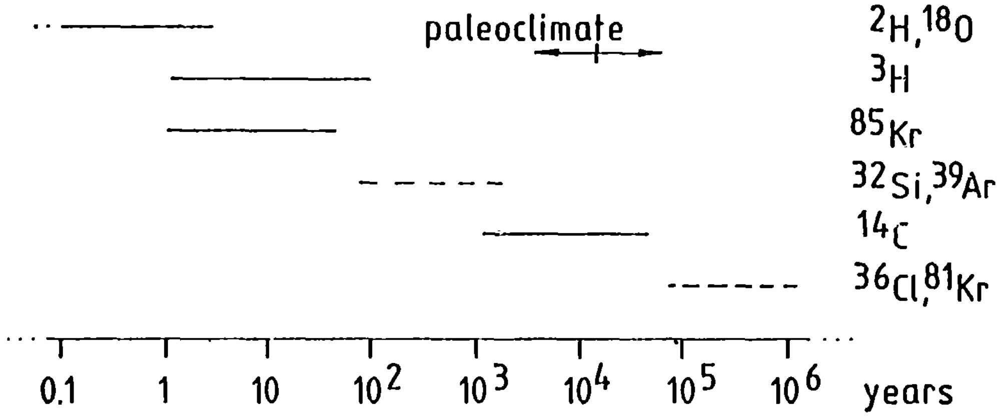


Figure 6: Dating ranges of environmental isotope techniques already in use (——) and under development (----), the exact range depending on the interpretation model used.

In the case of stable isotopes ^2H and ^{18}O, time differentiation is based on differences in concentration as shown in Table 1 which are mainly due to temperature-dependent isotope fracturation in the water cycle (e.g. IAEA 1981a) and consequently characterize the groundwater with respect to time and space and the climate during input. Fig. 7 shows the ^2H contents of individual precipitation events for an Alpine catchment area, the corresponding monthly means and the resultant seasonal variations. The extent to which such time-dependent variations of the ^2H and ^{18}O contents of the precipitation can be used to determine the residence time of the groundwater depends on the amplitude of the input function and, as in the case of all such interpretations, on hydraulic model assumptions. Thus, under humid climatic conditions, mean residence times of days to some years can be found.

Since isotope fractionation depends on temperature and air moisture, ^2H and ^{18}O contents of precipitation also reflects climatic variations. Fig. 8 shows that in eastern England, groundwater ages of more than 10 000 years with decreased ^{18}O contents as compared to recent waters are correlated. It may thus be possible to distinguish pleistocene from holocene waters (for further examples see, for instance, Moser and Rauert, 1980; Eichinger et al, 1984).

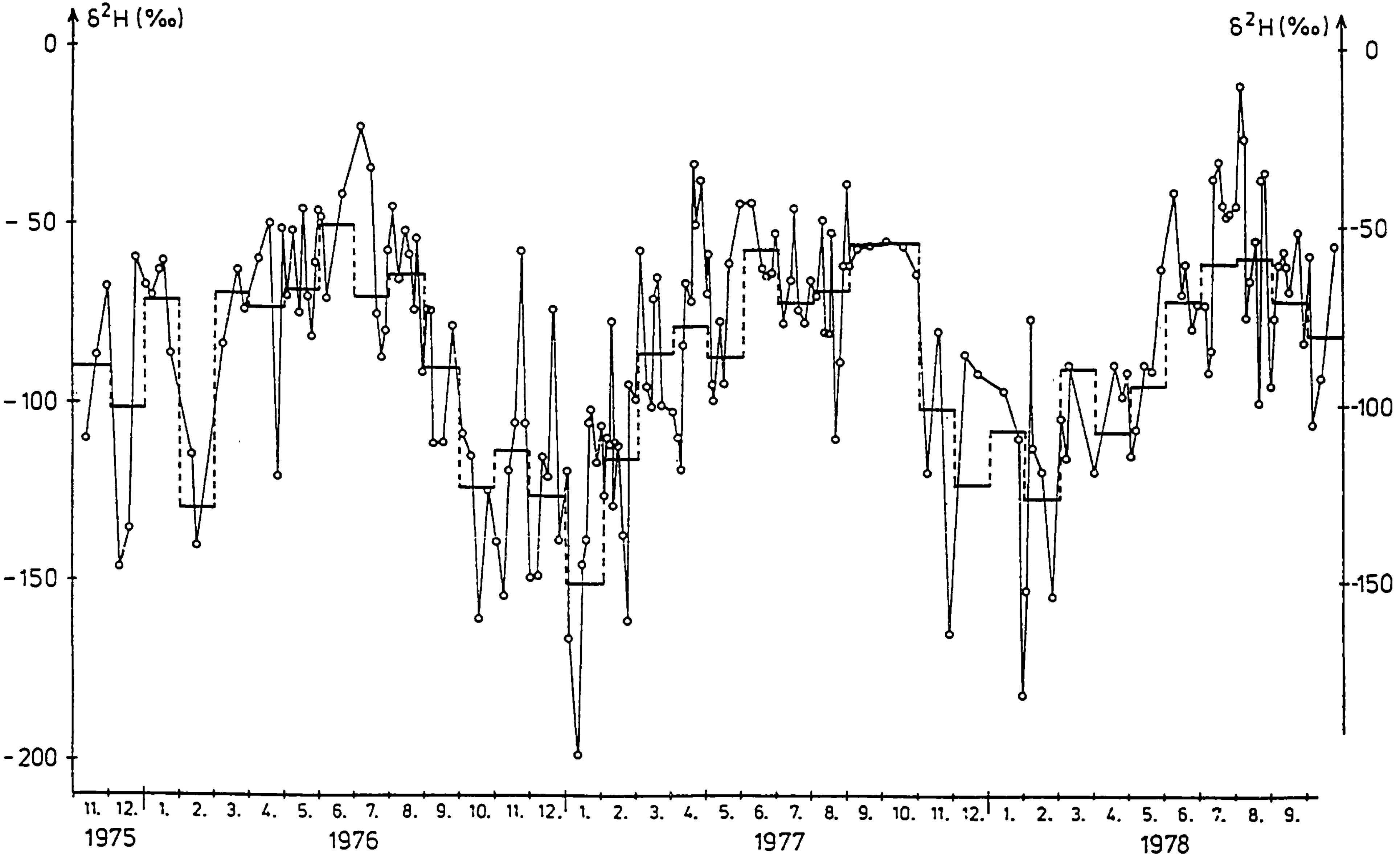


Figure 7: Seasonal variations of the 2H content of single precipitation events in a mountainous catchment area of 19 km2 (Upper Bavaria, Federal Repuvblic of Germany). In addition, the weighted monthly means of the deuterium contents are indicated as step functions (Hermann & Stichler, 1982).

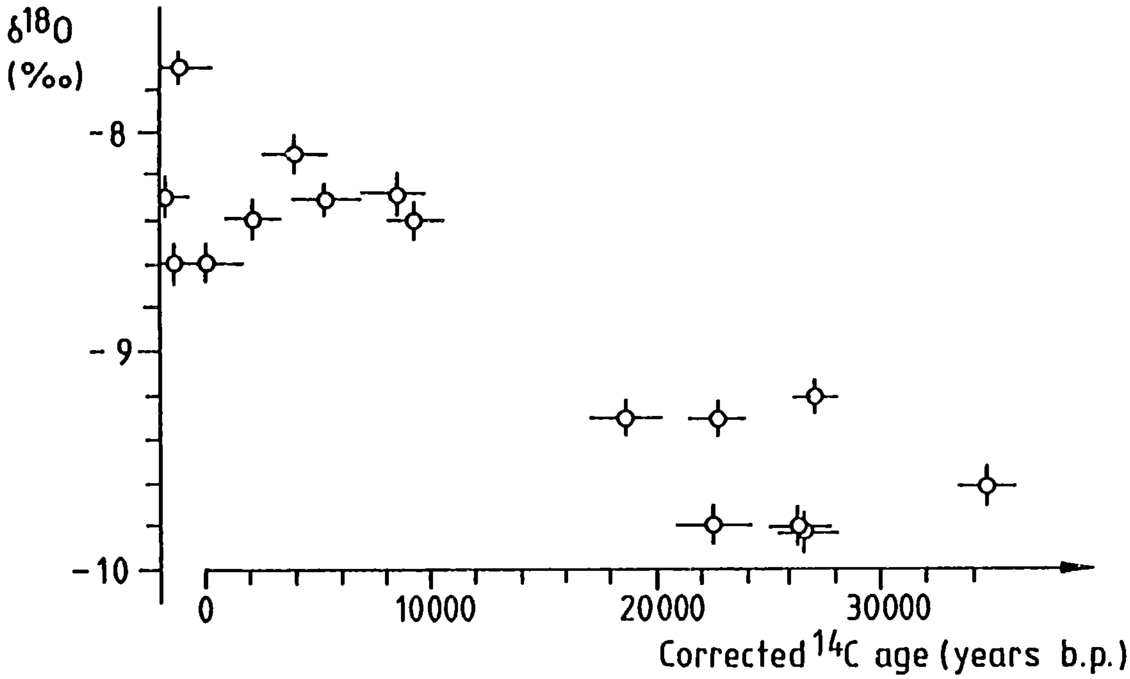


Figure 8: 18 0 contents of groundwater from the unconfined and confined area of a Triassic non-marine sandstone aquifer in eastern England, in relation to the geochemically corrected 14C age (according to Bath et al. 1979)

The radioactive isotopes ^{3}H and ^{85}Kr are largely of anthropogenic origin: ^{3}H originated from the nuclear bomb tests between 1952 and 1962 which injected tracer into the stratosphere. Since then it has been transported to the atmosphere with a seasonal periodicity and rained out since 1963 with from year to year decreasing, and later on with little changing annual mean concentrations (Fig. 9). The knowledge of this input function is provided on a global scale by the IAEA/WMO sampling network (IAEA 1981b and 1983c) and in addition by many national activities.

^{85}Kr is released from nuclear plants into the air and becomes distributed uniformly in the atmosphere. In contrast to ^{3}H, the ^{85}Kr concentration in the air and therefore also in the precipitation, increases monotonously without seasonal variations (Fig. 10).

^{3}H and ^{85}Kr contents of groundwaters are, according to the form of their input function, suited for a differentiation of residence times up to about 100 years, depending on the hydraulic model used for interpretation. Fig. 11 shows, in the case of the exponential model, the ^{3}H and ^{85}Kr contents of groundwaters with different mean residence times calculated from known ^{3}H and ^{85}Kr input functions (Fig.9 and 10). The measurement of ^{85}Kr content needs much more expenditure than that of ^{3}H. However, single ^{85}Kr analyses can be used successfully for clearing up ambiguities and uncertainties in the determination of residence times caused by the form of ^{3}H input function (e.g. Salvamoser, 1982). In other respects, a sufficiently long time series of measurements of ^{3}H (and/or ^{85}Kr) contents from a single groundwater sampling point can be useful for evaluating the validity of the applied model as well as the error of the calculated residence time.

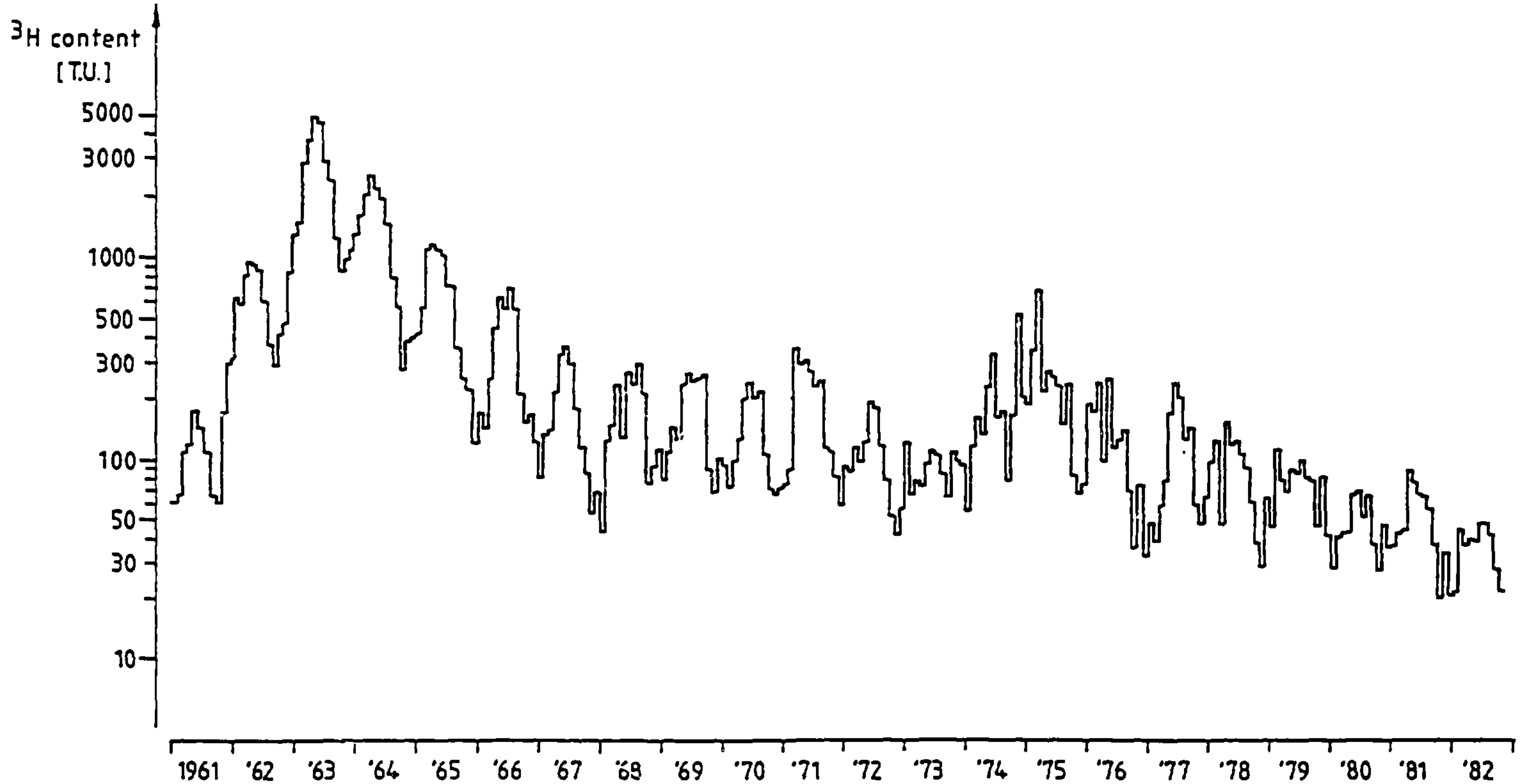


Figure 9: Monthly means of 3H content of precipitation in the catchment area of the river Rhine (according to Weiss & Roether, 1975) from data collected since 1974 in Upper Bavaria

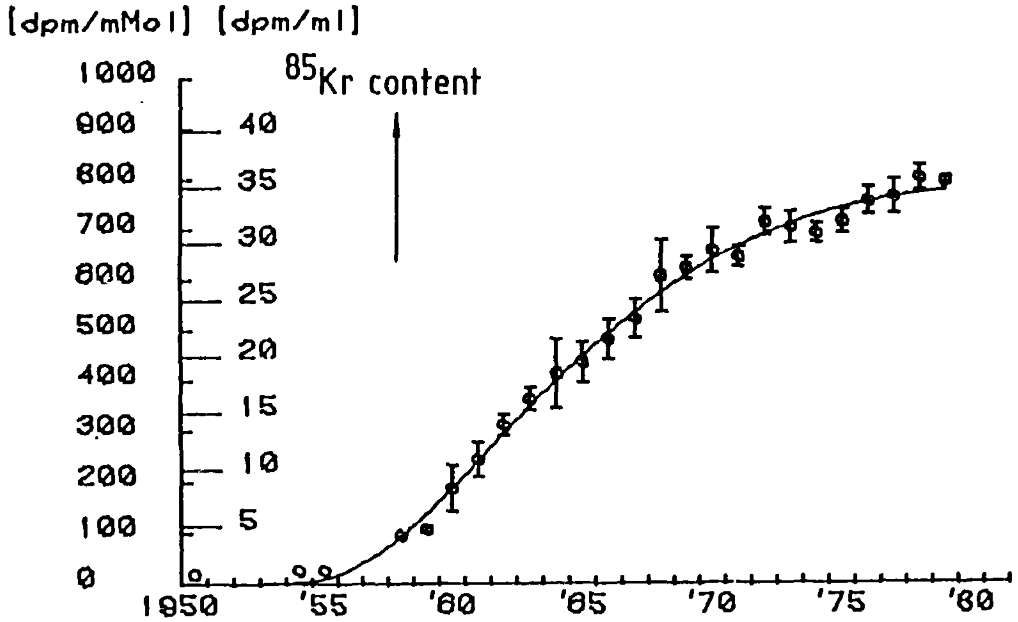


Figure 10: Annual means of atmospheric 85Kr concentrations between 40 and 60 northern latitude (Salvamoser, 1982); mMol and ml refer to krypton (STP).

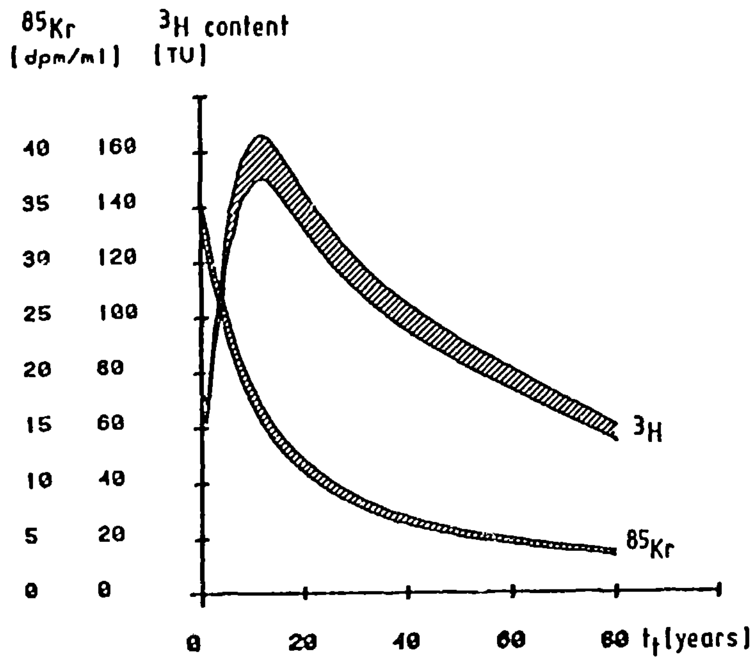


Figure 11: 3H and 85Kr contents of groundwater for different mean residence times tt calculated from 3H and 85Kr input functions (Figs. and 10)by means of the exponential model for groundwater samples taken in 1979 (Salvamoser 1982)

The radioactive isotope ^{14}C is produced in the atmosphere by cosmic-ray interaction. According to the model of Munnich (e.g., 1968) it enters the soil air and soil water mainly via the decomposition of plants and forms calcium bicarbonate and CO_2 in the groundwater. Using the law of radioactive decay, the ^{14}C model age of a sample from (deep) groundwater is calculated from the ratio of the initial ^{14}C content c_o of the groundwater at the time of recharge and the ^{14}C content of the groundwater under investigation. c_o often lies between about 60 and 100% modern. This uncertainty of c_o is due to, among other effects, the geochemistry of the recharge area, the possible ^{14}C content of soil carbonates, the dissolution of limestone by humic acids, and carbon isotope exchange between the soil gas and water. Furthermore, ^{14}C can be lost from the groundwater through isotopic exchange with the carbonate in the aquifer, or the ^{14}C content can be diminished by a mixture of CO_2 of fossil biogenic or magmatic (volcanic) origin. The various methods for isotopic and geochemical corrections of ^{14}C dates have been reviewed, for example, by Fontes and Garnier (1979) and by Eichinger (1981). Major parameters of these models are the concentrations of the dissolved inorganic carbon (HCO_3 , CO_2) and the ratios of the stable carbon isotopes, $^{13}C/^{12}C$, in the soil gas, carbonate rocks and groundwater. Additional complications in ^{14}C dating of groundwater which exist also in dating with other cosmogenic radionuclides, are possible diffusion and/or convective transport of ^{14}C through low-permeable layers which separate horzons of groundwater with strongly distinct ^{14}C contents and/or hydraulic heads (Klitzsch et al., 1976; Geyh & Backhaus, 1979). Despite all these problems at the present time the ^{14}C method is the only means for providing hydrogeologists with order-of-magnitude estimates of groundwater ages between about one thousand years and a few tens of thousands of years.

The radioactive isotopes ^{32}Si and ^{39}Ar, having half-lives intermediate between those of ^{3}H and ^{14}C, could be important for dating groundwater with the hydrologically significant age range between 100 and 1000 years. Many questions exist concerning ^{32}Si including the exact value of half-life, the contribution of ^{32}Si produced by cosmic radiation in the soil and by nuclear bomb tests, and the complex silica geochemistry. Until now, dating with ^{32}Si is at most, useful for establishing relative ages of water in a single aquifer (cf. Davis & Bentley, 1982).

Though the rare gas argon dissolved in groundwater does not react with the solid aquifer matrix, ^{39}Ar ages measured so far proved to be often much younger than the pertinent ^{14}C model ages. This discrepancy could be due, inter alia, to subsurface production of ^{39}Ar according to the reaction $^{39}K(n,p)$ ^{39}Ar (Loosli & Oeschger, 1979). On the other hand, one also has to consider whether the ^{14}C model ages evaluated are too high. Indeed, examples show that the reduction of ^{14}C model ages by geochemical corrections brought the pairs of ^{14}C and ^{39}Ar ages into the range of possible admixture models (Eichinger, 1981; Forster et al., 1984).

The radioactive isotopes ^{81}Kr and ^{36}Cl are used for dating of very old groundwaters within a time scale of 10^5 to 10^6 years. ^{18}Kr has the advantages of being inert and of originating probably only in the atmosphere and shallow soil horizon induced by cosmic radiation. As natural ^{18}Kr concentrations in groundwater are very small, gas samples extracted from water volumes of 10^3 m^3 were considered to be required for radioactivity counting (Oeschger, 1978). Most recently a new detection techniques, the resonance ionization spectroscopy, which combines laser technique and mass spectrometry, seems to allow the sample size to be reduced to a few liters of water. The first measurements using this technique can be expected in the near future. (Loosli, personal communication).

The development of mass-spectrometric techniques for nuclide identification using accelerators, has provided an excellent means for the measurement of natural ^{36}Cl concentrations in a few liters of water. Problems of geochemical interpretation are considered to be less than with ^{14}C, because chloride in groundwater is neither derived normally from, nor reacts with, the solid matrix of the aquifer (Davis & Bentley, 1982). Airy et al. (1984) showed the applicability of such ^{36}Cl measurements in an extended study of the Great Artesian Basin, Australia, which led to hydrologically reasonable groundwater ages up to 10^6 years. However, extensive studies combined with measurements of other radionuclides are still necessary to prove the ^{36}Cl dating method as a useful tool in hydrological investigations.

Additional information on groundwater age differentiation could be provided by other isotope methods, the results of which are even more difficult to interpret than the before mentioned isotopes. The accumulation of radioactive decay products in water may be a measure of the transit time, and the measurement will become even easier the older the water is. There were attempts to use the accumulation of ^4He, originating from the decay of U and Th in the rock for groundwater dating but almost all ^4He model ages obtained so far turned out to be distinctly older than corresponding ^{14}C model ages (e.g. Bath et al, 1979). This might be due, inter alia, to the admixture of helium which seeps upwards from deep geological sources. It should also be mentioned that the other He isotope, ^3He, which is the decay product of ^3H, might be useful for dating young groundwater. Concerning old groundwater, only qualitative dating up to about 1.5×10^6 years seems to be possible by measuring the $^{234}U/^{238}U$ activity ratio and considering the disequilibrium of these radionuclides in circulating groundwater. For details of this method as well as for the potential utilization of chemical disequilibria (e.g. amino acid racemization) and of anthropogenic chemicals like halocarbons (e.g. Freon) in groundwater dating, we have to refer to literature (e.g. Davis & Bentley, 1982).

In the last few years measurements of environmental isotope contents were increasingly resorted to in the case of all practical problems, the solution of which presupposes knowledge about groundwater flow. Such problems are, for instance, groundwater development and balances in regionally extended aquifers, in particular in arid areas but also in other climates with high water requirements; in karst areas, in particular with view to the frequently and necessarily simultaneous problem of drinking water supply and waste water discharge, and in thermal and mineral water aquifers in particular with a view to their use and protection. Investigations of the communication of surface water and groundwater, in particular of bank filtration of rivers, saltwater intrusion in coastal areas and of groundwater movement in the vicinity of disposal sites for radioactive or other wastes assist in the protection of groundwater and environment.

