

T. A. K. REVIEW

NATURAL AND ARTIFICIAL TRACERS IN THE STUDY OF THE HYDRODYNAMICS OF KARST

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1. INTRODUCTION

The idea of tracing the underground path of water by observations made on the surface goes back to ancient times. Straw, leaves and dyes have been introduced into one sinking point and then observed in an adjacent source, thus establishing the connection of the two and the direction of the flow.

The first remarks concerning the use of tracers to investigate underground waterflow belong to the Roman historian Josephus Flavius (A.D. 100—37) who showed in his work "The Jewish War" that in A.D. 60 Philip, the tetrarch of Trachonitis, established the origin of the Jordan river (namely the Banias spring) using chaff as a hydrological tracer. Actually, the tetrarch had introduced chaff into the Ram Crater Lake and thought he found it again in the Banias spring. Employing environmental isotopes (D, ^{18}O) 2,000 years later, Mazor (1976) demonstrated that the Banias spring is not supplied by Ram Crater Lake waters. Calculations reveal that the capacity of the lake is two orders of magnitude too small to be the feeder of the Banias spring and, furthermore, evaporation tags the lake water with chlorine, deuterium and oxygen-18 enrichments that are not found in the Banias spring. (The latter resembles the regional water recharged on the slopes of Mount Hermon). Philip's merit, however, is unquestionable as he virtually put into practice an idea the fruits of which are reaping at present.

The first through experiment conducted with tracers in a karstic area dates to 1877 when Knopp and Ten Brink used fluorescein to establish a direct connection between water losses in the Danube and the spring of the river Aach, a tributary to the Rhine — a classical example of karstic piracy (Paloc, 1975). The first labelling on a karst in Romania was made in 1904 by Romanian geologist Mihașia who, using powdered coal as a tracer, established a hydrological link between the Cîmpe-nească Cave and the Boiu spring.

Numerous labellings, using fluoresceine and rhodamine B as tracers were performed by Viehmann (1966), Rusu (1979, 1981), Orășeanu (1985 a, 1985 b,) Sencu (1986) and others.

However, the study of the hydrodynamics of karstic waters with the help of tracers has been encouraged only in the recent decades as an outcome of the spectacular development of speleology.

At present, we may say that whereas in any other area of hydrology, tracer methods may be employed along with equivalent methods of investigation, in the case of karsts the tracer-based approach is absolutely necessary owing to the unparalleled results it may yield.

The results and analysis of numerous tracer works on karsts, the recent progress made in the field of tracers and of methods used to identify and measure them, as well as the processing of the information they supply and the advancement of knowledge in general on karstic aquifers and their hydrodynamics cast clear light on the efficiency and prospects of tracing in karst (Atkinson et al., 1973; Gaşpar, 1973; Bleahu, 1974; Mangin, 1974a; Mangin, 1974b; Mangin, 1975; Molinari, 1976; Bakalowicz, 1979; Komatina, 1984; Mijatovici, 1984).

2. HYDRODYNAMIC BEHAVIOUR OF THE KARST

A karstic system that acts as a drainage unit may be divided in two zones or sub-systems — an unsaturated zone or zone of infiltration and a saturated zone or waterlogged karst (Mangin, 1975; Blavoux, 1980) as is schematically shown in fig. 1. In this conceptual scheme on the functioning of a karstic aquifer, imagined by Mangin, endokarstic condensation was introduced.

According to Mangin (1974), in the unsaturated zone, the flow appears in two modes, the first being two-phase (air-water), the second being an actual run-off. The problem of capillary barriers bears an important part in the karst too.

The karst inlet represents the amount of water that seeps into the underground owing to precipitation (precipitation-evapotranspiration), to which add, with a considerable share, the infiltrations from possible non-karstic aquifers and endokarstic condensing. (fig. 1). Precipitations penetrate the whole surface of the karst in the form of either slow, diffuse infiltration or rapid infiltrations concentrated through karstic holes (fissures, faults, solution channels) woting to the runoff on the runoff on the karst surface. Furthermore, there is also the water derived from sources outside the system (rivers, lakes, ponds, leakage from aquifers) which penetrates inside through characteristic karstic forms.

Filtration seepage (or percolation water) is very important in the study of the functioning of a karstic system but may be assessed with approximation. Neither labellings on the karst surface with the help of artificial tracers nor the attempts at a mathematical modelling yielded any satisfactory results. Percolation water is defined as that proportion of runoff following precipitations in a limestone area which does not enter the channel of a surface stream, either by direct runoff or through flow, prior to sinking underground.

The relative significance of percolation waters in limestone areas will vary with geological structure, lithology, climate and degree of karstification; it will be largely a function of the degree of hydraulic homogeneity and anisotropy with respect to porosity (Drew, 1968). One

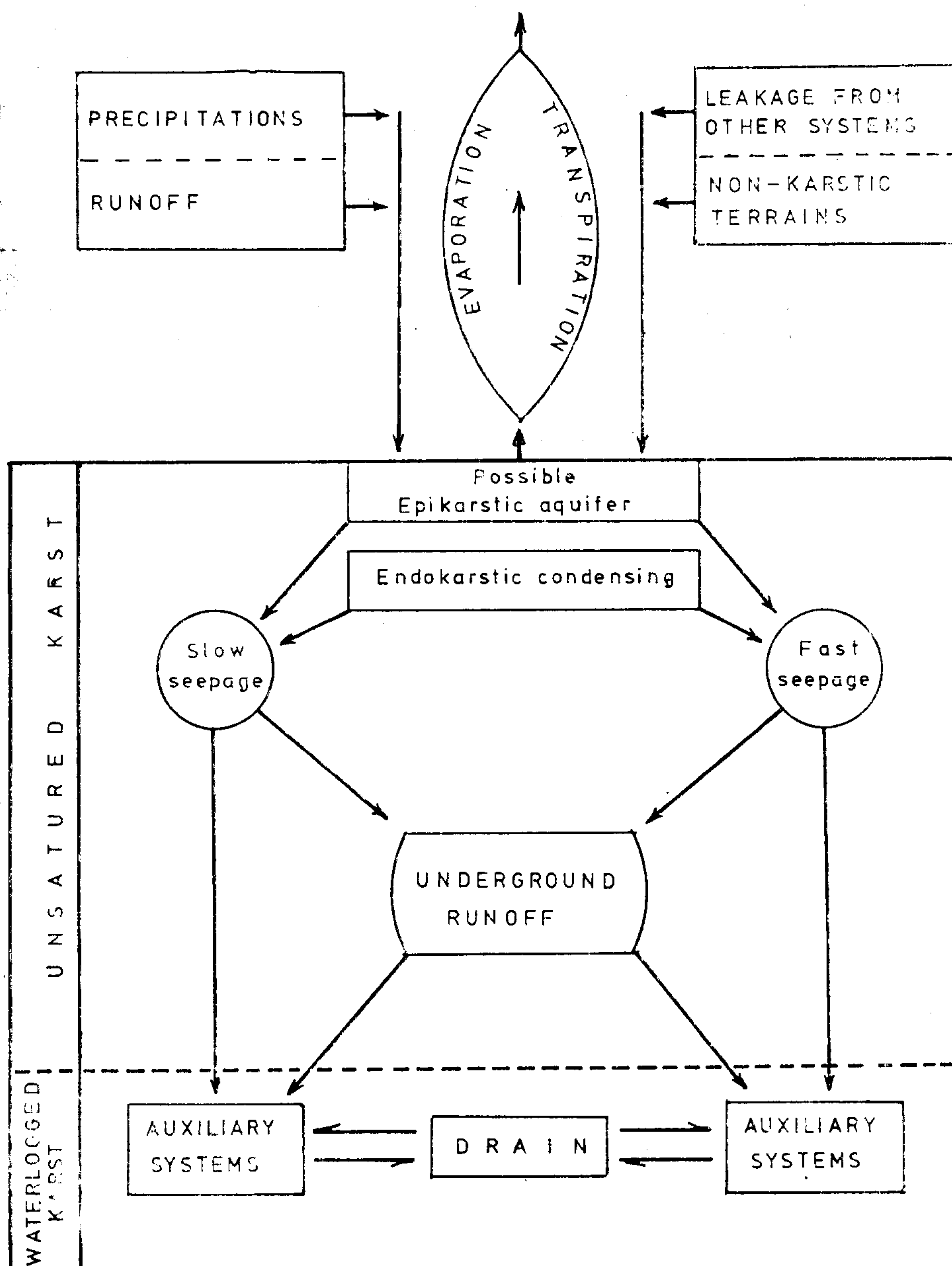


Fig. 1. Water dynamics through a karstic system. Conceptual scheme imagined by Mangin and adopted by Bakalowicz. We have introduced the endokarstic condensing.

major difference between swallet and percolation waters is that the latter will pass through the soil mantle before reaching the bedrock (except in pavement areas) and this will obviously affect its rate of flow and degree of diffusion. Suggested rates of flow of soil moisture

vary between 0.03—150 cm/h depending on the soil type, structure, state of wetness, intensity of rainfall and the nature of the overlying vegetation.

The rates of flow of percolation water vary considerably between areas of similar limestones, depending on the soil type and degree of integration and development of sub-surface channels.

Near the surface a belt of altered and cracked rock may allow temporary water storage. This epikarstic aquifer is responsible for a postponed percolation with highly mineralized waters. A conceptual sketch of a karstic aquifer was imagined by Paloc (1975) in fig. 2.

The infiltrations into the underground (percolation water and swallet water) continue their route in the epikarstic zone. In the case of abundant precipitations, this area may become saturated and thus act as a first temporary aquifer for meteoric waters.

The organization of vertical drainage in the unsaturated zone is achieved both through a fast percolation through fractures and tubular holes and through slow percolation through small fissures.

Furthermore, underground streams with a free level (sometimes under pressure) are frequently met in the unsaturated zone and some of them make a substantial contribution to cave formation.

The lower part of a hydrokarstic structure is the saturated zone or the waterlogged karst, whose constitution is heterogeneous containing a drainage network and sunken conduits in which a rapid flow develops. According to Drogue (1983), these drains are linked to reserves or slow-flow blocks, which are called sub-systems.

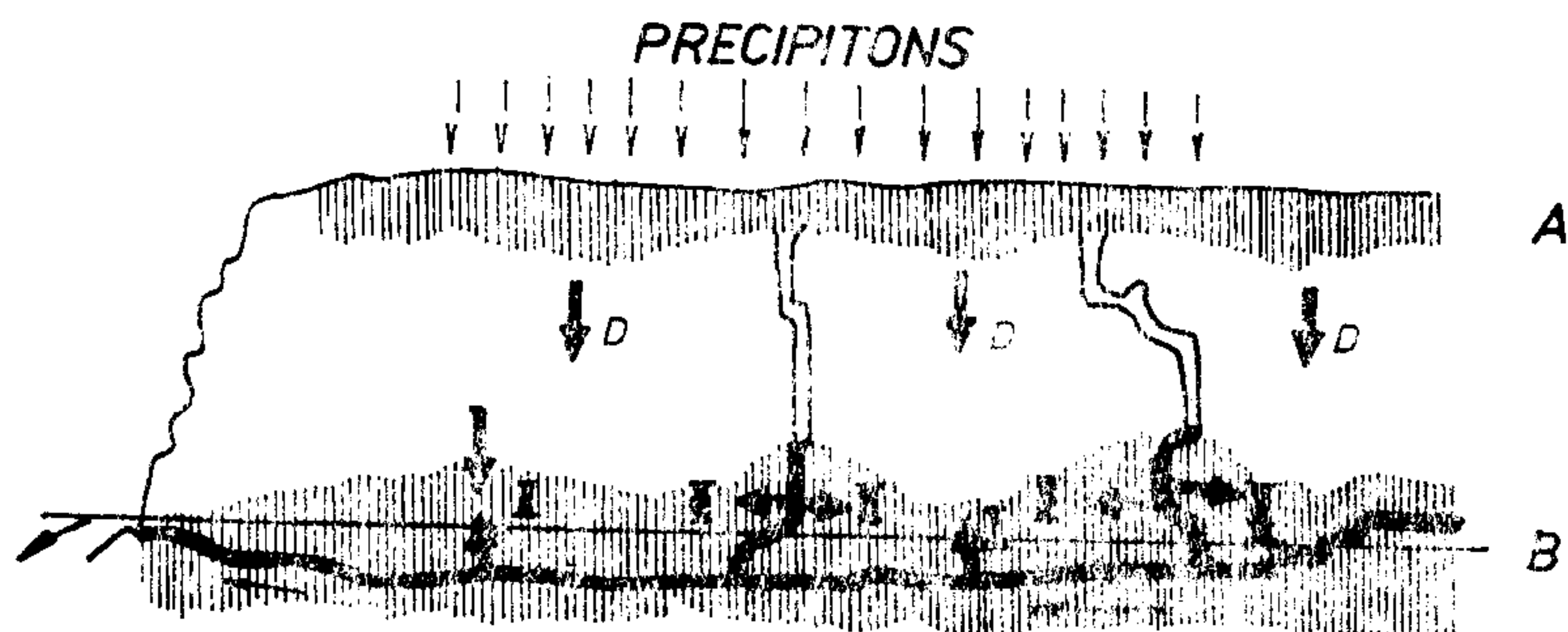
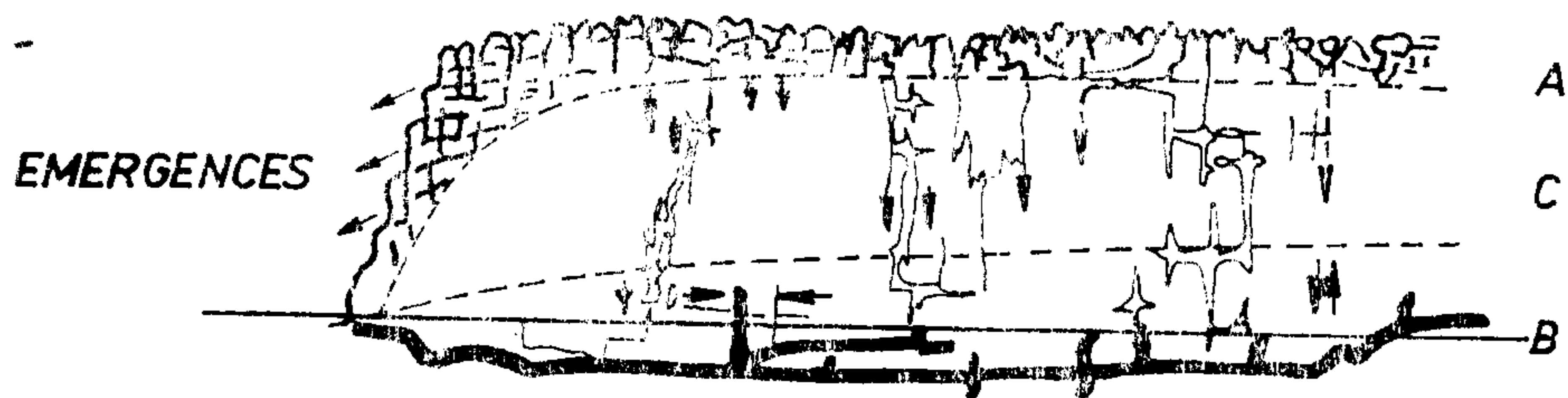
Mangin (1974) suggests a rather different image of the karst. This image should be understood as it accounts for the different behaviour of a karst after a number of labellings were made in different hydrogeological conditions. Thus, drains are considered to be linked to karstic formations, called auxiliary systems, wherein water moves at a lower speed. The more distant they are from the main drain, in which flow is rapid, the slower the velocity.

The auxiliary systems are groups of large-size fissures, galleries and cavities (high storage capacity reservoirs) connected to a drainage network. They develop variable flow relations with the drains, according to the hydrodynamic charge of the latter. Thus, they are supplied by drains during water-rise periods and, in their turn, supply the drains when water decreases and in periods of low flow. They are dependent on drains and the water infiltrated from the rest of the karst has a minor importance; that is why, these auxiliary systems make a whole, with the drain as their outlet. Their hydrodynamic behaviour is very different and their links with the drain entail highly different charge losses.

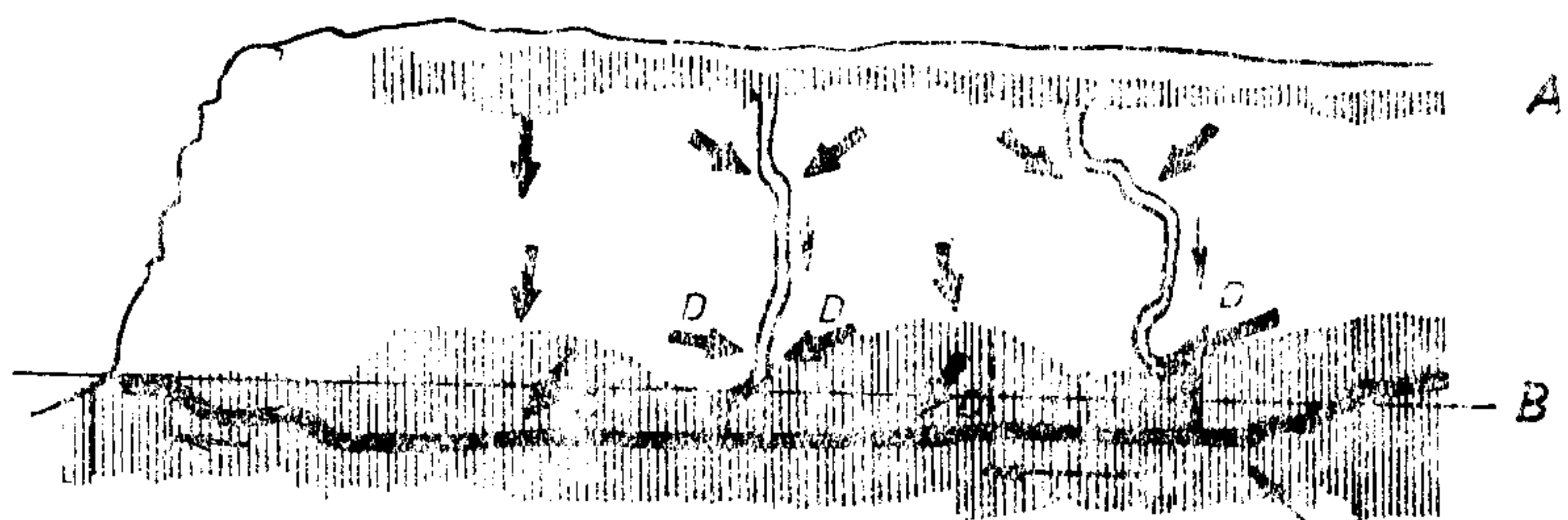
If there are no underground branches of the main drain to guide water to other exurgences, then the discharge it conveys will increase as the spring is being approached.

In low-flow periods the auxiliary systems supply the main drain in an upstream-downstream direction.

During heavy rainfalls, the karstic system is put under pressure. Water velocity in the main drain increases and part of the water pene-



Flow regime during high flow



Flow regime during low flow

SATURATED ZONE

A. Storage zone

C. Transfer zone

B. Storage zone

Flow through pipes

Flow through fissures

I. Injection

D. Drainage

Fig. 2. A cross-section scheme of a hydrokarstic structure. Conceptual sketch of flow through a karstic aquifer imagined by Paloc.

trates the auxiliary systems. If the access involves a charge loss (as in the case of galleries with high roughness, cavings, branches, bends, slopes, etc.), water will have to consume part of its energy to penetrate the auxiliary systems, which will first occur where energy is maximum, i.e. downstream.

The phenomenon under consideration progresses slowly upstream, according to the amount of water that penetrated the karst. Water may penetrate some of the intermediary auxiliary systems first if its access does not imply a high-energy consumption.

After a long period of low flow, the recharge of the sub-systems may take several years. Accumulation in the lower part of the karst depends on both supply and discharge possibilities. Recharge is not achieved after the first rainfalls that follow the low-flow period, but much later, and progressively, as discharge possibilities are saturated.

Given these circumstances, what will the fate of a tracer pulse be according to the hydrodynamic behaviour of the karst? If during a labeling operation the tracer penetrates the auxiliary systems, the whole amount of tracer will be recovered after a long period: either continuously, a large dispersion of the tracer cloud being thus achieved, or intermittently, according to the length of the interval of high-flood succession.

Therefore, the hydrodynamic functioning of a karstic aquifer is closely dependent on both its inner organization and the supply volume. Consequently, according to hydrological conditions, either rapid or slow flow may occur in the same karst. So, for instance, in periods of water rise, when the system is put under pressure, the network of underground channels inject water in the fissures, holes and interstices of the karstifiable rock, while in the low-flow periods they act as drains. Adding to all this are the large karstic holes wherein underground water accumulates and which can influence water transit or not, depending on the conditions that prevail at a given moment. Therefore, it is imperative to know the way auxiliary systems operate, that is whether they supply or are supplied by the main drain.

The importance of the auxiliary systems results from the fact that they provide for reserves; their links with the drain influence the general mode of flow. The way these auxiliary systems operate is responsible for the heterogeneous behaviour of the hydrokarstic system in time and space.

The direction of flow of underground waters is the deciding factor of the karstic evolution of karstic aquifers; variations in lithology, faults and fissures are only secondary in importance.

The direction of circulation modifies with the change in the aquifer water table. On a certain level of the underground layer water will follow a certain direction of flow. In karsts, however, when its level rises water may flow in other directions as well, according to the solution channels it intercepts.

Water circulation through karstic structures may be of several kinds:

— filtration seepage (predominantly in the upper zone of the aquifer);

- flow with free-surface ;
- hydraulic system under pressure ;
- combined flow (partially under pressure and partially with free surface).

Underground courses occurring in the aquifer zone obey to the hydraulic laws of the open channel flow. Groundwater flow in the waterlogged zone for the majority of the cases corresponds to flow in the pipes of systems under pressure.

The karstic springs that make the system outlet are supplied through a rapid circulation owing to the subterranean flow through the drains of the waterlogged karst, as well as through a slow circulation originating either in the drainage of karstic blocks of low permeability or in the deepest ascending channels.

The participation of each of the components of the discharge of the karstic emergence varies obviously from the hydrogeological conditions of a maximum flood wave to the severest low flow.

According to Blavoux (1980) during periods of floods the epikarstic aquifer concentrates the diffuse flow towards the vertical channels which collect part of the waters of swallow holes as of surface losses. A delayed infiltration from the epikarstic aquifer also occurs. The rapid flow continues through drains at the level of the waterlogged karst.

When flow occurs through fractures, bedding planes, joints and intergranular pores, it has a diffuse and laminar character and motion is slower than that of a surface stream with a similar gradient. In the case of laminar flow, flow rate is proportional to the hydraulic gradient, permeability and effective porosity and may have a value of only several centimeters per year (Stringfield and Le-Grand, 1969).

After analysing numerous karstic structures, Atkinson (1985) suggests a third category, namely circulation through karstic fissures, that is a reticulate network of joints and bedding planes roughly 10 cm wide, which were created through dissolution. The portional contribution of each type of flow to a given karst can only be estimated.

The classification proposed by Atkinson — and suggestively rendered in fig. 3 — undoubtedly corresponds to a reality frequently encountered in practice.

3. GROUNDWATER FLOW ANALYSIS IN HYDROKARSTIC SYSTEMS

In general, most methods adopted for estimating water supply may be useful in studies of the hydrology of carbonate terrains but no method is applicable to all conditions. Thus, for instance, Meinzer (1932) describes some methods that are applicable chiefly though not exclusively, to aquifers under water-table conditions and others applicable chiefly to artesian and non-artesian aquifers in which water moves at a considerable distance away from the inlet to the discharge areas.