In this connection, in addition to a combined application of measurements of different environmental isotope contents, correlations with hydrochemical, hydrogeological and hydraulic parameters are increasingly used for the solution of problems. For details of numerous case studies of that kind, reference is made to the afore-mentioned monographs (Moser & Rauert, 1980; IAEA, 1983a 1983b) as well as to the Proceedings of the Symposia on isotope hydrology regularly held by IAEA (e.g. 1974, 1979, 1984). The outcome of that work shows, however, that work is still required to further develop the measuring techniques, to study the input concentrations and, in the case of radionuclides, possible underground production of the environmental tracers used. A principal problem still to be solved is the development of comprehensive models for data interpretation which account for the geochemistry of tracer behaviour and water-rock interaction as well as diffusion or dispersion processes and the hydrodynamics of groundwater flow including mixing processes in natural flow systems.

2.2 Determination of Groundwater Filtration Velocity and Flow Direction by Means of Single-Well Techniques

Single-well techniques involve the injection of a radioactive tracer into a borehole and detection of this tracer within the borehole during infiltration of the tracer into the aquifer. Single-well techniques have the advantage of using only small amounts of tracer. The distortion of the flow field around the borehole must be borne in mind and a correction applied when interpreting the results of single-well tests in terms of the aquifer system.

The borehole dilution techniques (e.g. Moser & Rauert 1980; IAEA, 1983a 1983b; Drost, 1983 1984) involve the instantaneous injection of a tracer (such as $^{82}Br^-$, $^{131}I^-$) into a sealed section of the borehole and the monitoring of the decrease in tracer concentration with time due to groundwater flow through the borehole (Fig. 12). In the case of a porous aquifer, the measurements provide an estimation of groundwater filtration velocity. By use of a collimated revolving detector, the direction of groundwater flow can also be determined. Fig. 12 shows a combined probe for the determination of filtration velocity and direction of groundwater flow. Both methods give valuable results in porous media only if no vertical streams dominate in the borehole and if the borehole stands in a hydrogeologically representative profile of the aquifer. The range of filtration velocity measurable by the dilution method is between some mm/day

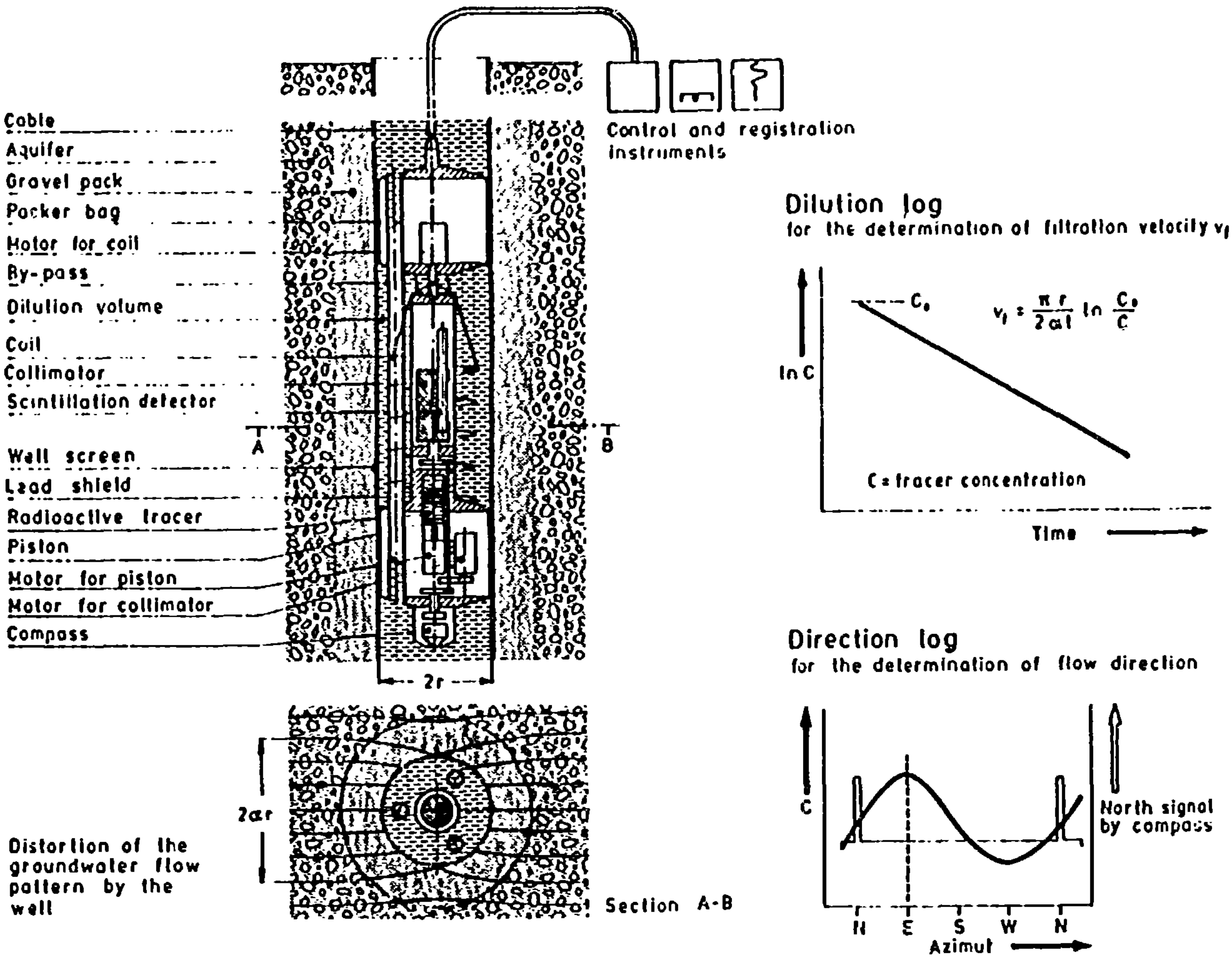


Figure 12: Tracerprobe and principle for measuring filtration velocity and flow direction of groundwater (Drost, 1983).

and some hundreds of m/day. In fractured rock this method may be used to obtain information on flow in specific fractures but detailed interpretation will depend on the geometry of the intersection of the fissure with the borehole. Vertical streams within the borehole can be investigated by releasing a tracer (such as $^{82}Br^-$, $^{131}I^-$) in the borehole and observing the movement of this tracer up or down the borehole e.g. by logging (e.g. Klotz et al, 1979; IAEA, 1983a; Drost, 1983). This technique allows identification of zones of water inflow and outflow the borehole profile and quantitative determination of discharge of these flows. All single-borehole techniques have been widely applied for local hydrological problems such as groundwater resources studies, environmental and groundwater protection, and civil engineering (e.g. Moser & Rauert, 1980; Klotz et al, 1979; IAEA, 1983a; Drost, 1983 1984).

2.3 Determination of the Velocity of Groundwater and the Dispersion of the Groundwater Aquifer by Means of Multiple-Well Techniques by Applying Radioactive or Activable Tracers

Multi-well tracer techniques involve introducing a tracer solution into the aquifer in one or more boreholes and observing the concentration time distribution of the tracer groundwater down-gradient from the injection location. As a result of this process in the non-pumped aquifer the distance velocity and hydrodynamic dispersion and in the pumped aquifer effective porosity can be determined (see, e.g., IAEA 1983d, Moser & Rauert 1980). In the case of karst-hydrologic investigations such measurements supply knowledge about water paths, flow and residence times as well as about catchment areas of a karst water system. For reasons of radiation protection the use of radioactive tracers in the case of such investigations can be allowed only where advantages as compared to traditional hydrological tracers (dye tracers, salt) can be expected. This applies in cases in which, e.g., water marked with ^3H is used as largely adsorption-free ("ideal") reference tracer or in the case of a multi-tracer experiment (e.g., karst investigations) in which the wide range of available tracer substances can be enlarged by the addition of radionuclide tracers (e.g., Bauer et al, 1976; Zojer, 1983). Inactive tracer substances with subsequent activation have, in practice, been applied only in a few cases because of the relatively high expenditure required (e.g., Batsche et al, 1970; Behrens et al., 1976).

3. CONCLUSIONS

Development in the field of the application of nuclear techniques for the investigation of water movement in the unsaturated and saturated zones over a period of about 25 years shows that these methods today take an established position next to hydrogeologic, hydrochemical and hydraulic methods in hydrology. In many cases these methods provide evidence, which neither wholly nor in part can be obtained by means of conventional methods, at least not directly. This is particularly true for the time differentiation of groundwaters. Application of nuclear techniques combined with conventional methods tend to eliminate erroneous conclusions as may often result when considering a natural system unilaterally. Objections to nuclear methods for reasons of expenditure do not hold good in most cases, since analyses of environmental isotopes (^2H, ^{18}O, ^3H, ^{13}C, ^{14}C) have become routine and therefore, in general, require no higher expenditure than complete water chemical analyses; the use of intentionally added radioactive tracers corresponds in terms of expenditure, in the case of single-well techniques, to other conventional borehole-procedures and also in the case of multiple-well techniques approximately to the expenditure to be incurred for tracing experiments with conventional tracers. It is therefore to be expected that nuclear techniques will be increasingly applied in hydrology.

4. REFERENCES

AIRY, P.L., H. BENTLEY, G.E. CALF, S.N. DAVIS, E. ELMORE, H. GOVE, M.A. HABERMEHL, F. PHILLIPS, H. SMITH, T. TORGERSEN (1984): Isotope Hydrology of the Great Artesian Basin, Australia. - In: Proc. Intern. Conf. Groundwater and Man, Sydney, in print.

BATH, A.H., W.M. EDMUNDS, J.N. ANDREWS (1979): Paleoclimatic trends deduced from the hydrochemistry of a Triassic sandstone aquifer, United Kingdom. In: Isotope Hydrology 1978, IAEA, Vienna, p. 545-568.

BATSCHE, H., F. BAUER, H. BEHRENS, K. BUCHTELA, H.J. DOMBROWSKI, R. GEISLER, M.A. GEYH, H. HOTZL, F. HRIBAR, W. KASS, J. MAIRHOFER, V. MAURIN, H. MOSER, F. NEUMAIER, J. SCHMITZ, W.A. SCHNITZLER, A. SCHREINER, H. VOGG, J. ZOTL (1970): Kombinierte Karstwasseruntersuchungen im Gebiet der Donauversickerung (Baden-Wurttemberg) in den Jahren 1967-1969. - Steirische Beitr. z. Hydrogeol. 25, 5-165

BAUER, F., H. BEHRENS, F. BERNOT, B. BUKVIC, S. BUSER, M. DEDANT, F. DROBNE, R. GOSPODARIS, P. HABIC, H. HOTZL, F. HRIBAR, W. KASS, M. KOLBEZEN, P. KRIVIC, F. LEWICKI, V. MAURIN, J. -J. MISEREZ, H. MOSER, M. MOZETIC, M. PIRS, V. RAJNER , D. RANK, W. STICHLER, M. TRATNIK, R. VERBOVSEK, J.G. ZOTL, Martina ZUPAN, M. ZUPAN, K. ZRIBIK (1976): Markierung unterirdischer Wasser - Untersuchungen in Slowenien 1972-1975. - Underground Water Tracing - Investigations in Slovenia 1972-1975), Ljubljana.

BEHRENS, H., H. MOSER, E. WILDNER (1976): Investigation of groundwater flow with the aid of Indium-EDTA-complex using neutron activation for the determination of the tracer. - In: Modern Trends '76, Proc. 1976 Intern. Conf. Modern Trends in Activation Analysis, Munchen, p. 1093-1099; s. also: J. of Radioanalytical Chem. 38 (1977), 491-498.

DAVIS, S.N. & H.W. BENTLEY (1982): Dating groundwater, a short review. - In Nuclear and Chemical Dating Techniques (Ed. L.A. Currie), Washington D.C., p. 187-222

DROST, W. (1983): Single well techniques. - In: Tracer Methods in Isotope Hydrology, IAEA-TECDOC-291, Vienna, p. 7-16.

DROST, W. (1984): Einbohrlochmethoden zur Bestimmung der Filtergeschwindigkeit und Fliessrichtung des Grundwassers. Wasser und Boden 1984, 149-153.

EICHINGER, L. (1981): Bestimmung des Alters von Grundwassern mit Kohlenstoff-14; Messung und Interpretation der Grundwasser des frankischen Albvorlands. - Diss. Univ. Munchen.

EICHINGER, L., W. RAUERT, W. STICHLER, B. BERTLEFF, R. EGGER (1984): Comparative study of different aquifer types in Central Europe using environmental isotopes. - In: Isotope Hydrology 1983, IAEA, Vienna, 271-289.

FONTES, J.C. & J.M. GARNIER 91979): Determination of the initial 14C activity of the total dissolved carbon: a review of the existing models and a new approach. - Water Resources Res. 15, 399-413.

FORSTER, M., H. MOSER, H.H. LOOSLI (1984): Isotope hydrological study with carbon-14 and argon-39 in the Bunter Sandstones of the Saar region. - In: Isotope Hydrology 1983, IAEA, Vienna, 515-533.

GEYH, M. & M. BACKHAUS (1979) : Hydrodybnamic aspects of carbon-14 groundwater dating. - In: Isotope Hydrology, 1978, IAEA, Vienna, p. 631-643.

GUPTA, S.K. & P. SHARMA (Eds) (1979): Current Trends in Arid Zone Hydrology (Proc. Symp., Ahmenabad, 1978), New Delhi.

HERRMANN, A. & W. STICHLER (1982): Surface runoff separation and discrimitation of subsurface storage systems using environmental isotopes. - Beitr. Hydrologie, Sonderheft 3; 233-252.

IAEA (1970): Neutron Moisture Gauges. - Tech. Rep. Ser. 112, Vienna.

IAEA (1971): Nuclear Well Logging in Hydrology. - Tech. Rep. Ser. 126, Vienna.

IAEA (1974): Nuclear Techniques in Groundwater Hydrology, Vienna.

IAEA (1979): Isotope Hydrology 1978, Vienna.

IAEA (1981a): Stable Isotope Hydrology - Deuterium and Oxygen-18 in the Water Cycle, Tech. Rep. Ser. 210 (Eds: J. Gat & R. Gonfiantini), Vienna.

IAEA (1981b): Statistical Treatment of Environmental Isotope Data in Precipitation, Tech. Rep. Ser. 206, Vienna.

IAEA (1983a): Guidebook on Nuclear Techniques in Hydrology, 1983 Edition. - Tech. Rep. Ser. 91, Vienna.

IAEA (1983b): Isotope Techniques in the Hydrogeological Assessment of Potential Sites for the Disposal of High-Level Radioactive Wastes. Tech. Rep. Ser. 228, Vienna.

IAEA (1983c): Environmental Isotope Data No. 7: World Survey of Isotope Concentration in Precipitation (1976-1979), Tech. Rep. Ser. 226, Vienna.

IAEA (1983d): Tracer Methods in Isotope Hydrology. - IAEA-TECXDOC-291, Vienna.

IAEA (1984): Isotope Hydrology 1983, Vienna

JAKUBICK, A. (1972): Untersuchung der Wasserbewegung in teilweise gesattigten Boden - Tritium Tracermethode zur Bestimmung der Grundwasserspende. - Diss. Univ. Heidelberg.

KLITZSCH, E., C. SAONNTAG, K. WEISTROFFER, E.M. EL-SHAZLY: Grundwasser der Zentralsahara. Fossile Vorrate. - Geol. Rdschau 65, 264-287.

KLOTZ, D., H. MOSER, P. TRIMBORN (1979): Single-borehole techniques - present status and examples of recent applications. - In. Isotope Hydrology 1978, IAEA, Vienna.

LOOSLI, H.H. & H. OESCHGER (1979): Argon-39, carbon-14 and krypton-85 measurements in groundwater samples. In: Isotope Hydrology 1978, IAEA, Vienna, p. 931-947.

MATTHESS, G., A. PEKDEGER, H.D. SCHULZ, H. RAST, W. RAUERT (1979): Tritium tracing in hydrochemical studies using model lysimeters. In: Isotope Hydrology 1978, IAEA, Vienna, p. 769-785.

MOSER, H. & W. RAUERT (1980): Isotopenmethoden in der Hydrologie. - Berlin - Stuttgart.

MOSER, H. & W. RAUERT (1983): Determination of groundwater movement by means of environmental isotopes: State of the art. - In: Relation of Groundwater Quantity and Quality (Proceedings of the Hamburg Symposium, August, 1983), IAHS Publ. No. 146, 241-257.

MUNNICH, K.O. (1968): Isotopen-Datierung von Grundwasser. - Naturwiss. 55, 1558 -163.

MUNNICH, K.O. (1970): Isotope studies on groundwater movement in the unsaturated and saturated soil zone. - In: Proc. Symposium on Trace Elements in Drinking Water, Agriculture and Human Life. Middle Eastern Regional Radioisotope Centre for the Arab Countries and Goethe Institut, Cairo, p. 108-122.

MUNNICH, K.O. (1983): Moisture movement in the unsaturated zone. - In: Guidebook on Nuclear Techniques in Hydrology, 1983 Edition. Tech. Rep. Ser. 91, IAEA, Vienna, p. 203-222.

MUNNICH, K.O., W. ROETHER, L. THILO (1967): Dating of groundwater with tritium and 14C. - In: Isotopes in Hydrology, IAEA, Vienna, p. 305-320.

MUNNICH, K.O., C. SONNTAGE, D. CHRISTMANN, G. THOMA (1980): Isotope fractionation due to evaporation from sand dunes. - Zfi-Mitt. 29, 319-332.

OESCHGER, H. (1978): Some cosmic ray produced radionuclides of interest in dating old groundwater. - In: Workshop on Dating Old Groundwater (Ed. S.N. Davis). Arizona, 129-135.

RAO, S.M. (1983): Use of radioactive tracers in studies on infiltration through unsaturated zone. - In: Tracer Methods in Isotope Hydrology, IAEA-TECDO C-291, Vienna, p. 47-66.

SALVAMOSER, J. (1982): 85Kr im Grundwasser - Messmethodik, Modelluberlegungen und Anwendung auf natürliche Grundwassersysteme. - Diss. Univ. Munchen

SONNTAG, C., G. THOMA, K.O. MUNNICH, T. DINCER, E. KLITZSCH (1980): Environmental isotopes in North African groundwaters - the Dahna sand dune study (Saudi Arabia). - In: Arid-Zone Hydrology: Investigations with Isotope Techniques, IAEA, Vienna, p. 77-84.

THOMA, G. N. ESSER, C. SONNTAG, W. WEISS, J. RUDOLPH, P. LEVEQUE (1979): New techniques of in-situ soil-moisutre sampling for environmental isotope analysis applied at Pilat sand dune near Bordeaux. - HEPT modelling of bomb tritium propagation in the unsaturated and saturated zones. - In: Isotope Hydrology 1978. IAEA, Vienna, p. 753------768.

WEISS, W. & W. ROETHER (1975): Der Tritiumabfluss des Rheins 1961-1973. - Deutsche Gewasserkl. Mitt. 19, 1-5.

ZIMMERMANN, U., K.O. MUNNICH, W. ROETHER, W. KREUTZ, K. SCHUBACK, O. SEIGEL (1966): Tracers determine movement of soil moisture and evapotranspiration. - Science 152, 346-347.

ZOJER, H. (199983): Groundwater flow in Karstic aquifers. - In: Tracer Methods in Isotope Hydrology, IAEA-TECDOC-291, Vienna, p. 165-172.

PART II

SOIL MOISTURE MOVEMENT DETERMINED BY PHYSICAL METHODS

by G. Morgenschweis

PART II SOIL MOISTURE MOVEMENT DETERMINED BY PHYSICAL METHODS

LIST OF FIGURES

INTRODUCTION

Water in the unsaturated zone, which extends from the soil surface down to the groundwater table, is generally referred to as soil moisture. It forms a connecting link between atmospheric, surface and subsurface components of the hydrological cycle with all possible interrelations. Thus soil water affects such important hydrological processes as:

- Infiltration and percolation and the resulting groundwater recharge

- Surface detention including interception and overland runoff

- Capillary rise, evaporation and transpiration as well as water consumption by plants and the formation of runoff in catchment areas.

Significant qualitative processes take place between soil and water or water constituents and substratum. Since soil water determines the fundamental behaviour of both soil and water, it is not surprising that many methods have been developed in the last few decades in, for example forestry, agriculture, environmental sciences, engineering and industry in order to measure soil moisture. The basic information obtained using these methods is the water-content distribution with respect to depth and time at a location as shown in the centre of Fig. 1, taken from Greacen et al. (1981).

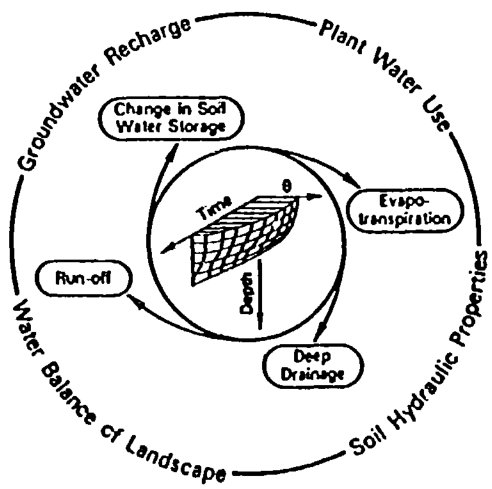


Figure 1: Schematic diagram of the applictions of soil-water measurement values. Central to this figure is the water content-depth- time relationship (Greacen et al., 1981)

Furthermore, this diagram summarizes the applications of soil moisture data ranging from water balance studies in catchment hydrology over soil-plant water relations and the determination of soil hydraulic properties needed for soil water movement studies to groundwater studies with emphasis on capillary rise and groundwater recharge.

But soil water content as a function of time and depth is normally not sufficient to yield information on soil-moisture movement, since soil moisture moves - due to the principles of unsaturated flow - in response to a number of forces such as gravity, soil suction, vapour pressure and temperature, gradient. This means that for the determination of soil-water movement soil moisture data are needed in conjunction with estimates of soil hydraulic properties such as soil suction, conductivity and diffusivity. On the theory of soil moisture movement cf. to the fundamental works of e.g. Buckingham (1907), Richards (1931), Childs & Collis-George (1950), Klute (1952), Philip (1954, 1955), summarized in Philip (1969).

On the other hand, for a better interpretation of these complex relationships, simulation models for water transport have been developed and applied to a greater extent in recent times, particularly in the field of hydropedology and hydrology (cf.section 3.3).

1. SOIL-WATER CYCLE

For a better understanding of the complex relations, the soil-water cycle is shown schematically in Fig. 2. Using the same symbols, the short-term soil- water balance of a place site, neglecting lateral subsurface inflow and outflow, is cited (for symbols see Fig. 2).

(1) $$QI + QK - QET - QP = \Delta S$$

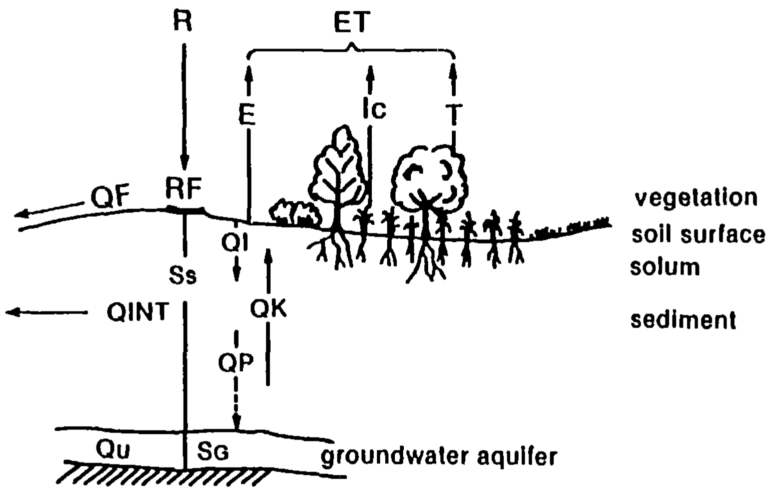
Where QI = infiltration, QK = capillary rise, QET = evapotranspiration, QP = deep percolation and ΔS = change in soil-water storage.

When incorporated into:

(2) $$R = QF + QI$$

Where R means rainfall and QF overland runoff, we obtain

(3) $$R = QF + QET - QK + QP + \Delta S$$



R = rainfall OF - overland runoff RF = surface detention
OINT = interflow Ou = subsurface runoff Ss = profile storage
So = groundwater storage E = evaporation Ic = interception
T = transpiration ET - evapotranspiration OI = infiltration
OP = percolation OK = capillary rise

Figure 2: Soil-water cycle

Viewing the relationship between input and output of water over an interval of several years, in the humid climate of Europe the ΔS-term is neglected in many cases because it is assumed to equal 0.

QI, QF, QET and QP are flow rates per time interval at the upper or lower boundary of the unsaturated zone; in this way the flow through the soil surface represents infiltration and soil evaporation resp. evapotranspiration if vegetation is included, and the flow at the lowest boundary (the groundwater surface) indicates the groundwater recharge and the capillary rise at sites with near-surface groundwater tables.

In addition to problems of water-supply of the plant-root zone the term S is of interest because of its importance in determining QP and QET. Data for ΔS alone, however, are not sufficient for its determination. Short period variations in the water content during the growth period have a considerable effect on ten-day and monthly balances.

2. MEASUREMENT METHODS

All components of the soil-water cycle in equ. (3) and the corresponding processes of soil moisture movement are dependent on soil moisture content and its variation in depth and time. Hence suitable field data on soil moisture are needed. Consequently, the next section deal with methods of soil-moisture measurement.

2.1 Soil-moisture measurement

Currently the most frequently used techniques in the field are

2.1.1. Thermogravimetric method:

With the help of a soil auger volume-known soil samples are taken at various depths in the field; in the laboratory the actual water content is then determined gravimetrically by weighing, drying and reweighing. The result is the volumetric soil-water content.

This direct method is simple and economical for short-term investigation programmes and is still the standard for the calibration of all other methods. When a mid-term or long-term study is performed, however, the frequent augering destroys the measurement site and disturbs the natural environment (Reynolds, 1970a, 1970b, 19070c).

Only weighable lysimeters allow the continuous measurement of the change in soil moisture with time by recording changes in the weight of a soil block. Beside some methodological problems (oasis-effect, boundry problem at the surrounding walls, disturbed soil-suction profiles at the bottom of the lysimeter), the method involves considerable technical and financial efort and, this is why it is not in general use. Aspect of this method are discussed in detail in DVWK (1979).

2.1.2 Neutron diffusion method:

The neutron method is nowadays the most frequently used indirect technique of measuring soil-water content; for this reason, it will be discussed in the following in more detail.

It is a non-destructive field method based on the slowing-down, thermalization and diffusionof fast neutrons emitted from a source by elastic scattering with hydrogen nuclei in the soil. Since the hydrogen nuclei of the soil are approximately proportional to the water content, the flux of slowed-down neutrons near the detector is a measure of soil moisture.

The measurement is normally performed by lowering a probe (see Fig. 3), which consists of a radioactive source and a detector to the required depth in an access tube into the ground. Soil water content is then calculated from the count-rate of the slowed neutrons and a calibration curve, which should be specific to the particular measurement profile or site. (For more details on the principle of the neutron moisture probe is referred to IAEA (1970), Couchat (1974), Neue (1980), Greacen et al (1981), Morgenschweis (1983).

The main advantages of the radiometric method compared to gravimetric sampling are those of fast assessment values without destroying the measurement profile as well as of precision and cost, especially if used in a long-term and large investigation program. The advantages of this physically-based measurement system can be reduced to a minimum by two main imperfections:

1. Poor installation of access tubes and

2. Calibration procedures and curves which do not meet the physical and physico-chemical requirements of the instrument and the medium measured.

Concerning point 1) reference is made to the publication of Eeles (1969), Bell (1976), Morgenschweis & Luft (1981), Greacen et al (1981) where the different possible bore techniques and the intruments needed to install access tubes are described in detail.

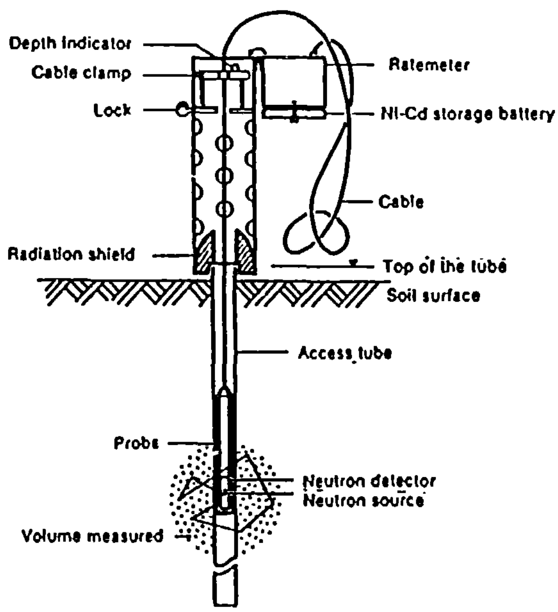


Fig. 3 Schematic diagram of a neutron moisture probe

The most serious source of bias in the neutron method derives from unadequate calibration procedures (point 2). this is why, a practicable calibration concept is presented here in detail:

The calibration is complicated by the fact that soil elements with a high neutron absorption probability as B, Cl, Li, Ca, Fe, K and organic matter, clayey minerals, silt and especially the bulk density of the porous medium influence the process of neutron diffusion.

Thus Olgaard (1965) and Couchat (1967) used for their model calculations of their fundamental studies more than 30 soil and instrument parameters that influence neutron gauge readings, but soil density proved to be the most important one. (cf. for example, Lorch (1963), Eeles (1969), Hanus et al. (1972), Vauchad et al. (1977). As a result of the calibration function for a neutron probe is

$$\Theta = f(N, \gamma)$$

(4) with

Θ = volumetric soil water content (vol% H_2O)
N = countrate of the neutron probe (Imp·s^{-1})
γ = dry bulk density (g·cm^{-3}).

To the question which method for calibration is to be chosen (as field and laboratory calibration, calibration using theoretical methods), the statistical treatment of the calibration data seems the crucial point.

In principle, equ. (4) can be approximated either with linear or non-linear multiple regression analysis using the polynomial approach (e.g. Hanus et al. 1972, Greacen et al. 1981), or with parameter estimation procedures. Couchat (1974) and Vachaud et al. (1977) derived from neutron-physical measurements an empirical function of the neutron diffusion dependent on moisture and density; their simplified reverse function stood the test as the basic equation of a neutron-probe calibration function.

(5) $$\Theta = (N - g\cdot\gamma - d) / (a\cdot\gamma + b)$$

The soil-physical parameters a, b, d and g can be approximated using an optimizing estimation procedure (Hartley, 1961). The main advantage of the parameter estimation procedure is that it needs only relatively small random samples (10 -2 20 samples).

In Fig. 4, the calibration function for a loessian measurement site in Southern Baden for a Wallingford neutron probe type IH II is presented (Morgenschweis, 1983). It was derived from a total of 180 volume-known scores from 30 to 300 cm depth (at least 5 parallels at each depth) which were averaged to random sample of 29 mean values (cf. table 1).

With the help of an optimizing procedure (a modified GAUSS-NEWTON iteration) the calibration function was determined with a standard error of the model s = 1.0 vol% H_2O taking into consideration dry bulk density in a range between 1.2 and 1.8 g.cm^{3-}.

In the meantime, this concept has been used in several research programmes in West Germany with different types of neutron probes and has provided satisfactory results with relatively little field and laboratory work.

Worth noting in this context is the remark by Greacen (1981), that, whatever calibration procedure is chosen, sound practice in the volumetric sampling of soil is the sine qua non for sound neutron meter calibration.

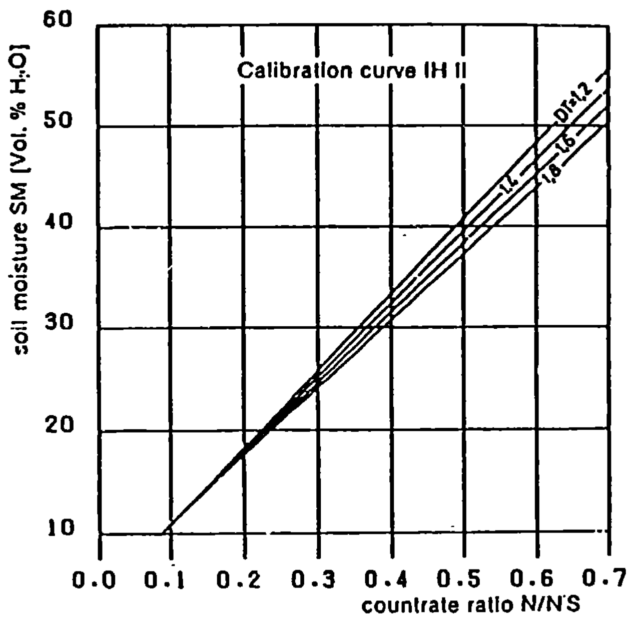


Figure 4: Moisture calibration curves of the neutron moisture probe Wallingford IH II for different dry soi

A disadvantage of the neutron method is its poor vertical resolution and therefore its inability to detect discontinuities and sharp changes in water content as a function of depth. This is true, for example, of measurements near the water table and in the uppermost 20 cm below the soil surface, where neutrons escape to the atmosphere when the neutron meter extends above the surface of the soil.

To overcome this disadvantage separate calibrations for the surface layers (Greacen et al., 1981), correction functions to increase the reduced countrate ratio (Morgenschweis, 1983), extension trays (Sharme & Tunny, 1972) are suggested. After all, the assessment of top soil moisture by using a neutron probe remains a problem.

Furthermore a once determined calibration function should be checked and maintained using adequate procedures. The instruments should be adjusted regularly to remove any bias due to electronic instabilities of the probe, for example by using control standards (e.g. a water drum (Bell, 1976) or polyethylene cylinders (Luft, 1981) and reference curves or the "relative countrate" principle(cf. Bell, 1976). For other possibilities see Greacen et al (1981) and Wendling (1985).

Following all the recommendations for installation and calibration, the neutron moisture probe is able to estimate the moisture content of the soil with an overall accuracy of lower than 2 vol% H_2O.

2.1.3 Gamma-ray transmission method:

Another radiometric technique is the gamma-ray transmission method (van Bavel, 1959; Lorch, 1967, 1971). The attenuation of gamma-rays is a density-dependent phenomenon and changes in density are proportional to changes in water content provided that the pore system is rigid (non-swelling or non-shrinking). The method can detect vertical changes of the order of only a few centimetres. In soils with varying bulk density (non-rigid pore systems), measurement can be carried out by using two sources, either a neutron and gamma source or two gamma sources with different energy levels (Corey et al. 1971).

There are other methods of soil moisture assessment such as

- electrical resistance units (Bouyoucous et al, 1940),
- heat conductivity instruments (Schulte im Walde, 1975),
- tensiometers (cf. chpt. 2.2),
- ultrasonic and
- electromagnetic method (Topp et al., 1980).

Common to all these methods is the fact, that they either do not fulfill the requirements in precision and handling, or are still being developed, so that it is too early to recommend them for practical use (cf. Schmugge et al. 1980).

To summarize this review of the direct and indict methods of soil-moisture measurement: there are, in the opinion of the author, two essential methods; on the one hand, gravimetric sampling as a standard for the calibration of other methods and as the most simple and economic method for short-term studies and, on the other hand, the radiometric technique (neutron and gamma-ray) which satisfies almost ideally the requirements of hydrologists as regards the physical determination of soil moisture.

2.2 Soil-moisture tension

As stated above, the movement of water in the zone of aeration cannot be explained by changes in soil-water content alone, since, in contrast to the saturated zone, gravity is not the dominant force but rather soil suction or soil tension (which are synonymous terms) by which water is held in comparatively moist soils.

This means that under normal circumstances and temporarily ignoring the effects of gravity, there will be a movement of soil moisture from moist soil to dry soil, or in terms of soil tension, from an area of low suction to an area of high suction. Thus, it is necessary to measure the change of moisture content and of suction with depth and time.

2.2.1 Tensiometer:

Tensiometers have been used to indicate soil moisture tension since the early 20's (Gardner, 1922, Richards, 1949). With the help of porous-clay cells, which are filled with water and connected to a pressure measurement system, e.g. a mercury manometer, this suction force of the soil is measured in situ and its variations can be recorded continuously. Tensiometers operate, however, only up to about 0.85 atm tension because dissolved air and the impurities in the soil water reduce the water's tensile strength (Don Kirkham, 1964). This means that tensiometers measure only the capillary component of soil moisture suction and that it cannot be used in dry soils or in top soil layers which show a wide range of water content variation with time.

To obtain information on soil tension higher than about pF 2.9 (pF is the logarithm of soil moisture suction, as defined by Schoffield (1935)), it is necessary to make laboratory use of porous plates or pressure membrane apparatus as described by Richards (1947). Another method is the use of an osmotic tensiometer ("Osmometer") as developed by Peck & Rabbidge (1969), which is filled with as osmotic solution instead of water and which makes the measurement of soil-moisture suction possible up to pF 4.2 (wilting point).

New developed pressure transducer tensiometers allows digital recording and its application is not restricted to frost-free periods (Strebel et al., 1970, 1973). But the above-mentioned physically based restrictions remain the same.

In controlled plot studies tensiometers are nowadays a successfully used measurement technique. (For more details see Richards (1949), Benecke (1982).

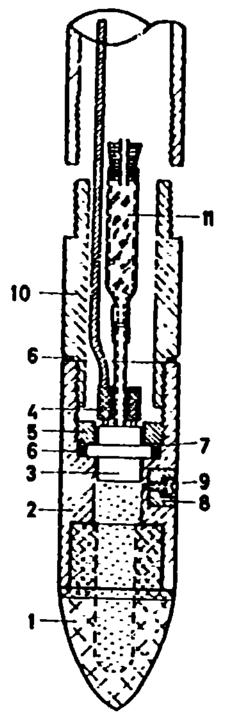
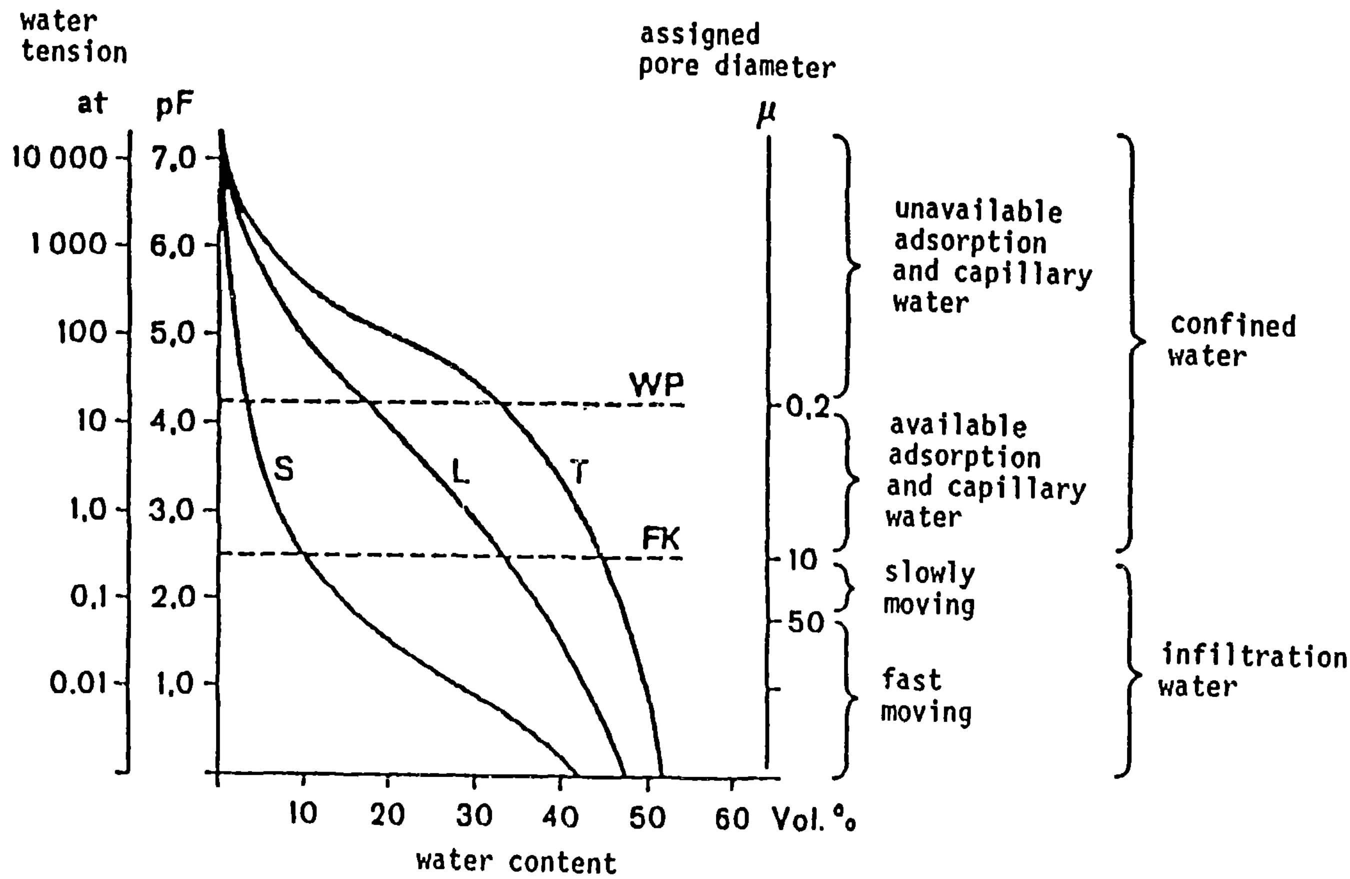


Figure 5: Schematic diagram of a pressure transducer tensiometer (Strebel et al., 1973).

2.2.2 Soil-Moisture Characteristic Curve

Under field conditions in a saturated soil, the hydrostatic potential and the tension are zero. As suction is increased, water is drawn out of the soil because pores of a certain diameter cannot retain soil water against the suction applied and will empty. Thus, increasing suction is associated with a decreasing soil-moisture content. The amount of water remaining in the soil at an equilibrium is a function of the pore size and volume and hence a function of the matric suction (cf. Fig. 6). This function is normally measured experimentally with soil scores using e.g. Richards' method with desorption. Its graphical presentation is termed, according to Childs (1940) "soil-moisture characteristic" or often soil-moisture - tension relationship. Examples of moisture characteristics for sand, loam and clay are shown in Fig. 6. If this function is known, soil tension can be estimated from measured soil moisture values.



Wilting point (WP): water content of the soil at which most plants start wilting (except typically dry and saline plants)

Field capacity (FK): maximum volume of confined water

Between WP (pF > 4.2; > 15 at) and FK (pF < 2.5; < 0.3 at): water available for plants

pF = -∞: condition of full water saturation in the case of prevented infiltration or condition of reservoir or ground water

pF = $\log_{10}$ cm water column

Figure 6: Soil-moisture characteristics of a sandy soil (S), a loamy soil (L) and a clayey soil (T) (adapted from Scheffer & Schachtschabel, 1981)

This function, however, is not generally a unique and single-valued one, because of the hysteresis phenomena, meaning that equilibrium soil water content at a given suction is greater in drying (desorption) than in wetting (sorption) a soil. Fig. 7 illustrates the hysteresis effect. For more details on hytsteresis and its causes cf. Poulovassilis (1962), Philip (1964), Hillel (1971).

The combined use of simultaneous measured soil moisture and soil tension data for determining soil moisture movement will be discussed in Section 3.

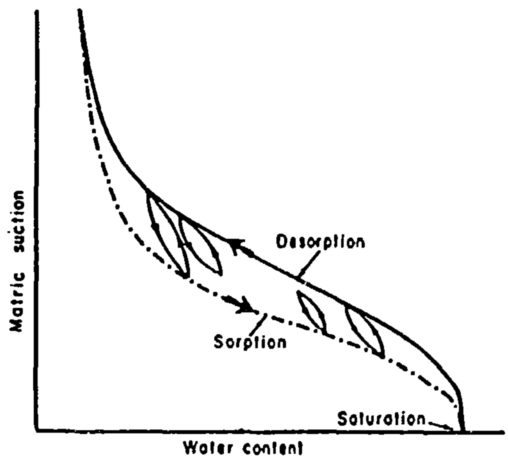


Figure 7: Hystosis phenomena of the suction-water content curves in sorption and desorption (Hillel, 1971) 2.3 Unsaturated conductivity and diffusivity

2.3 Unsaturated conductivity and diffusivity

To solve the basic equations of unsaturated flow as used in the simulation models discussed in section 3.2, knowledge of the unsaturated hydraulic conductivity and the diffusivity in dependance of suction or water content are generally required.

In principle, this information can be obtained from either :

a) experimental measurements in the laboratory, e.g. using the falling head or constant head method or the hot air method (cf. Klute, 1965; Gardner, 1956; van den Berg et al., 1986) or

b) experimental measurements in the field, e.g. using infiltration experiments (cf. Hillel & Gardner, 1970) or

c) using empirical functions as first approximation (cf. Childs & Collis-George ; 1950), Philip, 1955; Bruce & Klute, 1956). The distributed simulation model presented in section 3.2.2 uses such an empirical function for the estimation of the $k(\theta)$ and $D(\theta)$ function. Its graphical presentation is shown in Fig. 10.

Following Hillel (1971) it should be stated that until now there is no reliable way to predict these functions. Thus it is not surprising, that the above publications show very differing, even contradictory graphs.

3. DETERMINATION METHODS OF SOIL-MOISTURE MOVEMENT

Using soil-moisture content and tension as basic data and taking different boundary conditions into account, more or less complex computation methods have to be used to determine the components of soil-moisture movement, such as infiltration and deep percolation (downward direction), capillary rise and evaporation or evapotranspiration (upward direction).

3.1 Zero-flux plane method

During the growing season under not too humid climatic conditions, a plane of zero-flux (where the hydraulic gradient = 0) occurs below the root zone. If soil water and soil suction are simultaneously measured as a function of time between the soil surface and the groundwater table, an accurate determination of QP and QE is possible under these conditions. Using the zero-flux plane, and the groundwater table as a boundary layer, the water content variations can be integrated with time and give directly the deep percolation flux QP.

The integration between the zero-flux plane and soil soil surface results in the evaporation QE, or evapotranspiration QET when calculated with vegetation.

For periods without a zero-flux plane, the capillary water flow at a distinct depth below the root zone has to be determined by Darcy's law and this depth is used then as a boundary for integrating the water content variations. The relation between hydraulic conductivity and soil-water suction of the different soil layers needed for this approach can be determined by field measurements during periods without vegetation cover (Hillel et al., 1972) or on undisturbed soil cores in the laboratory using different methods (Renger et al., 1974; van der Berg et al., 1986).

Capillary rise QC from the groundwater table can be determined analogously (after a report of Strebel, 1985).

3.2 Deterministic simulation models

To quantify soil-water movement and its components. deterministic mathematical models have proved to be extremely successful. A great number of such physically-based models have been developed and published within the last 2 decades (e.g. Freeze, 1971; van der Ploeg et al., 1974; Wind & van Doorne, 1975 ; Hillel, 1977; Feddes et al., 1978; Duynisveld et al., 1983; Morgenschweiss, 1984). Hence, as it is imposible to present even in outline the most important developments, it seems more appropriate to outline the principles and different philosophies of soil-moisture movement modelling by taking two contradictory types as examples, a lumped two-soil zone model and a distributed analytical based model.

3.2.1 Two-soil zone lumped model

The approach adopted here is that described by Fleming (1975. 152 ff). Lumped parameter models of soil-moisture movement are based on the solution of the continuity equation of flow into and out of a soil moisture profile. Fig. 8 shows the general concept of such a lumped model, where a small unit of area within a catchment is taken and a soil column of it is considered, which can be subdivided into several zones. On the left of Fig. 8 the hydrological processes taking place within the soil profile are shown in a simplified manner.