The hydrological study of a karstic aquifer should mainly supply answers to the following questions (Stringfield and Le Grand, 1969; Burdon, 1967) ;

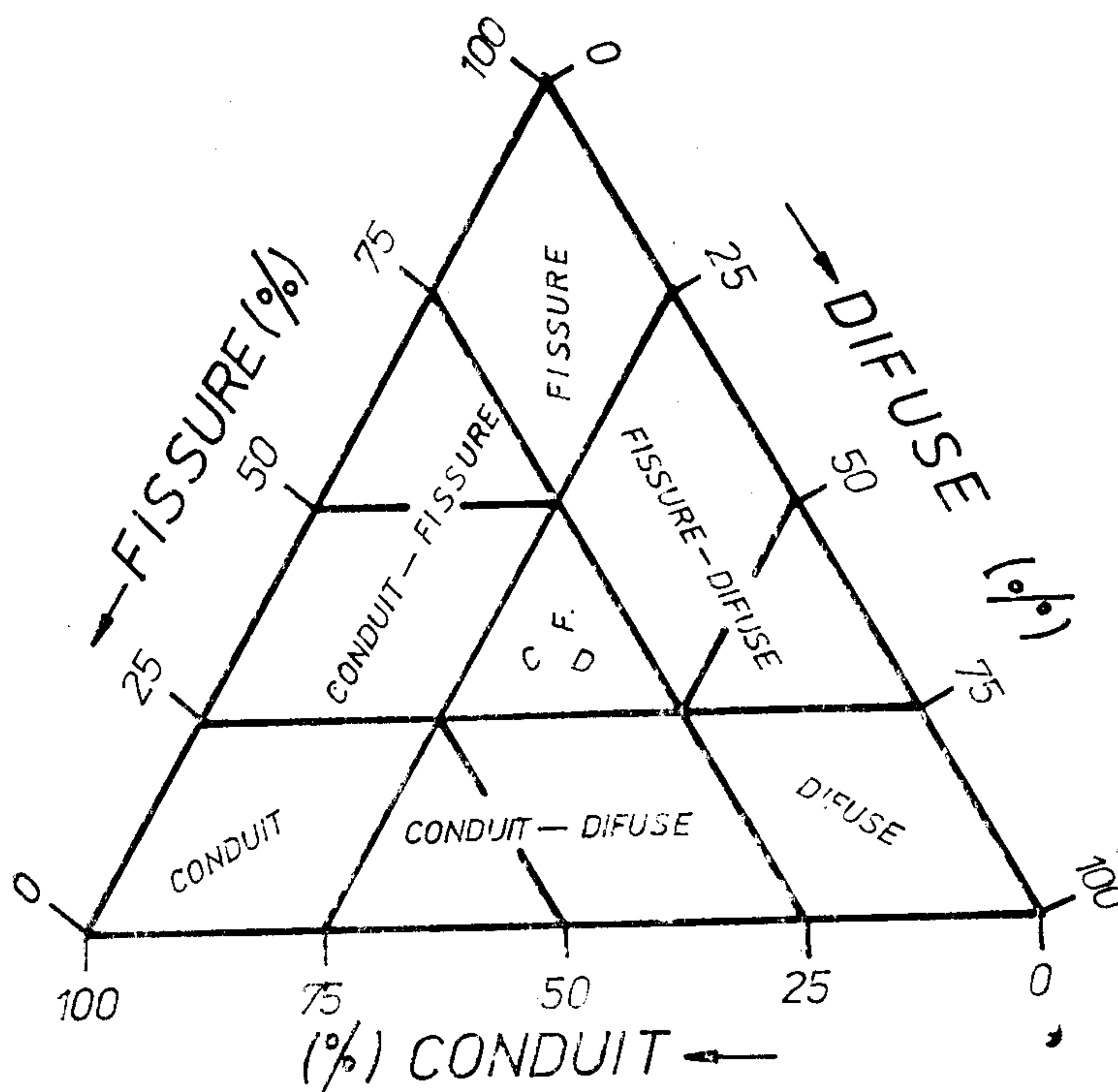


Fig. 3. Flow through a karstic aquifer. A classification proposed by Atkinson.

- the catchment area, the sources and the mode of recharge ;
- the origin of waters (meteoric, contribution by nonkarstic aquifers, contribution by surface or other sources ;
- the correlation between recharge and emergences ;
- the existence of an organized drainage, existence and functioning of the auxiliary systems ;
- the infiltration routes and their expansion ;
- water divide and diffuence areas ;
- water exchange in the underground, the nature of flow and the dispersivity of the aquifer ;
- the existence and location of underground basins, branches of the main stream, siphons, etc. ;
- the mean transit time, residence time distribution and water velocity ;
- estimation of groundwater reserves ;
- rainfall runoff analyses ;
- the behaviour of the system during flood and low-flow periods ;
- the evolution of the hydrokarstic system, phenomena of karstic piracy ;
- the quality of the water, the degree of pollution and pollution sources, the vulnerability of the karst ;

The contribution of (natural and artificial) traces in the resolution of these problems is of major importance. However, the tracer investigation of hydrokarstic systems and data interpretation are possible only within a thorough research conducted with the help of conventional methods, which include :

- the geologic, tectonic and micro-tectonic study of the area (fig. 4) ;
- the hydrogeological study of the area, caves, potholes, ponors and dolines included ;
- the characteristics of vegetation ;
- investigations through drillings and with the help of piezometers ;
- measurement of precipitations throughout a several-year cycle ;
- measurement of the discharges of insurgences, emergences and waterflows which pass through the area, in characteristic points ;
- measurement of seepage and of evapotranspiration with the help of lysimeters both in areas under vegetation and in barren zones ;
- variation in the temperature of springs ;
- evolution of minor and major ions ;
- measurement of the electrical conductivity of water ;
- variation in the concentration of environmental isotopes (D , ^{18}O , 3H , ^{14}C) in the cycle under study ;
- analysis of free and dissolved gases ;
- bacterial and microbial load, microfauna ;
- measurement of the natural radioactivity of waters.

The experimental method of investigation of hydrokarstic structures with the help of tracers consists of the stimulation of the system with an input signal and measurement of the output response. The input signal is the (natural or artificial) tracer and materializes in its mode of injection which can be accidental, random, continuous, discontinuous, in the form of pulse, step, or a combination of them.

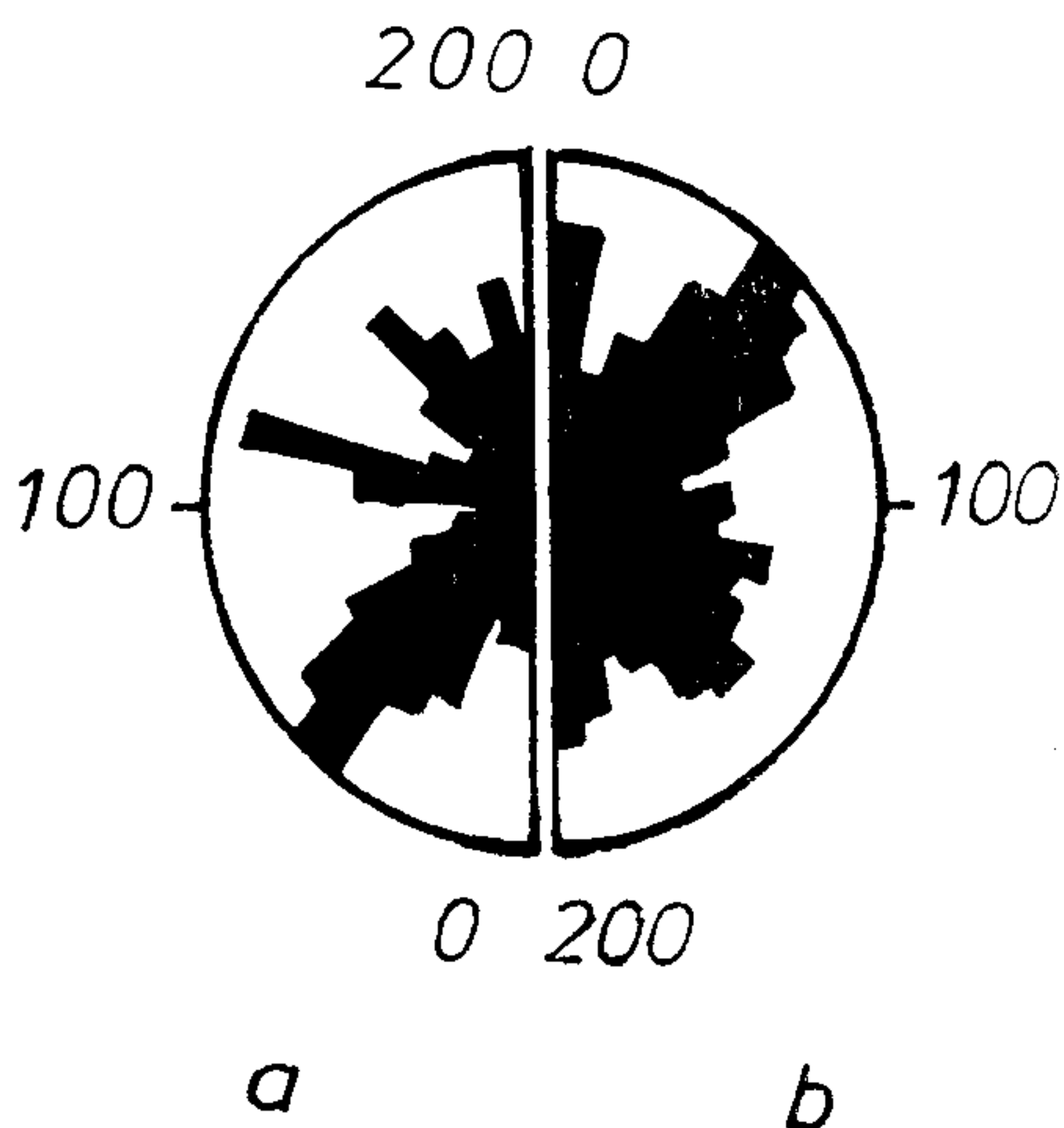


Fig. 4. Azimuthal distribution of cumulated lengths : a — fractural features (fault and overthrusts) ; b — exokarstic features (unsymetric sinkholes, sinkhole valleys, dry active valleys, krstic capture depressions)

4. TRACER METHOD TO INVESTIGATES HYDROKARSTIC SYSTEMS

The tracer method is a technique which furnishes information about a karstic system or some part of it through observation of the behaviour of a specific substance, the tracer, that has been added to the system. The tracer method usually presupposes the use of a tracer to label a specific phase or part the system, or make them easily identifiable.

There is no such thing as a perfect tracer. Thus, for instance, rhodamine WT, an excellent tracer in the study of the dynamics of karstic waters, cannot be used in the study of endokarstic condensing for the simple reason that fluorescent tracers cannot trace water during the evaporation-condensation process. However, the concept of an ideal tracer proves useful in the selection of artificial tracers, the search for environmental tracers and, more particularly, the development of mathematical models.

An usual classification of hydrological tracers includes natural and artificial tracers.

4.1. *NATURAL TRACERS*

Natural tracers are all the chemical or biological species, all the isotopes which can label water naturally. There is a great diversity of natural isotopes in the environment, which are also called environmental isotopes, and they label water in precipitations throughout the hydrological cycle.

4.1.1. CHEMICAL COMPOSITION OF WATER

Chemical analyses are important in understanding the rock-water interactions and thus evaluating the history of groundwater, although quantitative considerations like storage conditions and underground residence time must be backed up by hydrologic measurements and age determinations by radioisotope methods. Thermodynamic computations including saturation calculations and the calculation of the relation of the water to a specific gas phase (e.g. CO_2) are important tools for clarifying the complex reactions in natural aquifer systems (Goldbrunner and Leditzky, 1986).

The karstic aquifer is characterized by intimate relationships between its structure and functioning. Consequently, the chemical components of water may supply outstanding information on the origin of water, the probable nature of the terrains travelled by water and of the pollution between the inlet and outlet of the karstic area.

In a karstic zone, the content of dissolved ions in groundwater varies over a large range of concentrations and relative abundancies. Rainwater contains ions of dissolved sea-spray, dust and atmospheric gases, includ-

ing CO_2 . While passing through the soil water becomes enriched with biogenic CO_2 which enables it to decompose and dissolve carbonates such as limestone, chalk, dolomite, marl and also silicates, olivine, orthoclase, mica and clay minerals (Mazor, 1976, Coman, 1984). These decomposition processes take place in the soil horizon, through the unsaturated zone and finally in the aquifer. Similarly, halite, gypsum and other minerals are dissolved in various amounts. Exchange reactions with silicates and carbonates and to the colourful chemical compositions found in groundwater.

A primary step in a hydrological survey is, therefore, a chemical analysis of the dissolved ions. An essential analysis includes Ca^{++} , K^+ , Na^+ , Mg^{++} and Cl^- , SO_4^{--} , and HCO_3^- .

The chemical concentrations of karstic waters are subjected, in time and in the same phases, to a two-fold influence — one which is due to seasonal climatic rhythm and the other to flow rate variations at karst outlets. That is why, the study of seasonal and episodic chemical variation during and in-between various hydrological events is very important for understanding the characteristic elements of the karst under study.

The uniformity or complexity of a karstic aquifer may be traced by chemical analysis of several water sources geographically spread over a studied aquifer, by repeated seasonal sampling or by successive sampling during pumping tests (Bakalowicz, 1979; Miserez, 1976; Marin, 1984; Povară and Marin, 1984).

One of the most characteristic natural tracers of karstic waters is electrical conductivity. Bakalowicz (1974) studied the relationship between the electrical conductivity of a given water and its mineralization and came to the conclusion that a linear correlation exists between them. As each ion is involved in electrical conductivity owing to both its nature and concentration, the slope coefficient of the linear regression is characteristic of the association of ions in the waters of an emergence and provides for a geochemical definition of the aquifer under study.

Müller and Plancherel (1982) studied the distribution of the values of electrical conductivity of waters in various regions and noted that a relationship exists between water mineralization and the altitude of the respective regions: mineralization increases when the altitude of the area of supply decreases.

Comparisons between karstic waters in various regions show that whereas the absolute values of water mineralization are influenced by the altitude of the supply area, the variations round the average are due to flow conditions determined by the structure of the reservoirs. Consequently, water mineralization depends not only on altitude but also on permeability conditions and water residence time in the respective karstic formation.

The chemical constituents of water result from the rock-water interaction. That is why, in some cases the recharge areas of karst waters can be determined according to their chemical composition related to the drained rock type (e.g. dolomite, gypsum-magnesium, sulfate content) Zojer (1983).

Furthermore, under favourable circumstances, flow routes and interconnections may be established. Analysing the chemical composition of waters in shallow holes, drill holes and springs over a period of at least one year allows several analogies between the behaviour of certain ions or substances, the maximum and minimum of concentration being advanced or delayed in time according to hydrogeological conditions.

In this context, we should note that in ordinary chemical analyses a number of precious items of information may be overlooked. That is why, it is recommended that the water fingerprint should be determined with the help of activation analysis. The identification of traces of elements might allow for analogies between shallow holes and springs, and, therefore, prove aquiferous interconnections. In the case of certain karstic waters — highly mineralized ones in particular — or in case of geothermal waters, measurement of the natural radioactivity of waters may be relevant for their origin. The variation in radioactivity according to the special distribution of springs may supply data on the dynamics of the karstic waters in the area.

4.1.2. POLLUTION TRACERS

They are injected into groundwater by men, but not for the purpose of solving hydrogeological problems.

The study of the quality of the waters contained in karstic reservoirs may show the persistent character of certain pollutants. They may be found owing to the industrialization process undergone by the respective areas, the location of mining units, the chemicalization of agriculture, the operation of poultry rearing or animalbreeding complexes and urban developments. Pollution tracers are either injected by man in the underground or penetrate there in a natural way with the assistance of hydro-meteorological factors. Besides particular pollutants, specific to certain areas, nitrates or heavy metals, which are to be found in ever larger amounts in continental waters, may be used as tracers. Adding to all this is a whole range of substances which, as an outcome of civilian and military activities, were released in the atmosphere at a planetary level and in a relatively short period and also participate in the hydrological cycle (T, ^{14}C , freon⁻¹²).

4.1.3. ENVIRONMENTAL ISOTOPES IN THE STUDY OF REGIONAL GROUNDWATER FLOW

Environmental tracers are defined as isotopes or substances whose natural abundance variations may be used for hydrological studies. The environment contains a series of isotopes whose concentration varies according to the mode of production (either natural or artificial) and to environmental conditions which the investigator cannot control directly. These tracers label water naturally, tracing it throughout the hydro-meteorological cycle, in atmosphere, in precipitations, in surface and underground waters.

Ideally, some of the more significant environmental isotope ratios that may be used in groundwater studies include D/H, T/H, $^{14}\text{C}/^{12}\text{C}$,

$^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{234}\text{U}/^{238}\text{U}$, $^{32}\text{S}/^{34}\text{S}$ and $^{32}\text{Si}/^{28}\text{Si}$. In practice however, for karstic waters, use is confined to the stable isotopes of water, deuterium and oxygen-18, and the radioactive isotopes tritium and carbon (Wallick and Toth, 1976).

Under ideal conditions, a study of the space distribution of stable isotopes and tritium and radiocarbon in groundwaters from karstic zones yields the following information for the groundwater regime :

- Water age at any point ;
- Mean flow velocity and drainage directions ;
- Mean residence time of water within the i -th flow system ;
- Qualitative age of groundwater at a point a given flow system ;
- Spatial and temporal distribution of recharge events ;
- Spatial extent and order of flow systems ;
- Degree of homogeneity (i.e. mixing properties) within a flow system ;
- Stagnant zones ;
- Separation of flow components.

The first studies with the help of the environmental isotopes were conducted in Turkey, where the main water resources come from karstic reservoirs with major springs of up to $50 \text{ m}^3/\text{s}$ of discharge and benefitted from the advantage of maximum tritium concentrations in the atmosphere, which provided for a net differentiation between various water sources (Dincer and Payne, 1965 ; Yurtsever, 1979 ; Ozis and Yurtsever, 1982).

An exemple of the possibilities of the method is given by Fontes (1983) who made detailed studies of flood events in a karstic zone with the help of tritium and stable isotopes and established the following correlations :

- the isotope content of the flood discharge is independent of that of the rainfall causing it ;
- summer rainwater enriched with heavy isotopes accumulation in low altitude, isolated reservoirs available for storage ;
- heavy autumn rains remove summer waters as separate pulses corresponding to the discharge of isolated reservoirs ;
- when heavy rains fall during late autumn or winter, the reservoirs of the lowest part of the karst are homogeneously refilled with the water of the immediately preceding storm ;
- at the beginning of each flood, a small enrichment in heavy isotopes first reflects the discharge of waters stored at low altitude ; then, the isotope content decreases as the waters coming from higher altitude reach the outlet.

One of the largest karstic sources in the world, Fontaine de Vaucluse, was investigated with the help of environmental (and artificial tracers too) and its origin, recharge area and flow mechanisms were established (Evin et al. 1967 ; Flandrin and Paloc, 1969).

Association of other parameters of karstic waters (chemism, temperature, salt content, etc.) and the use of mathematical models to most faithfully fit experimental data will lead to a most veridical interpretation of the karstic phenomena under study (Bakalowicz et al. 1974, Blavoux et al., 1979, Siegenthaller et al., 1979). Thus for instance fig. 5 shown an

analogy of the variations in the deuterium content in time, as observed by Blaga (1979)¹ in three categories of waters the Șapte Izvoare Reci karstic springs and the Ghizela and Scorillo thermal drill holes, supplied from limestone (Băile Herculane area). These springs belong to a mixture of waters described by the relation :

$$\delta D = -6,971.54 d \quad (r = -0.997)$$

where d is the average density of the salt content. Subsequent determinations with artificial tritium and fluorescein attested to the existence of a common component which supplies the two types of waters.

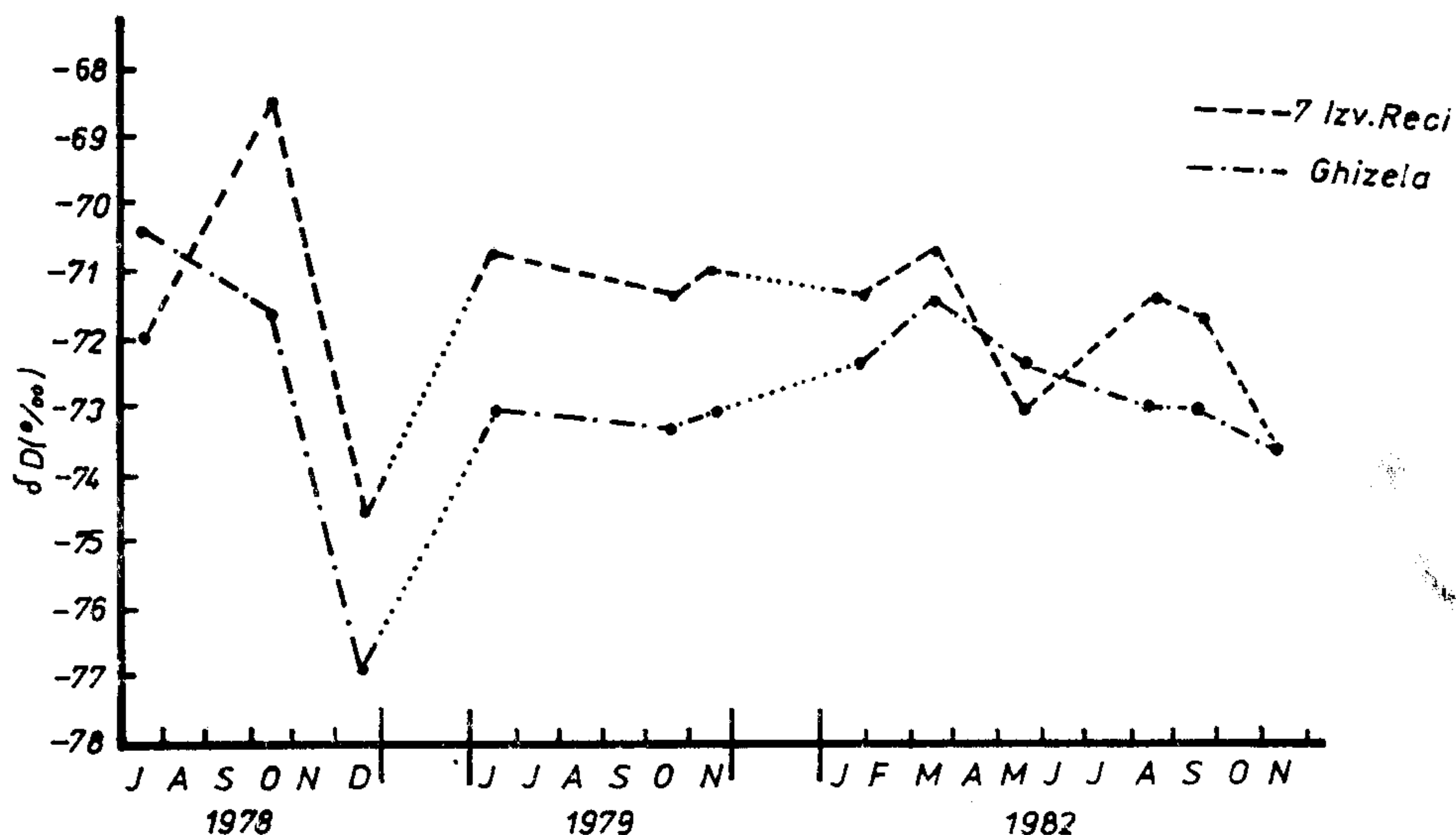


Fig. 5. δD -time variation for Ghizela and 7 Izvoare Reci sources. A good parallelism between their δD -time variations are shown, underlining meteoric characteristic of these waters.

4.1.4. PHYTO- AND ZOO-PLANKTON AND WATER MICROFAUNA

In certain conditions, phyto- and zoo-plankton and the live organisms that make up the microfauna of certain aqueous systems may be used as tracers. During floods, part of the microfauna which populates various karstic formations is carried by water, thus becoming a natural tracer.

In this respect, Moeschler et al. (1982) report that during a high-discharge event, the floating fauna (hydras, mollusca, crustaceans) was sampled using fine-meshed nets. A very good correlation was observed between biological and physical-chemical parameters yielding information on the discharge mechanisms.

4.2. ARTIFICIAL TRACERS

Artificial tracers are generally defined as those deliberately introduced into the hydrokarstic system to investigate groundwater flow.

¹ BLAGA L. (1979) — Private communication.

An usual classification of these tracers proceeds according to the methods of detection employed. Thus, radioactive tracers (as well as activable tracers after activation) are detected and measured according to their radiation. When a tracer is detected and measured through the optical analysis of fluorescence (through *spectrofluorometry*, for instance), then we have to deal with fluorescent dye tracers.

Furthermore, the chemical composition of tracers is a basis of classification: *chemical* and *saline tracers*, *dyes*, *epilamens*.