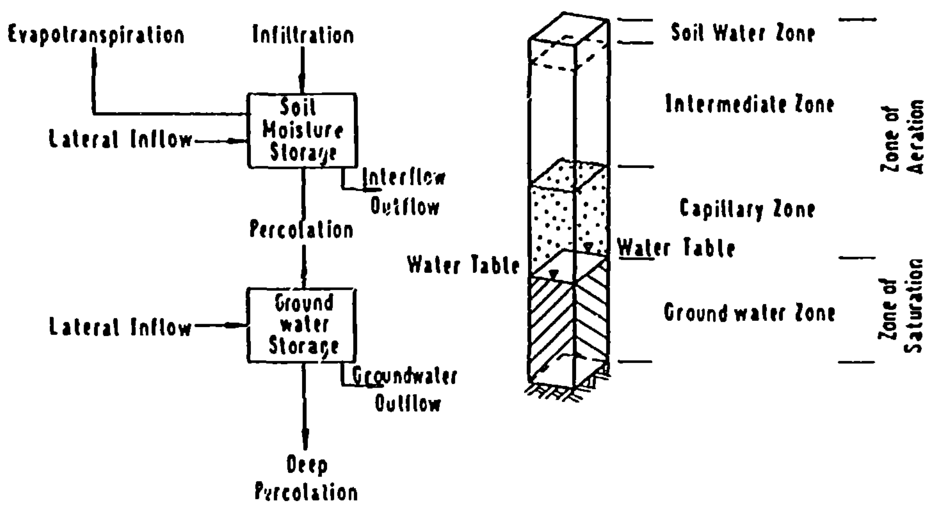


Figure 8: General concept of a lumped model of soil-moisture movement (Fleming, 1975)

Within the well-known "Stanford Watershed Model IV" (Crawford & Linsley, 1966) soil-moisture movement is modelled as a two soil-zones system: The upper soil zone (from a few centimeters or to decimeters) of soil which reacts immediately to rainfall and which controls the formation of overland flow and infiltration; and the lower soil zone which represents the soil moisture storage capacity, from just below the surface down to the capillary fringe. Both the upper and the lower zones are assigned parameters which represent nominal values of storage capacity. These are assigned based on parameter estimation. Rainfall is divided between surface detention and gross infiltration. The gross infiltation includes infiltrated water assigned to the lower zone and that assigned to interflow. Some fraction of the water assigned to surface detention enters the upper zone soil storage. This fraction is computed based on the ratio of actual soil moisture in the upper zone to the nominal soil-moisture storage. Percolation takes place from the upper zone to the lower and groundwater zones based on the function in equ. (6)

$$D_r = 0.1 \times Inf \times UZSN \left[\frac{UZS}{UZSN} - \frac{LZS}{LZSN} \right] \quad (6)$$

where D_r = drainage from the upper soil zone
Inf = an infiltration rate parameter
UZS = actual upper zone soil-moisture storage
UZSN = normal upper zone soil-moisture storage
LZS = actual lower zone soil-moisture storage
LZSN = normal lower zone soil-moisture storage

A fraction of the water accumulating in the lower zone from direct infiltration and percolation from the upper zone enters the groundwater zone. This percentage is based on the functions in equ. (7) to (9).

$$P_g = 100\,\frac{LZS}{LZSN}\left(\frac{1.0}{1.0+z}\right)^z \quad \text{for } \frac{LZS}{LZSN} < 1 \tag{7}$$

$$P_g = 100\left\{1.0 - \left(\frac{1.0}{1.0+z}\right)\right\}^z \quad \text{for } \frac{LZS}{LZSN} > 1 \tag{8}$$

$$z = 1.5\left\{\frac{LZS}{LZSN} - 1.0\right\} + 1.0 \tag{9}$$

where P_g = percentage of moisture entering groundwater storage from the lower zone

The above treatment of soil moisture is a simplification of what in reality is a highly complex phenomenon. In distributed catchment models, however, the lumped approach is often to be found, as i.e. in the above cited Stanford Watershed Model, the USDAHL-model, the EGMO-model (Dyck, 1981) or in agricultural hydrology (Renger & Strebel, 1982).

3.2.2 Distributed simulation model

In contrast to the above lumped approach the distributed models divide the soil profile into a number of compartments (depth increments) (cf. Fig. 9) and solve the basic partial differential equations of flow in the unsaturated or saturated zone for each compartment continuously using a suitable time interval.

Morgenschweis (1984) gives among others an examples of a distributed simulation model describing the one-dimensional vertical unsaturated soil-water water movement through heterogeneous soils. The model solves the basic differential equation that is based on a diffusion analogy (Remson et al., 1971):

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left(D\,\frac{\partial\theta}{\partial z}\right) + \left(\frac{dk}{d\theta}\right)\frac{\partial\theta}{\partial z} = D\,\frac{\partial^2\theta}{\partial z} + \left(\frac{\partial D}{\partial z} + \frac{dk}{d\theta}\right)\frac{\partial\theta}{\partial z} \tag{10}$$

where θ = total measured water content (vol% H_2O),
z = vertical rectangular coordinate,
$k = k(\theta)$ = standardized unsaturated hydraulic conductivity ($cm \cdot s^{-1}$),
$D = D(\theta)$ = soil-moisture diffusivity ($cm^2 \cdot s^{-1}$).

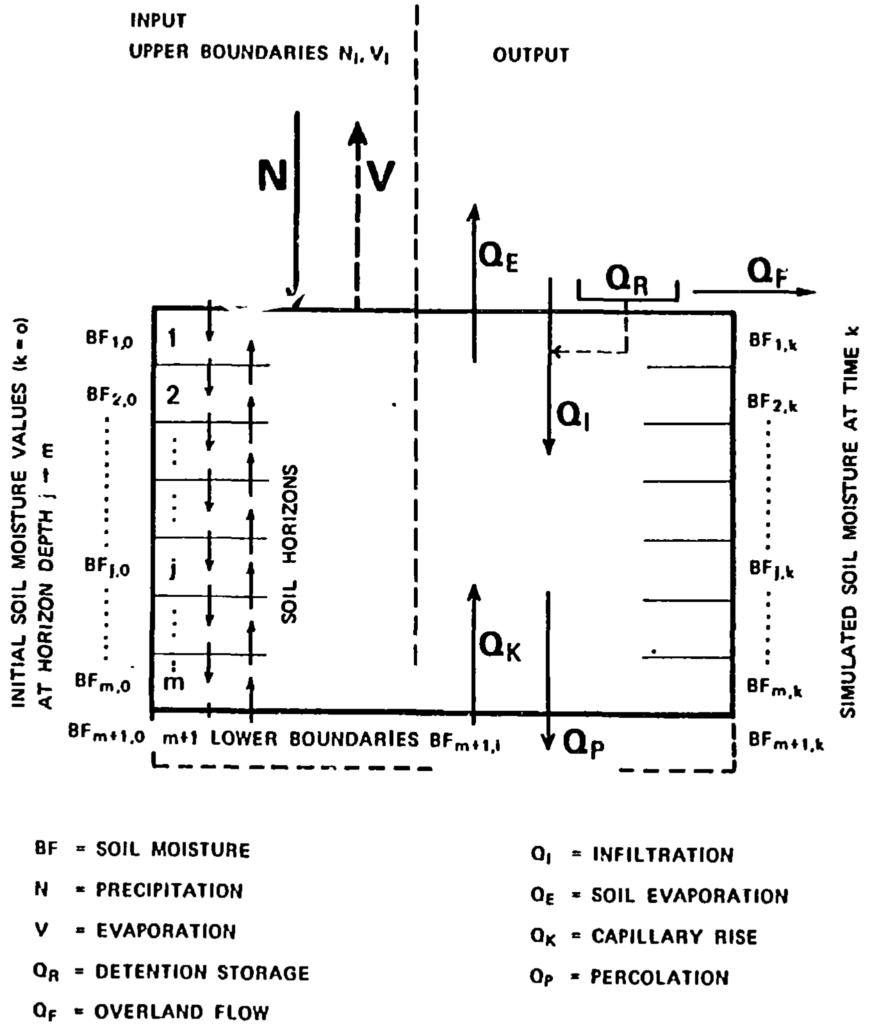


Figure 9: Schematic diagram of a distribution, multi-layered, one-dimensional soil-moisture model with boundary and initial conditions Morgenschweis, 1984)

It is solved numerically with the help of finite differences according to the Liebmann scheme with backward difference approximation. The procedure proved to be rapidly convergent and showed a good stability behaviour.

The model results in flow rates per time interval (hour, day, etc.) at the upper and lower boundaries, first for each compartment and later for the total balanced soil profile. In this way the flow through the compartment at the soil surface represents infiltration and soil evaporation, and the flow at the lowest boundary indicates the groundwater recharge.

For a better understanding of the results compiled in the following tables, it should be explained that the model assigns negative values to soil evaporation (-) and capillary rise (-) while giving positive values to infiltration (+) and percolation (+).

A detailed explanation of the model used, including detailed information on boundary and initial conditions for the numerical solution, and on model refinements, is given in Morgenschweis (1981).

To give an idea of the data needed for the model, the input data are listed:

- <u>time-variant data</u>

a) soil-moisture values per depth increments of 20 cm (e.g. 10 m deep access tubes) used method: neutron moisture and gamma-ray density probe, once per week.

b) precipitation used method: rain recorder digitally punched on papertape every 5 min.

- <u>time-invariant input data</u>

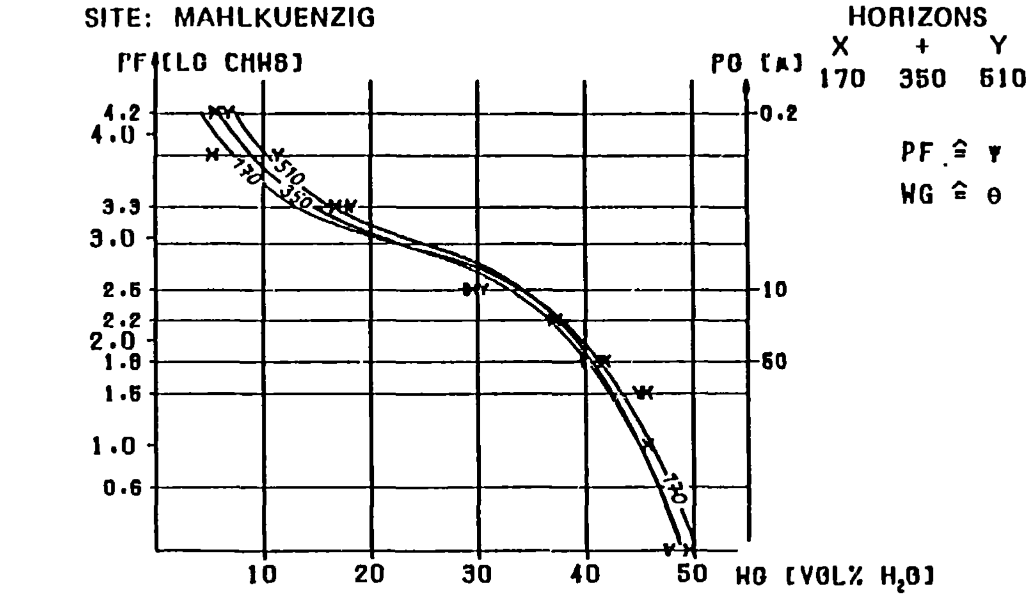
measured values or functions::
a) grain-size distribution of each 20 cm increment
b) total pore space volume
c) wet/dry bulk density
d) saturated hydraulic conductivity
e) desorption curves of the soil moisture - tension relation

estimated values or functions:
f) unsaturated hydraulic conductivity $k(\theta)$, evaluated for each incremental depth by an emperical power function according to Averjanov (1950, cited in Luckner & Schestakow, 1975) and later successfully tested by Mualem (1978), (cf. Fig. 10).
g) soil-moisture difussivity values $D(\theta)$ for each horizon were estimated according to

$$D = D(k,\Psi,\theta) = -k(\theta)(d\Psi/d\theta) \qquad (11)$$

whereby the soil tension is differentiated with respect to saturation θ and with hydraulic conductivity k as a parameter (cf. Fig. 10).

Fig. 10 depicts soil moisture-tension, unsaturated hydraulic conductivity and diffusivity for different horizons.



× $PF = -1.1179(10^{-4})HG^3+7.7676(10^{-3})HG^2-2.0733(10^{-1})HG+4.0379$ $S = 0.22$

+ $PF = -1.2576(10^{-4})HG^3+8.6909(10^{-3})HG^2-2.4286(10^{-1})HG+5.3415$ $S = 0.33$

Y $PF = -1.4390(10^{-4})HG^3+1.0416(10^{-2})HG^2-2.8408(10^{-1})HG+5.7622$ $S = 0.25$

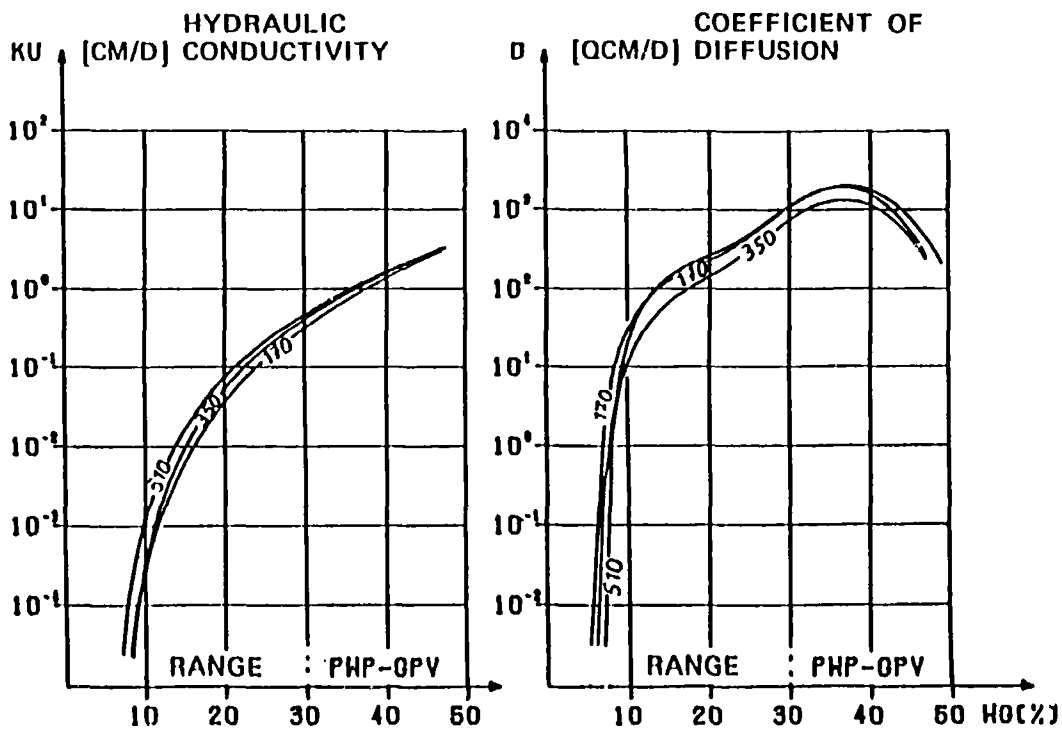


Figure 10: Examples of soil-moisture characteristics logΨ(θ), ku(θ) and D(θ) (170, 350 and 510 cm depth) of a loessian site (WG equals volumetric moistureθ) (Morgenschweis, 1984).

The multi-layered model was used to analyze soil-moisture movement in a small loessian catchment area in Southern Germany near Freiburg, which is well-known from long-term experimental studies (Luft et al., 1983).

Taking as an example the simulation results of a high terrace site (30 m thick loess terrace) the influence of a specific rainfall event on the soil-water movement will be discussed. During the period July 27 - August 16, 1973, a storm deposited 35 mm of rainfall with a maximum intensity of 22 mm hr -1. To simulte this event, the model needed to distinguish between the measured precipitation and the water which actually infiltrated (i.e. overland flow and surface detention had to be considered). The effect of this rainfall on the soil-moisture distribution in the depth profile had to be simulated using precipitation data per 5 min. The resulting hourly soil-water distribution over a period of one day is plotted in Fig. 11.

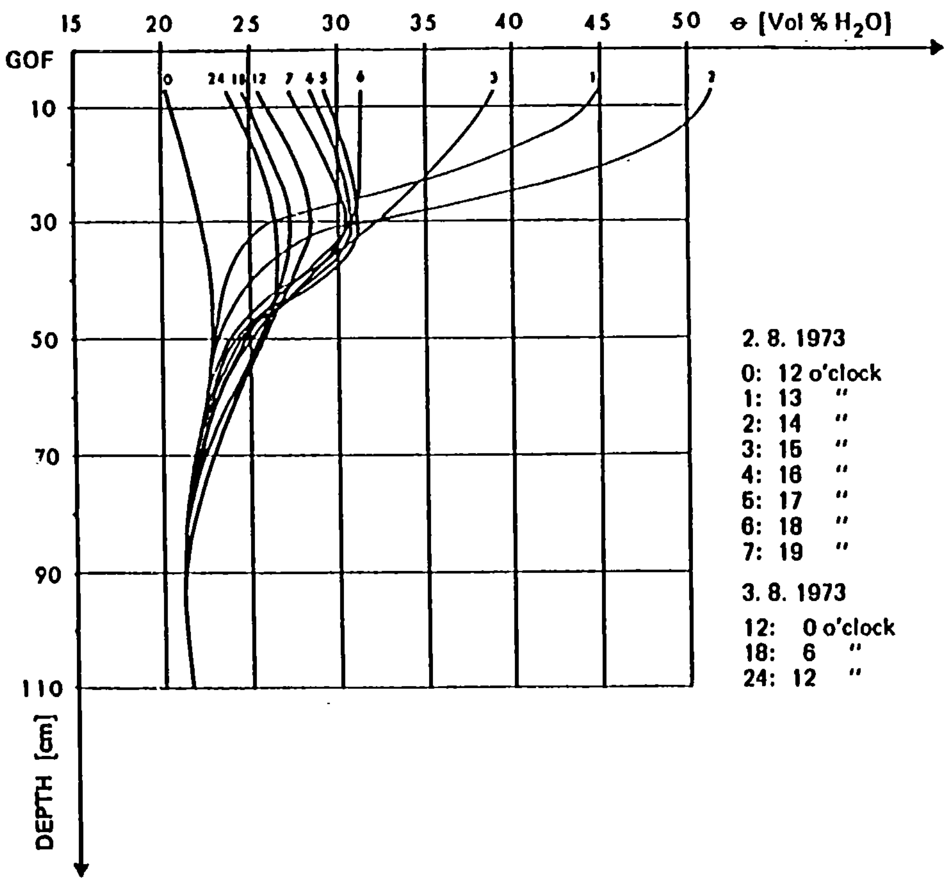


Figure 11: Water-content profiles during infiltration after storm rainfall at a loessian site (Morgenschweiss, 1984).

Furthermore daily soil-water balances and distributions of tensions and fluxes of different representative sites were simulated. For details see Morgenschweis (1981, 1984).

In addition, Fig. 12 shows the simulation results of Jansson (1980) using a similar distributed model. The simulation was performed continuously for two summer half-years.

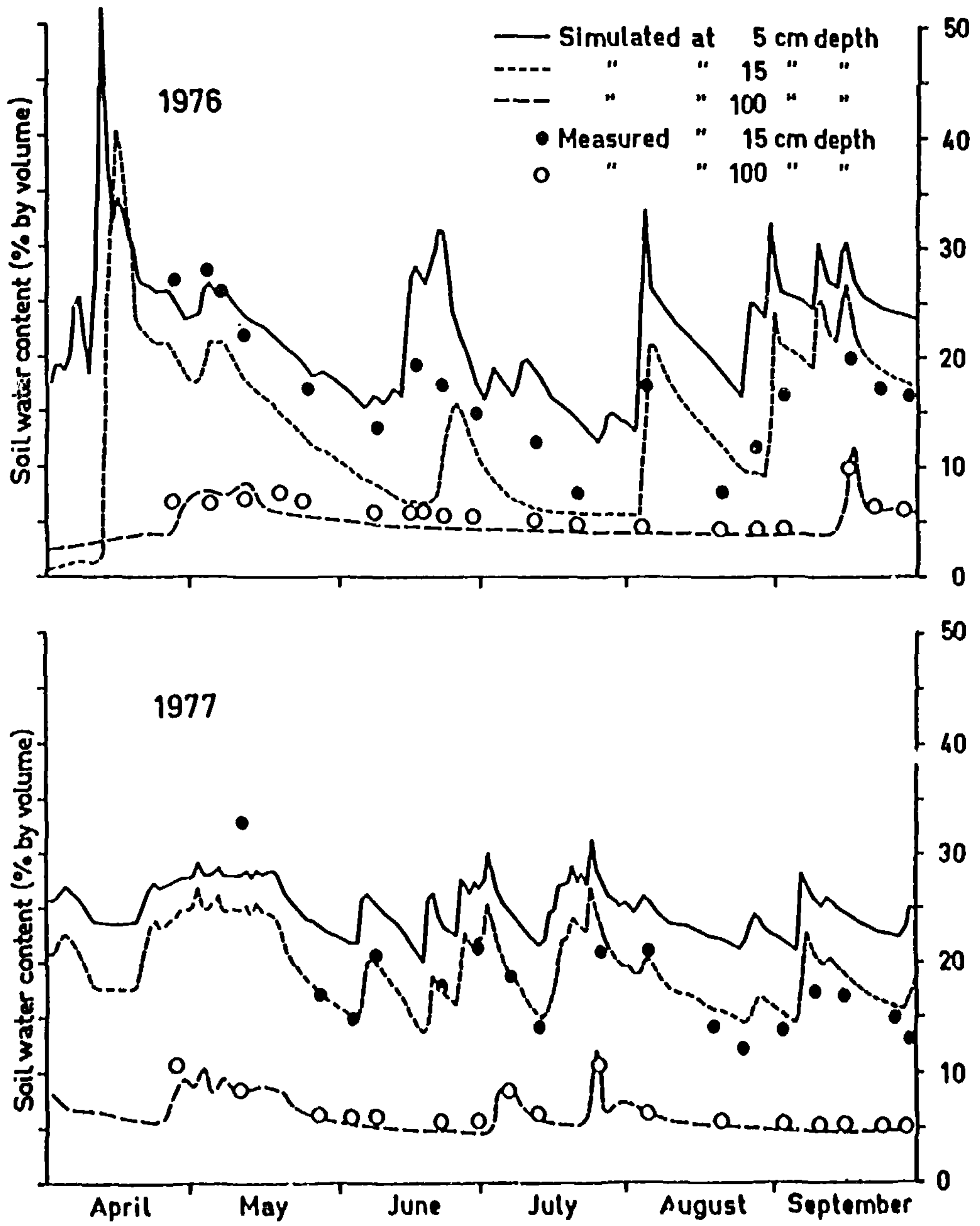


Figure 12: Simulated and measured water-content of two summer half-years in soils at Jadraas/Sweden (Jansson, 1980).

Most of the soil-moisture simulation models solve the basic differential equation numerically using the finite difference procedure, only a few authors try to use finite elements; most of them are one-dimensional conception. Two-dimensional models, as described in Hornung et al. (1980) theoretically are very rare or are being developed. On the other hand, the combined and simultaneous modelling of the unsaturated and the saturated flow have been developed in the last decades.

4. VARIABILITY WITH SPACE

As well as the above-mentioned measurement as the determination methods yield results for soil-water components on a point or small plot scale under specific soil, plant and groundwater conditions. For larger areas, complete landscapes or catchment areas, additional data (preferably presented on detailed or semi-detailed maps) about the soil, groundwater depth, vegetation cover and climate conditions are to be considered. Especially important in soil maps are the hydraulic characteristics of the mapped soil units or at least data on soil-texture and texture layering from which approximate hydraulic parameters can be derived (Sharma & Luxmoore, 1979). On the other hand soils vary significantly, both horizontally and vertically, and it is extremely difficult to collect information on areal soil-moisture movement.

To determine the variation of soil moisture and soil hydraulic properties in space great efforts are being made on world-wide scale by means of remote sensing. According to Schmugge et al., (1981), Meier (1981), Schultz (1986) the application of the microwave method seems to be the most effective investigation trace of the future. Nevertheless all indirect measurement methods need a calibration with point measured values. Hence, suitable field data are required.

On how to transform point measured values into areal values (e.g. mean basin soil moisture) and the necessary networks installation, reference is made to Toebes & Ouryvaev (1970), Greacen et al (1981).

5 REFERENCES

BAVEL, C.H.M., VAN: Soil densionmetry by gamma transmission. Soil Sci. 87 (1959) 50-58

BELL, J.P. Neutron Probe Practice. Natural Environment Research Council, Institute of Hydrology, Wallingford (1973, 1976) No.19

BENECKE, P. Wasserhaushalts - und Bodenfeuchtmessungen mit Lysimetern, Neutronensonden und Tensiometern. 13. DVWK-Fortbildungs lehrgang. Andernach (1982).

BOUYOUCOUS, G.J., MICK, A.H. An electrical resistance method for the continuous measurement of soil moisture under field conditions. Michigan State College Agricultural Experiment Station. Techn. Bull. 171 (1940)

BRUCE, R.R., KLUTE, A. The measurement of soil water diffusivity. Soild Sci. Soc. Amer. Proc. 20 (1956), 458-462.

BUCKINGHAM, E. Studies on the movement of soil moisture, USDA Bur. Soils Bull, No. 36, 1907.

CHILDS, E.L. The use of soil moisture characteristics in soil studies. Soil Sci. To (1940), 239-252.

CHILDS, E.C. An Introcution to the Physical Basis of Soil Water Phenomena. Wiley, New York, N.Y. (1969) 493 pp.

CHILDS, E.C., COLLIS-GEORGE, N. The permeability of porous materials. Proc. R. Soc. London, Ser.A, 201 (1950)

COUCHAT, P. Determination de la courbe d'étalonnage de l'humidimetre à neutrons à partir de l'analyse chimique des sols. Proc. Symp. on Isotopes and Radiations Techniques in Soil Physics. Istanb. IAEA, Vienna (1967) 67-82.

COUCHAT, P. Mesure neutronique de l'humidité des sols. Thesis, Institut National de Polytechnique, Toulouse (1974)

COREY, J.C., PETERSON, S.F. WAKAT, M.A. The measurement of 137Cs- and 241 Am-attenuation to determine soil density and soil moisture. Proc. Soil Sci. Soc. America 35, (1971)

CRAWFORD, N.H., LINSLEY, R.K. Digital Simulation in Hydrology, Stanford Watershed Model IV. T.R. 39. Stanford, Calif., Dept. of Civil Engineering, Stanford University (1966)

DON KIRKHAM, C.F.C. Soil Physics. In: VEN TE CHOW (Ed.) Handbook of Apoplied Hydrology. New York, London (1964), 5-1 -5-26

DUYNISVELD, W.H.M., RENGER, M., STREBEL, O. Vergleich von 2 Simulationsmodellen zur Ermittlung der Wasserhaushaltskomponenten in der ungesattigten Bodenzone. Z. dt. Geol. Ges. 134. (1983), 679-686.

DVWK (Hrsg.): Empfehlungen zum Bau und Betrieb von Lysimetern. DVWK Regeln zur Wasserwirtschaft (1979) H. 114

DYCK, S. (Ed.): Angewandte Hydrologie. Teil 2; Berlin (1982)

EELES, C.W.O.; Installation of access tubes and calibration of neutron moisture meters. Institute of Hydrology, Wallingford (1969) 7

FEDDES, R.A., KOWALIK, P.J. & ZARADNY, H.: Simulation of field water use and plant yield. Centre for Agric. Publ. and Doc. Wageningen, Netherlands (1978)

FLEMING, G. 1972. Computer Simulation Techniques in Hydrologa. American Elsevier, New York, N.Y., 333 pp.

FREEZE, R.A.: The mechanism of natural groundwater recharge and discharge, 1. One-dimensional vertical, unsteady, unsaturated flow above a recharging or discharging groundwater flow system, WWR, 5: 153-171, 1969.

GARDNER, W.R. Calculation of capillary conductivity from pressure plater outflow data. Soil Sci. Soc. Amer. Proc. 20 (1956) 317-320

GARDNER, W.R. et al. The capillary potential function and its relation to irrigation practice. Phys. Res. 20 (1922), 196

GREACEN, E.L. (Ed.). Soil water assessment by the neutron method. CSIRO Australia (1981).

HANUS, H., SUSS, A. & SCHURMANN, G. Einfluss von Lagerungsdichte, Ton - und Schluff - sowie Humusgehalt auf die Wassergehaltsbestimmung mit Neutronensonden. A. Pflanzenernahrung, Bodenkunde 132, 4 - 16, 1972

HILLEL, D., Soil and Water - Physical Principles and Processes. Academic Press, New York (1971) N.Y. 288 pp.

HILLEL, D. & GARDNER, W.R., Measurement of unsaturated conductivity and diffusiity by infiltratio through an impending layer. Soil Sci. 109 (1970).

HILLEL, D., KRENTOS, V.D., STALINANOU, Y., Procedure and test of an internal drainage method for measuring soil ydrualic characteristics in-situ. Soil Sci. 114, 395-400.

HILLEL, D., Computer simulation for soil-water dynamics: A compendium of recent work. Int. Develop. Res. Center Ottawa/Canada, 214 p., 1977.

INTERNTIONAL ATOMIC ENERGY AGENCY (IAEA). Neutron Moistoire Gauges. Technical Report No. 112, vienna (1970).

KLUTE, A., A numerical method for solving the flow equation for water in unsaturated materials. Soil Sci. 73 (1952), 105-116.

KLUTE A., Laboratory measurement of hydraulic conductivity of saturated soil. In: Methods of soil analysis. Amer. Soc. Agron. Monograph 9 (1965), 21-221.

LORCH, S., Messungen des Wassergehaltes im Boden mit der Neutronensonde. Zeitschrift f. Geophysic 29 (1963), 261-308.

LORCH, S., Automatische Registrierung der Feuchtedichte und der Wassergehaltsanderung eines Bodens durch Messung der Absorption von Gammastrahlen. Z. Pflanzenernahr.. Bodenkunde 130, 136-151, 1971.

LUCKNER, L. and SCHESTAKOW, W.M., Simulation der Geofiltration. VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1975, 358 pp.

LUFT, G., Anmerkung zur Kalbrierungvon Neutronentiefensonden fur Bodenfeuchtmessungen. Deutsche Gewasserkundliche Mitt. 25 (2), 60-61 (1981).

LUFT, G., MORGENSCHWEIS, G. & VOGELBACHER, A., Influence of large-scale changes of relief on runoff characteristics and their consequencesfor flood control design. IAHS Publ. No. 147 (Proceedings of the Hamburg Symposium, August 1983).

LUFT, G., MORGENSCHWEIS, G. Neutrontiefensonde und die Erfassung der Bondenfeuchte. Wasser und Boden (1981) Heft 11, 5455-550.

MEIER, R. Fernerkundungsmethoden zur Erfassung der Bodenfeuchtigkeit im hydrologischen Einzugsgebiet Rietholzbach. Mitt. Versuchsanstalt Wasserbau, Hydrol. Glazil, Eid. Tech. Hochschule (E.T.H.), Zurich, Nr. 45, 115 pp.

MORGENSCHWEIS, G. Zum Bodenwasserhaushalt im Losseinzugsgebiet Rippach/ Ostkaiserstuhl, Beitr. Hydrol., 7 (1980) 23-97.

MORGENSCHWEIS, G. Mehrschicht-Simulationsmodell der vertikalen ungesattigten Bodenwasserbewegung.Beitr. Hydrol. Sonderh., 2: 265 - 292 (1981).

MORGENSCHWEIS, G., LUFT, G. Einrichtung von Bodenfeuchtemesstellen und Kalibrieurng einer Neutronensonde am Beispiel der Wallingfordsonde Typ IH II. Deutsche Gewasserkundl. Mitt. 25. (1981), H. 3/4, 84-92.

MORGENSCHWEIS, G., LUFT G. Vorstellung und standortspezifische Kalibrierung der fur pedohydrologische Gelandearbeit entwickelten Neutronensonde Wallingford IH II. DVWK-Schriften Heft 50 (1983).

MORGENSCHWEIS, G. Soil-water movement and balance in thick loess soils and its model simulation. Journal of Hydrology 67 (1984), 339-360.

MUALEM, Y. Hydraulic conductivity of unsaturated porous media: Generalized macroscopic approach. Water Resour. Res., 14 (2) (1978), 325-334.

NEUE, H.U. Methodischer Vergleich von Neutronentiefensonden anhand von Modelluntersuchungen und mehrjahrigen Bodenfeuchtemessungen auf Loss-, Sandloss und Geschiebelehmstandorte. Diss. Hamburg (1980)

OLGAARD, P.L. On the theory of the neutronic method for measuring the water content in soil. Riso Rep. no. 97 (1965)

PECK, A.J., RABBIDGE, R.M. Direct measurement of moisture potential: a new technique, Proc. Wageningen Sympos. on Water in the Unsaturated Zone, 1: 165-170, IAHS/Unesco (1969)

POULOVASSILIS, A. Hysteresis of pore water, an application of the concept of ndependent Domains. Soil Sci. 93 (1962), 45-412.

REMSON, I., HORNBERGER, G.M., MOLZ, F.J. Numerical Methods in Subsurface Hydrology. Wiley-Interscience, New York (1971).

RENGER, M. GIESEL, W., STREBEL, O., LORCH, S. Erste Ergebnisse zur quantitativen Erfassung der Wasserhaushaltskomponeneten in der ungesattigten Bodenzone. Wasserhaushaltskomponeneten in der ungesattigten Bodenzone. Zeitschrift f. Pflanzenernahrung, Bodenkunde 126 (1970), 15-35.

RENGER, M., STREBEL, O. Beregungsbedurftigkeit der landwirtschaftlichen Nutzflachen in Niedersachsen. Geol Jb. F13 (1982).

REYNOLDS, S.G. The gravimetric method of soil moisture determination. Part I: A study of equipment and methodological problems. J. of Hydrology 11 (1970), 258-273.

REYNOLDS, S.G. The gravimetric method of soil moisture determination. Part II: Typical required sample sizes and methods of reducing variability. J. of Hydrology 11 91970), 274-287.

REYNOLDS, S.G. The gravimetric method of soil moisture determination, Part III: An examination of factors influencing soil moisture variability. J. of Hydrology 11 91970) 288-300.

RICHARDS, L.A. Capollary conduction of liquids through porous mediums, Physics, 1: 318-333 (1931).

RICHARDS, L.A. Pressure-membrane apparatus, construction, and use, Agric. Eng., 28. 451-454 (1947).

RICHARDS, L.A. Methods of measuring soil moisture tension. Soil Sci. 68 (1949). 95-112.

SCHEFFER & SCHACHTSCHABEL: Lehrbuch der Bodenkunde. Stuttgart (1981).

SCHMUGGE, T.J., JACKSON, T.J., MCKIM, H.L. Survey of methods for soil moisture determination. Water Resources Research 16, No. 6, 961-979 (1980).

SCHOFIELD, R.K. The pF of the water in soil, Trans. 3rd Internat. Cong. Soil Sci., 2. 37-48 (1935).

SCHULTE IM WALDE, M. Kontinuierliche Feuchtemessungen in Boden und Bodenlysimetern mittels Wärmeleitfahigkeitssonden. Mitteilung der Deutschen Bodenkundlichen Gesellschaft 22 (1975), 101-112.

SHARMA, M.L., LUXMOORE, R.J. Soil Spatial variability and its consequences on simulated water balance. Water Resources Research 15 (1979), 1 1567-1573.

STREBEL, OL. Moisture and groundwater movement determined by physical methods (Hannover, 1985) (Unpublished).

STREBEL, O., GIESEL, W. RENGER, M. LORCH, S. Automatische Registrierung der Bodenwasserspannung im Gelande mit dem Druckaufnehmertensionmeter. Z. Pflanzenernahr., Bodenkunde, 126 (1970) 6-15.

STREBEL, O., RENGER, M., GIESEL, W. Soil-Suction measurements for evaluation of vertical water flow at greater depths with a pressure transducer tensiometer. J. Hydrology 18 (1973), 367-370.

TOBBES, C., OURYVAEV, V. Representative and experimental basins. An international guide for research and practice. Unesco-Guide, Paris (1970)

TOPP, G.C., DAVIS, J.L., ANNAN, A.P. Electronic determination of soil water content measurements in coaxial transmission lines. Water Resources Research 16 (1980) 3. 574-582.

VACHAUD, G., ROYER, J.M., COOPER, J.D. Comparison of methods of calibration of a neutron probe by gravimetry or neutron-capture model. J. of Hydrology 34 (1977), 343-356.

VAN DEN BERG & LOUTERS, T. An algorithm for computing the relationship between diffusivity and soil moisture content from the hot air method. J. of Hydrology 83 (1986) 149-159.

VAN DEN PLOEG, R.R., BEESE, F., STREBEL, O., RENGER, M. Unsteady unsaturated u-dimensional moisture flow in soil: a computer simulation program. Soil Sci. Soc. Amer. Prof. 38 (1974).

WARD, R.L. Principles of Hydrology. London, 2nd Ed. (1975).

WIND, G.P., VAN DOORNE, W. A numerical model for the simulation of unsaturated vertical flow of moisture in soils. J. of Hydrology 24 (1975), 1-20.

PART III

TRACER TECHNIQUES

by H. Zojer

PART III TRACER TECHNIQUES

LIST OF FIGURES

INTRODUCTION

An important part of the water cycle is represented by the movement of water in the underground, whether as soil moisture in the unsaturated zone or as groundwater in water saturated rocks. Tracer technology is the most appropriate method of following water movement. Tracing techniques have been developed with the last 5 years by the progress of hydrochemistry, and chemistry and isotope physics in particular.

On the one hand, tracers are used artificially; they are injected into the water cycle by man. On the other hand, the natural components within the water cycle, e.g. dissolved chemical solids or environmental isotopes, can be applied. Between these two main groups of tracers can be placed a class of tracing constituents (e.g.tritium,waste water) although their infiltration into the underground is not intended for hydrogeological purposes In addition, it can be stated that a number of environmental or natural tracers can also be injected artificially, such as radioactive isotopes and dissolved solids.

The history of tracer hydrology has been influenced decisively by the "International Working Group for the Application of Tracer Methods in Hydrology", and especially by the synoptical development of artificial tracing with isotope techniques. Routine investigations carried out by scientists from different countries were reported and discussed in several "Tracer Symposia": 1966 in Graz (Austria); 1972 in Freiburg i.Br. (Federal Republic of Germany); 1976 in Bled (Yugoslavia) and 1981 in Bern (Switzerland). The 5th Symposium is being organized in Athens (Greece) 1986.

1. NATURAL CHEMICAL TRACERS IN THE WATER CYCLE

Groundwater quality greatly depends on the large variety of rock-water interactions, which eventually can be reflected in equilibrium models.

The process of dissolution is determined by a series of criteria which must be considered as a whole. One is the time of contact between the moving water and the rock and, furthermore, the face of the contacted solid or unconsolidated rock. The rock-water interactions are also influenced by the dissolving ability of the water and vice versa by the readiness of the rock to release particles, i.e. to be dissolved. In carbonate rocks,CO_2 and its partial pressure are important requirements for increased chemical reactions.

Dissolved solids can be used in this way as natural tracers due to the rock geochemistry in the recharge areas of springs and wells. So parameters like calcium, magnesium sulfate and other ions as well as the varying relationships between them, can indicate the location of recharge areas and can help to conceive hydrodynamic models. Special emphasis is given to this by E. Eriksson (1981).

2. METHODOLOGY OF ARTIFICIAL CHEMICAL TRACERS

There are a certain number of requisites for the artificially injected chemical tracers:

- The tracers should not, or minimally, appear naturally in the investigated groundwater system.

- The tracers must be soluble in water.

- The tracers must be harmless with regard to hygienic-medical considerations, so that the water may still be used

- The tracer stability concerning physical, chemical, photochemical or biological interference should be assured.

- The tracers must not influence the natural hydraulic properties of the sub-surface water.

- When underground, the tracer should not be retained by absorption, chemical reaction with rocks, ion exchange or sedimentation.

- The tracers must be easily detected.

2.1 Inorganic chemical tracers (salt tracers)

2.1.1 Types of salt tracers

Inorganic salts, like NaCl (sodium chloride) and KCl (potassium chloride), have been used for underground water tracing for a long time. These tracers have been successfully applied in the Alpine karst by G. Kyrle (1928), and in the fifties by V.Maurin & J. Zötl (1959). The greatest progress in the utilization of salt tracers has been made in the large scale experiments in the central Styrian Karst (Austria (H. Batsche et al., 1970), in the classical Istrian karst (M. Zupan & H. Behrens, 1976) and in the Swiss Jura (I. Müller & W. Käss, 1980).

Other inorganic chemical tracers have also been used successfully in the past. As an example, the underground flow of the Vipava river and the Timavo (Istria) was detected in 1907 by lithium, cezium and stronthium chlorides (G.Timeus, 1911).

The salt tracers are generally well soluble. It has to be presupposed that for quantitative tracing experiments, it is necessary to analyze the salt before dissolution in order to obtain information on the distribution of the ions (e.g. Na+, K+, Li+, Cl-). It can then be seen that the percentage of anion chloride, when used with sodium or potassium, is slightly higher than 50%. On the other hand with an LiCl solution, the percentage of the anion rises to more than 80%.

Other inorganic chemical tracers not combined with chloride are nitrate and nitrate complexes, but high background concentrations and health considerations in connection with waster water disposal sometimes prevent the utilization of these tracers. In saturated zones, in a few cases, Borax - injected as HBO_2 - is used. The solubility is poor and the local high background due to sewage disturbs the transit of the injected tracer. (T. Harum & Ch. Leibundgut, 1981).

The application of salt tracers is naturally limited. They cannot be injected in the vicinity of salt mines or salinary wastes or coastal areas, where sea water intrusions could effect brakish springs or could raise the salinity of the groundwater in general. 1 Furthermore, using NaCl or KCl, large quantities of salt have to be dissolved to prove the underground water circulation. Even in very small areas, some hundred kilogrammes of the salt tracer have to be injected. For KCl, a smaller amount of tracer needs to be injected due to the lower background of potassium in natural waters compared with sodium. Large scale experiments would require enormous quantities, like in 1969, when 50 t of NaCl were injected into a Danube sinkhole near the town of Tuttlingen (Federal Republic of Germany). It is clear that with such a large amount of tracer, the limit of application possibility is nearly reached. In summary, the problems appear to be exclusively in connection with the injection. A successful test can be carried out when the transport facilities, as well as sufficient water for the dissolution of the salt and the injection, are guaranteed.

2.1.2 Detection of Salt Tracers

The determination of the ions, sodium potassium and lithium in the laboratory will be carried out by flame photometer or atomic absorption, whereas chloride is detected volumetrically or by ion chromatrography.

When using NaCl or KCl for a tracing experiment, the dissolved solids, of chloride, sodium and potassium have to be analyzed. In opposition to this, when using LiCl as a tracer, only lithium needs to be detected because of the smaller amount of injection material, causing only a slight increase of Cl-, which is not significant.

The seasonal variations of the natural background have to be taken into account when calculating or estimating the quantity of material to be injected. For other artificial tracers not usually included in the water cycle (e.g. fluorescent dyes) such considerations can be neglected.

One of the greatest advantages of salt tracers is their direct or indirect detection in the field by :

-conductivity measurements, or by
-using ionselective electrodes.

Knowledge of tracer concentrations directly in the field permits, if necessary, immediate changes in sampling intervals at the conclusion of the experiment.

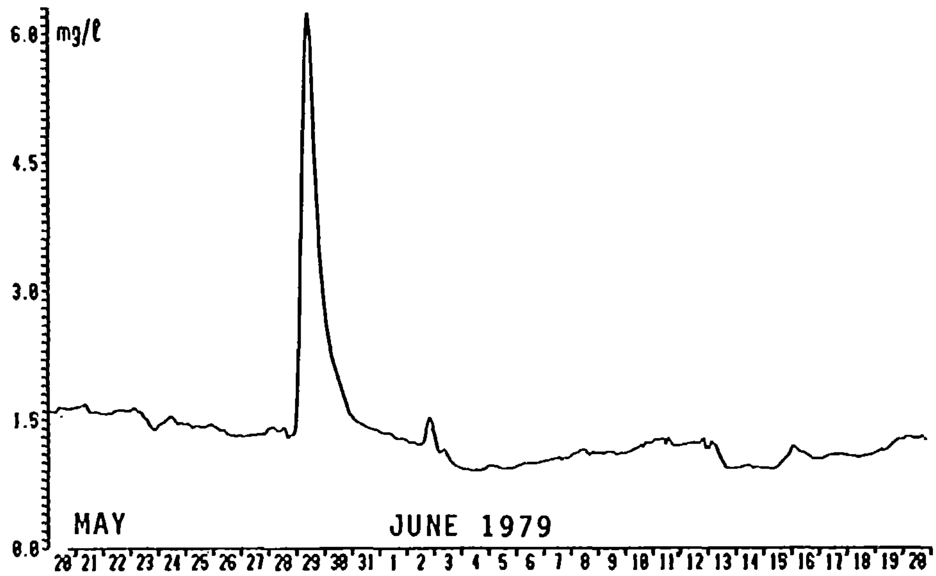


Figure 1: Tracing experiment using NaCl: Passage curve of sodium recorded by ionsensitive electrode (I.Müller & W.Käss, 1980).

2.1.3 Cation exchange phenomena

Responsible for ion exchange within rock-water interactions are organic substances and different mineral components, especially clay minerals, which are sedimented generally in very small fractions. The first group is located as residues in the weathering zone become acid in character; the latter, described by H. Leditzky (1978), shows that in particular Vermiculite and Montmorillonite have a high exchange capacity (expressed in mval/10 g solid). The primary mineral is glimmer, later on converted to clay minerals.

Under such conditions, water with a high content of the ions sodium, potassium or lithium will be altered in so far as these cations are partly replaced by calcium and/or magnesium. These facts have to be taken into account when using salt tracers, when the liquid comes into contact with clay minerals. Therefore Ca and Mg also have to be detected in order to get a quantitative control of the input - output relationship. Such experiments were described by C.Job (1972), W.Kollmann (1979) and H. Leditzky (1981) (Fig. 2).

The ion exchange process appearing in salt tracing experiments, which is a reversible reaction, can be stated as follows (F.Schwille, 1954):

$$\frac{Ca}{Mg} A + 2\ NaCl \rightleftharpoons Na_2A + \frac{Ca}{Mg} Cl_2$$

A = exchange capacity

The chloride and nitrate ions show only little aptitude for ion exchange. For this reason the chloride ion is a good trace substance for the movement of water in the underground.

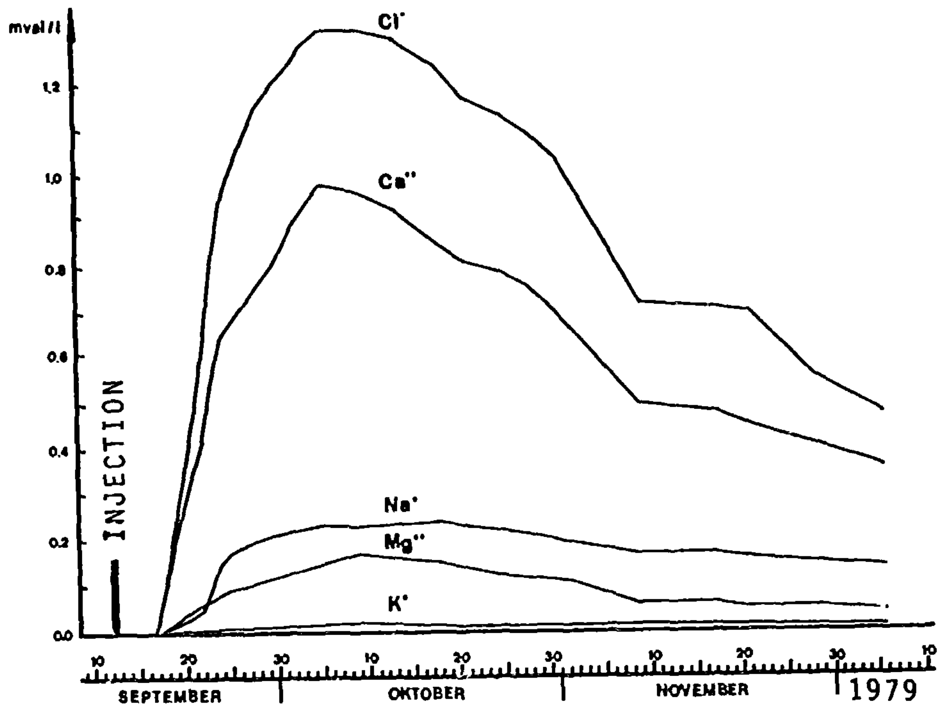


Figure 2 Ion concentrations of a tracing experiment injecting NaCl (H.Leditzky, 1981).

2.1.4 Requisite Properties for use of Salt Tracers

- good solubility
- large amount of tracer (NaCl, KCl) is necessary
- large quantity of water for dissolution of the tracer and the subsurface transport is essential; therefore restrictions will originate in karst areas with lack of water
- the background is usually relatively low but fluctuating
- chemically resistant
- changes of hydraulic characteristics could occur in the saturated zone of unconsolidated rocks; under such conditions, a retention of the tracer can also be expected, which is negligeable in non-saturated karstic zones
- the detection of salinity in the field can be carried out very easily by conductivity measurements
- restrictions are given due to ion exchange, for LiCl in particular, because of the compratively low amount of tracer to be injected this means that the ion, replacing the lithium is hardly detectable.

2.2 Fluorescent dye tracers

The first successful tracing experiments were carried out using salt and dye tracers after negative tests with oil products and floating substances.

At the beginning of dye tracing, materials such as "fuchsine", "kongored", "safranine" or "anilinred" were applied, but mostly with negative results. Later on sodium fluorescein (uranine) became the most appropriate dye tracer. An important point in the development of dye tracing experiments was the year 1877, when for the first time the connection between the sinkholes of the Danube near Immendigen and the Aach-spring was proved by the supply of uranine.

The progress of dye tracing technology is based on a more accurate detection of the tracers and an enrichment of the smallest dye tracers by special treatment. Whereas previously investigations were directed more or less to the discovery of underground connections of water, nowadays the evaluation of tracing experiments also has to include the quantitative results concerning underground storage capacity and transient time of the fluid.