According to their nature, tracers may also be *biological tracers* live beings (bacteria) or dead beings (spores, plants, etc.).

All hydrological tracers may be used in investigations of karstic waters. They can be selected according to the following requirements:

- they should be *conservative*, therefore stable in time, and should not deteriorate at contact with the investigated medium (water, air, rocks);
- they should be easily detectable and measurable in high dilutions;
- they should not change the hydraulic conditions of the traced water;
- they should provide for an analysis of the distribution of residence times;
- they should not cause pollution of karstic waters of the springs beyond permissible standards in force;
- they should not be toxic to either the population or the fauna of the karst;
- they should not lead to the emergence of toxic or carcinogenic by-products following physical or chemical degradation;
- they should be readily soluble in water;
- they should be available on the market and inexpensive.

Naturally, not all tracers meet all these requirements.

The following tracers, however, have broad applications and, consequently, they are listed according to the methods employed for their detection and measurement, namely: chemical tracers, fluorescent dye tracers, radioactive and activable tracers, spores, bacteriophages, etc.

4.2.1. CHEMICAL TRACERS

This category of tracers offers a wide range of possibilities, for which reason they have been extensively used in hydrology. As chemical substances may be measured according to various techniques — conductometry, chemical analysis, colourimetry, fluorometry, radiometry, activation analysis, laser analysis, olfactometry, a.o. — measurement methods are a criterion of tracer classification. On the other hand, some tracers are so important in hydrology that they make up a special category: fluorescent dye tracers, radioactive tracers, activable tracers.

The other chemical tracers, though still used in practice, have a lesser importance owing to:

- the relative high cost of laboratory detection and measurement tests;
- difficulties in finding substitutes or compounds that can be detected in concentrations comparable with those of fluorescent dye tracers or radioactive tracers;

- natural or artificial occurrence in surface and underground waters in high concentrations, which limits the sensitivity of analytical methods;
- non-conservative behaviour in the traced medium;
- pollution of the karstic system;
- toxicity for men or live beings from karst;
- changes in the original hydraulic conditions, owing to the injection of substantial amounts of tracers as a direct result of high detection limits.

a) Sodium chloride (NaCl)

It is the cheapest of all tracers. Its solubility in 15°C water is of 360 g/l. The minimal detectable concentration is of $5 \cdot 10^{-8}$ g/ml by measuring the Cl^- ions content in conditions of a small natural *background*. This tracer can be analysed through either chemical titration or conductimetry. Water conductivity, however, varies with temperature ± 2 —3 per cent for each degree centigrade so that for an accurate measurement (error ± 1 per cent) the difference in the temperature of two samples included in a chain of measurements must not exceed $\pm 0.1^\circ\text{C}$. Mention should be made that for a conductivity of natural waters of 1,000 M/cm the minimal concentration that can be measured is 10^{-5} g/ml and 10^{-6} g/ml when conductivity stands at 100 MΩ cm. On the other hand, natural variations in conductivity prejudice the accuracy of measurements because of their frequency and amplitude. Nevertheless, NaCl has proved succesful in investigation of hydrokarstic structures (Gaspar et al., 1984). In such cases, however, when short water courses or *swallow holes* are labelled — which call for large amounts of tracer — labelling cannot be achieved through impoules but through constants-discharge injection. Figure 6 gives comparative diagrams showing the variation of Cl^- , Rhodamine B and ^{131}I used as tracers to investigate the Cioroaiete Tîrcului cave.

b) Sodium dichomate ($\text{Na}_2\text{Cr}_2\text{O}_7$)

It is one of the tracers most commonly used to measure flow rates in rivers. Its main advantages are low cost, minimum measurable concentration of 10^{-6} g/ml directly on samples, and 10^{-8} g/ml after re-concentration, with an accuracy of ± 3 per cent. The analysis is conducted through colourimetry (Molinari, 1969). Karstic water dynamics in Toplița brook (Pădurea Craiului Mountains) was studied by us with sodium dichromate and the transfer curve obtained is given in fig. 7.

c) Sodium iodide (NaI).

It is readily soluble in water and little retained by the medium travelled. To detect and measure it, the catalytic microdosage is employed through the kinetic method with the help of an analyser. Concentrations of 10^{-9} g/ml can be measured with an error of ± 15 per cent. The *minimal detectable concentration* may be lowered to $2 \cdot 10^{-10} \pm 50$ per cent g/ml, but the limit of the method, in terms of metrology, coincides with the limit of the natural iodine content of the measured waters which, with rare exceptions, does not exceed 10^{-9} g/ml.

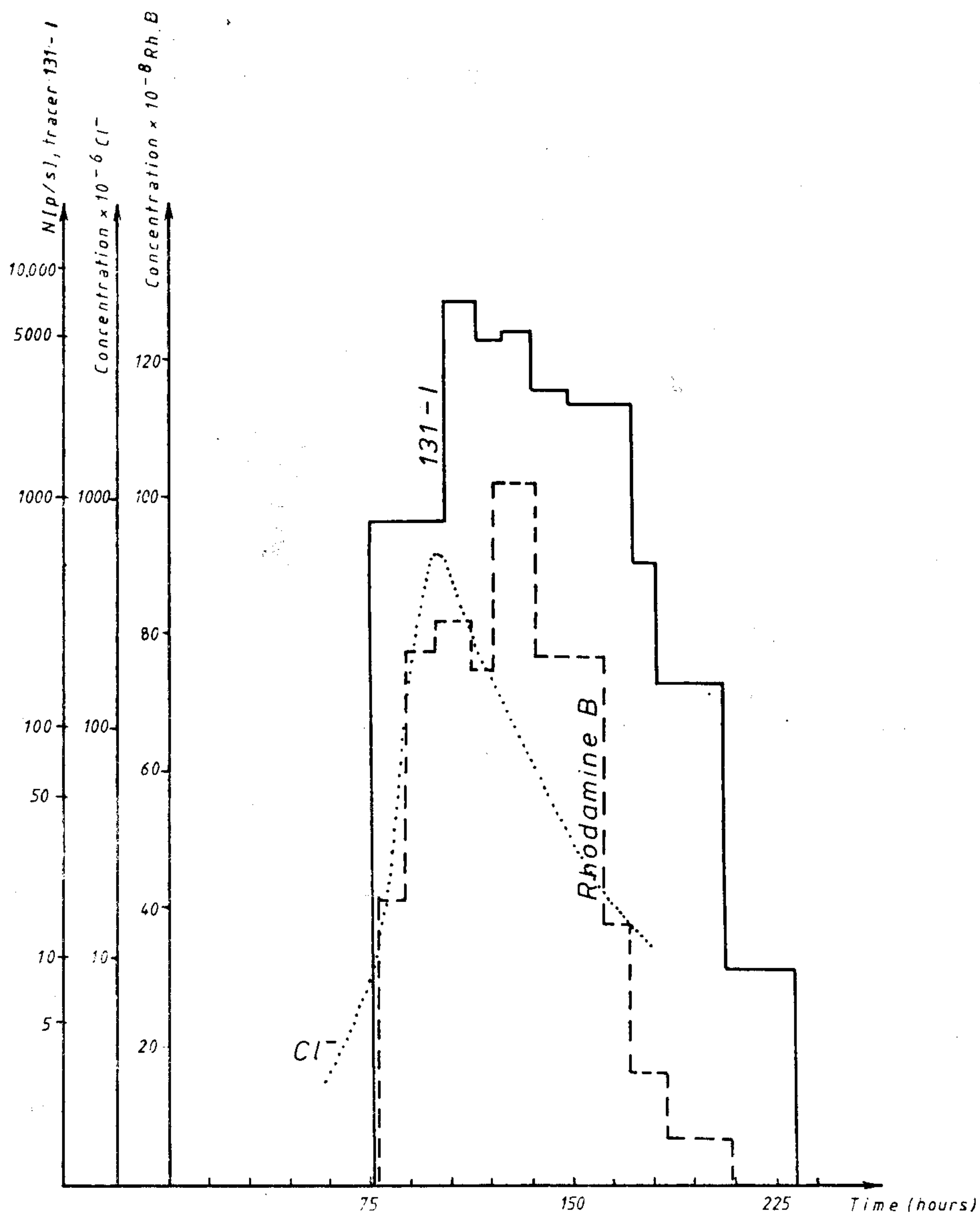


Fig. 6. Three simultaneous labellings using chemical, fluorescent and radioactive tracers. Comparative diagrams.

4.2.2. FLUORESCENT DYE TRACERS

All the fluorescent dye tracers used in hydrology and hydrogeology are organic substances; most of them belong to the family of dyes deriving from xanthene.

The tracer properties are based on the chemical structure of special compounds consisting of the frequently occurring elements: C, H, O, N,

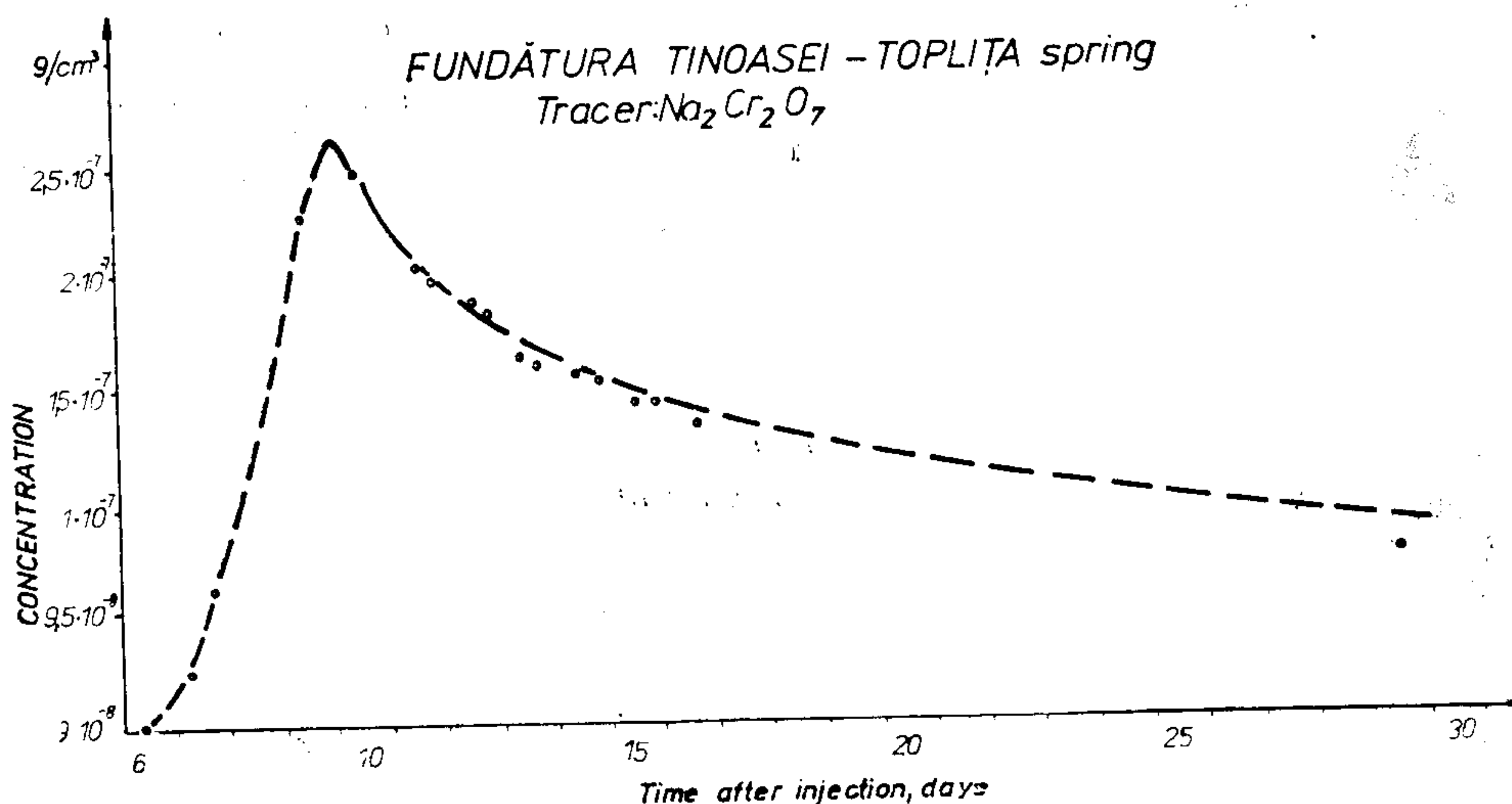


Fig. 7. The behaviour of sodium dichromate used to trace karstic water dynamics.

and S. The tracer properties can be severely changed or completely lost when the chemical structure of the dye molecules is changed or destroyed through chemical or other attacks.

Fluorescent dye tracers boast a remarkable property — they can be detected and measured *in situ* in small concentrations of 10^{-10} — 10^{-11} and, in some cases, even of 10^{-12} g/ml. Other advantages of fluorescent dye tracers: they are relatively cheap and not toxic, they are not mutagenic and they are fit for labelling.

a. *Uranine* $\text{C}_{20}\text{H}_{10}\text{O}_5\text{Na}_2$: It is the oldest fluorescent dye tracer used in hydrology. In point of ionic form, it is an anion with the molecular weight of 376.15. Its structural formula is given in fig. 8. It is less soluble in water: 25 g/l, but it dissolves well in water and ethanol: 300 g/l, or in water-and ammonia solution.

The minimum detectable concentration in the case of both uranine and the other tracers is obviously dependent on both the measuring device and the measurement method employed. In the case of uranine, it currently varies from 10^{-11} to $2 \cdot 10^{-12}$ g/ml. (Feuerstein and Selleck, 1963; Behrens et al. 1976). Maximum excitation wave length is 431 nm and maximum emission is 512.5 nm.

b. *Rhodamine B* ($\text{C}_{28}\text{H}_{31}\text{O}_3\text{N}_2\text{Cl}$) has been extensively used as a tracer, especially after proving successful in tracings to simulate or label pollutants in open sea. It appears in cationic form with a molecular weight of 479.02 and its structural formula is given in fig. 9. Though an organic dye which is strong and stains any material it comes into contact with, it is less soluble in water: 20 g/l. In acetone it dissolves 95 g/l, in acetic acid — 300—400 g/l and in methanol 100 per cent — 800 g/l. The minimum detectable concentration in the presence of the background, at 20°C , and measured on 5 ml samples, is of 2.1×10^{-11} g/ml. Maximum excitation wave length is 553.5 nm and maximum emission is 512.5 nm.

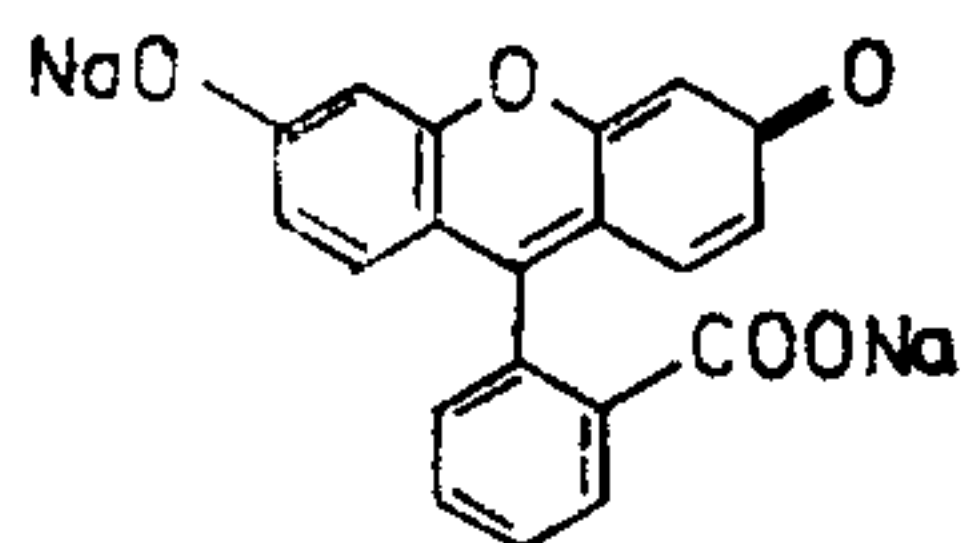
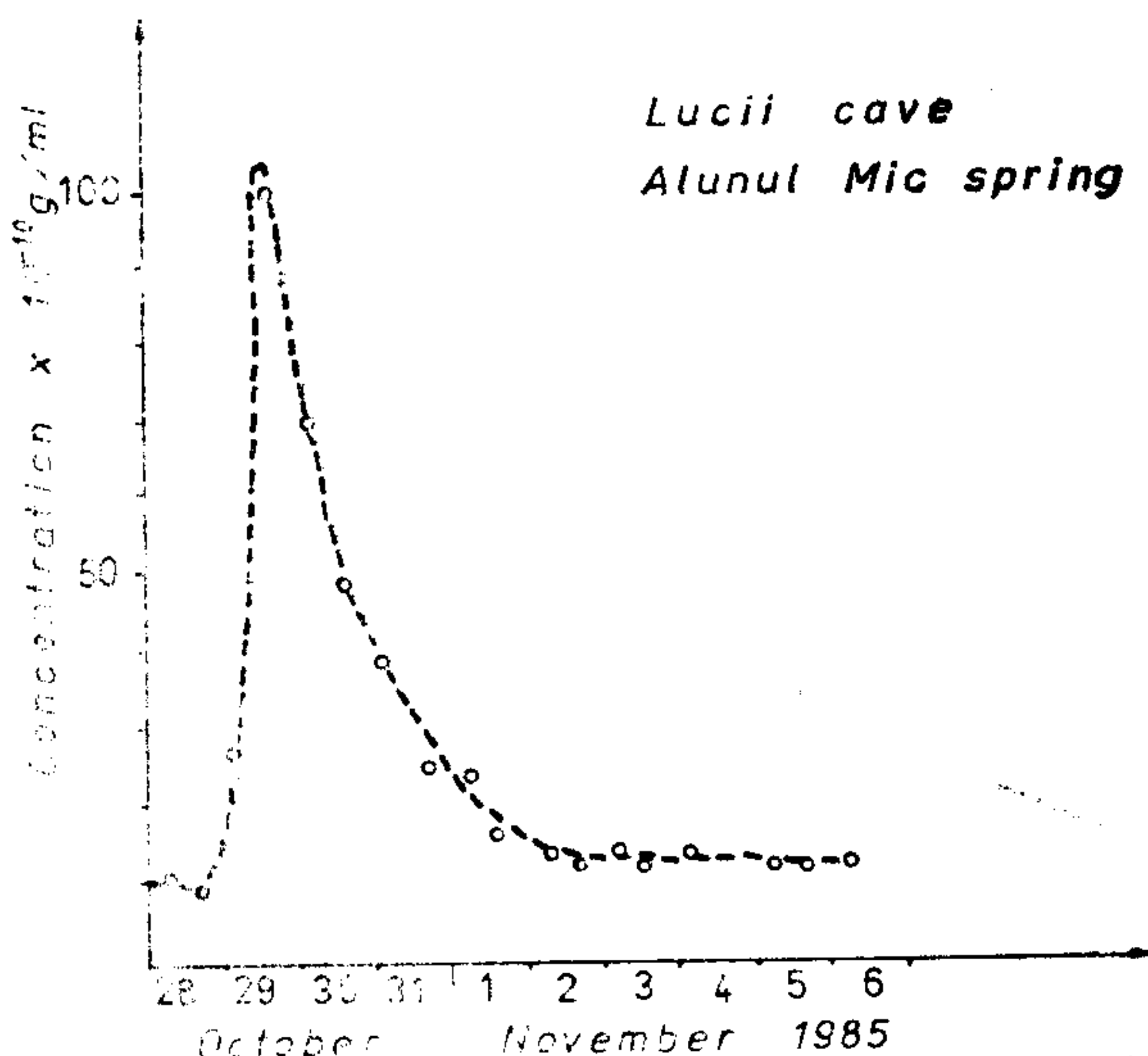


Fig. 8. Transfer curve of uranine in the Luncii cave experiment. The structural formula of uranine (up).

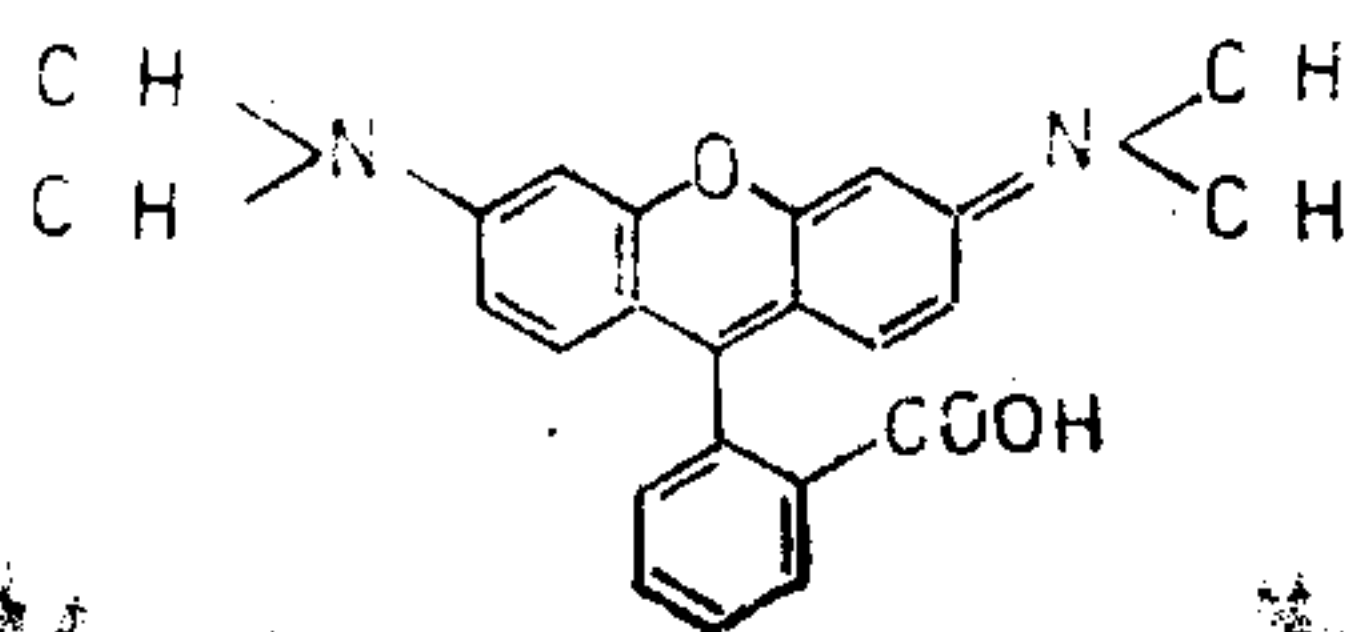


c. *Rhodamine Wt* $C_{29}H_{29}O_5N_3Na_2Cl$. The structural formula of rhodamine Wt is given in fig. 10. It has a molecular weight of 566.5 and appears in anionic form. Its minimal detectable concentration ranges from $5 \cdot 10^{-11}$ to $1 \cdot 10^{-11}$, though possibilities exist to improve detection sensitivity. Apparently, it is the fluorescent dye tracer boasting most qualities (Laurent and Gibert, 1981).

d. *Other fluorescent dye tracers*. Noteworthy in the large family of rhodamines are other components used as hydrological tracers such as sulforhodamine B and sulforhodamine G, rhodamine 6G, amidorhodamine G. The minimum detectable concentrations in the case of these substances vary with the device and methods employed. There is a limit of 10^{-10} — 10^{-11} g/ml for amidorhodamine B and of $2 \cdot 10^{-11}$ — $5 \cdot 10^{-12}$ g/ml for amidorhodamine G extra.

Other xanthene dye type used for karstic waters is eosine or tetrabromofluorescein ($C_{20}H_6Br_4O_5Na_2$). It is readily soluble in water and ethanol, in various proportions, according to the purity of the product. Minimum detectable concentration is 10^{-9} g/ml.

Other hydrological fluorescent tracers are amidoflavine, brillantsulfoflavine (stilbene derivative), lissamine (aminoketone dye type), pyranine (pyrene dye type), a.o., but they are used on a smaller scale. The minimum detectable concentration is roughly of 10^{-6} g/ml for amidoflavine and 10^{-9} g/ml for pyranine.