2.2.1 Spectral properties

Fluorescent dyes have the property of being able to absorb light of certain wavelengths (excitation of absorption spectrum) and to emit at the same time light with higher wavelengths (emission of fluorescence spectrum) according to the law of STOKE, a part of the quantum physics. The excitation as well as the emission spectra are characteristic for each fluorescent dye, and furthermore, they are constant. Therefore they can be identified by means of their spectral properties.

R.Benischke (1983) compiled the spectral data of the main fluorescent dyes comparing different experiences of authors:

	Excitation maximum (nm)	Emission maximum (nm)
Uranine	484 - 493	512 - 516
Eosine	515 - 517	535 - 540
Amidorhodamine G	530 - 536	552 - 557
Rhodamine B	544 - 555	575 - 578
Tinopal CBS-X	about 350	about 430

The excitation and emission of uranine, amidorhodamine G and rhodamine B is shown in Figure 3.

Finally, scatter effects have to be considered, especially the RAMAN scattering. A part of the absorbed light is transformed in a scattering energy, which appears in a constant distance higher than the excitation wavelength, independent from the wavelength of emission. Avoidance of RAMAN's overlapping and emission can be created by varying the excitation wavelength or by simultaneous scanning. The RAMAN-effect only appears at very low detection limits.

Generally fluorescence spectra will be excited at a fixed wavelength, at which the tracer has a high absorption of light. If the excitation is selected at the maximum wavelength of excitation and emission,one has to take into account, that together with a decrease of tracer concentration the fluorescence peak will disappear in the scattering light of the background until it cannot be detected definitely. To exclude such effects it could be moved with the excitation to shorter wavelengths, although RAMAN scattering could effect secondary peaks and could appear as a fluorescent dye which anyhow has to be neglected.

As H.Behrens (1983) summarized, tracer properties are also based on the structure of the widely occurring elements carbon,hydrogen, oxygen, nitrogen and sulfur. They could be altered and their application lost, when, for any reason, this structure of dye molecules is disturbed.

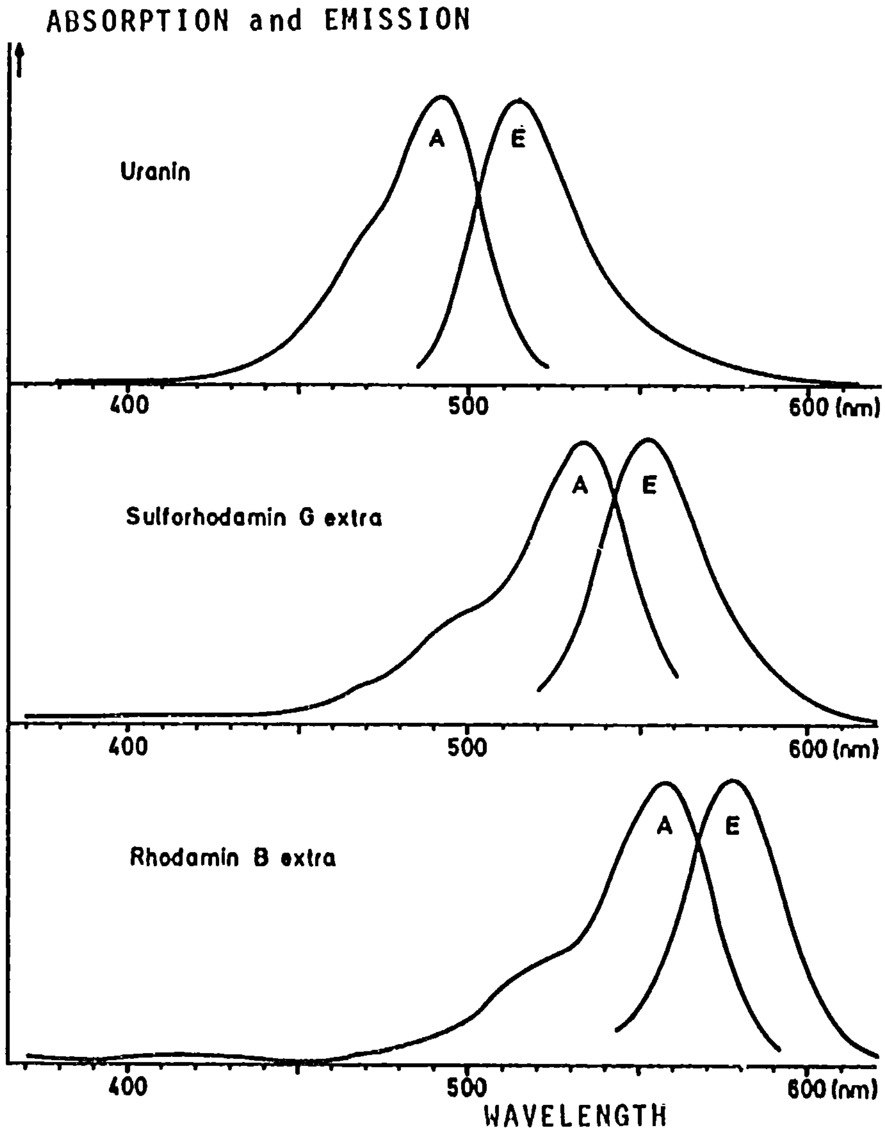


Figure 3 Excitation (A) and emission spectra (E) of some fluorescent dyes (H.Behrens, 1971).

2.2.2 Subsurface behaviour

To characterize the fluorescent dye tracers as an ideal tool to follow up underground water ways, some requirements concerning temperature and chemical stability, pH-dependence, photochemical degradation, biological influences and health hazards should be considered

The fluorescent dye tracers appear as most resistant in respect to chemical decomposition, as all of them are from organic origin (H.Behrens, 1983). On the other hand, fluorescent dye tracers are subjected to different sorption phenomena due to their chemical composition. In this connection the main influence originates from the absorption, defined as sorptive amount of retading tracer depending ion rock-water interactions in the underground. The reason for such phenomena is given by the fact that molecules of fluorescent dyes are directed to solid aquifer material by polarization effects. Taking into account that all dye molecules are ions, uranine and eosine,in neutral and alkaline aqueous solutions exist as anions. They cannot be absorbed by minerals, uranine in particular. With increasing acidity, e.g. clay, absorption processes increase without reaching reasonable figures. The rhodamine dyes, on the other hand, generally show a strong retardation in an acid environment, even in the case of amidorhodamine G, although it is of anionic character. The absorption of rhodamine B by clay minerals is extraordinarily high, so that this tracer cannot be used in the underground in such an environment.

The absorption behaviour of different fluorescent dyes has also been tested in the laboratory (Ch.Leibundgut, 1981) using uranine and the optic brightener tinopal (as anionic composition ABP and as cationic MSP) in a clean sandy granular medium (no clay minerals) and in soil, enriched with clay minerals and organic substances. The retardation of uranine in the sand is nearly zero, comparing with tinopal ABP which is a little higher. The cationic tinopal MSP on the other hand shows an output of less than 2% related to the input quantity. Similar results are given for tinopal MSP when carrying out the expriments in soil. In this matter the absorption rate of uranine also rises to nearly 50%. Investigations by I.Laidlaw & P.Smart (1982) of absorption from fluorescent dyes from different supplying manufacturers show that the red dyes (acid red, rhodamines) are retained in sandstone up to 25%, in peat up to 80% without great differences within the group of products.

Concerning stability with regard to temperature variations, uranine can also be considered as the most constant fluorescent tracer. Compared with rhodamine B, the fluorescence intensity decreases less than 4% when the temperature of aquatic fluid is increased by 10 C, whereas the loss of intensity for rhodamine B can be more than 30% within the same temperature range. The highest numbers of destabilization caused by temperature effects are characteristic for the optic brighteners, thus preventing their application as tracers on some occasions.

Variations of the pH-value in aqueous fluids cause reversible changes of dye molecule structures, the extent is different for various dye tracers. The pH-dependence of uranine is very significant. Below pH 9 the uranine intensity decreases and pH drops to below 6; uranine intensity will alter until it is no longer detectable at usual excitation and emission wavelengths. Under such conditions excitation maximum at 490 nm disappears even in slightly acid solutions (Figure 4).

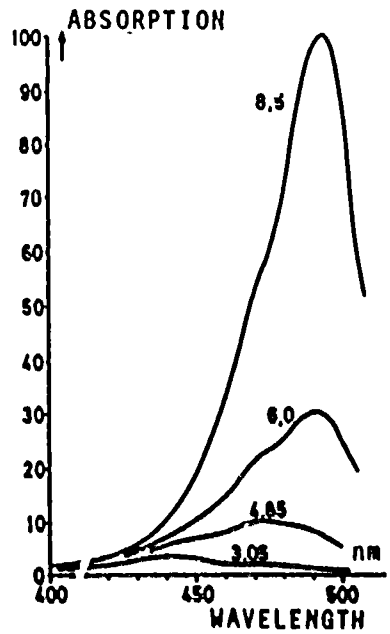


Figure 4: Variations of the excitation spectrum of an uranine solution parallel with changes of pH (H.Behrens, 1971).

Compared with uranine, the pH-dependence of eosine is not very significant. As shown in Figure 5, pH higher than 6 do not cause any changes of the eosine intensity at the given excitation - emission adjustment (515/537 nm). Even at pH 4, intensity of fluorescence is still in the magnitude of 70%. I.Laidlaw & P.Smart (1982) investigated the relation between pH and fluorescence intensity of different rhodamine dyes In general the sulphuric substituted dyes (e.g. amidorhodamine G) are nearly stable downwards to a pH of approximately 3, rhodamine B and especially rhodamine WT show a slight loss of intensity at pH lower than 5.5.

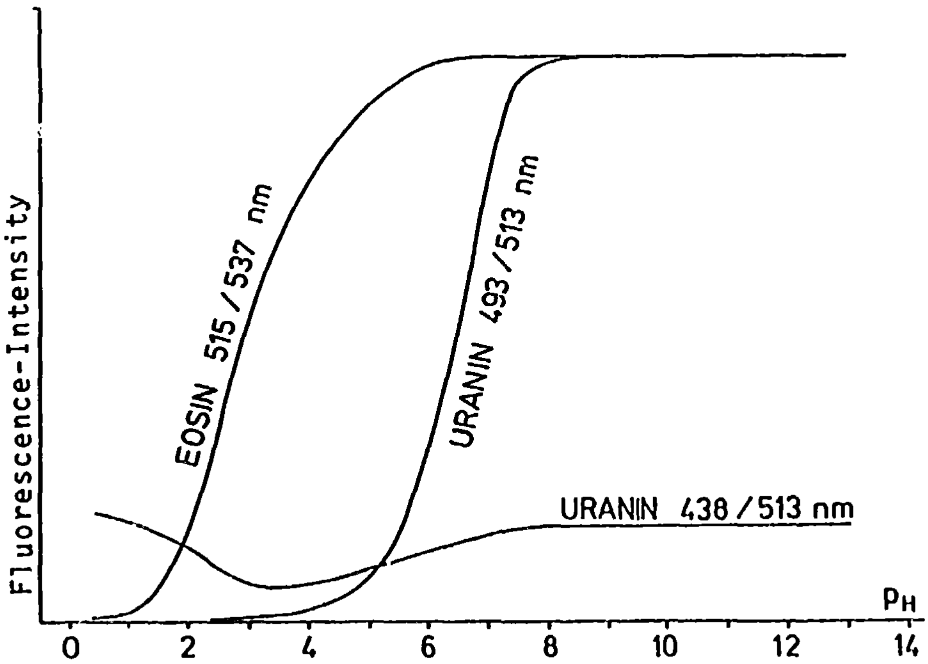


Figure 5: Dependence of the fluorescence intensity of uranine and eosine on pH; the uranine was excited at two different wavlengths (H.Behrens,1982).

Another problem which could arise with fluorescent tracers is the photodecomposition by irradiation with natural and artificial daylight induced by ultraviolet radiation. The most photosensitive tracer is eosine, followed by uranine, amidorhodamine G and rhodamine B in that order (Figures 6 and 7).

Investigations by H.Behrens and G.Teichmann (1982) show that photochemical degradation is not dependent on the intensity and the duration of light effects: the photosensitivity is effected by more complex reactions in the aquatic environment for a part of the fluorescent tracers. On the one hand, the dyes pyranine, tinopal uranine and eosine show a linear degradation in a semilogarithmic scale of concentration and time of radiation due to a constant velocity óf photochemical decomposition. The different rhodamine fluorescent dyes (rhodamine WT, sulforhodamine B, rhodamine B, amidorhodamine G) on the other hand,are subjected to an increasing velocity of degradation versus the time of light exposure. It seems that different dissolved solids within the fluid could at least influence this phenomenon. Beyond that, additional effects, e.g. suspended material and changes of light in relation to different depths of water could be of some importance.

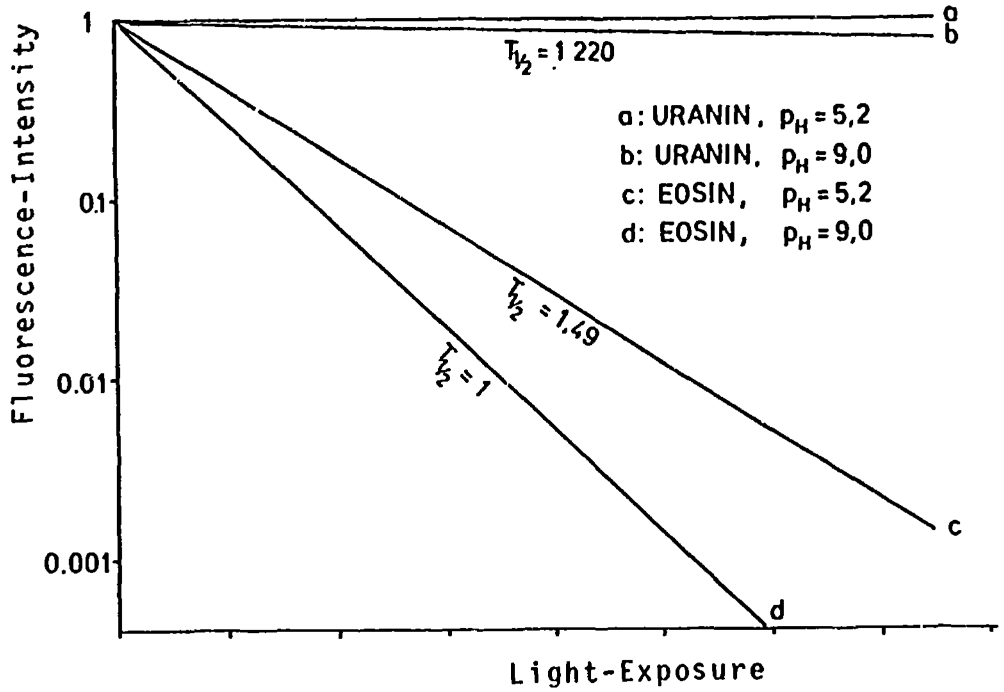


Figure 6: Relative decay of fluorescence intensity of uranine and eosine solutions exposed to daylight; T1/2 = halflife related to the eosine solution at pH = 9 (H.Behrens, 1982).

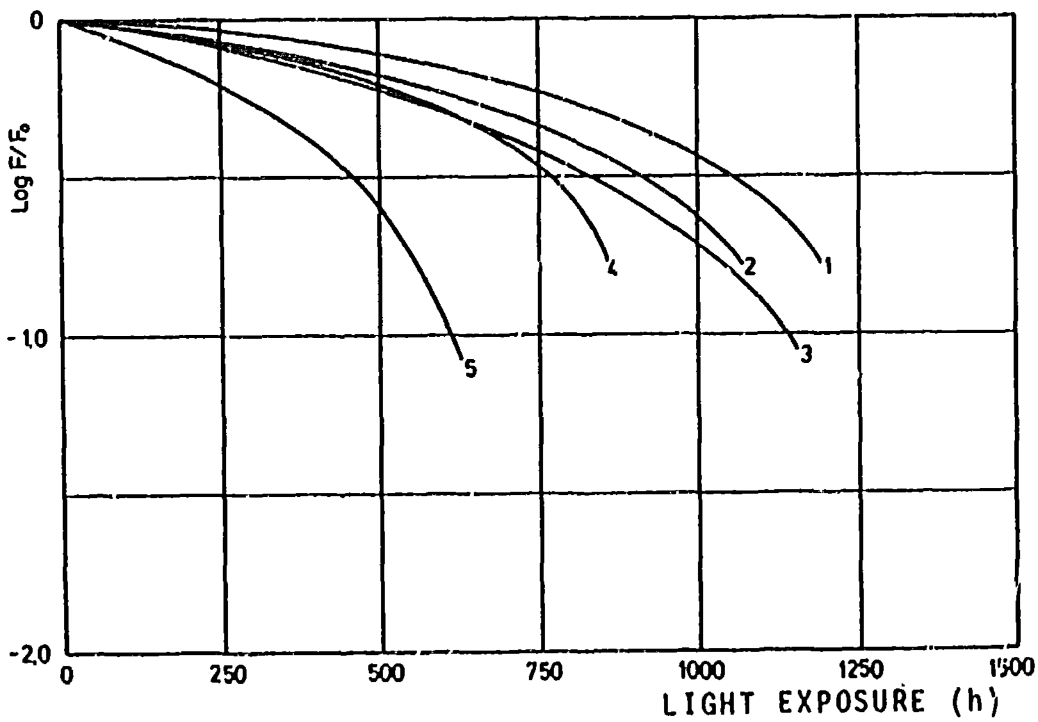


Figure 7: Decay of fluorescence intensity of aqueous solutions of - sulfo-rhodamine B (1), rhodamine B (2), amlorhodamine G (3) brillant-sulfoflavine FF (4) and rhodamine 6G (5) exposed to artificial daylight (H.Behrens & G.Tiechmann, 1982).

In addition, tracer stability can be influenced by biochemical decomposition of the dyes. M.Zupan (1982) has investigated the effects of bacteriologfical and chemical pollution on the decomposition of fluorescent dyes, especially in combination with phenol and nitrogen substances. Practical results show some observations on losses of fluorescent dye tracers in polluted karst water caused by microbiological activites (H. Behrens & M.Zupan, 1976). These empirical results have to be transferred to the knowledge of cause-effect-relationship.

No health hazards have been reported so far in connection with the application of fluorescent dyes in the water cycle, but rhodamine B, a cationic dye, shows very high toxic effects. Also, concerning mutagenicitiy (P.Smart, 1982) rhodamine gives conflicting results when investigated in very high concentrations and under extended exposure.

2.2.3 Detection of dyes

In the early beginnings of dye tracing, the concentrations were detected by the naked eye using comparable solutions, which is only possible when the concentrations are higher than 10 ppb in clear water. Later, the content was determined by ultraviolet lamp half-quantitatively in connection with relative standards. Problems arise when the water samples are polluted with suspended material. Filtering procedures are then necessary.

Nowadays there are many different instruments available by which dye tracers can be detected very precisely. The progress of accurate measurements started with the development of filter fluorometer. The excitation of the fluorescence will occur at that wavelength at which the dye will be mostly absorbed. The adjustment of the wavelength is fixed during the whole measuring procedure. As this is different for each particular dye, special changeable interference filters are used for the selection of the excitation. The instrument can be adjusted by certain screen openings which should be constant during the measurements. In this way, the tracer content of single water samples can be detected by means of a stream cell. The latter permits automatic recording of the concentration related to the time. The accuracy of measurement could be hindered by suspended material in the water, such disturbances can be elimated in the laboratory by appropriate treatments (e.g. filtering).

Apart from simple fluorometric methods with measurements at fixed wavelengths, the special fluorometry allows a parallel control of detectable tracers. A precise description was carried out by H. Behrens (1973). The excitation and emission wavelength at its maximum usually has a more or less constant distance of 20 - 25 nm within the spectrum. Thus it should be possible to measure all fluorescent tracers in one operation only by parallel and simultaneous application of the excitation and emission monochromator moved in 25 nm intervals. So only one sample is necessary for the detection of all tracers contained in the water. The advantage of identifying fluorescent tracers simultaneously by spectral scanning is emphasized by the fact that one can also practically ignore the light scattering of the background at low concentrations. So the RAMAN scattering appears almost non-existant in synchronous scanning.

Selective detection of individual fluorescent dye tracers in one sampled mixture according to combined tracing experiments is limited by the overlap of the particular spectra (H.Behrens, 1982, W.Käss, 1982). The problems in this case occurs in identifying the dye components separately and quantitatively in the fluid, taking into account that they appear in different concentrations (Figure 8). Tracers situated at some distance from each other with the spectrum, e.g. uranine and rhodamine B, can be detected by easily without any correlative interference. For dyes which are closer together within the spectrum (e.g. amidorhodamine G and rhodamine B) there is generally some overlapping and corrections should be calculated(H.Behrens, 1982; Figure 9). If the tracers are very close neighbours (uranine - eosine; eosine - amidorhodamine G) they cannot be identified satisfactorily without additional separation methods.

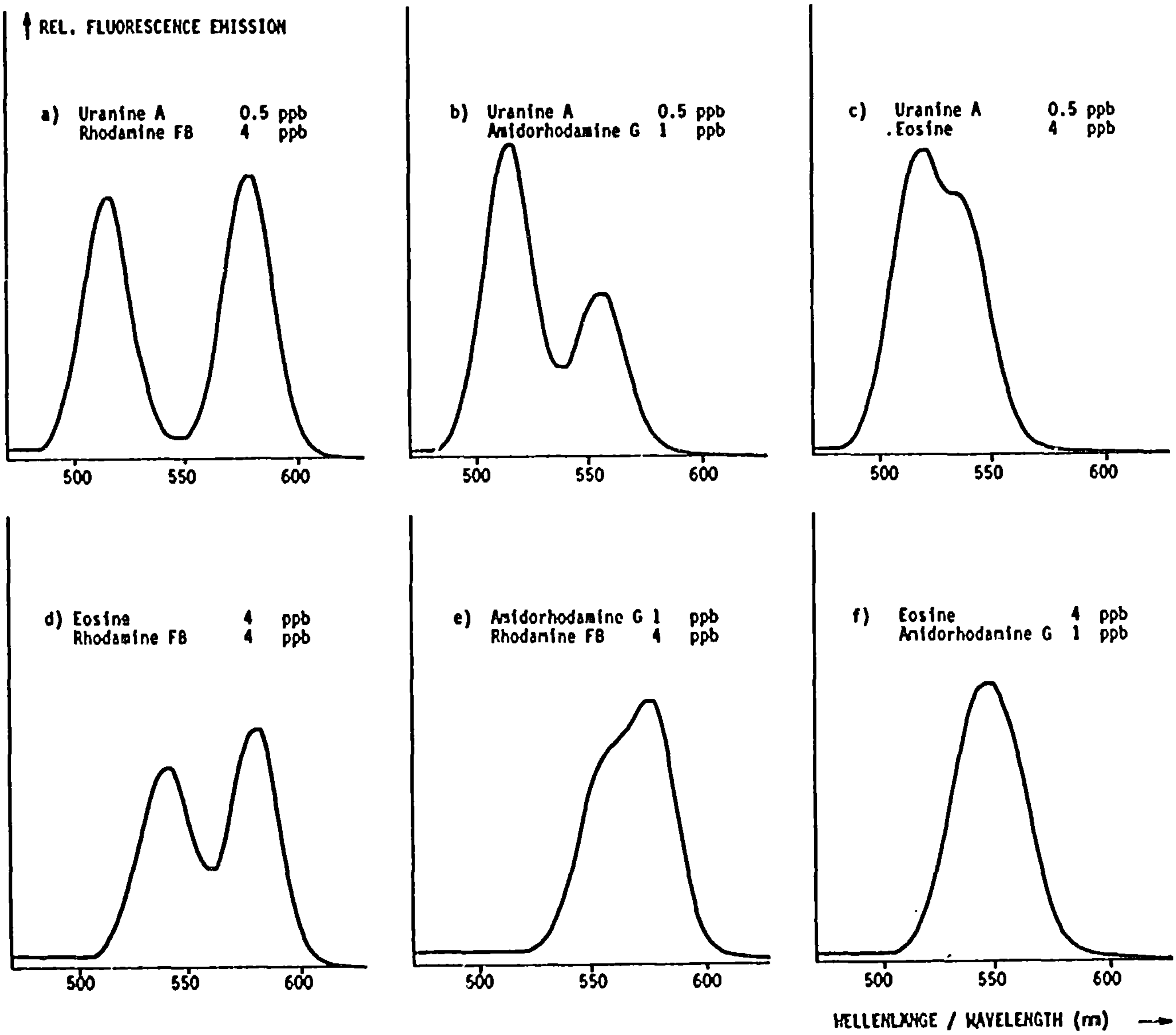


Figure 8: Fluorescence spectra of different fluorescent dye mixtures in aqueous solutions; taken off at simultaneous displacement of excitation and emission wavelengths in constant distance of 25 nm (H.Behrens, M.Supan & M. Zupan, 1976)

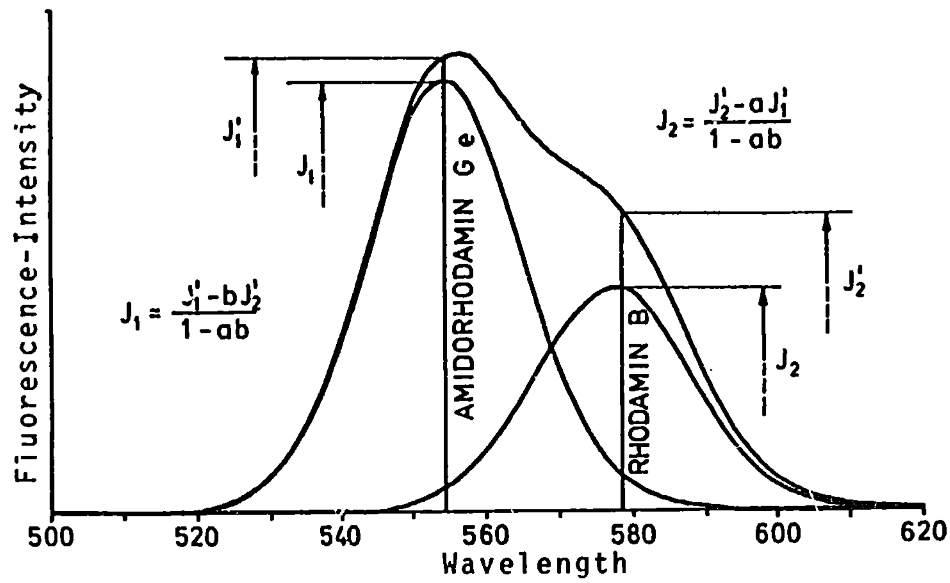


Figure 9: Correction procedure for the determination of concentrations of single components from the fluorescence spectrum of an amidorhodamine G and rhodamine B mixture (H.Behrens, 1982).