Coiba Mică cave
Tăuz spring

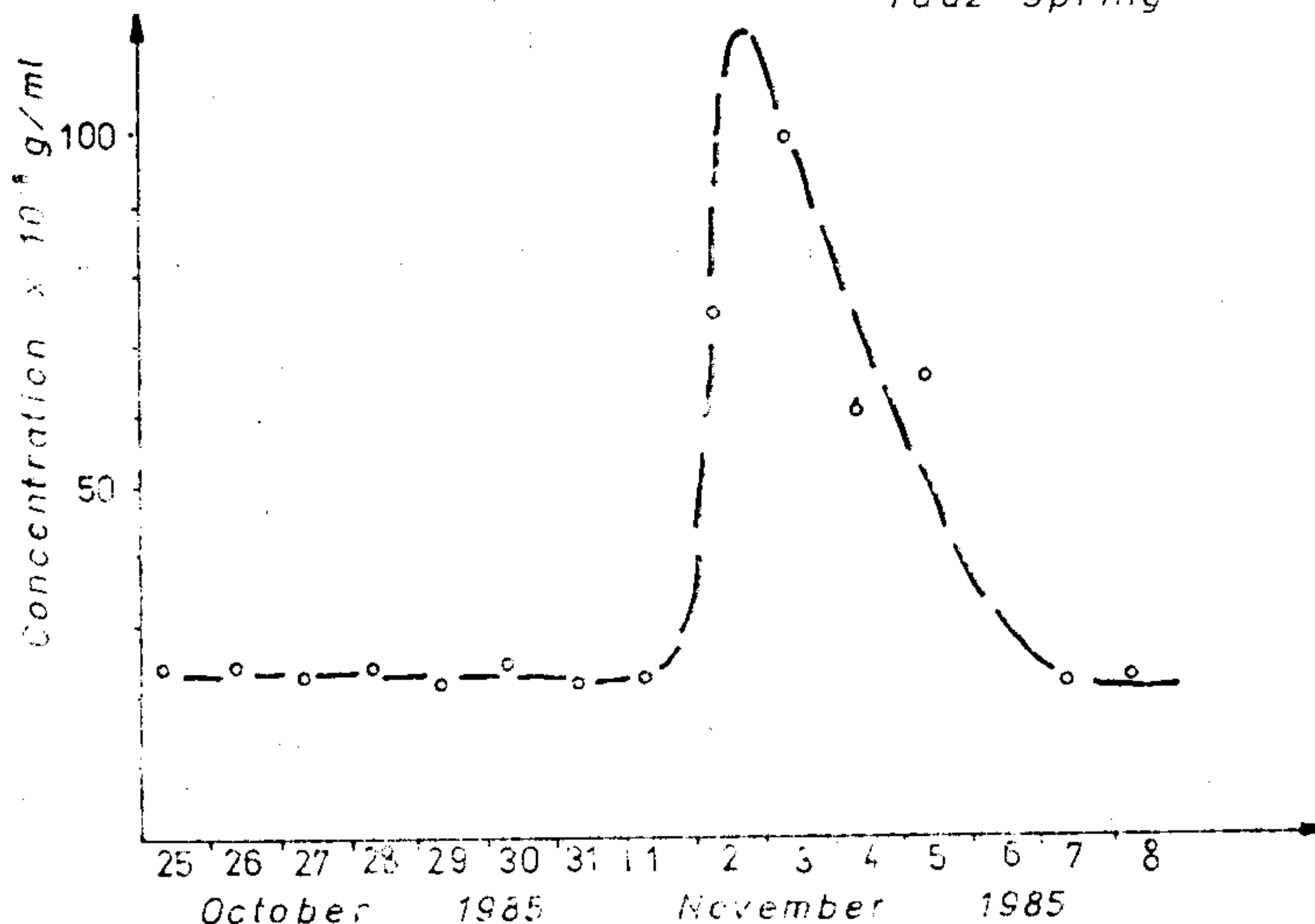


Fig. 9. The chemical formula and concentration-time variation of rhodamine B in the Tăuz experiment.

e. *Optical brighteners*. There is a number of optical agents which are used in industry to bleach paper, textile fibres, etc. Noteworthy among the tracers employed are : photine CV, fluolite BW, leucophor BS, leucophor C, chalcofluor white ST, tinopal ABP, tinoual CBS-X, stralex. They are colourless in aqueous solution.

The detector for collection of samples is cotton (which may be detected with the help of passive detectors made of cotton wool and packed in muslin-cotton bags). At present, the minimum detectable concentration is 10^{-10} g/ml and possibilities exist to further lower it through chemical treatment of the samples. Thus, for instance if the water sample

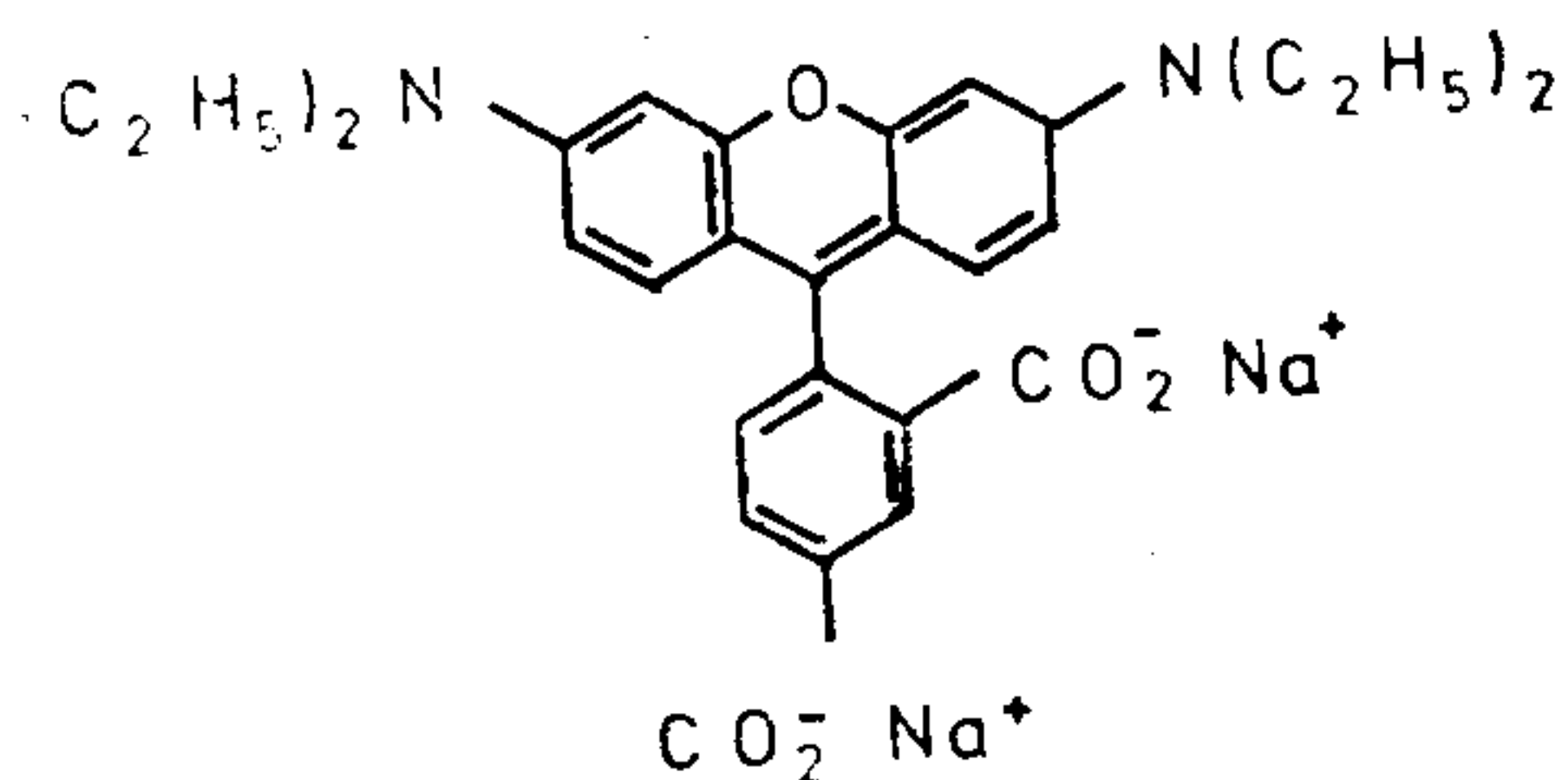


Fig. 10. The structural formula of rhodamine Wt.

that contains the tracer is diluted with glycerol (fig. 11) in a proportion of 1 : 1, the fluorescence of tinopal increases 60 times (Schumacher, 1982). Using water samples and spectrofluorometric analysis, the detection limit may be lowered to 10^{-12} g/ml, in the case of pure waters, naturally. Unlike the other fluorescent dye tracers, the background of bleaching optical agents in surface and underground waters has been growing continuously owing to industrial pollution.

f. *Detection and measurement of fluorescent tracers.* Fluorescent dye tracers are still very sensitive and the least expensive tracers to observe underground waters in karstic terrains. The simultaneous application of various fluorescent dye tracers nearly always causes considerable analytical problems. The selective detection of individual fluorescent dye tracers in mixtures of several dyes is limited by the overlap of the spectra. Therefore additional separation steps must be introduced into the analytic procedure.

In high concentrations, all the fluorescent dyes are visible to the naked eye, separately. Various methods are employed to measure eye in concentration of 10^{-7} g/ml; with the help of a fluoroscope, it can samples. Thus, for instance, fluorescein (uranine) is visible to the naked be detected in concentrations of 10^{-8} g/ml; through fluorometry, the detection limit may be lowered to 10^{-10} , while through *spectrophotometry*, it drops below 10^{-11} . This sensitivity, however, may be attained in cases of independent occurrence of singular tracer in pure, natural waters where no other tracers can influence the spectrofluorometric assessment (Bauer et al., 1976).

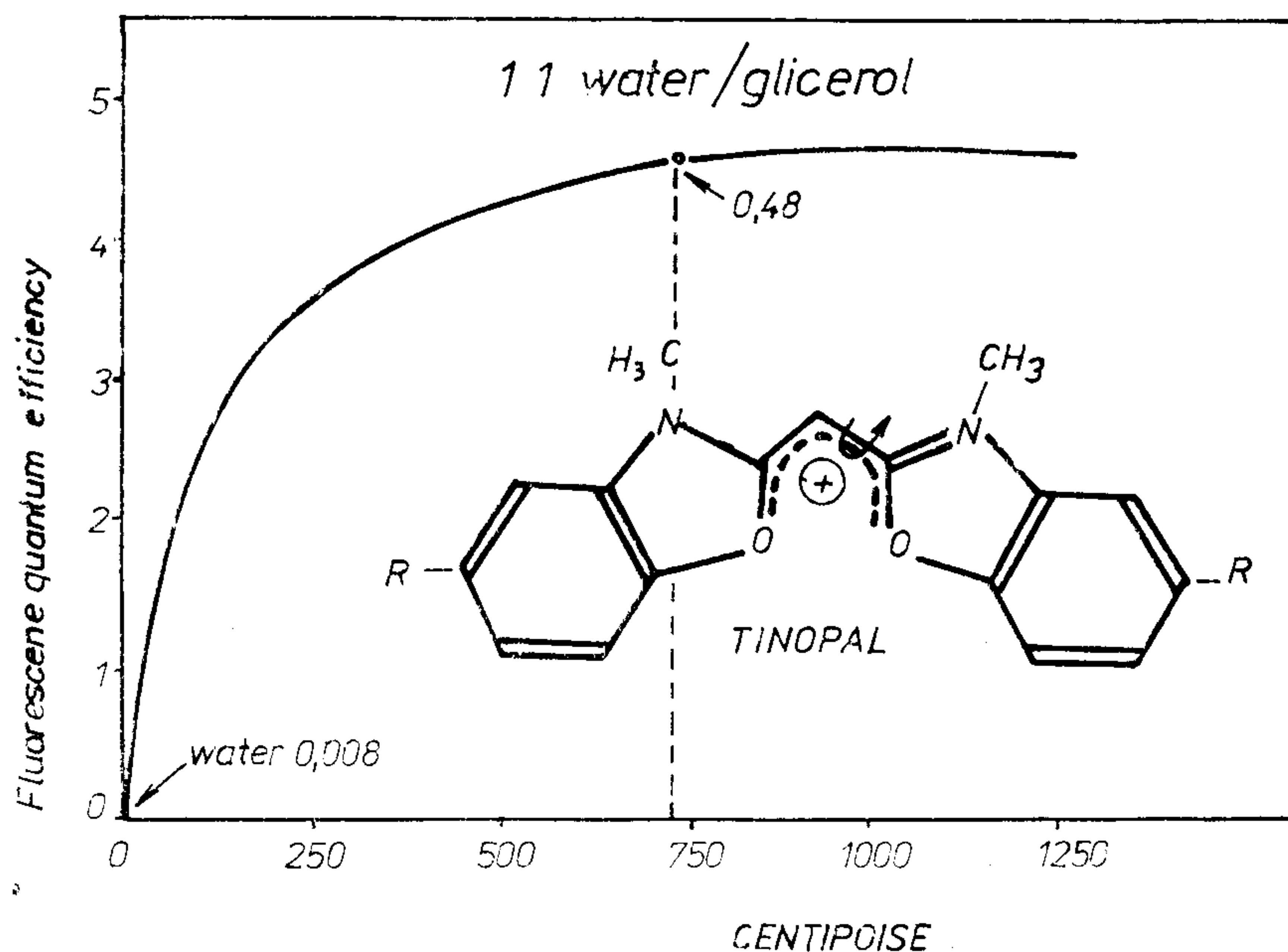


Fig. 11. Fluorescence quantum efficiency of Tinopal as a function of glycerol concentration in water. Structural formula of a tinopal-type fluorescer (Schumacher, 1982).

The relationship between the intensity of fluorescence radiation and the concentration of a fluorescent dye tracer is not rigorously the same for all tracers but it may be considered linear when first assessed. For precision measurements, the device should be standardized for all instrument ranges and recently prepared solutions, in known concentrations, should be used. These solutions alter rapidly and stable, quinine-based samples are needed for a subsequent verification of the installation.

Following the simultaneous use of several tracers, which was largely dictated by hydrological reasons (e.g. operations of multiple tracing in karsts), the question of spectral separation of dyes featuring fluorescence has been given special attention in the last few years (Behrens, 1983; Ackermann et al., 1982). With a view to measuring various tracers in the same water sample, optical and ion exchange methods, as well as thin-layer chromatography have been developed. In order to increase detection sensitivity, the fluorescent components found in water are separated and concentrated on *active coal*.

Analysing the spectral data of fluorescent dye tracers, one may note that there are tracers that can be detected and measured in fine mixtures, without mutual interference. This is the case of uranine and rhodamine, irrespective of their concentration. Likewise, tinopal can be determined independently in the presence of other fluorescent dyes because its fluorescence maximum occurs in the ultraviolet region of the spectrum. Moreover, it does not influence the assessment of any other fluorescent dye. However, the optical brightener tinopal CBS-X is disturbed by the fluorescence of organic matters in natural waters.

Relatively small disturbances occur in the following combinations of dyes: uranine-amidorhodamine G and eosine-rhodamine B; stronger mutual interference can be found in mixtures of uranine-eosine and amidorhodamine G-rhodamine B.

Recent research shows that the fluorescent dye tracers in a mixture can be measured individually through the guided application of pH modification, of adsorption agents and the influence of light on the solution containing the respective mixture.

Spectral analysis — in the position of both emission and excitation spectra — also supplies qualitative information, while the intensities of the spectra provide quantitative information concerning the tracers that are being measured.

Thus, in the case of two spectrally close tracers, such as rhodamine B and amidorhodamine G, superpositions occur: a correction calculus for absorption spectra establishes the proportions of the tracers in the respective mixture (Käss, 1976).

The method may be correspondingly applied to mixtures of several dye tracers. Errors of measurement, however, increase as the number of components rises. In the case of mixtures of spectrally extremely close fluorescent dye tracers (e.g. fluorescein-eosine or eosine-amidorhodamine G), an irreproachable analysis can be made only by resorting to a separation method (Käss, 1982).

4.2.3. RADIOACTIVE TRACERS

They proved superior to non-radioactive tracers whenever the latter were unsatisfactory from technological or economic point of view. The choice of suitable characteristics of radioactive emissions will be influenced by a number of factors including the duration of the test, the logistics of tracer supply, radioprotection requirements for the tracer prior to injection and the location and method of measurement.

Considered as an ideal tracer for water, tritium emits low-energy beta particles (0.018 MeV) and can be easily transported and handled without radiation hazards. First karst labelled using tritium as a tracer was performed by Burdon et al., 1963 in Greece. However, a major disadvantage in its use in field studies is the inability to measure very low concentrations in the field. Samples have to be taken to the laboratory for measurement by liquid scintillation or gas-counting methods.

Radioactive tracers having penetrating gamma rays allow measurement of samples of large volumes with a correspondingly high detection sensitivity. Also, for multitracings in karst, the simultaneous detection of several different tracers may be achieved by gamma-ray spectrometry. So, in a multitracing performed in Vașcău Plateau, two radioactive tracers, Iodine-131 and Bromine-82 appeared simultaneously in Boiu spring and were measured independently (fig. 12 and 13).

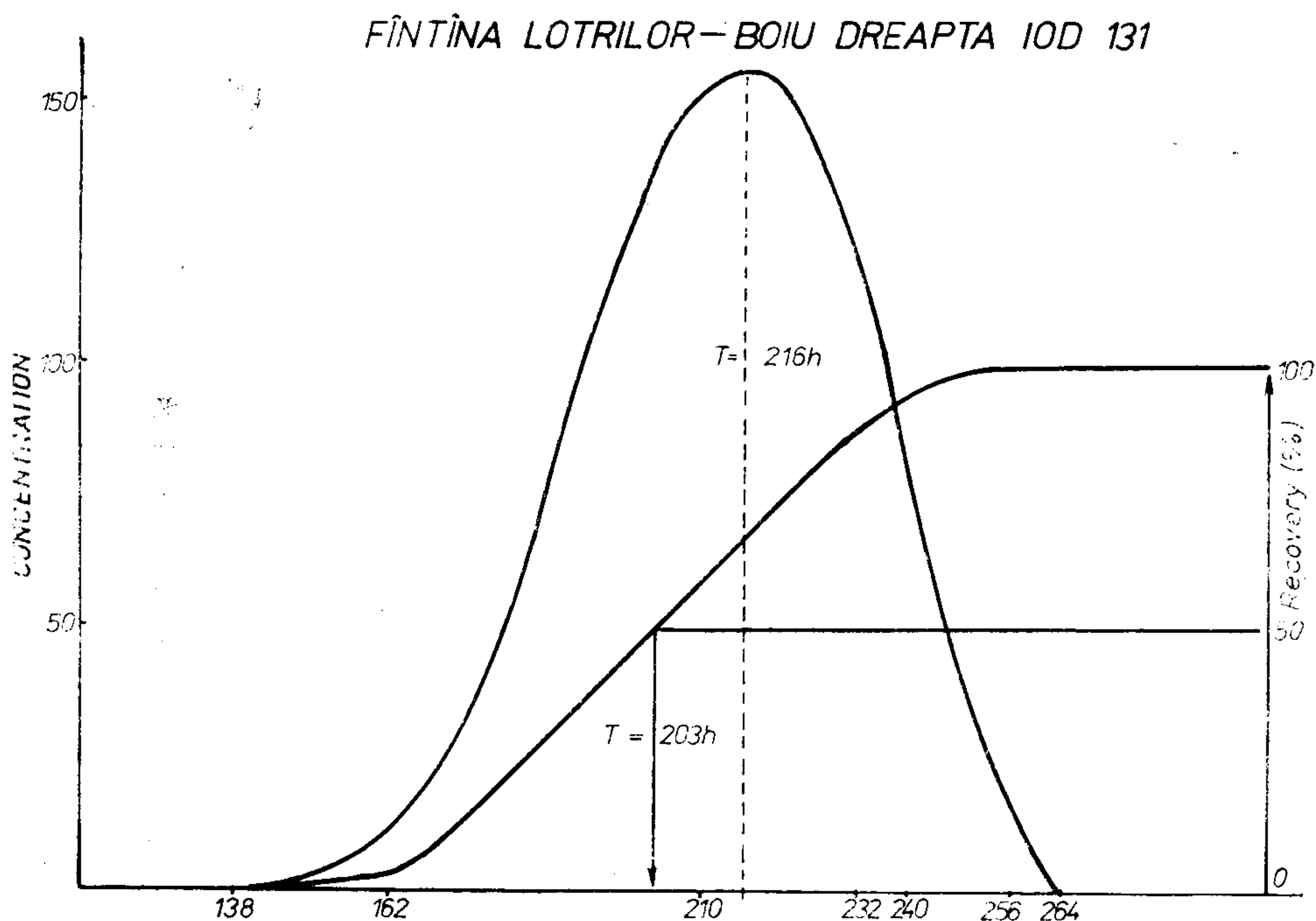


Fig. 12. Concentration-time variation of ^{131}I used as a tracer in karstic zone of Vașcău Plateau.

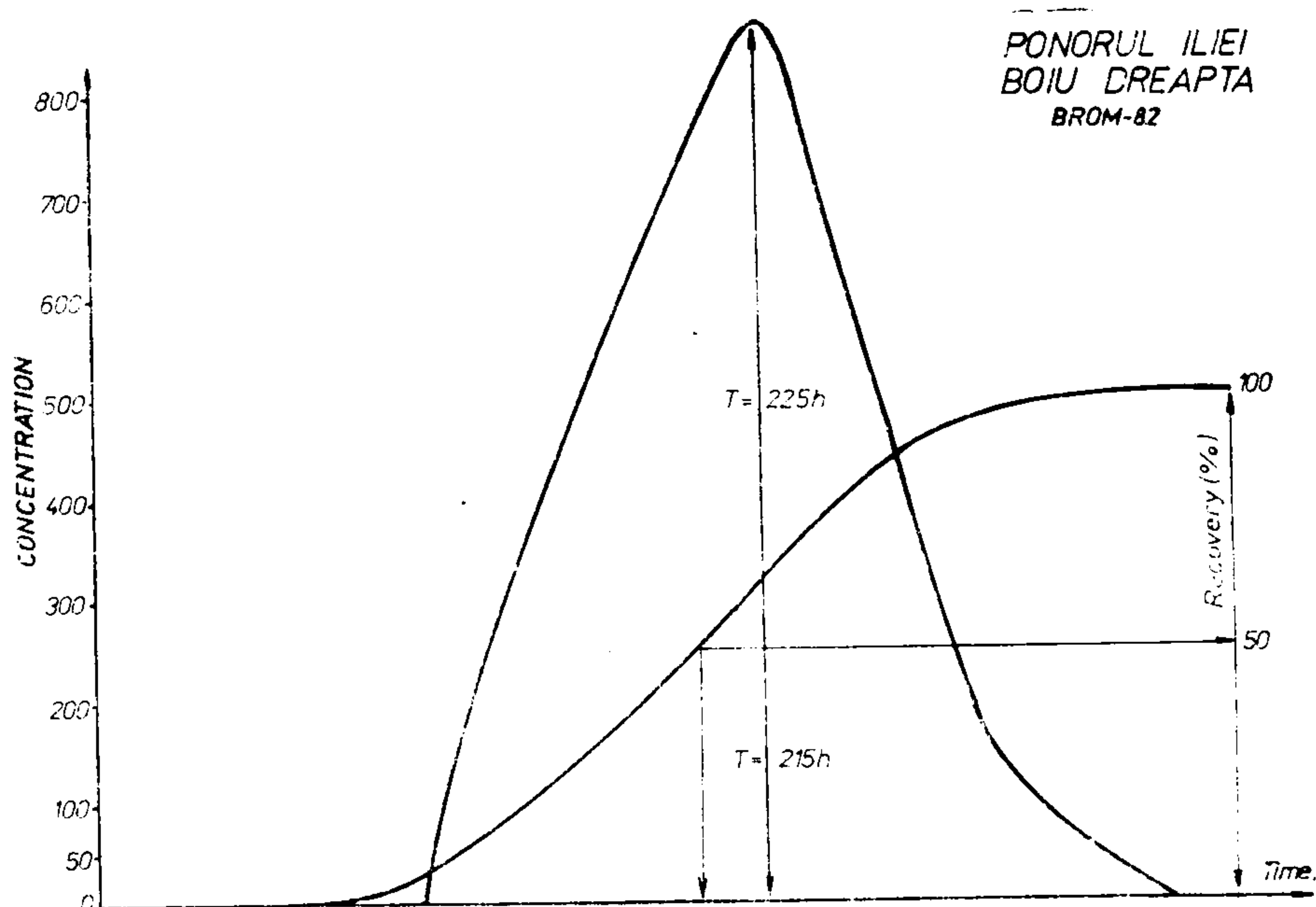


Fig. 13. Multitracing experiment in Vașcău Plateau. A diagram representing the variation in time of the concentration of ^{82}Br used as a tracer to label the Ilii sinkhole. The tracer was concentrated on an ion exchanger, Vionit AT-1.

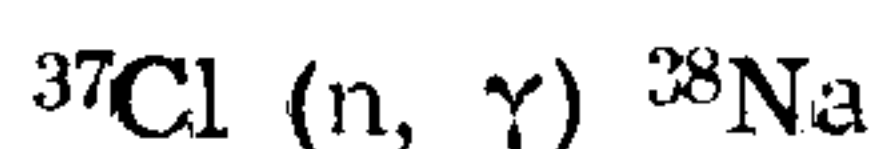
As possible radioactive tracers for ground water field experiment and for hydrokarstic structures in particular we agree to ^{82}Br , ^{131}I and ^{51}Cr -EDTA only.

4.24. ACTIVABLE TRACERS

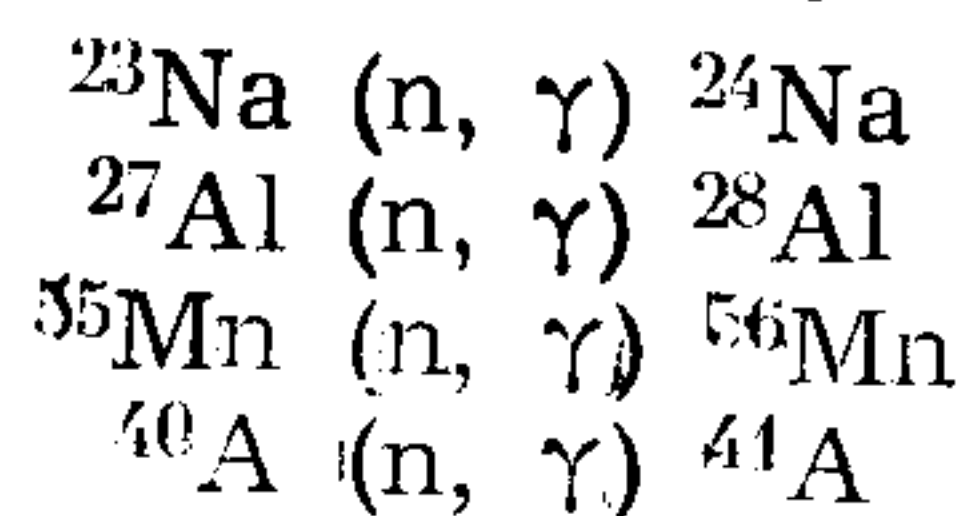
The problem of half-life in the use of radioactive tracers for investigation of hydrokarstic structures can, in principle, be avoided if inactive nuclides are used as tracers and the samples activated for analysis of the resulting radioactivity. The activation analysis is easily performed but it requires a strong neutron source (e.g. a nuclear reactor) and adequate detection equipment (a spectrometer). The atoms of most elements give rise by irradiation to radioactive species of the same elements. The elements can be identified by determining the radioactive properties of the respective radioactive nuclides produced, the activity obtained being a measure of their concentration in the water. During water activation analysis, some typical nuclear reactions due to elements contained by the salts usually solved in water, are produced. In the case of ^{37}Cl — an element usually contained by water — the typical reaction is :



or



Other typical reactions for water activation analysis are :



Obviously, other reactions are possible but they are not important in the following discussion.

A certain radioactive isotope is identified by its characteristics : type and energy of the emitted radiations and half-life. The half-life can be determined by measuring the counting rate for beta and gamma-radiations. The beta radiation energy can be determined by adsorbition and the gamma ray energy by spectrometry. The characteristics of the typical isotopes resulting from thermal neutron water irradiation are given in tables.

The neutron activation analysis may become a quantitative one because the total activity of a certain radioactive isotope from an irradiated sample is a quantitative measure of the stable element it comes from. However, the quantitative relationships depend on many factors. The induced radioactivity of the water samples is proportional to the concentration of the stable element it comes from, to the activation probability of the element and to the intensity of the thermal neutron flux. The induced activity depends also on the relative abundance of the stable isotopes of the element.

Chemical elements in this group of tracers must be present only in negligible quantities in the hydrological system under investigation to eliminate significant background. In this respect it must also be ensured that the radionuclide selected for detection cannot be formed from any element other than the actual tracer element. As an example, lanthanum used as an activation-analysis tracer is detected by activation as ^{140}La . When samples are irradiated with neutrons, however, ^{140}La is also formed by nuclear fission from the traces of uranium that are contained in most waters.

Thus, simple anions have been applied as activable tracers, whereas cations are not suitable because of their retention by ionic exchange. Of special importance are the anionic complexes of several metals ; as chelating agents, EDTA, DTPA or DCTA have been used.

In actual practice, irradiation (e.g. in a nuclear reactor) is usually preceded by separation of the substances contained in the water, for example by evaporation, precipitation ion exchange. Following irradiation, radiochemical separation may be necessary to remove interfering radionuclides formed from the main substances contained in the water sample.

High-resolution gamma spectrometry with Ge(Li) detectors has greatly improved the detection of activable tracers. It permits the necessary chemical separation procedures to be reduced to a minimum. *a. Bromine* is commonly used as activation analysis tracer because of its favourable tracer characteristic. Background values must be checked and a sufficiently high activation dose selected to guarantee measured tracer values that are clearly above background. This tracer is chemically stable in groundwater and sample solutions. The minimum detectable concentration of bromine is below 10^{-9} g/l.

b. Iodine is used as a rule in the form of NaI or KI. I^- may be dosed by activation analysis. Iodine-128 thus produced has a half-life of 25 minutes. In the absence of background, the minimum detectable concentration is 10^{-10} g/ml. This tracer was used to label the Albioara ponor (Pădurea Craiului Mountains — Romania), Fântina lui Ghiță (Vașcău Plateau) and Izoi ponor (Codru-Moma Mountains). The late labellings are presented in fig. 14 and 15.

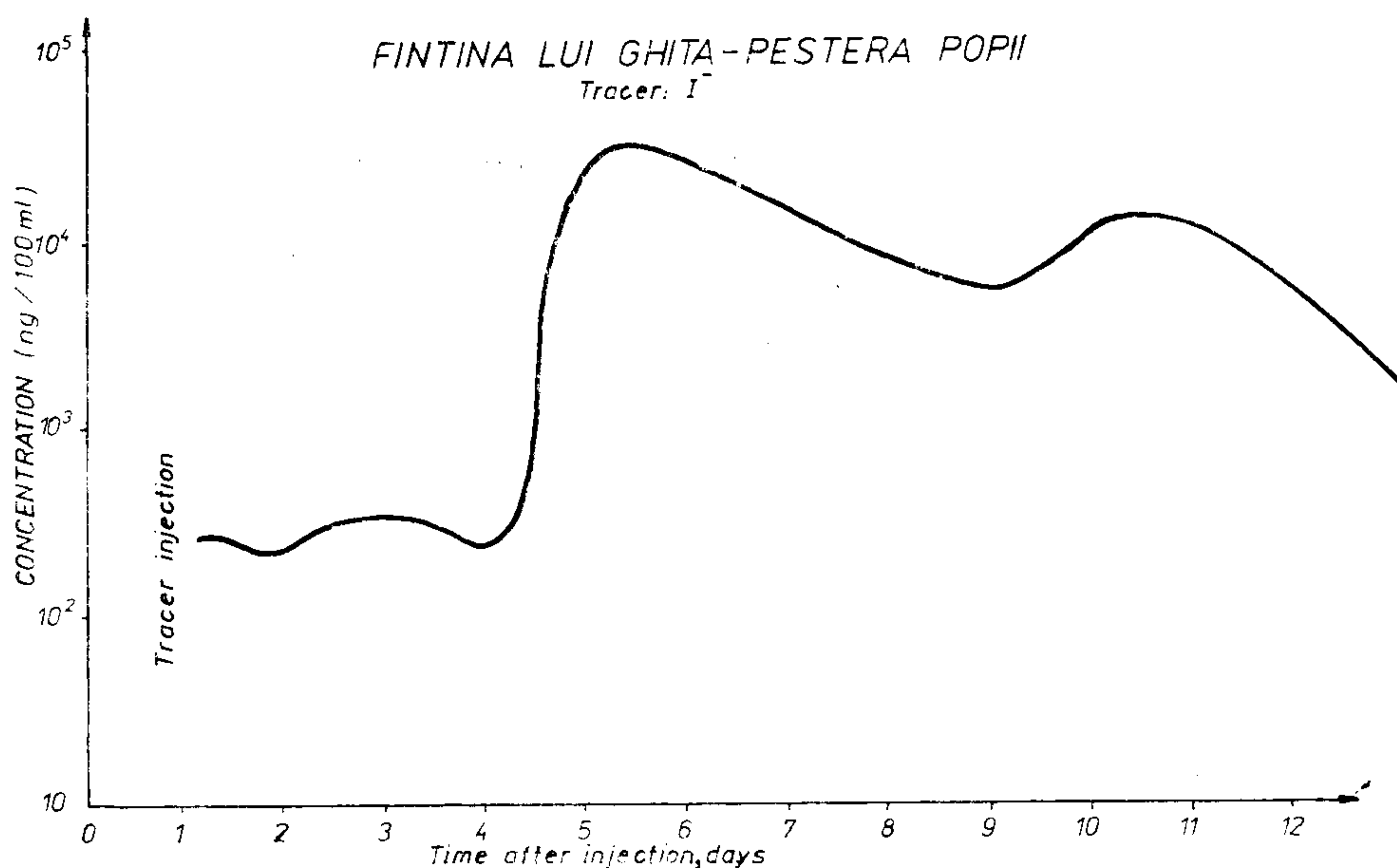


Fig. 14. Use of I^- as activable tracer. The background and the concentration-time variation in a multitracings experiment performed in Plateau Vașcău.

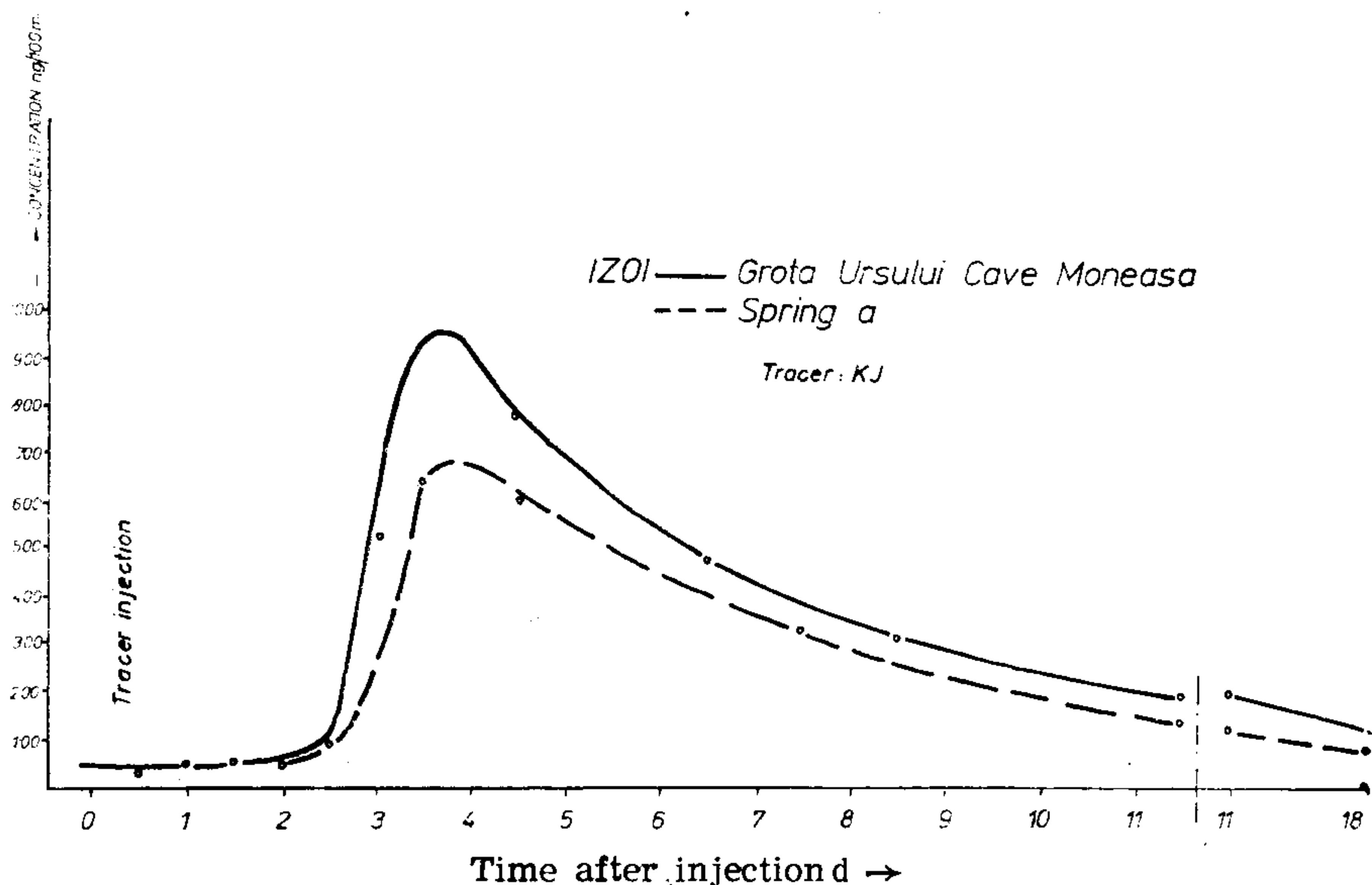
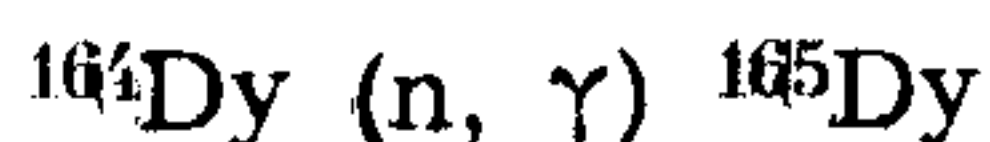


Fig. 15. Karstic diffuence labelled with I^- as activable tracer.

c. *Dysprosium*, used in the form of an EDTA complex it features fine tracer characteristics and a high-sensitivity detection. The detection reaction is :



Its presence in underground waters is extremely rare. The minimum detectable concentration of Dy is $5 \cdot 10^{-13}$ g/cm³. The results of a labelling using Dy-EDTA as a tracer performed in Padiș (Bihor Mountains) are presented in fig. 16.

d. *Indium* : With the exception of the areas that contain In deposits, this element is absent from surface and underground waters. As a tracer for water in hydrological investigations. In should be used in a chemical form which is perfectly soluble in water and does not react either with the aqueous medium or with underground rocks. The chemical combination meeting all these requirements is In-EDTA or In-DPTA.

The minimum detectable concentration of indium in water depends on a number of major parameters, among which are : the amount of sampled and analyzed water, the size of the neutron flux the duration of irradiation, the number of simultaneously irradiated samples, the efficiency and resolution of the spectrometric system, as well as the nature of labelled waters.

Theoretically, for 100 ml of analyzed water, in conditions in which five samples are irradiated for 20 minutes under a flux of $5 \cdot 10^{11}$ n s.sq. cm and a spectrometric system boasting an efficiency of 7 per cent and an energy resolution of 2.7 keV is employed for measurement, the obtained detection limit of indium in water is lower than $1 \cdot 10^{-12}$ g/ml. Figure 17 shows the variation curve of indium in the Cerna karstic spring after

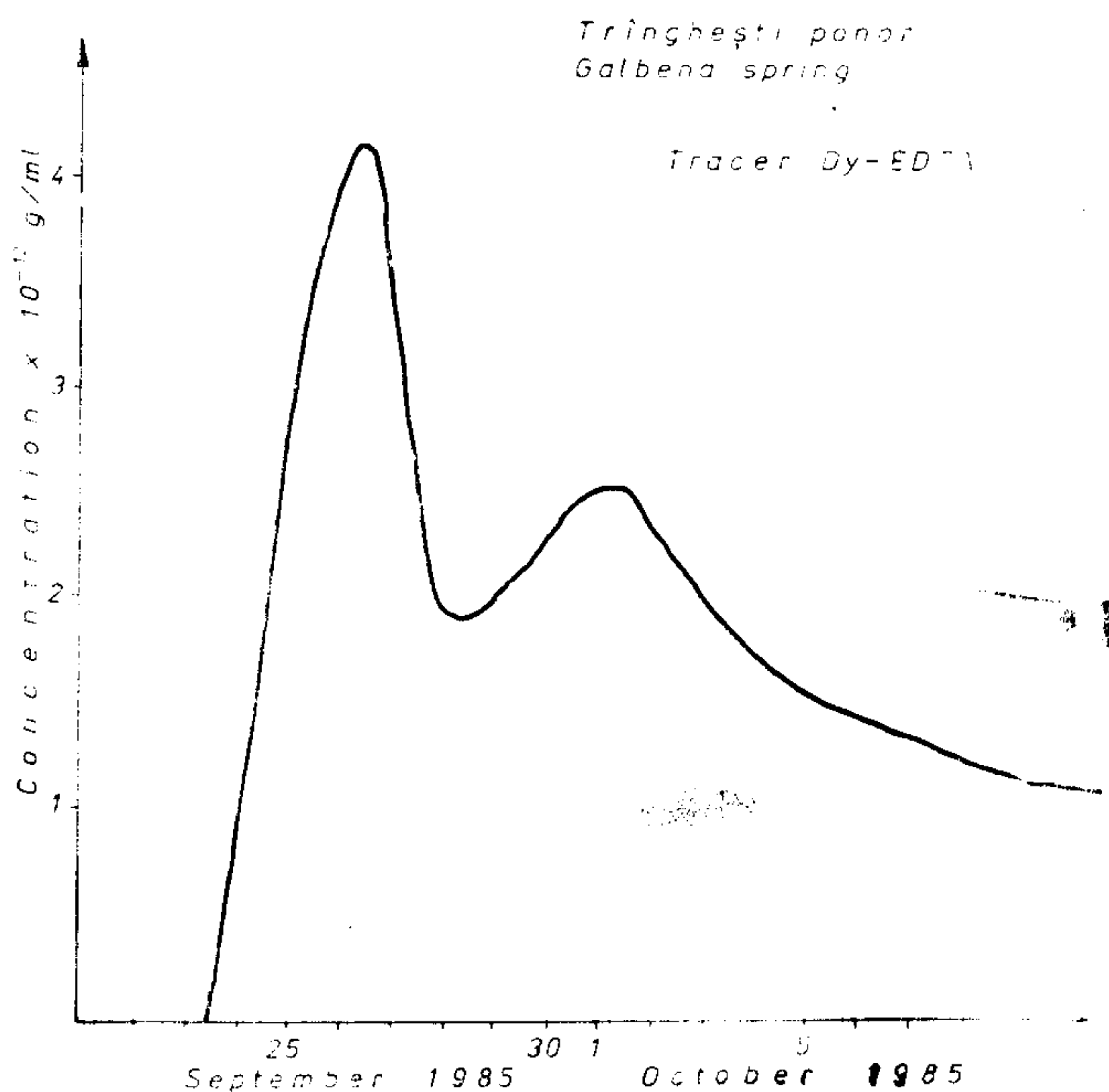


Fig. 16. A good tracer for karstic water labelling: Dysprosium-EDTA as activable tracer. The Padiș experiment.

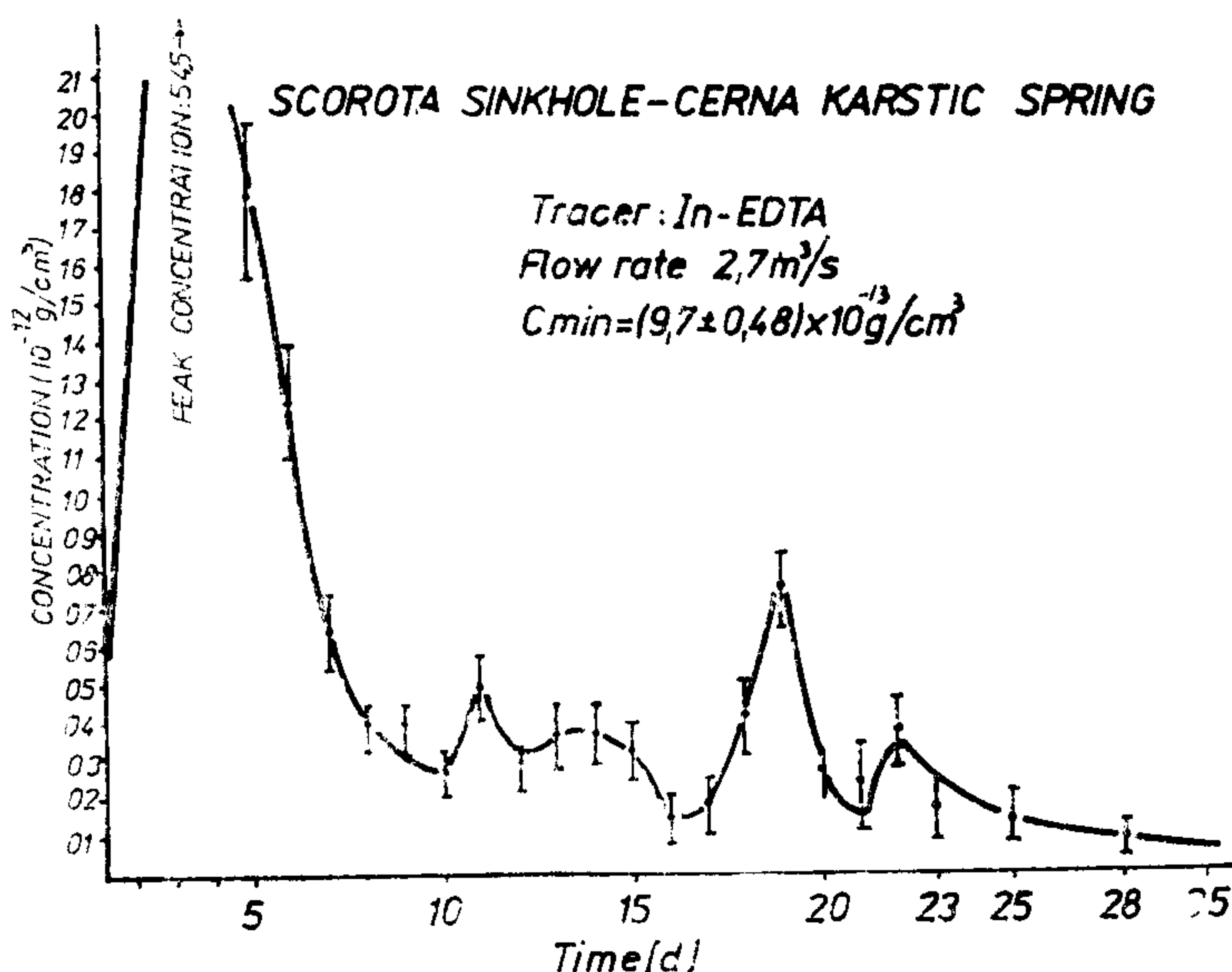


Fig. 17. Indium-EDTA may be considered as a reference tracer to label karstic waters. Cerna karstic spring experiment.

the labelling made in the Scorota sinkhole. The measured values and the errors of measurement are also shown. (Gaşpar et al. 1984).

The major advantage of this tracer is that, owing to its extremely low detection limit, it can label emergences of very low flow rates which cannot be labelled by any other tracer, be it fluorescent, chemical or radioactive (with the exception of tritiated water): an artificial lake or natural reservoir of 1 billion cu.m may be labelled using 1 kg of In-EDTA. The detection limit can be lowered below $1 \cdot 10^{-12}$ g/ml using a volume of water larger than 100 cu.cm for analysis and a larger neutron flux for irradiation (Behrens et al., 1977, Gaşpar et al., 1985b).