Some such treatments are based on artificial changes of pH, since the fluorescence intensity of uranine particularly, is very much effected by this parameter. If the sample is acidified, the uranine intensity more or less disappears . For eosine similar effects are considered at a low pH. Thus, eosine reacts to acidification at pH lower than 5 in opposition to uranine, which loses fluorescence intensity even at neutral pH. All these processes are reversible.

Besides pH, undesirable differences in absorption behaviour can be used for selective determinations. Laboratory tests (H.Behrens, 1982) show good results regarding absorption phenomena of rhodamine dyes applying glimmer sand. This procedure is suitable especially for the separation of eosine and amidorhodamine G.

In a similar way, photodecomposition can also be utilized for the separation of tracers, as this phenomenon is affected differently by various dyes.

Another possibility for tracer separation is the method of "Thin layer chromatography" (F.B.Bub & H.Hötzl, 1979; G.Ackermann,F.B.Bub & H.Hötzl, 1982). The principle of this method is the different effects of an absorbance and an eluens layer - deposited on a glass plate - on the fluorescent dyes. The measurements will be carried out by a specially adapted fluorometer. The tracers will be identified by the different distances (Rf-value) which the dyes cover in the absorbent body.

LIMITS OF DETECTION

These very much depend on the method applied and also on the instruments used. R.Benischke (1983) gives some data based on the synchronous scan method:

Uranine	0.001 - 0.025 ppb
Eosine	0.05 - 0.5
Amidorhodamine G	0.001 - 0.05
Rhodamine B	0.01 - 0.5
Tinopal	around 0.4

The data of the thin layer chromatography are derived from F.B.Bub & H.Zotl (1979):

Uranine	0.12 ppb
Eosine	1.0
Amidorhodamine G	0.05
Rhodamine B	0.02
Tinopal	2.5

2.2.4 Use of charcoal indicators

This method is based on the ability of activated charcoal to absorb fluorescent dyes in liquids and was first described by F.Bauer (1967). For this purpose 4 - 5 g of activated charcoal are put in small bags (size 10 x 3 cm) of nylon gauze with a mesh width of 0.67 mm. Before filling the bags with charcoal, the material has to be sorted and washed until only grain sizes with a diameter of about 1.5 mm remain. Charcoal dust has to be eliminated because of the risk of contamination by leaving the bag in the nylon net during the laboratory procedures to prepare and measure the charcoal sample.

The main characteristics are as follows:

- The concentration of the eluates from activated charcoals can be up to 1.000 times higher than the maximum concentration of water samples measured from the same site and period. From this fact it can be concluded that dye tracers can be identified with the help of charcoal at a concentration level which is distinctly below the detection limit for water samples. This effect can be explained by the fact that the water sample is being collected during a brief moment while the charcoal bag is exposed for a longer period in the water and can therefore sum up dye tracer substances.

- The qualitative clarification of subsurface drainage is possible with a very low personnel expenditure. In remote areas or springs difficult to reach (e.g. in caves, gorges), where a systematical direct water sampling is not feasible this method is applicable with much success.

- In some cases the only qualitative data obtained can be disadvantageous. The results cannot be related to the amount of tracer input and output to calculate storage capacities. Finally, it is useful to combine both the direct measurements of water samples and charcoal indicators.

After filling the charcoal bags they are exposed in the water current, where a rapid flow through the bag has to be guaranteed, as well as a large contact area between the surface of the charcoal and the water

After sampling the bags, the charcoal has to be dried and later extracted by mixtures of fluids (R.Benischke, 1983):

- for uranine: a solution of ethylalcohol (96% vol.) and KOH (15%) in a 1 : 1 ratio

- for multifluorescent dyes (uranine, eosine, amidorhodamine G, rhodamine B, tinopal): a solution N-N dimethylformamid (DMF) and distilled water in a 4 : 1 ratio. It is sometimes necessary to increase the pH. The maximum emission can be slightly shifted to a higher wavelength.

LIMITS OF DETECTION

R.Benischke (1983) compiled the data using DMF as extraction liquid:

Uranine	0.1 ppb (pH 7)
Eosine	0.1
Amidorhodamine G	0.1
Rhodamine B	0.1
Tinopal	10

3. STRUCTURE OF THE TRACING EXPERIMENT

To carry out an experiment applying chemical tracers one has to divide the work into three parts: preparation, realization and evaluation.

3.1 Preparation

3.1.1 Selection of injection points

To carry out a tracing experiment without problems in any case, an essential prerequisite must be a systematic hydrogeological mapping (general geology, springs, wells, boreholes, karstic phenomena). As the tracers should be injected into active sinkholes (natural inflow of water e.g. caves), dolines, shafts, joints, fissures or boreholes, the selection of the input sites depends on various criteria:

- The extent of the investigation area;
- For the case of a combined tracing experiment: the areal distribution of injection points and their availability;
- The season: because water is essential for injection (in mountainous areas: melting time; in arid zones: rainy season);
- The transport of tracers (especially in remote areas);
- The objective of the tracing experiment (formulation of the hydrogeological problem)

3.1.2 Selection of tracers

This question is relevant not only to chemical, but also to all artificial tracers. The following aspects should be taken into consideration:

- the geological features: estimation of rock permeability

- the lithology: absorption, ion exchange

- the water chemistry: ion exchange,pH environment, influence of mines and of sea water intrusion

- the locality of injection points: transport problems for salt tracers in particular, availability of water for injection

- the availability of tracers, e.g. could be problematic in developing countries

- the collection of samples: points to be selected due to the location of injection sites

- the expected duration of the experiment: change of the season during long-terms tests

- the laboratory facilities: instrumentation (possibly transferable into the field)

- the cost of the tracers: should be as low as possible

- the quantities of tracers expressed as estimated relationships under equal conditions (assumed):

NaCl, KCl - dye tracers (except tinopal)	100 : 1 to 500 : 1
Tinopal - other fluorescent dye tracers	10 : 1
Tinopal - LiCl	1 : 1 to 1 : 2

3.1.3 Organization of tracing tests

After the selection of the tracer and input points, some work has to be carried out before injection:

-preparation of injection points: e.g. preflushing the dry sinkholes by water from a conduit or by rainwater or melting of snow;

-for a test in shallow aquifers using boreholes: cleaning of the pipes and screens by pumping;

-insertion of charcoal bags in observation springs, boreholes, wells;

-working out a plan for sampling (could be changed during the experiment);

-collection of pre-experiment water samples for the knowledge of background concentrations of tracers to be injected (should be taken several times).

3.2 Realization

- Injection of tracer(s): In order to avoid contamination, persons concerned with injection material must be excluded from other duties during the experiment (sampling, laboratory work).

- Collection of samples: Using different sized bottles (according to the measuring facilities). They should be glass or plastic with a smooth surface. The schedule of sampling (direct water samples, charcoal) should be variable due to changes in field conditions and the progress of the experiment.

- Field measurements:
  - (a) for NaCl and KCl: by conductivitymeter
  - (b) for fluorescent dyes: by transportable field fluorometer (with a fixed adjustment of the wave length)

(c) discharge measurements at springs and streams for the quantitative evaluation

- Laboratory measurements:
  (a) for salts: by flame photometer, atomic absorption, titration, ionic chromatography
  (b) for dyes: by fluorometer (different types see chapter 2.2.3).

3.3 Evaluation

- Qualitative evaluation

(a) In the unsaturated zone: proof of subsurface connection of water ways (e.g. in karst or basalt areas), depending on the geological structure rock permeability, difference in elevation between input and output and their lateral distance.

(b) In the saturated zone: proof of flow velocity and flow direction (e.g. in combination with the determination of protected areas for public water supply).

- Quantitative evaluation:

  Besides the knowledge of subsurface connections for investigations of the water balance and drainage systems, it is absolutely necessary to calculate underground storage capacities applying the input-output mass balance carried out by the tracing experiment (Figure 10).

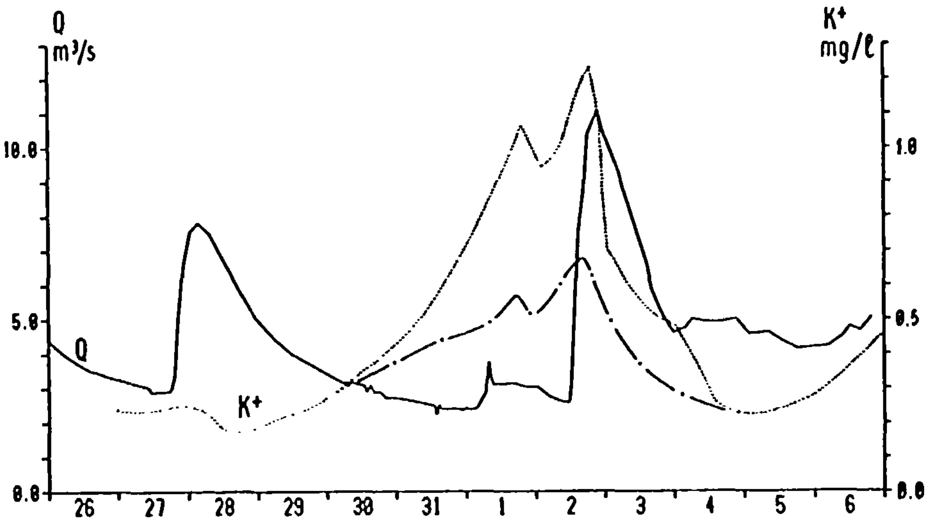


Figure 10: Passage of potassium (K+) at a tracing experiment in the Swiss Jura - Areuse spring in May/June 1979; Q = discharge of spring; semicolons = hypothetic background of natural K+. (W.Käss and I.Müller, 1980).

4. CASE STUDIES

The object of some case studies is not only to present the results of a tracing experiment, but also to describe synoptical investigations of both natural and chemical tracers.

CASE STUDY 1: Unsaturated zone (qualitatively)

Region : *Petzen massif (Austrian-Yugoslavian border)*
Geology : *Triassic limestones and dolomites*
Objective : *Knowledge of recharge areas of springs as well as of subsurface water connections with a mine*
Results :

Hydrochemical and isotopical data were compared. The results obtained by the application of natural and artificial tracers concur:

(a) The natural tracers add to the knowledge of the general subsurface drainage of the Petzen massif, but they cannot separate the areas of infiltration, which are connected with the different springs.

(b) It has been shown by the combined tracing experiment that the two springs with the lowest deuterium content have quite different recharge areas. This would indicate that the whole massif is divided into two blocks with their own particular hydrogeological drainage. From the higher elevated areas in the centre of the massif the subterranean water movement in the unsaturated zone of the karst body is directed mainly to the east (springs on the Yugoslavian side of the border and a lead-zinc mine, which is located 300m below the surface valley drainage system), but also radially to the north and the south. Springs in the northern part with the highest deuterium content were not touched by the artificially injected tracers. Their recharge areas are situated very locally.

(c) The results of this tracing experiment show that the application of salt tracers is very limited because of lack of available water during the injection. This fact did not affect the success of the experiment, because two different tracers were injected in one input site.

REFERENCES

ZOJER,H. 1983. Groundwater flow in karstic aquifers. Tracer methods in isotope hydrology. IAEA-TECDOC 291, Vienna.

GOSPODARIC,R.; HABIC,P.; RAMSPACHER,P.; STICHLER,W.; STRUCL,I.; ZOJER,H. Die Entwässerung der Petzen. Klagenfurt (in press)

CASE STUDY 2: Unsaturated Zone (quantitatively)

Region : Central Styrian karst (Austria)
Geology : Paleozoic limestones
Objective : Knowledge of subsurface drainage
Results :

This investigation area, located some 20 km north of Graz, comprises the basin of Semriach and the limestone Tanneben plateau reaching westwards to the Mur valley near Peggau (Figure 11). The water disappearing east of the paleozoic limestone area in the Lurbach sinkhole traverses the karst massif of Tanneben and re-emerges in the springs of the Lur cave system - the final brook is united by the Schmelzbach - and in the Hammerbach spring at the bottom of the Peggau face.

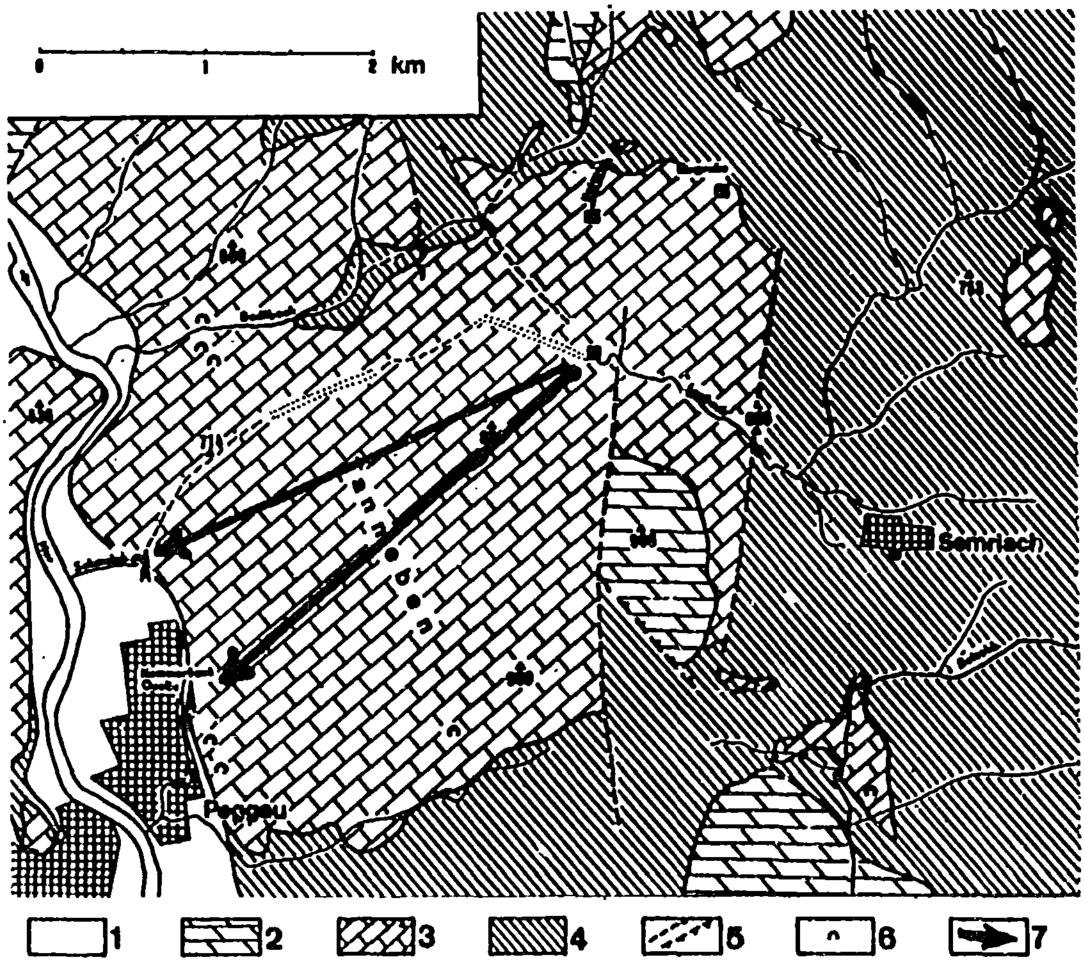


Figure 11: Central Styrian Karst; hydrogeological features; 1 = Quaternary deposits, 2 = Devonian dolomites in general, 3 = Devonian limestones, 4 = Devonian shale series, 5 = Important faults and overthrusts, 6 = Important caves, 7 = direction of subsurface flow (H.Zojer; J.Zötl. 1974.)

A number of tracing experiments have been conducted in the Lur system between Semriach and Peggau. Three points of view have to be considered when judging these tests: the first experiments, until 1959, nearly exclusively focussed on proving an interconnection between the springs in the Mur valley and the higher level waters in the east. With this fragmentary knowledge, it was later tried to use new tracers jointly with well-known materials in order to test their practicability for karst water investigations in general. Finally, it had become possible through such comparison to give quantitative proof, i.e. to gain access to the active storage area by means of discharge of the springs and passage time of the tracers, and to make input-output comparisons of various tracers.

The tracing test of September 1983 can be considered as a quantitative experiment and as an example for a dry weather period. Since low water conditions prevailed, the re-appearance of the tracing material injected in the Lurbach sinks could be observed only in the Hammerbach spring, the samples collected at the Schmelzbach remained negative. The calculation of the total output of the tracers at Hammerbach spring upto 15 September 1983, 12H00, resulted as follows:

	Input	Output	
	kg	kg	% of input
Sodium	226	125	55
Potassium	309	105	34
Chloride	641	390	61
Uranine	3.00	2.13	70

The peak of the concentration time-curve of the tracers sodium, potassium, chloride and uranine could be registered between 66 to 69 hours after injection. The different output rates of the salt tracers can be explained by ion exchange processes especially of potassium, maybe also of sodium to a lesser degree. This caused an increase of calcium and also slightly of magnesium) during the experiment, although these cations were not injected artificially.

Quite different results were obtained by a tracing experiment in 1975. The injection material was the same as above. The months of August and September of this year had thunderstorms with intensive rainfall and floods. The area of Semriach suffered a heavy flood during which the tourist installations for the cave were totally destroyed.The first traces of uranine in the Hammerbach spring appeared about twelve hours after the injection, the maximum of the uranine output was measured sixteen hours after injection, the total output of uranine was 1799,5 g. i.e. 60% of the injected quantity. In the Schmelzbach spring the first traces of uranine appeared about sixteen hours after injection. The total output of uranine in the Schmelzbach spring was 601.3 g. which was 20% of the quantity injected. The sum of the total output of uranine reached 80% of the injected quantity, thus representing a very high percentage.

REFERENCES:

ZOJER,H. 1973. The significance of quantitative statements in connection with combined investigations of karst water. UN Water Conference. TP 43, Mar del Plata.

ZOJER,H. 1983. Report on the 9th "Postgraduate Training Course on Groundwater Tracing Techniques." Unpubl. report, Graz.

CASE STUDY 3: Unsaturated Zone (Quantitatively)

Region : *Kibwezi (Kenya, East Africa)*
Geology : *Crystalline basement, covered partly by different basalt generations (Figure 12)*
Objective : *Educational demonstration, knowledge of underground storage*
Results :

In Eastern Africa young (Tertiary and Quaternary) basalt flows are to be found everywhere. They usually follow shallow valleys of the crystalline base rock and thus also contain groundwater flows which, depending on the thickness and irregularity of the basalt flow, also appear on the surface as scum-covered jungle pools. Not infrequently, the jungle ends where the flow leaves off, and the emerging groundwater forms the source of a perennial superficial riverlet. Villagers often consider this to be a superior living area.

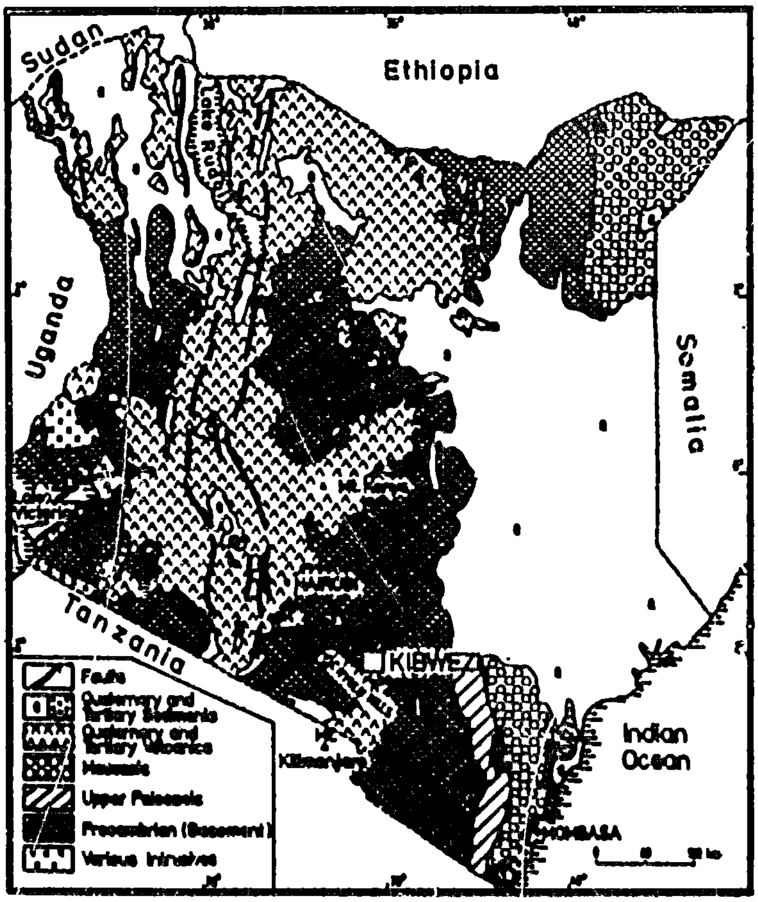


Figure 12 Generalized geological map of Kenya (P. Hacker, H. Zojer & J.G.Zötl, 1983).

In one such flow in the vicinity of the locality of Kibwezi, 400 kg sodium chloride, 5 kg blue dyed lycopodium spores and 2 kg uranine (sodium fluorescein) were injected into a sinkhole of a jungle pool, and the water outlets of the source area at the end of the basalt flow observed.

The point of input and the course outlets observed were relatively close together (350m in a straight line), but the seepage of the last surface pool was chosen deliberately to show the flow speed of the groundwater in the basalt flow. Intermediate pools slow the flow to a greater or lesser degree, depending on their size.

The results of this test, performed in January 1980, show a surprisingly high flow speed in the noncontinuous underground course of the basalt flow, as well as evidence of lack of a filter effect of the fissures and joints in the basalt. Maximal flow speeds around 350 m per hour and an average passage of 30 m per hour leave no doubt that the water is in no way protected from pollution of any sort, which paves the way for the spread of bilharziasis.

The marking experiment may also be viewed as a complete technical success, as emergence of 62- 72% of the injected tracer could be demonstrated, the storage capacity was calculated as approximately 800 to 1.200 m3.

REFERENCES:

HACKER,P.; ZOJER,H.; ZÖTL J.G. 1984. A combined tracing experiment in the basalt area of Kibwezi, Kenya. Hydrogeology of volcanic , terrains, Poona, India.

CASE STUDY 4: Saturated Zone

Region : *Shallow aquifer (South of Graz, Austria)*
Geology : *Quarternary gravels*
Objective : *Educational demonstration, flow direction and flow velocity of groundwater*
Results :

In comparison with results obtained by a radioactive tracer (99 Tc), a tracing experiment with a fluorescent dye was caried out on 8 September 1983. A quantity of 40 g uranine was injected into a central filter tube at a depth of approximately 3 m and the samples from 8 wells located in a semicircle were taken for the analysis of the dye. The results of the tracing experiment indicated the flow direction to be 145 from the north which is in fair agreement with the result of the single dilution test. The distance velocity referred to the ratio of distance to the time of maximum concentration and was computed to be about 15.6 m/d.