4.2.5. LYCOPODIUM SPORES

In 1926 the spores of club moss *Lycopodium clavatum* were first used as a hydrological tracer. These spores are small cellulose bodies 30—35 microns in diameter. They are commercially available and may be dyed in up to five different colours. They are employed in investigations of karstic structures, mainly in strongly corroded systems (Hötze et al., 1976; Gardner, 1976; Gray, 1976).

Lycopodium spores have densities lower than that of normal stream water and thus travel faster than the mean velocity of water.

The measuring technique employed in their case is counting. In the points of emergence the spores are collected with the help of large plankton nets. If silt is present, these nets clog up quickly; their cloth is delicate and may be easily torn by flood waters. After collection and

washing, the spores are analyzed and counted with the help of a stereo-microscope.

The *Lycopodium clavatum* spores do not share the surface properties of those found on pathogenic micro-organisms and may be poor indicators of pollution travel even if they are fine tracers of water motion. Another major disadvantage is that the dust of the spores is explosive and, therefore, they must be handled with care. The detection limit is of 1 spore in 10^6 .

4.2.6. BACTERIOPHAGES

Bacteriophages have proved useful as water tracers in karstic terrains. They have a number of advantages; the phage is not toxic and non-pathogenic to man and domestic animals, it is specific for its bacteria; assay is simple and rapid, and it boasts fine survival characteristics.

Because of host specificity, phages can be mixed, injected together and then distinguished on different hosts, thereby permitting simultaneous multiple tracings.

Phages feed of the bacteria of which they are parasites, and the host organism is subsequently destroyed. This provides the means whereby the phages may be detected in the samples. A small quantity of each sample is introduced into a plate of jelly-like bacteria and is then incubated. Each phage feeds of the bacteria, multiplying itself at the same time and leaving a clear area of dead bacteria on the milky surface of the plate. A manual count of the clear patches then establishes the concentration of phages in the sample.

Methods are available for the concentration of phages from large volumes of water. Using these techniques, it is possible to detect as many as 1—2 phages in a 20-litre volume of water. Furthermore, it should be pointed out that the samples may be conserved through freezing and measured later on, according to needs.

4.2.7. GASEOUS TRACERS

The use of gaseous tracers (smoke, gas) in karstic hydrogeology and the investigation of caves is a relatively new method. In this case, the notion of tracer no longer has its conventional acceptation. These gases move mostly through the system of karstic channels whose recent activity is expressed in the form of vertical circulation and a small number of concentrated courses.

Smoke or gas is injected through wells or karstic holes situated above the aquifer zone and, with the help of an artificial circulation or of the natural circulation of the air, the tracer is guided towards the remote areas of an interconnected system of karst voids which leads to their identification.

The gases employed should be lighter than the air and slightly absorbed by water and, with a view to facilitating detection, they should be radioactive, highly odorized or perfectly visible. As the tracer is lighter than the air, and highly penetrating, it will be able to cut a route

of rapid access to the surface using fractures, fissures, karstic channels and wells.

As a rule, fumigating substances that release large amounts of smoke are used as tracers; smoke may have a certain colour, that may be easily differentiated from fog. As compared to radioactive gases, it has the considerable advantage that it is not dangerous to either the experimenter or the population in the respective area.

When studying certain phenomena of karstic piracy that need labeling, des Marais (1981) resorted to volatile tracers. Thus, when a cave stream was inaccessible to water tracing, passages were delineated by use of sub-surface air flows driven by the „chimney effect“, and ethanethiol vapours as a tracer. The same tracer (viz. ethanethiol had been previously used in the King Blair cave (U.S.A.) and a link with a swallow sinkhole was established (Sperka, 1969).

5. INTERACTION BETWEEN ARTIFICIAL TRACERS AND HYDROKARST MEDIUM

In karstic systems water is a complex medium which may contain ions, colloids and sediments that drift on the bottom or are held in suspension, whose origins are extremely varied, and live beings from the plant and animal kingdoms (phytoplankton, sponges, bacteria; microbes; viruses, zooplankton, microcrustaceans, plants and animals). Qualitatively speaking, waters are polluted either naturally or artificially with the most diverse substances, in various proportions.

The general mechanism of interaction between tracers and the rocks in the underground medium are: filtration, physical adsorption, chemical adsorption, colloidal precipitation, ion exchange, chemical reactions and isotope exchange. These factors, the influence of the chemical nature of the water (degree of pollution) and the hydraulic behaviour of the karstic system contribute to lower tracer concentrations in time and space.

The interactions between the rocks in the underground and tracers are the latter's general reactions with the solid phase. Other chemical reactions between tracers and the elements of the solid phase are rare. An altogether different situation develops when a tracer comes into contact with the liquid phase. Whereas, naturally, waters can have a pH value, a temperature and a salt content that are greatly varied, owing to pollution the chemical composition of water may modify to such an extent that phenomena occur conducive to either the delay or the total reduction of the tracer. An example is the use of dichromate in hydro-metry (André et al., 1964). Polluted media may turn hexavalent chromium ions into trivalent ions, thus hindering dosage through colourimetry.

Radioactive or activable chemical tracers must boast a great physico-chemical stability so that they may not react at contact with the traced owing to its pollution. An example in this respect is the In-EDTA tracer. Used to label karstic waters in a period of low flow, the tracer could be measured 180 days after labelling, as fig. 18 shows (Orășeanu et al.,

1984). Although the medium was polluted owing to the penetration of waters resulting from bauxite processing into the karst and the contact between these waters and the tracer was long enough to have favoured retention, the tracer, however, was recovered in a proportion of 85 per cent (8.5 g from the 10 g used for labelling). The retention of the 1.5 g of In-EDTA may rather be accounted for by hydrological causes, frequent in the case of labellings in low-flow periods, when the tracer is trapped by auxiliary systems of the karst.

Fluorescent dye tracers, which boast a number of altogether remarkable features also have the serious disadvantage that their behaviour is influenced by the chemical nature of the investigated medium. Noteworthy among the most frequently employed fluorescent dye tracers are xanthenic compounds.

In the group of xanthenic dyes a proton in the methylic groups is replaced by a benzenic cycles. The uranine group (uranine and eosine) is characterized by phenolic and quinonic functions of the xanthenic cycle and the carboxylic function of the benzenic cycle. In the group of rhodamines, the xanthenic cycle is the carrier of a tertiary aminic and a quaternary ammonium function. They may be carboxylic (rhodamines) or sulfonic (sulforhodamines). These features impart characteristics on fluorescent dye tracers and also influence their behaviour. So, for instance, sulforhodamines B and G behave the way anions do. Eosine, uranine and rhodamine Wt show both anionic and cationic features (Rochat et al., 1975 ; Laurent, Gibert, 1981). Rhodamines B and 6G behave as cations.

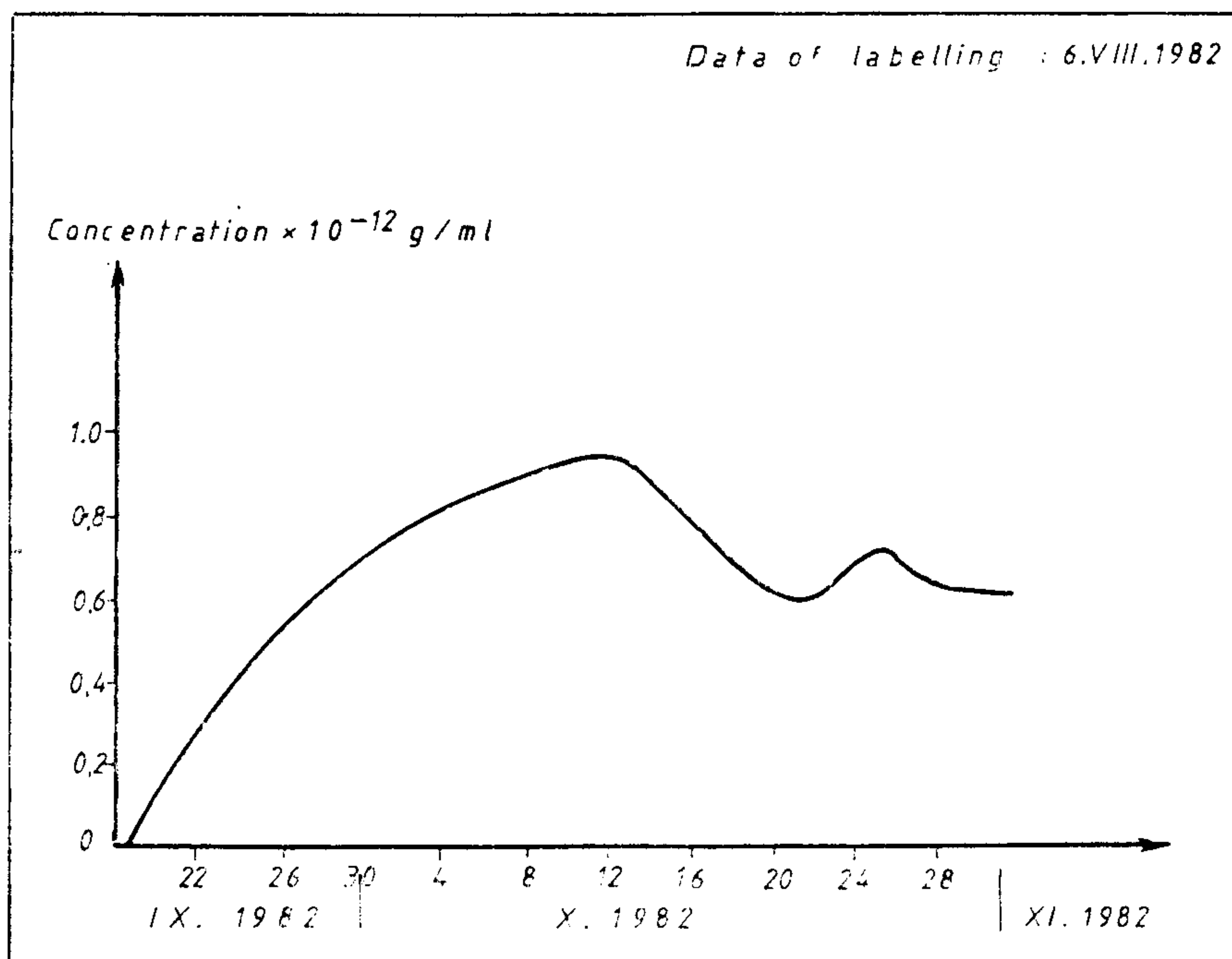


Fig. 18. The time behaviour of In-EDTA used as a tracer. The Vida experiment.

The use of fluorescent dye tracers in a medium with a strong ionic concentration may result in partial tracer loss.

Fluorescein, which may be found in five different monomeric forms, may pass to the dimeric form according to the pH value of the medium. Each of the structural forms will have different fluorescence characteristics. (Fluorescein may be also decolourized by contact with humus, clay minerals and calcite).

In exchange, the use of fluorescent dye tracers in media with high salinity (chlorinated medium) has no negative effects on them (André et al., 1976). When the medium contains sodium iodide, or when (active or inactive) sodium iodide and fluorescent dye tracers are simultaneously used, adding to the phenomena related to the rise in ionic concentration (modifications in diffusion intensity and in the absorption and emission spectra) are :

- a notable inhibition owing to the high sodium iodide concentrations ;

- a chemical degradation in the presence of iodine (for instance fluorescein turns into a non-fluorescent iodate derivative). The respective phenomenon also affects rhodamines : the fluorescence of rhodamine B and sulforhodamine B may be reduced in the presence of NaI (and of other fluorescence extinguishers) when its concentration exceeds 10^{-6} g/ml.

Analysing the behaviour of fluorescent dye tracers as to the chemical composition of waters (pH value, ionic charge, extent of pollution, etc.) and in interactions with the solid phase, one may note different manifestations (Feuerstein, 1963). The difference in behaviour is accounted for by the ionic nature of these tracers. Thus, the cationic form will provide for tracer fixation on most soils, on clays and colloids in particular.

Examining the absorption and desorption isotherm of rhodamine B and uranine, an excellent reversibility in uranine and a substantial, mostly irreversible, sorption in rhodamine B may be noted. Sulforhodamine and rhodamine Wt boast a behaviour similar to that of uranine.

In exchange, whereas in the case of fluorescein measurement is affected both by pH value and pollution extent, in the case of rhodamine B and sulforhodamine B the content of salts does not exert a significant influence when the pH value ranges from 5 to 10. The range of pH values is even wider — from 3 to 11 — in the case of sulforhodamine G.

Another fluorescent tracer, pyranine, shows excessive variations in fluorescence with pH changes in the range normally encountered in natural waters. This might prove a serious problem in quantitative applications to waters of variable quality.

To trace underground water in karstic systems, the tracers should be conservative (the tracer substances must be stable against physical, hydrochemical as well as microbial attacks). The basic properties of a tracers depend on their chemical and physicochemical structure. If this structure remains stable in experimental conditions, the tracer may be used in quantitative assessments.

As certain radioactive or non-radioactive isotopes (which can be detected with the help of the activation analysis), tested in their cationic form, proved an unsatisfactory behaviour, they were complexed. Nevert-

heless, the performance of anionic complex tracers is dependent on the stability of the complex. The dissociation of these complexes is characterized by the stability constant, K_s (Behrens, 1983). In table 1, MA_n is the molar concentration of the complex and M and A the molar concentration of the metal ion and of the ligand.

Table 1

The stability constants of chelate complexes in neutral aqueous solutions

| Complex | Stability constant $K_s = [MA_n] / [M][A^n]$ |
|------------------------------------|---|
| Co (CN) ₆ ³⁻ | 10 ⁶⁴ |
| Co-EDTA | 10 ³⁶ |
| In-EDTA | 10 ^{24.9} |
| Cr-EDTA | 10 ²⁴ |
| Sc-EDTA | 10 ²³ |
| Bi-EDTA | 10 ^{22.8} |
| La-DPTA | 10 ^{19.5} |
| Dy-EDTA | 10 ^{17.6} |
| La-EDTA | 10 ^{15.4} |
| Mn-EDTA | 10 ^{13.8} |

A relative criterion to assess the stability of complexes is the $K_s = 10^{20}$ limit. Therefore, In-EDTA, where $K_s = 10^{24.9}$, may be considered a very good tracer.

Photochemical decay has a great importance in tracer stability, because all fluorescent dye tracers are subjected to decomposition owing to natural light. Sensitivity to light, however, differs substantially from one fluorescent dye tracer to the other (Smart, Laidlaw, 1977, Atkinson, Smart, 1981, Laidlaw, Smart, 1982). The decrease in concentration of a fluorescent dye tracer under the impact of light follows the relation :

$$I = I_0 \exp - \left(\frac{0.693t}{t_{1/2}} \right)$$

where I is fluorescence after the t time of irradiation and I_0 denotes the fluorescence at the time $t = 0$ and $t_{1/2}$ is the half-life of fluorescence intensity.

This phenomenon has a special importance as it restricts the applications of fluorescent dye tracer to underground flow alone. On the other hand, storage of samples containing fluorescent dye tracers in areas exposed to light may lead to the degradation or total disappearance of tracers. So, for instance, uranine-containing water samples collected from karstic exurgences in day time showed lower fluorescence when compared with a reference sample, a situation which did not occur in the case of samples that had been collected at night.

The irreversible photodegradation of tracers in solutions is due to the dissolved oxygen or ferric ions in particular. Owing to studies conducted on uranine (Lingvist, 1960) losses through photodecomposition could be assessed. Thus, the half-life of fluorescence in distilled water

is of 11 hours, while photochemical degradation may reach even 25 per cent per hour in polluted waters. It is noteworthy that degradation is independent of the concentration of the tracer. In exchange, degradation increases with the intensity of irradiation, being roughly 5 times higher on a clear summer day than that on a day with a cloudy sky (Molinari, 1969).

In brief, the situation of other fluorescent dye tracers is as follows : eosine decomposes under the impact of natural light faster than uranine does and has a $t_{1/2}$ of 6 hours. Rhodamines behave differently. Thus rhodamine B has a fluorescence half-life of 780 hours, but may reach values of 2.24 percent in polluted waters. In exchange, sulforhodamine B has a $t_{1/2}$ of 820 hours (the photochemical degradation of a sample exposed for a total 24 hours to strong sunshine was of only 1 per cent). From this point of view, sulforhodamine G boasts an almost identical behaviour. Among the other rhodamines, rhodamine 6G decomposes a little faster ($t_{1/2} = 375$ hours) and then the half-life of fluorescence intensity increases under the impact of light. Amidorhodamine G has the $t_{1/2} = 770$ hours and rhodamine Wt has the $t_{1/2} = 1,300$ hours, which makes it a more stable tracer.

The situation of other fluorescent dye tracers is variable. Thus half-life in the case of tinopal CBS-X is of 17 hours, of pyranine is of 47 hours, while brilantsulfoflavine FF has a photochemical stability which is 200 times higher than that of eosine and a t equal to 1,200 hours (Klotz, 1982).

Not all hydrological tracers are stable at temperatures higher than that of the environment. The most relevant case is that of fluorescent tracers. So, fluorescence intensity varies inversely with temperature, though this rate depends on the dye (Smart, Laidlaw, 1977). For instance, degradation of fluorescein starts at 25 degrees centigrades ; at a temperature of 200°C fluorescence disappears altogether (Fabricol, Pauzancre, 1981). Degradation is not instantaneous, however. Experimentally, total degradation occurs in ten days at a temperature of 200°C. As a rule, thermal waters are highly mineralized and, in this case, the stability of fluorescein is not affected by the chemical composition of water but only by its temperature.

Radioactive and activable tracers in compounds used in hydrology are generally stable at temperatures found in practice with the exception of ^{82}Br in the BrNH_4 combination. As bromine volatilization starts at 18°C, it cannot be used to label thermal waters. On the contrary, ^{131}I in the form of NaI boasts fine stability at temperatures of up to 130°C. In-situ tests showed a fine percentage of tracer recovery after a 48-hour residence in the underground at a temperature of 130°C. As for the influence of the temperature of the tracer solution on measurements, it can be noted that small differences in temperature as to a reference sample may have substantial negative effects on certain classes of tracers. Fluorescent dye tracers are the most sensitive of all. Thus, rhodamine B and sulforhodamine B show a 3 per cent variation in the measured value per each degree centigrade. In exchange, hydraulic fluorescein varies only 0.4 per cent with the same temperature gradient. Sulforhodamine B is not influenced at all.

The last factor in lowering of tracer concentration in karstic systems is the interaction with biomass.

This process shows to the full in surface and karstic waters in particular where all conditions for intense biological activities are met. Of equal interest is tracer retention through other processes by algae or even through mere superficial contamination of vegetation.

Degradation of fluorescent dye tracers may occur owing to microbial activity, more particularly when they penetrate polluted waters. The most affected of them is uranine.

Iodine, a highly useful hydrological tracers, may stand a series of chemical transformations through processes induced by microbial activities in both surface freshwater and soil water.

Though not sufficiently investigated, the microbial conversion of tracers should be considered, as it leads to their gradual degradation. According to some authors, tracer biodegradability is an advantage and a criterion for selection. An example in this respect are optical brighteners which disappear from surface waters under the joint impact of sun rays and biological activities (Smart, 1982).

6. TRACER TOXICITY

Two aspects of tracer toxicity are important: first, deleterious effects on karstic and surface water life and second, the limitations which should be considered where human (and the entire ecological chain) consumption of the labelled water from karstic aquifers is a possibility. In assessing the biological risk on living organisms in karst, the amount and tracer concentration and the duration of experiment should be considered.

When tracing is achieved at high discharges, the duration of experiment is short and great concentrations may appear in karstic springs. Obviously, these springs contain water of very good quality. The tracer concentration at karstic outlets should appear below the limits permissible for drinking water. This is very important, especially for chemical and radioactive tracers. For other tracers, whose concentrations are missing from standard in force, the toxicity of compounds to man is normally investigated on laboratory animals; safe dosage levels are then scaled up, and an additional safety factor is incorporated.

When labelling is performed in conditions of low discharges, tending to low flow, tracer dispersion is high. The tracer penetrates into karstic holes, siphons and secondary channels where it may remain for some time, according to hydrometeorological conditions.

Tracer concentration in these zones of virtually stagnant waters with an extremely slow velocity may acquire substantial values. Having enough time to interact with the rock, the tracer will be fixed to the walls and floors of the cavities through physical and chemical processes, that is exactly at the point where the microfauna of the karst develops.

For these reasons, the tracer used should boast the features of an ecological tracer, that is, it should not lead to changes in environmental

conditions or to the emergence of mutations, and should not destroy the life that develops in the karst.

Of the tracers in use, radioactive tracers meet the requirement for an ecological tracing. Lower organisms are influenced only by large doses of radiation which cannot be produced by activities in use, limited by sanitation norms in force in all countries.

The only tracers that may pose ecological problems are the chemical and fluorescent dye tracers. Of the chemical tracers, certain salts, such as NaCl or KCl, call for large amounts for one labelling (more than 500 kg normally). These tracers may create a saline medium in underground cavities, a medium which might influence normal living conditions.

As for fluorescent dye tracers, they made the object of numerous studies of toxicology. The final conclusion was the need to limit the amounts of injectable tracer into the karst (Smart, 1982).

7. TRACING OF KARSTIC WATERS

7.1. TRACER INJECTION

The aim of the tracer injection is to stimulate the karstic system so that an output response function apt to supply most complete information on the system may be obtained. That is why labelling must not modify the hydraulic characteristics of the karstic system.

The way in which a tracer is introduced in a ponor or sinking point may have a deciding influence on the whole experiment. The smaller the amount of tracer, the lower its impact upon hydrodynamic and ecological conditions, although tracer detection and measurement might prove a difficult metrological problem.

Of the modes of injection in use, three are worthy of mention (fig. 19).

a. *Instantaneous point injection* (by δ -input signal). The response of the system to this signal is usually a curve with a Gaussian form, as the analysis of the transfer curve obtained on an experiment plot when labelling the Valea Popii ponor (Pădurea Craiului Mountains) shows (fig. 20) Suchlike labelling cannot be performed in any conditions. For low and very low discharges, the only tracers fit for δ -pulse injection are the radioactive or activable tracers, as the amounts injected are insignificant and do not upset the hydraulic conditions of the system either at the inlet or in the underground ;

b. *Step injection*. It represents the sum of pulses, with the tracer introduced into the insurgence using a device at a constant discharge. This system is employed when large amounts of substance (the case of chemical tracers, for instance) are needed for the performance of labelling. Injection discharge, q , should be lower than a tenth of the inflow, Q_0 . The introduction of the tracer takes long in the case of low-discharge insurgences and large amounts of substance are necessary. Besides being

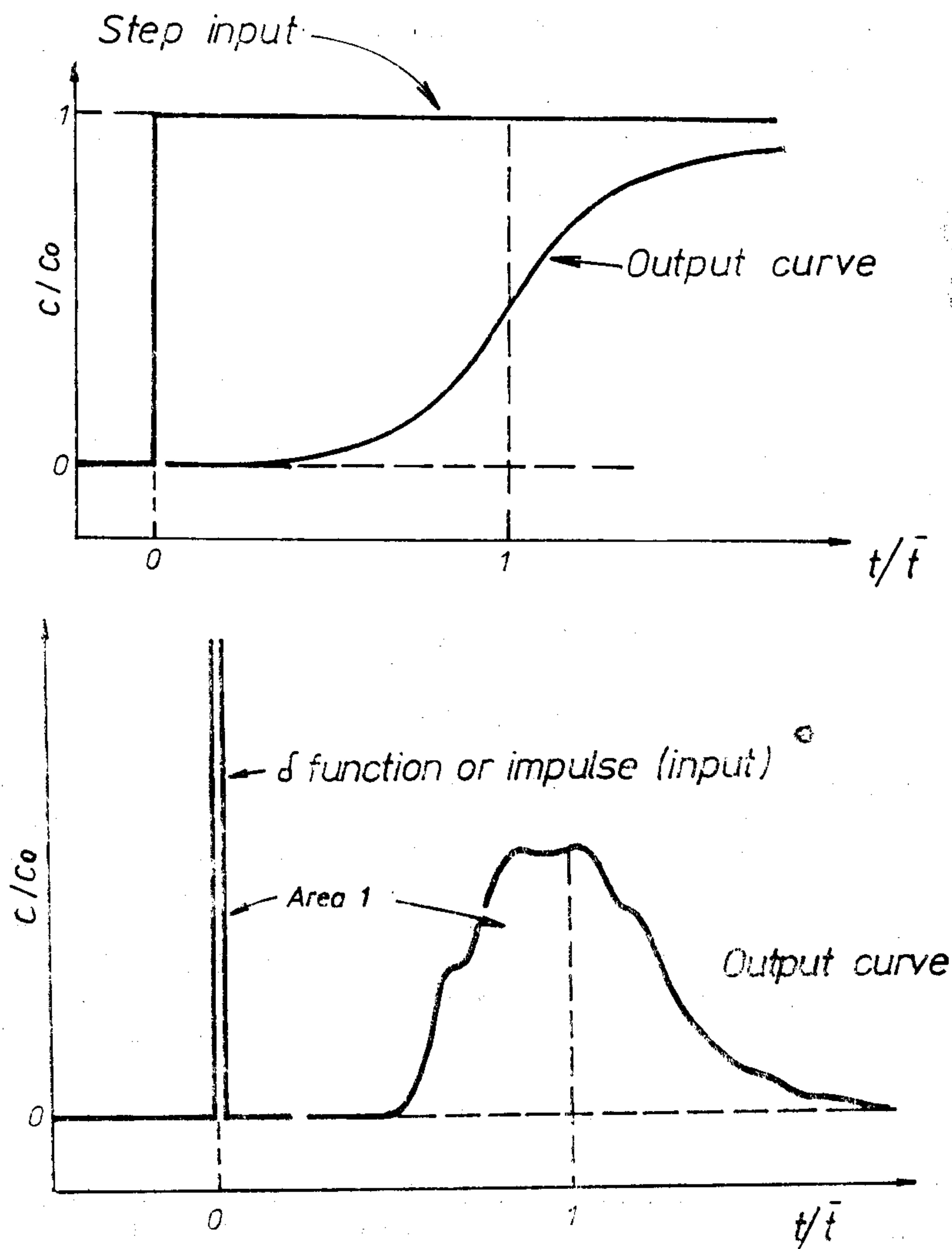


Fig. 19. Tracer injection : step signal and δ (Dirac function) signal.

uneconomical, it has the disadvantage that it may lead to negative results because of tracer dispersion below detection limits.

The response of the system to this labelling is a signal of the step type, if transit is short, or of any other form. Figure 21 shows the time variation of tracer concentration in the IAS-Mangalia mezothermal spring after the labelling of the Kara-Oban sinkhole with a constant tracer discharge (Gaşpar, 1981).

c. *Random labelling.* At present it is employed only when qualitative results are expected (for instance, to demonstrate the existence of an interconnection), the discharge of the insurgence is low and the tracers (dyes or salts) are available in large amounts. Tracer concentration in

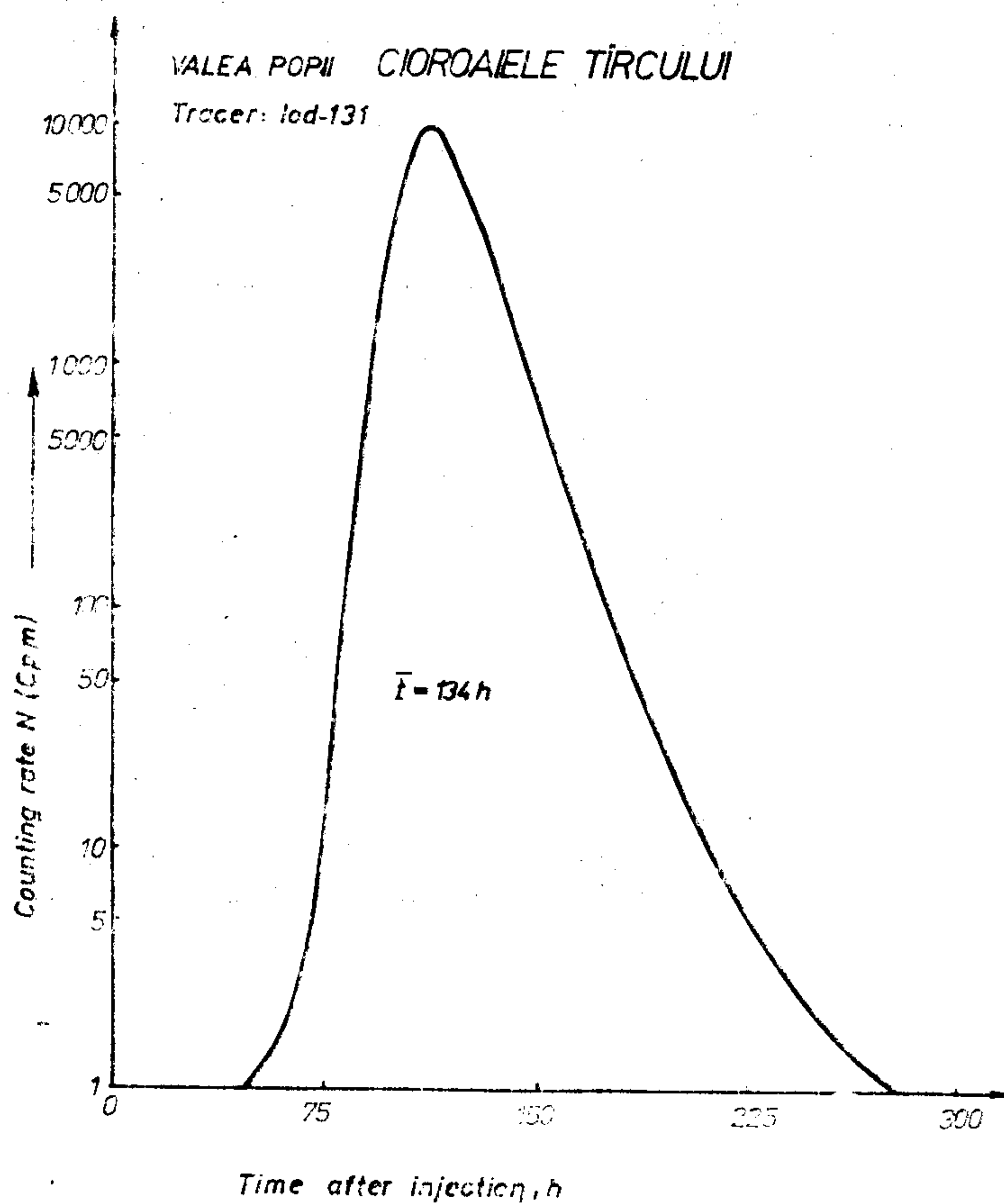


Fig. 20. The output curve of a tracer after labelling by δ -input signal. The flow rate of labelled ponor: 0.1 l/s.

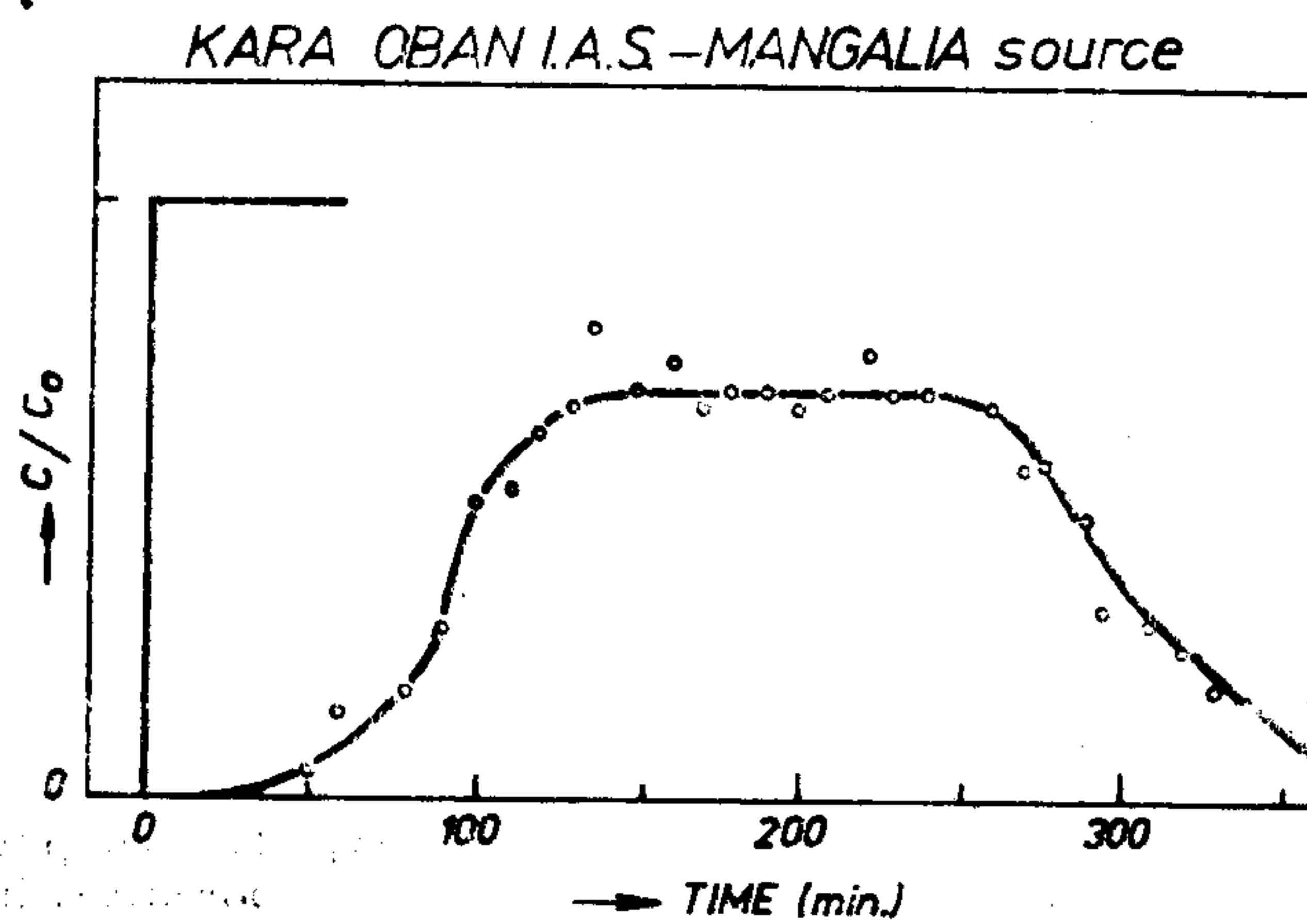


Fig. 21. Step input and tracer output curve in the Kara Oaban experiment.

the labelling points varies according to water dissolution capacity, which, in turn, varies with the temperature of the medium; the labelling operation may take hours or days. The response of the system to such a signal will be random, as well, and in these circumstances the only aspect of interest is the presence of the tracer in the emergence under study in concentrations that differ substantially from the value of the background.

A labelling operation is not simple and, besides tracer injection, it includes :

— preparation of the labelling area, which means the creation of an access route to the ponor, the removal of the organic depositions, which tend to absorb the tracer from the very beginning in the point where its concentration is at its highest. To introduce a certain amount of water after labelling with a view to "activating" the ponor is a mistake which can only result in tracer loss through the wall effect, absorption reject, dispersion etc.

In case radioactive isotopes are used, the introduction of the tracer should be preceded by the introduction of the carrier.

When labelling is performed in ponors with partial discharge loss or when the sinking point is located in a flooded area or at the bottom of a lake, additional installations and devices are employed which assist tracer injection through the agency of a perforated pipe that penetrates under the layer. In this case, it is recommended that a certain amount

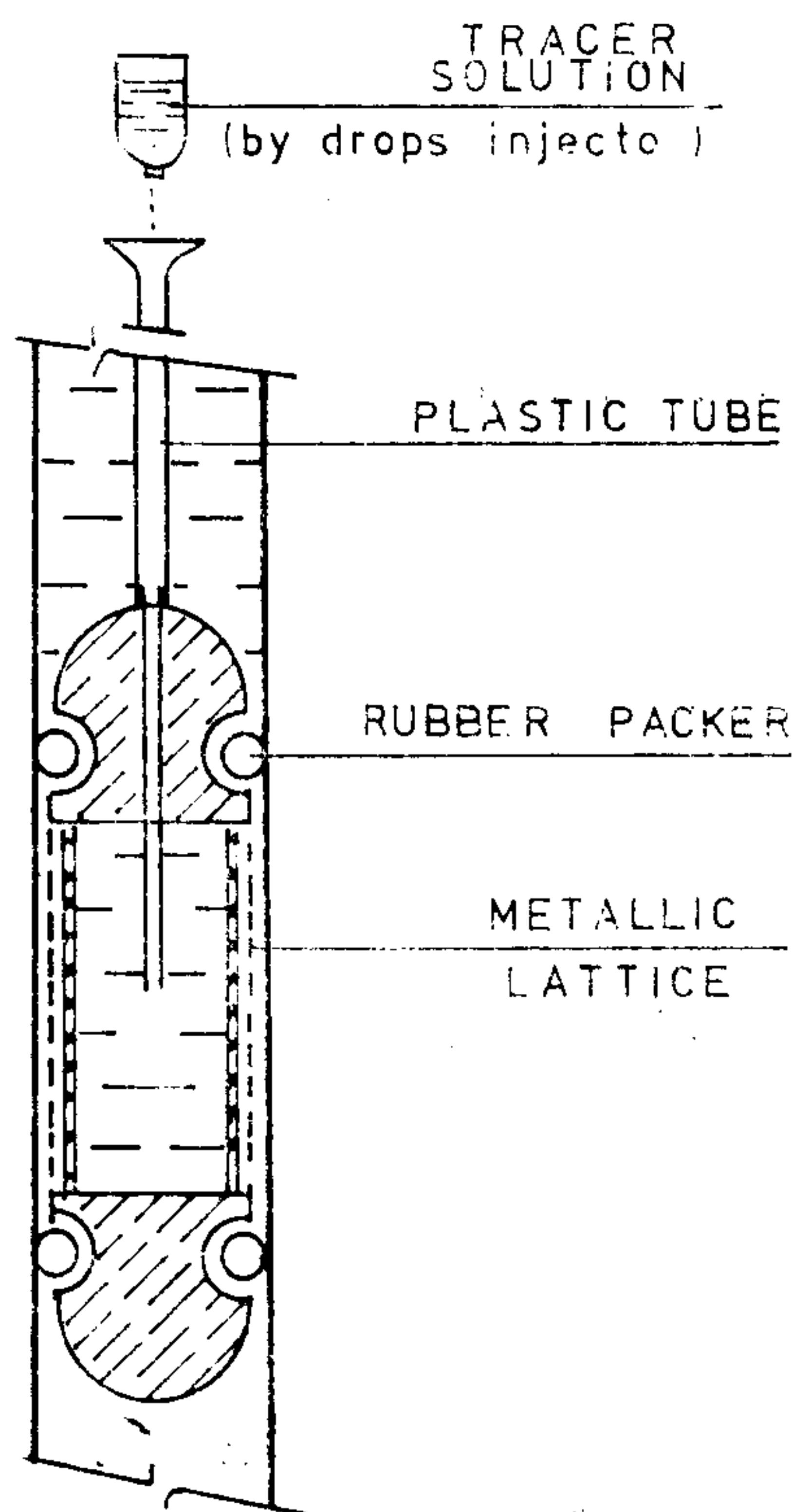


Fig. 22. Equipment for tracer injection in boreholes having vertical currents.

of water be introduced into the pipe to favour tracer penetration into the underground.

If the tracer employed is not a dye, a small quantity of fluorescein or rhodamine B can be used to verify the efficiency of the respective labelling. When the insurgence point is an estavellas (a karstic formation that may operate both as a ponor and a spring) labelling should be performed at a moment when there is no possibility that the tracer be moved backwards.

In the case of labellings in wells the existence of currents and their direction (ascendent, descendent) is determined, the areas with holes (boasting maximum permeability) are identified and isolated with packers and then the tracer is introduced (fig. 22). After the tracer has been completely injected into the borehole pipe it should be followed by the injection of the amount of water required to ascertain if the entire amount of tracer has left the pipe and penetrated into the underground.

Tracer injection may be performed in dry sinkholes too, obviously for the sole purpose of establishing certain interconnections. In the absence of a natural flow, an occasional flow is created until hydraulik links are established; artificial flow should continue after the tracer has been injected as the probability of detecting the tracer depends on the duration of the continuity of the flow (Sencu, 1977).

— Tracer dissolution and dilution are operations that often require a large water volume. If the tracer is not dissolved entirely the inflowing amount of tracer is smaller than the amount that has been injected and, therefore, cannot be used in balance computations, even if recovery curves are obtained in emergences. Furthermore, the dissolution in time of the tracer carried by water and retained owing to the difference in density nearby the injection point will entail an artificial elongation of the tracer cloud, which conveys a false image of the hydrological characteristics under study.

— Decontamination and waste removal, which refers to individuals equipment and means of transport. Decontamination measures should be most strict. So, for instance, in case spores are used the presence of a single spore is considered sufficient to indicate the existence of an interconnection; the possibility of conveying an erroneous information enhances considerably if the the same individual performs both injection and the sample taking operation.

— Surveillance of emergence points, which starts when labelling operations do, or after a short interval, according to experiment conditions.

7.2. TRACER QUANTITIES USED IN KARST WATER TRACING

The quantities of dyes that should be injected into the water in tracer studies can only be approximately calculated or estimated. Nevertheless, such estimates can prevent gross errors. There is an optimal amount of tracer to investigate a karstic structure but it depends on a number of variable factors, such as: the labelled volume, the minimum detectable concentration of the tracer, the transit time in con-

nection of period of investigation (during low or high flow), the maximum allowable concentration of the tracer in drinking water, the out-flowing discharge of springs, the background etc.

A relation that was established more recently (Leibundgut, 1974, Leibundgut et al., 1982) and has been used in numerous dye tracer tests, starts from the analysis of the tracer wave in the monitoring point:

$$M_0[\text{kg}] = \frac{T[\text{h}]C_{\text{peak}}[\text{mg}/\text{m}^3]Q[\text{m}^3/\text{h}]A_c S_c}{2 \cdot 10^6}$$

where M_0 is the injector quantity of dye, T denotes the estimation of dye passage duration through the monitoring point, C_{peak} represents the maximum estimated concentration in the sampling point, Q is the spring discharge (in the case of determination in wells, the pumping flow rate), A is the adsorption coefficient and S denotes a safety coefficient.

In the case of tracers detected with the help of chemical analysis or activation analysis, Leibundgut's relation yields equally satisfactory results. In this case, however, the range of variation in the natural background, prior to, the experiment, should be known and the value of the maximum concentration expected in the measured emergence should satisfy the relation:

$$C_{\text{peak}} = 100 Bg$$

where Bg is the value of the background for the substance used as a tracer. This metrological condition provides a fine requisite for the statistical processing of experimental data.

As for In-EDTA, used as a tracer to investigate hydrokarstic structures, the analysis of numerous trials (Gaşpar et al., 1985) has led to an empirical relation -

$$M_0 = QTPK$$

where M_0 is the In amount required for one labelling (expressed in g), S is the sum of the flow rates of the emergences where the tracer might occur (in m^3/s), T denotes the time interval, as estimated by the investigator, needed for the tracer to pass through the monitoring point and for a value of at least 10 to be attained for the maximum/minimum concentration ratio (in days), P is the loss coefficient, expressed by the M_0/M ratio, where M is the In amount recovered, and K is a safety coefficient.

The use of coefficient P is justified as a certain amount of tracer may be retained in the auxiliary systems according to the hydrodynamic behaviour of the karstic system during the testing period. On the other hand, in the case of very long transit times, determined in particular, by a lack of precipitations and the continuous lowering of the water table, part of the tracer may be lost in various traps and it will be released later, after rainfall start, in general after measuring operations have ceased.

We believe that a value ranging from 1 to 3 for P may be considered as reasonable, the value of 3 not being exceeded in the abovementioned experiments. As for coefficient K , its value may be below 2.

Figure 23 shows a diagram for the optimal amount of indium needed in an experiment for cases frequently occurring in practice. So, for instance, 10 g of In-EDTA — a minimum detectable concentration of 10^{-12} g/cu.cm granted — may label a karstic structure which discharges through an emergence with an outflow of 1 cusec, the tracer cloud passing through the monitoring point for a period of 10 days if conditions are favourable. If labellings is performed at the beginning of a period of drought, the respective amount of indium would be enough only for a discharge of 150 l/s; for a discharge of 1 cusec, 16 g are necessary.

Henceforth, it is clear that in the afore-said example the probability of obtaining a positive result, without creating ecological or financial problems, will enhance substantially of the safety coefficient is raised and an amount of 25 g used.

More complicated problems occur in case radioactive tracers are used because of strict radioprotection norms. The experimenter is obliged to take every preventive measure so that the concentration attained in the spring water should be below the permissible upper limit for drinking water.

With a view to performing radioactive labelling yielding quantitative information on the hydrokarstic structure under investigation,

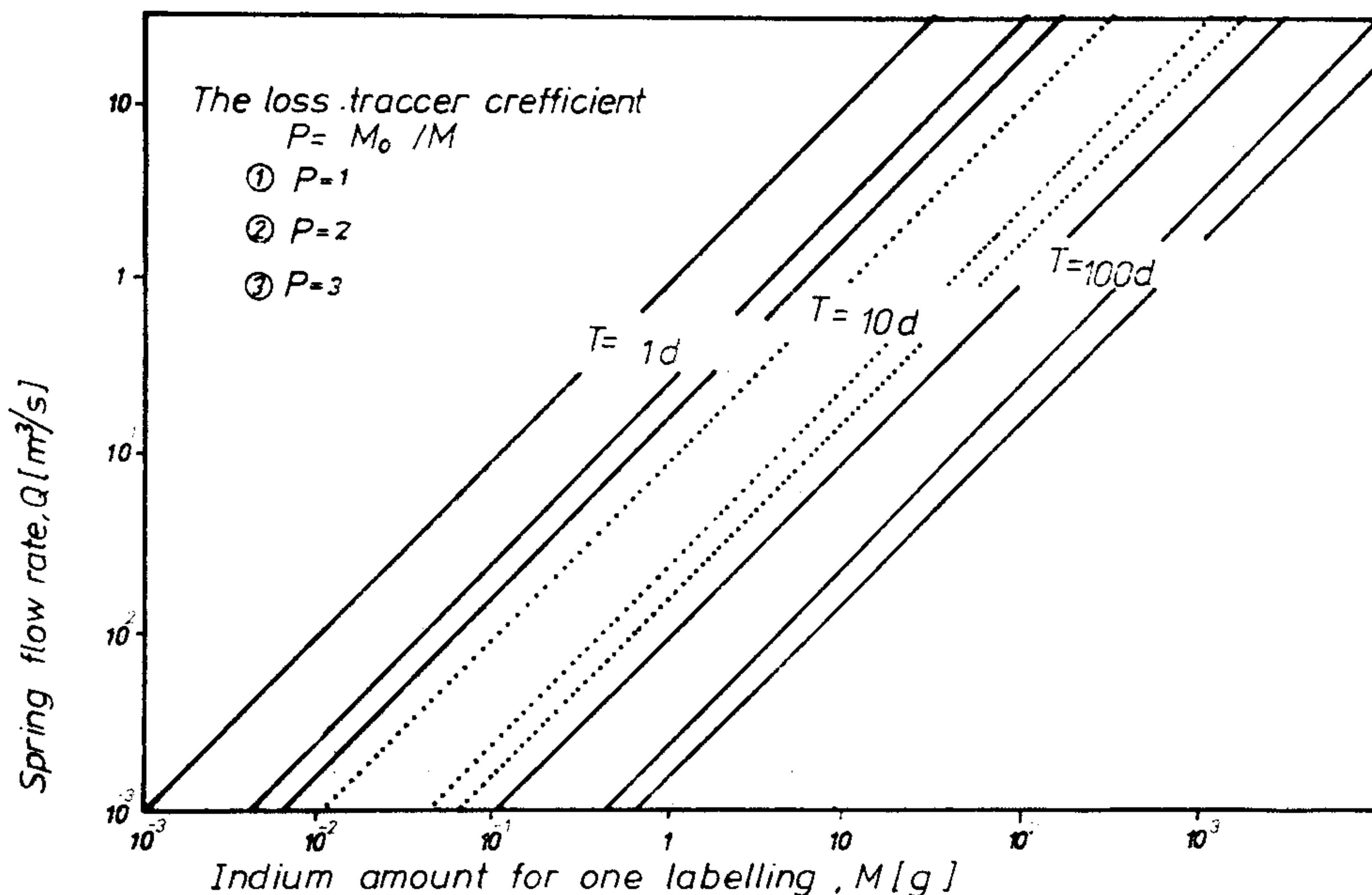


Fig. 23. Diagram to compute the Indium amount for one labelling.

it is necessary that the following conditions be achieved in the emergence point :

$$C(x,t) \geq C_{min} \leq C_{al}$$

where C_{min} is the minimum detectable concentration with the detection system employed, and C_{al} the maximum allowable concentration of the tracer used for the population exposure. In these conditions, the maximum activity necessary, A , for the experiment is :

$$A = \Omega C_{al} D^{1/2} x^{1/2} \exp(\lambda t)$$

where λ is the radionuclide disintegration constant, D denotes the hydrodynamic dispersion coefficient, x is the distance between ponor and springs, t denotes the estimated transit time, and Ω represents the cross section of the flow (fig. 24).