These tests and their comparison show that there is an additional need for parametrers referring to a larger scale, especially related to single borehole techniques. Tracing tests and pumping tests are therefore of a complementary character and necessary to obtain optimum information on the aquifer behaviour.

REFERENCES:

ZOJER,H. 1983. Report on the 5th "Postgraduate Training Course on Groundwater Tracing Techniques". Unpubl. report, Graz.

CASE STUDY 5: Saturated Zone

Region : Interalpine valley near Villach (Austria)
Geology : Quarternary (diluvial) sands
Objective : Localization of the protection area for water supply
Results :

The town of Villach is situated at the confluence of two interalpine valleys. Its public water supply is provided by a well in a shallow granular aquifer and also from karst springs. As the utilization of this groundwater field was extended, it became necessary to reconsider the protection of the groundwater against waste water and refuse deposits.

A combined tracing experiment was carried out in July 1983 injecting uranine, amidorhodamine G and LiCl in observation boreholes located at different distances from a central well, where groundwater had been pumped out during the test up to 100 l/s. From this investigation a maximum flow velocity of the groundwater in the area of the hydraulic depression was calculated with 7.5 m/d, from which data the protected area could be plotted. In this zone disposal and construction activities are now prohibited.

REFERENCES:

Forschungszentrum Graz. 1980. Bericht über den Markierungsversuch bei Urlaken Villach, Unpubl.report, Graz.

REFERENCES

ACKERMANN, G.; BLINDE, A.; FABIAN, E.; HÖTZL, H. 1982. Anwendung der Markierungstechnik zur Untersuchung der Entwässerungsfunktion eines Erzganges. Beitr. Geol.Schweiz, 28/II, Bern. p. 432-434.

ACKERMANN, G.; BUB, F.U.; HÖTZL, H. 1982. Erfahrungen mit der Dünnschicht-Chromatrographie beim Nachweis von Fluoreszenztracern. Beitr. Geol. Schweiz, 28/I, Bern. p.63-68.

ACKERMANN, G.; HÖTZL, H. 1984. Weiterentwicklung der Dünnschicht-Chromatographie für die Auswertung von Aktivkohle-Eluaten in der Tracertechnik. Steir.Beitr.Hydrogeologie, 36, Graz. p.103-114

BACK, W.; ZÖTL, J.G. 1975. Application of geochemical principles, isotopic methods and artificial tracers to karst hydrology. Hydrology of karstic terrains, IAH, Paris.

BATSCHE, H.; BAUER, F.; BEHRENS, H.; BUCHTELE, K.; HRIBAR, F.; KASS, W., KNUTSSON, G.; MAIRHOFER, J.; MAURIN, V.; MOSER, H.; NEUMAIER, F.; OSTANEK, L.; RAJNER, V.; RAUERT, W.; SAGL, H.; SCHNITZER, W.A.; ZÖTL, J. (1967). Ergebnisse der vergleichenden Markierungsversuche im mittelsteirischen Karst 1966. Steir.Beitr.Hydrogeologie, 18/19. p.331-406.

BATSCHE, H.; BAUER,F.; BEHRENS,H.; BUCHTELA,K.; DOMBROWSKI,H.J.; ISLER,R., GEYH,M.A.; HOTZL,H.; HRIBAR,F.; KASS,W.; MAIRHOFER,J.; MAURIN,V.; MOSER,H., NEUMAIER,F.; SCHMITZ,J.; SCHNITZER,W.A.; SCHREINER,A.; VOGG,H.; ZÖTL,J. 1970. Kombinierte Karstwasseruntersuchungen im Gebiet der Donauversickerung (Baden-Württemberg in den Jahren 1966-1969. Steir.Beitr.Hydrogeologie, 22. Graz. p. 5-166.

BAUER,F.; 1967. Erfahrungen beim Uraninnachweis mit Aktivkohle. Steir.Beitr Hydrogeologie, 18/19. Graz. p. 169-178.

BAUER,F. 1972. Weitere Erfahrungen beim Uraninnachweis mit Aktivkohle. Geol. Jahr. C 2. Hannover. p. 19-28.

BAUER,F. 1972. Untersuchungen über die Verwendbarkeit von zwei Fluoreszenzfarbstoffen im Rahmen eines Färbeversuches. Geol.Jahrb. C 2. Hannover. p. 61-74.

BAUER,F. 1976. Untersuchungen über die Verwendbarkeit von Tinopal CBS-X als Tracer. Papers 3th SUWT, Ljubljana. p.17-26.

BAUER,F.; BEHRENS,F.; BERNOT,F.; DECHANT,M.; HABIC,P.; GOSPODARIC,R., HÖTZL,H.; HRIBAR,F.; KASS,W.; KRIVIC,P.; LEWICKI,F.; MAURIN,V., PICININ,A.; PIRS, M.; TOPLISEK,M.; UDOVC,H.; VERBOVSEK,R.; ZIBRIK,K., ZÖTL,J.G.; ZUPAN,M.; ZUPAN.M. Realization and results of combined water tracing test 1975 in Slovenia. Underground Water Tracing, Ljubljana. p. 122-216

BAUER,F.; ZUPAN,M.; BEHRENS,H. 1976. Applicability of fluorescent tracers in Karst. Underground Water Tracing, Ljubljana, p.217-220.

BAUER,F.; BUB,F.P.; HÖTZL,H.; PEWRLEGA,W.; ZUPAN,M. 1980. Die Markierung von Fluoreszenztracern (Neuenburger Jura). Steir.Beitr.Hydrogeologie,32. Graz. p.57-76

BAUER,F.; BEHRENS,H.; KASS,W.; LEIBUNDGUT,Ch.; PERLEGA.W. 1981 Methodik und Ergebnisse der Tracerversuche (Langetental, Schweiz). Steir.Beitr.Hydrogeologie, 33. Graz. p.56-79.

BEHRENS,H. 1971. Untersuchungen zum quantitativen Nachweis von Fluoreszenzfarbstoffen bei ihrer Anwendung als hydrologische Markierungsstoffe. Geol.Bav., 64. Munchen. p.120-131.

BEHRENS,H. 1973. Eine verbesserte Nachweismethode fur Fluoreszenzindikatoren und ihre Anwendung zur Feststellung von Fliesswegen im Grundwasser. Ztschr.Deutsch.Geol.Ges., 124, Hannover, p.535-544.

BEHRENS,H. 1982. Verfahren zum qualitativen und quantitativen Nachweis von nebeneinander vorliegenden Fluoreszenztracern. Beitr.Geologie Schweiz, 28/I, Bern, p.39-50.

BEHRENS,H. 1983. Comparison of radioactive and non-radioactive tracers. Tracer methods in isotope hydrolgy, IAEA-TCDOC 291, Vienna. p. 173-186.

BEHRENS,H.; HÖTZL,H.; MAURIN,V. 1981. Die Markierung mit Fluoreszenztracern, Nachweismethoden und Ergebnisse (Muotatal, Schweiz). Steir.Beitr. Hydrogeologie, 33. Graz. p.198-219.

BEHRENS, H.; BÖGLI,A.; LEIBUNDGUT,Ch.; ZOJER,H. 1981. Die Markirung mit Salzen (Muotatal, Schweiz). Steir.Beitr. Hydrogeologie, 33, Graz. p.220-224.

BEHRENS,H.; TEICHMANN,G. 1982. Neue Ergebnisse über den Lichteinfluss auf Fluoreszenztracer. Beitr.Geol.Schweiz, 28/I, Bern, p.69-78.

BENISCHKE,R. 1983. Fluorescent dyes as means of water tracing, the use of charcoal indicators for the detection of the tracers in the underground. Unpubl. report PGTC, Graz.

BENOIT-GUYOD,J.L.; ROCHAT,J.; ALARY,J.; ANDRE,C.; TAILLANDIER,G.. (1979) Correlations entre les propriétés physico-chimicos et ecotoxicite de traceurs fluorescents xantheniques. Toxicologie Europ Research, 2.

BRAUNS,J.; HÖTZL,H. 1982. Kombinierte Pump- und Markierungsversuche zur Dimensionierung von Schutzzonen. Beitr. Geol Schweiz, 28/II, Bern. p.309-320.

BROUILLARD, J.F. 1975. Les applications de la spectrofluorimétrie a l'hydrologie. Spelunca, 9 Suppl., Neuchatel.

BROWN,M.C.; WIGLEY, T.M. 1969. Simultaneous tracing and gauging to determine water budgets in inaccessible karst aquifers. 5th Int. Congr. Spel., Proceedings, Stuttgart.

BUCHTELA,K.; JOB,C. 1970. Vergleichende Markierungsversuche mit Indium ADTE und Kalisalz in einem Bergsturzgelände bei Badgastein. Steir.Beitr. Hydrogeologie, 22, Graz. p.199-206.

CALMELS,A.; CHARRIERE,R.; FORNEAUX,J.C.; MOLINARI,J.; SARROT-REYNAULT,J., TALOUR,B. 1976. Multitracages dans les massifs karstiques du Vercors et de la Chartreuse (France). Papers 3rd SUWT, Ljubljana, p.101-112.

DAVIS,S.N.; THOMPSON,G.M.; BENTLEY,H.W.; STILES,G. 1980. Ground water tracers - a short review. Ground water, 18, p. 14-23

DOUNAS,A.; KALLERGIS,D.; MORFIS,A.; PAGOUNIS,M.; ZOJER,H. 1982.82) Die Ergebnisse eines Markierungsversuches im östlichen Kopais-Becken, Griechenland,Beitr.Geol.Schweiz, 28/I, Bern. p.161-168.

DUFFY,D.P.; Mc DONNEL, J.J.; WOLCHOK,R.L.; KRUGER.P.; ROBERTS,P.V. (1981) Tracer tests during artificial recharge of groundwater by direct injection. Techn.Rep.258, Stanford University, Stanford.

ERIKSSON,E. 1981. Hydrochemistry - chemical processes in the water cycle. Technical Documents in Hydrology, UNESCO, Paris, 100 p.

FEUERSTEIN,D.L.; & SELLECK,R.E. 1963. Fluorescent tracer for dispersion measurements. Journ.Sanit.Eng.Div.Amer.Soc.Civil.Eng., 89, p.1-21.

FOURNEAUX,J.C.; GRANGE,R. 1980. Utilisation de la spectrofluorimétrie et de la spoectrphotométrie pour la mesure des debits karstiques. Coll. Nat. Prot.eaux souterr., Besancon.

FOURNEAUX,J.C.; ROCHAT,J. 1982. Essais ("in situ" de quatre traceurs fluorescents. Beir.GeolSchweiz, 28/I, Bern, p.91-100.

Forschungszentrum Graz. 1980. Ergebnisse des Markierungsversuches Urlaken bei Villach (Kärnten). Unpubl. Rep., Graz. 9 p.

GLOVER,R.R. 1972. Optical brighteners - a new water tracing reagent. Trans. Cave Res.Group Great Brit., 14/2. p.8488.

GOLDBRUNNER,J.E.; RAMSPACHER,P.; ZOJER,H.; ZÖTL,J.G.; MOSER,H.; RAUERT,W. STICHLER,W. 1982. die Anwendung natürlicher und künstlicher Tracer in einem hochalpinen Magnesitbergbau. Beit.Geol. Schweiz, 28/II, Bern. p.407-422

GOSPODARIC,R.; HABIC,P.; RAMSPACHER,P.; STICHLER,W.; STRUCL,I.; ZOJER,H. (1985, in press) Die Entwässerung des Petzen-Karststockes (Kärnten-Slowenien). Carinthia II, Klagenfurt.

GUILBAULT,G.G. 1973. Practical fluorescence theory, methods, techniques. Marcel Dekker, New York.

HABIC,P.; GOSPODARIC,R. 1982. Tracerhydrologische Untersuchungen im Karst von Slowenien (NW Jugoslawien). Beitr.Geol.Schweiz, 28/I, Bern, p.169-176.

HACKER,P.; ZOJER,P.; ZÖTL, J.G. 1983. Ergebnisse eines kombinierten Markierungsversuches im Basaltgebiet von Kibwezi (Kenya). Steir.Beitr. Hydrogeologie, 34/35. Graz. p. 107-125.

HACKER,P.; ZOJER,H.; ZOTL,J.G. 1984. A combined tracing experiment in the basalt area of Kibwezi, Kenya. Hydrogeology of Volcanic Terrains, Poona, (India). p. 49-62.

HARUM,T.; LEIBUNDGUT,Ch. Ed. 1981. Tracerhydrologische Untersuchungen im Langetental (Schweiz). Steir.Beitr.Hydrogeologie, 33. Graz. p. 5-123.

HIBSCH, G.; KREFT,A. 1979. Determination of aquifer transport parameters. Journ.Hydraul.Div. ASCE 105, HY 9, p. 137-1151.

HOEHN, E.; ROBERTS,P.V. 1982. Tracer test interpretation in radially divergent groundwater flow. Beitr.Geol.Schweiz, 28/II, Bern. p. 297-308.

HÖTZL, H.; METZLER,F.; ROTHEGATTER,P. 1982. Die Kluftmarkierung, eine Anwendung der Markierungstechnik zur Ermittlung von Durchlässigkeitseigenschaften klüftiger Gesteine. Beitr.GeolSchweiz, 28/II, Bern. p. 381-394.

JOB,C. 1972. Ionenumtausch bei Salzungsversuchen. Geol.Jahrb., C 2, Honnover. p. 103-110.

JONES,W.K. 1976. Dye tracing in North America. Papers 3rd SUWT, Ljubljana. p. 101-112.

KANZ, W. 1981. A simple but effective method to determine groundwater flow velocities near pumping wells. Studies in Environmental Science, 17 - Qaulity of Groundwater. p. 703-706.

KÄSS,W. 1976. Salzversuche mit Kalisalz. Steir.Beitr.Hydrogeologie, 18/19, Graz. p.275-280.

KÄSS, W.; MÜLLER,I. 1980. Resultat des Markierungsversuches mit Salzen. Steir.Beitr.Hydrogeologie, 32, Graz. p.77-80.

KÄSS,W. 1982. Routinemässige Bestimmungen von zwei Fluoreszenzfarbstoffen nebeneinander. Beitr.GeolSchweiz, 28/I, Bern. p.51-62

KAUFMANN,W.J.; G.T.ORLOB 1956. An evaluation of groundwater tracer. Trans.Amer.Geoph.Union, 37. p.297-306.

KLIR,St. 1972. Untersuchungen uber den Intensitätsabfall des Fluoresceins. Geol.Jahr.,C 2, Hannover. p. 29-34

KLOTZ, D. 1982. Verhalten hydrologischer Tracer in ausgewählten fluvioglazialen Kiesen, Hangschutt-Kiesen und tertiären Kies-Sanden. Beitr. Geol.Schweiz, 28/II, Bern. p. 245-256.

KOLLMANN,W. 1979. Erfahrungen bei Salzmarkierungsversuchen und deren Auswertung unter Berücksichtigung von Ionenaustauschvorgangen. Steir. Beitr.Hydrogeologie, 31, Graz. p.143-150.

KUSSMAUL, H.; MÜHLHAUSEN,D. 1976. Use of chloride, borate and uranine present in Rhine river water as indicators in determining residence times and mixture rations in recovering potable water by the bank filtration method. Papers 3rd SUWT, Ljubljana. p. 124-132.

KYRLE,G. 1928. Kombinierte Chlorierung von Höhlengewassern. Spelaol. Monogr., 12, Wien.

LAIDLAW, I.M.S.; SMART, P.L. 1982. An evaluation of some orange fluorescent dyes. Beitr.GeolSchweiz, 28/I, Bern. p/113-118.

LALLEMAND, A.; PALOC,H. 1964. Possibilites d'utilisation d'un nouveau colorant, le "Pontacyl Brillant Pink B", pour l'étude des circulations karstiques. Spelunca, 4.

LEDITZKY, H. 1978. Interpretation von Ionenaustauschvorgängen beim Einsatz von Salzen zur Verfolgung unterirdischer Wasserwege durch Sedimentuntersuchungen. Steir. Beitr. Hydrogeologie, 30, Graz. p. 169-174.

LEDITZKY,H. 1981. Ionenaustauschphänomene beim Einsatz von Steinsalz als Markierungsmittel. Festschr. Zotl, Graz. p. 103-110.

LEHMANN,R. 1977. Evaluation von geeigneten Tracern für die Anwendung im Grundwasser unter spezieller Berücksichtigung der Adsorption. Ing. Bericht, Univ. Bern.

LEIBUNDGUT, Ch. 1974. Fluoreszierende Markierstoffe in der Hydrologie. Mitt. Naturforsch.Ges., 31, Bern.

LEIBUNDGUT,Ch. 1975. Färbeversuche im Grundwasser des Oberaargaus.Jahrb. Oberaargau 1975, p. 143-171.

LEIBUNDGUT,CH. 1981. Zum Asorptionsverhalten von Fluoreszenztracern. Festschr. Zötl, Graz. p. 111-130.

LEIBUNDGUT, Ch.; LUETHI, B. 1976. Bestimmung des Seihvermögens von Grundwasserleitern mittels Tracer. Papers 3rd SUWT, Ljubljana, p.141-148.

LEIBUNDGUT,Ch.; WERNLI, H.I.; 1982. Zur Frage der Einspeisemengenberechnung fur Fluoreszenztracer. Beitr.GeolSchweiz, 28/I, Bern. p.119-130.

LENDA, A.; ZUBER,A. 1970. Tracer dispersion in groundwater experiments. Isotope Hydrology 1970, Vienna. p. 619-636.

LOISELEUR, B. 1978. Campagne de coloration dans les préalpes de Schwyz. Stalactite, 28/1, Neuchatel, p.12-21.

LUFT, G.; MORGESCHWEIS,G. 1982. Ermittlung von Abstandsgeschwindigkeit, hydraulischer Leitfähigkeit und Dispersionskoeffizient aus Markierungsversuchen in kiesigen und schluffigen Aquiferen. Beitr.Geol.Schweiz, 28/II, Bern. p.283-296.

MAURIN,V.; ZÖTL,J. 1959. Die Untersuchung der Zusammenhänge unterirdischer Wässer mit besonderer Berücksichtigung der Karstverhältnisse. Steir.Beitr. Hydrogeologie, 1/2, Graz.

MAYER, S.W.; TOMPKINS,E.R. 1974. Ion exchange as a separations method. A theoretical Analysis of the Column Separations Process, Part IV, J.Amer Chem. Soc., 69, p.2866-2874

MOSER,H.; SAGL,H. 1967. Die Direktmessung hydrologischer Farbtracer im Gelände. Steir.Beitr.Hydrogeologie, 18/19, Graz. p.179-184.

OEZIA,U.; YURTSEVER,Y. 1982. An Outlook on Tracer Applications in Karst Hydrology of Turkey. Beitr. Geol. Schweiz, 28/I, P.149-160.

ORTLAM,D.; 1982. Ein Pollution-Tracer-Verfahren im Bereich der Waser bei Bremen. Beitr. Geol.Schweiz, 28/II, P. 269-274.

PERLEGA,W.; 1976. Der Nachweis von Fluoreszenzfarbstoffen mittels Aktivkohle. Papers 3rd SUWT, Ljubljana, p. 195-202.

POCHON,M.; SIMEONI,J.P. 1976. Nature et role traceur des troubles argileux dans deux sources karstiques (Jura tabulaire suisse). Ann. Scient.Univ. Besancon, 25, p. 321-339.

PREKA,N.; AVDAGIC,I.; LIPOLD,N.; KURPJEL,B. 1982. Stream pollution as a tracer for groundwater studies. Beitr.Geol.Schweiz, 28/II, Bern, p.257-268.

QUINLAN,J.F. 1976. New fluorescent direct dye suitable for tracing groundwater and detection with cotton. Papers 3rd SUWT, Ljubljana, p.257-262.

QUINLAN,J.F. 1982. Groundwater basin delineation with dyetracing, potentiometric surface mapping and cave mapping, Mammoth Cave Region, Kentucky USA. Beitr.Geol.Schweiz, 28/I, p.177-190.

QUINLAN,J.F.; SMART, P.L. 1976. Identification of dyes used in Water Tracing: a suggestion to improve communication. Papers 3rd SUWT, Ljubljana, p. 263-268

ROCHAT,J.; ALARY,J.; MOLINARI,J.; CHARRIERE,R. 1975. Separations physico-chimiques de colorants xanteniques utilisés comme traceurs. Jorn. Hydrology, 26, Amsterdam. p. 277-293.

ROCHAT,J.; ALARY,J.; FOURNEAUX,J.C. 1981. Compartement des traceurs fluorescents xantheniques, influence des principaux composants du sol. Spelunca.

ROUSSET,Ph. 1981. Resultats d'un tracage effectué sur le système karstique des sources d'Arbois-Bournillon (Vecors,France). Congr.Fed.Franc.Sepel., Seyssins.

SCHMASSMANN,H. 1972. Quantitative Auswertung von Kochsalzmarkierung in Schotter-Grundwasserströmen. Geol.Jahrb., C 2, p. 75-88

SCHWEDT,G. 1981. Fluorometrische Analyse - Methoden und Anwendungen. Verlag Chemie, Weinheim.

SEILER,K.P. 1979. Die Bedeutung der Lage des Markierungsortes zum Förderbrunnen für die Tracerdurchgangskurven. Jahresber. Inst.Radio-hydr., München, p.118-121.

SMART,C.C.; FORD,D.C. 1982. Quantitative dye tracing in a glacierized alpine karst. Beitr.Geol.Schweiz, 28/I, Bern. 191-200.

SMART, P.L. 1976. Use of optical brighteners/cellulose detector systems for water tracing. Papers 3rd SUWT, Ljubljana, p.203-213.

SMART,P.L. 1976. Catchment delimination in karst areas by the use of quantitative dye test. Papers 3rd SUWT, Ljubljana, p.291-298.

SMART,P.L. 1982. A review of the toxicity of 12 fluorescent dyes used for water tracing. Beitr.Geol.Schweiz, 28/I, Bern, p. 101-112.

SMART,P.L.; BROWN,M.C. 1973. Activated carbon for the detection of the tracer dye Rhodamine WT. Abstr.paper, 7th Congr. Spel.,Olomove, p.13-14.

SMART,P.L.; LAIDLAW,I.M.S. 1977. An evaluation of some fluorescent dyes for water tracing. Water Resources Research, 13/1, p.15-33.

TIMEUS,G. 1911. Sui mezzi d'indagine nell-idrologia sotteranea. Boll. Soc.Adr.Sci.nat., 15, Trieste, p.217-231.

TRIPET,J.P. 1976. Dye test in remote areas - application to the karst of Alta Verapaz, Guatemala. Papers 3rd SUWT, Ljubljana, p.299-310.

WHITE,W.B. 1967. Modification of fluorescein dye groundwater tracing techniques. Steir.Beitr.Hydrogeologie, 18/19, Graz, p.151-158.

WILSON,I.F. 1968. Fluorometric procedures for dye tracing. Tech.Water Res.Invest., US Geol.Surv., 3, CH A 12.

WRIGHT,R.; COLLINS,M. 1964. Application of fluorescent tracing techniques to hydrologic studies. Int.Amer.Water Works Assoc., 56.

ZOJER,H. 1977. The significance of quantitative statements in connection with combines investigations of karst waters. UN Water Conference, TP 43, Mar del Plata, 20 p.

ZOJER,H. 1983. Groundwater flow in Karstic aquifers. Tracer Methods in Isotope Hydrology, IAEA-TECDOC-219, p.165-172.

ZOJER,H. 1983. Report on the 9th Postgraduate Training Course on Groundwater Tracing Techniques. Unpubl.Rep., Graz. 10 p.

ZOJER,H.; ZÖTL,J. 1974. Die Bedeutung von Isotopenmessungen im Rahmen kombinierter Karstwasseruntersuchungen. Österr.Wasserwirtsch., 26, Wien, p.62-70.

ZÖTL,J. 1974. Karsthydrogeologie. Springer Verlag, Wien, 291 p.

ZUBER,A. 1983. Models for tracer flow. Tracer Methods in Isotope Hydrology, IAEA-TECDOC-291, Vienna, p.67-112

ZUPAN,M. 1982. Einfluss der Wasserverschmutzung an der Zerstörung der Fluoreszenztracer. Beitr.Geol. Schweiz, 28/I, Bern, p.79-90.

ZUPAN,M.; BEHRENS,H. 1976. Applicability of salts in karst. Underground Water Traciong, Ljubljana, p. 221-222.