Any labelling should contain a measure of risk since the activity of the experimenter depends on the hydrological conditions that prevail throughout the duration of the test. The fact should be pointed out that

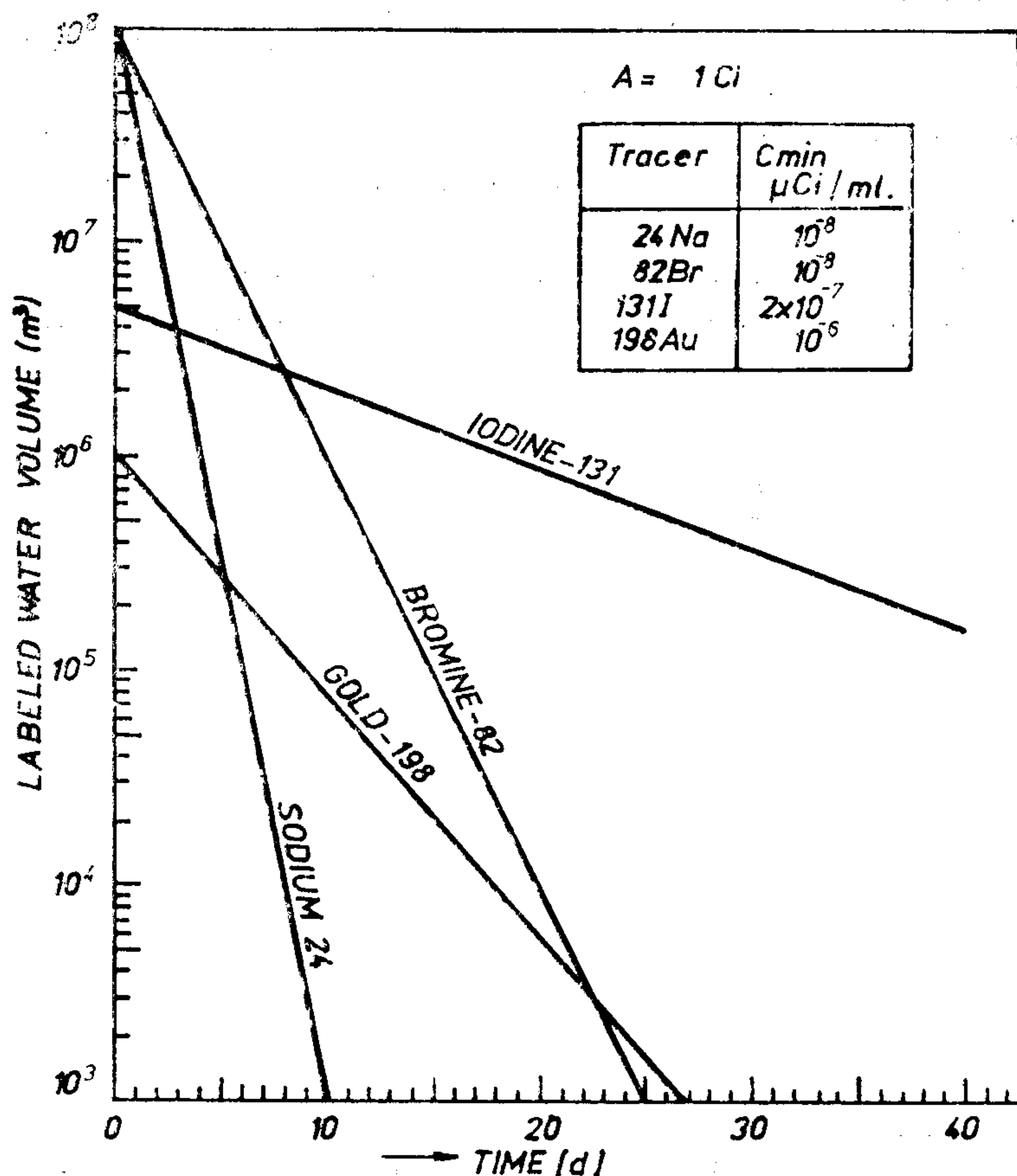


Fig. 24. The water volume which can be labelled using 1 Curie of radioactive substance.

rapid changes in hydrological conditions may either favour the experiment or cause its failure. The risk of failure appears whenever labelling is performed during low-flow periods. The tracer water may be stored in siphons, underground lakes and solution channels until the karstic structure becomes active again.

Thus, for instance, a labelling made with the help of In-EDTA in the Pădurea Craiului Mountains, in an area where average velocities of 30—40 m/day were frequent, for a transit distance of 4.8 km and a level difference of 135 m, the tracer needed 40 days to appear in the Toplița de Vida spring. Throughout this interval it penetrated deeply into the auxiliary systems, being carried toward the outlet after it had travelled them. This is apparent in the high dispersion of results, measurable Indium amounts being released from the karst during a 150-day interval after the first occurrence (Orășeanu et al., 1984).

7.3. MEASUREMENT OF TRACERS

The results of a labelling are primarily dependent upon an accurate inventory of all possible emergence: (continental and submarine) springs, (natural and artificial) lakes, rivers, estuaries, wells and boreholes, caves, underground mines where water inflows occur, as they all represent monitoring points.

Two methods are employed in practice: the continuous procedure (in situ) and the sampling procedure.

In situ detection is used for gamma active tracers, for fluorescent dye tracers and salts. The accuracy of determinations depends on the calibration of probes and devices (in the case of radioactive tracers in particular). When salts are used as tracers, their concentration may be assessed by continuously measuring either the conductivity or the resistivity of water. In case of in-situ assessments, graphic recorders are normally employed which accurately pinpoint the moment of tracer occurrence.

In situ detection gives rise to two extremely difficult problems for the operators. These concern the auxiliary electronic instrumentation and the detector itself. The electronic equipment for radiation counting has to meet very high exigencies: it should enable high sensitivity determinations; the accuracy of the measurements should be as high as that of sample measurements; it has to be light and easily carried by one person since the medium to be investigated may be in an inaccessible region; it should be sturdy, to resist mechanical shocks during transportation; it should have a longer functioning independence than the duration of the investigated phenomenon, it must work in conditions within an acceptable temperature range from -5 to $+40^{\circ}\text{C}$ in temperate regions or it must be tropicalized; it should normally function in variable conditions of humidity and pressure (e.g. in caves).

Detection on samples is a method very used in karst hydrology. The sampling must be performed with adequate apparatus, according to a

well defined technique, and at determined time intervals, in order to observe the phenomenon all along its course.

Sampling must not perturb the hydrodynamic conditions of the phenomenon to avoid the appearance of an unexpected concentration gradient. The samples must be placed in special containers which can not be contaminated and prevent retention or contamination of the tracer. Thus, water samples are collected in plastic rather than glass bottles of a given capacity, as the latter permit an undesirable isotopic exchange.

When the sample measurement method is applied an optimal sampling interval should be found so that the information supplied by the tracer may not be lost when transit is rapid and testing should not become uneconomical when transit is long.

Analysing the results of several labellings in karsts, one may note a dependence between average transit time, \bar{t} , and the interval of time during which the outlet returns the tracer, T . Generally, the following relation may be expected :

$$T = n\bar{t}$$

where n ordinarily acquires values ranging from 1 to 3. T is shorter than \bar{t} only in the case of recently formed karstic systems with short routes and sensible level differences.

The use of active carbon filters (for fluorescent dye tracers) and of ion exchangers (for radioactive tracers) provides for the use of very low tracer concentrations. Throughout the interval, the filters are active, the amount of accumulated tracer is large enough to be measured. This method provides for the measurement of concentrations which are not detectable through other methods (for instance, assessments of radioactive concentrations that are lower by several orders of magnitude than the maximum concentrations admitted in potable water).

When active carbon filters or ion exchangers are used, account should be taken of the fact that fixation yield depends on a number of factors such as the salt content of water, pollution degree, turbidity, discharge per unit volume and solution concentration and is inversely proportional to the last two. These filters concentrate both tracers and the fluorescent and radioactive substances regularly found in water. That is why gamma spectrometry is used to detect and measure radioactive tracers and differentiate them from natural radioactive substances accumulated on filters.

Calibration in field conditions is of special importance in the case of fluorescent dye tracers as the intensity of fluorescence depends on temperature, pH value and the degree of pollution of the measured water.

Because adsorption is continuous in time, a higher background fluorescence will result if longer exposures are used. Activated carbon detectors should be replaced every three or four days, at least, as otherwise dye adsorption is delayed, especially in a medium rich in organic substances.

8. VARIATION OF TRACER CONCENTRATION IN THE MONITORING POINTS

At the measuring point, the concentration distribution is determined along the measuring time.

Plotting the complete curve of tracer concentration at the karst outlet provides for the interpretation of its behaviour. The aspect of curve $C(t)$ supplies information on the phenomena occurring inside the karst and on the underground history of the waters labelled in ponors and insurgences.

Analysing these curves, Mueller (1982) assumes that the release of tracers from the karst obeys the same laws and types of exponential equations like those describing recession curves. He determined even the discharge coefficient of the recession curve, α , using the results of the experiments conducted with artificial tracers. This means that the aspects of the variation curve of the tracer according to time might be characteristic of flow conditions in a geological structure. Each structure might have its own, specific concentration-time distribution curve. If this hypothesis holds valid for the given karst, then the curve $C(t)$ might supply additional information on the volumes of stored water wherein tracers were dispersed.

But a plot of tracer concentration against time at a spring may

Multi-peak concentration-time curves may appear :

show one or multiple peaks under many circumstances.

— when water flows from a cave passage into the surrounding bedrock, remains there for a time and then flows in the reverse direction, back into the cave passage. Atkinson et al. (1973) suggests that water is stored in the fissure of the bedrock during the rising limb of a flood hydrograph and released on the falling limb. If traced water is stored and later released, a double peak of tracer concentration may result (figs. 25 and 26).

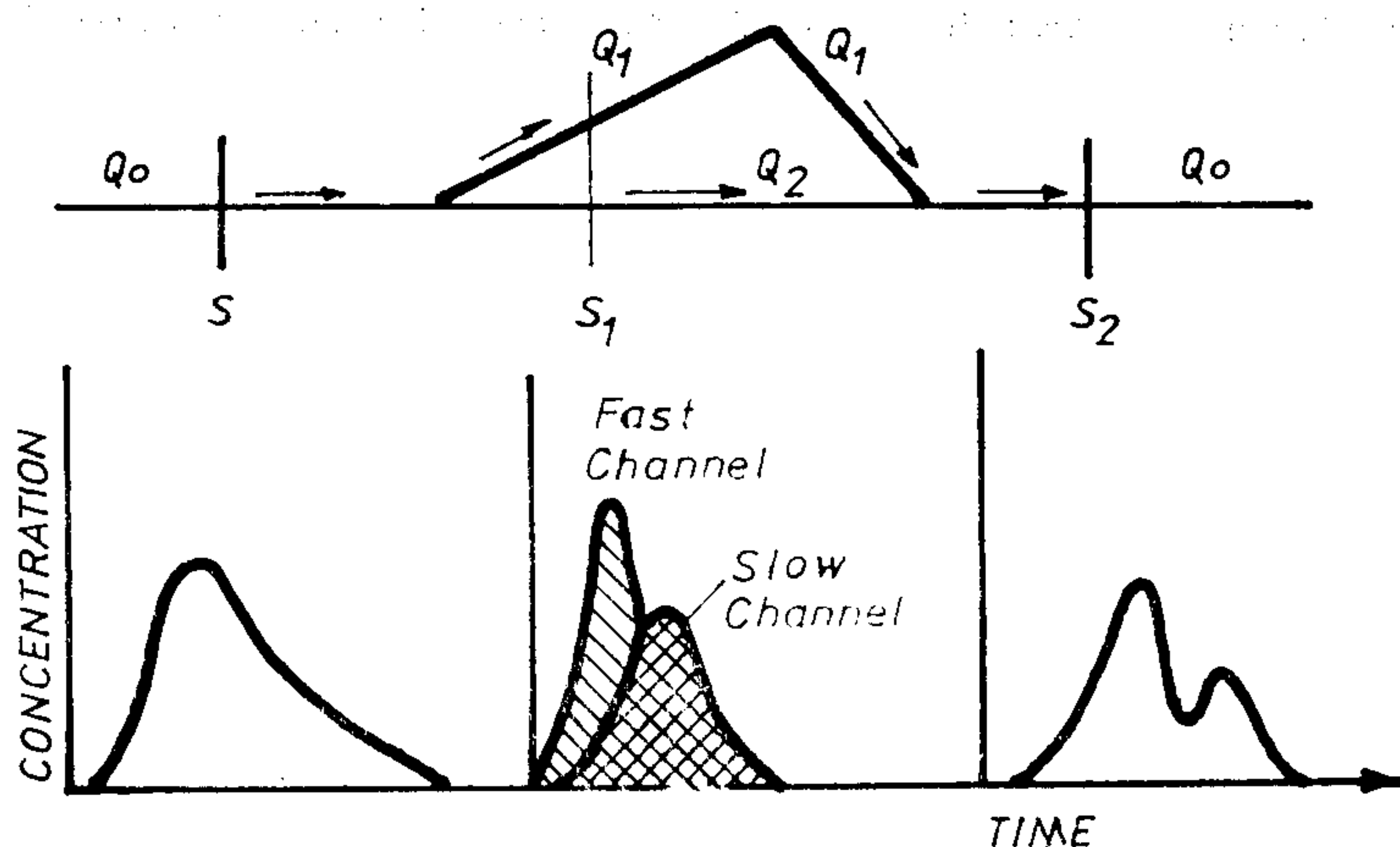


Fig. 25. Theoretical $C(t)$ curve for two branches of the initial current in the underground.

— in certain situations when the route contains a siphon that operates rhythmically, the concentration-time distribution curve will have peaks that are equally distanced in time. The peaks must have a descending amplitude but they may also feature anomalies.

— when, at a certain moment, waters divide in the underground and take various routes towards the same spring. The peaks may be well spanned from one another, virtually representing two concentration-time curves, according to the tracer transport velocity through the two channels. If from the slow channels the tracer penetrates into cavities containing underground lakes the time distribution of tracer concentrations will be a continuous curve with two peaks (fig. 27).

The intensity graphs point to certain characteristics of the karstified rock. The graph integrates these characteristics. At present, no method is available for separating on the graph the effects of hydrogeological parameters and main characteristics of karstic aquifers without doubt,

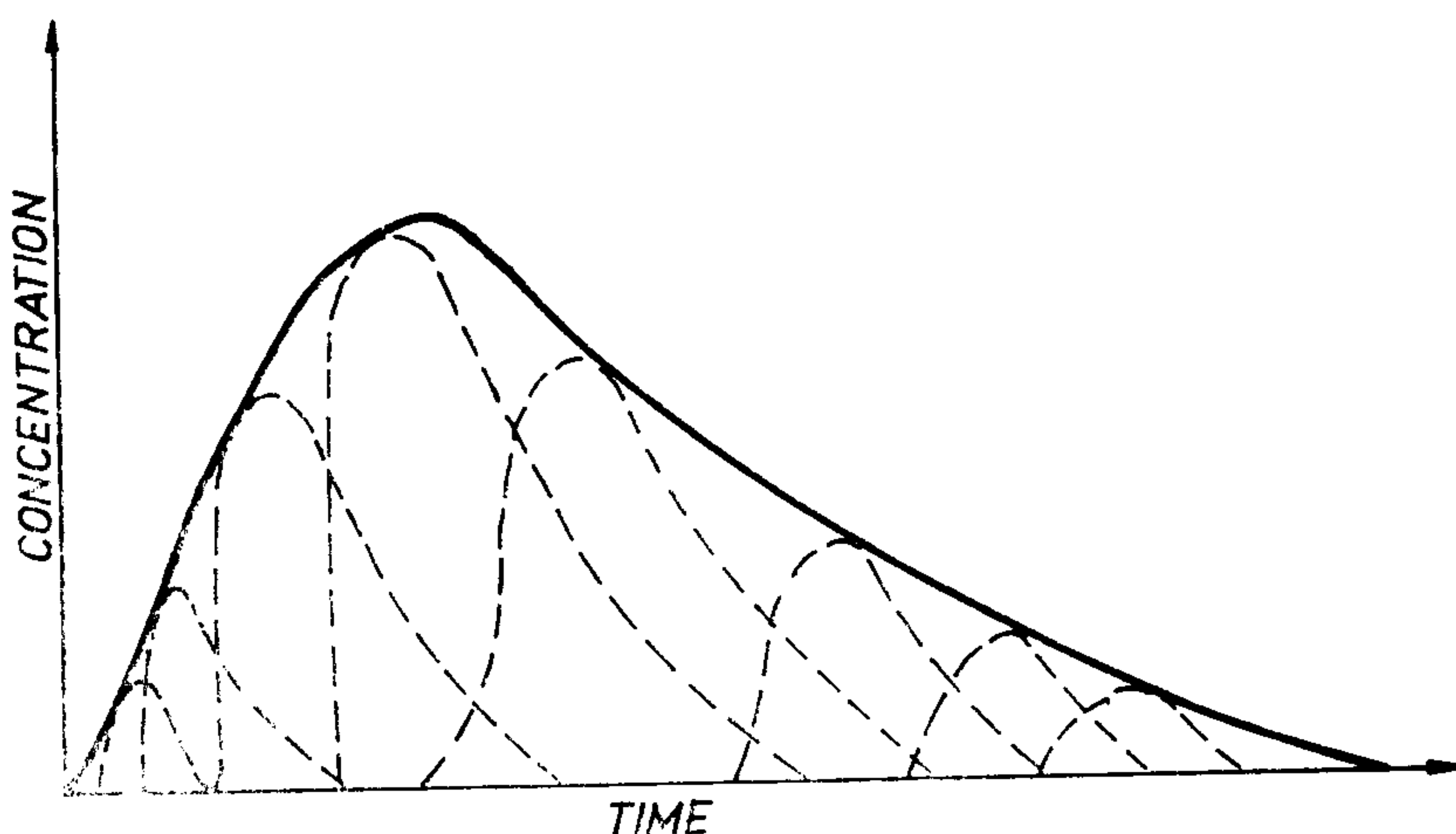


Fig. 26. Theoretical transfer curve for the case of a multichannel flow.

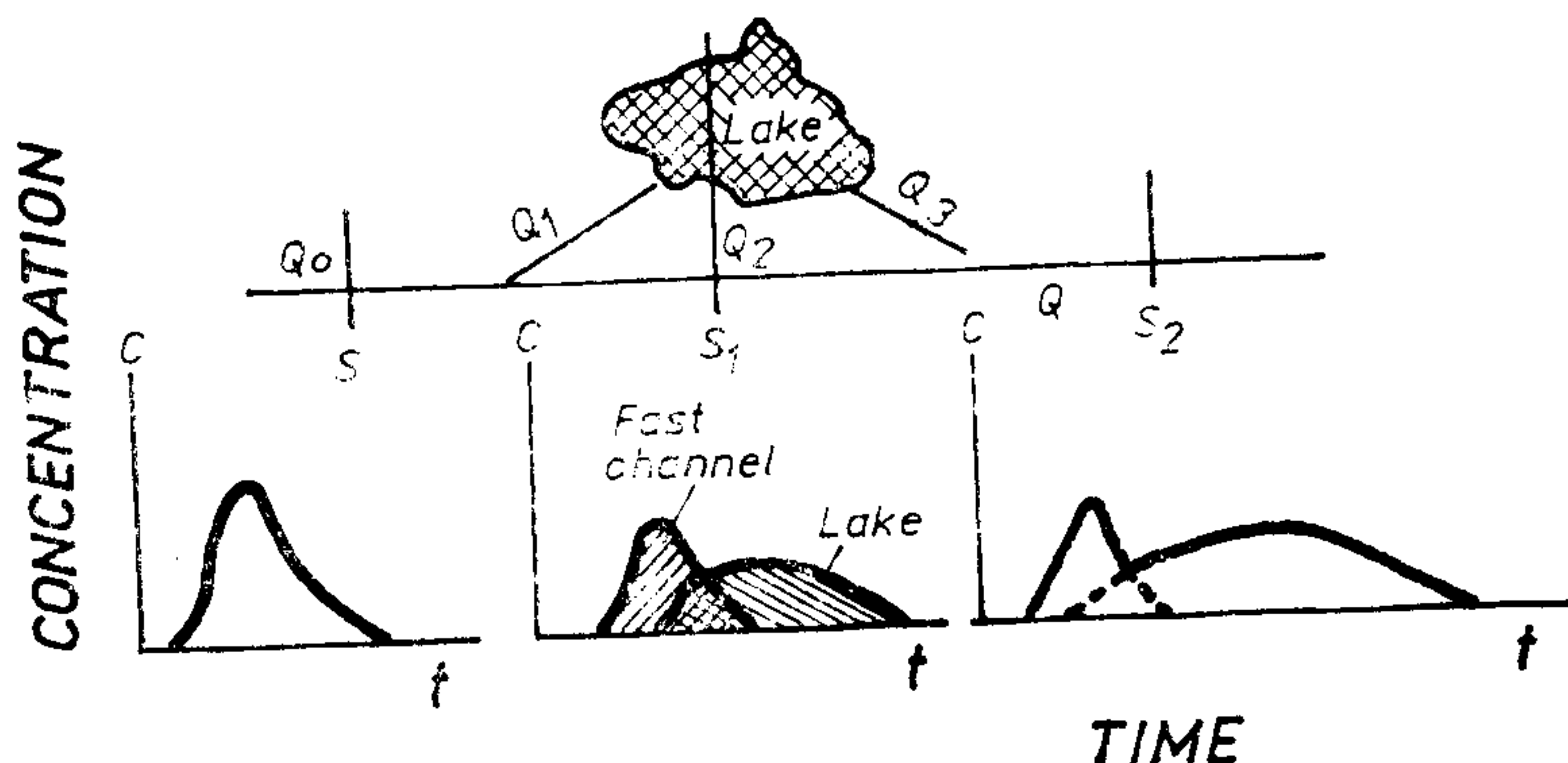


Fig. 27. The concentration-time distribution curve for the case one of the branches crosses an underground pool.

the shape of this graph primarily depends upon the geometry of the water conduit bearing the flowing water during tracing time (Milanovic, 1981).

However, considering a simplified case when the main stream divides in two on the swallet-spring route, the analysis of the residence time distribution (RTD) allows of the assesement of the amount of water that flows through the fast channel. So, for instance, in fig. 28 the area below curve $C(t)$ may be divided in two — A and B. Under steady-state hydraulic conditions, the short circuit coefficient will be :

$$\beta = \frac{A}{A + B}$$

The tracer concentration-distribution curve according to time provides for the quantitative processing of the pieces of information which tracers supply. Thus, if an amount of tracer M_0 is injected into a system and its concentration C , measured with time at output or another point in the system such that complete mixing has been achieved, then in steady-state conditions, consideration of mass balance requires that

$$M_0 = Q \int_0^T C dt$$

More often than not, however, the amount of recovered tracer is M , where $M < M_0$, as part of the tracer may penetrate into the auxiliary systems being released along with the postponed infiltration after an interval of time which is too long to allow of measurements.

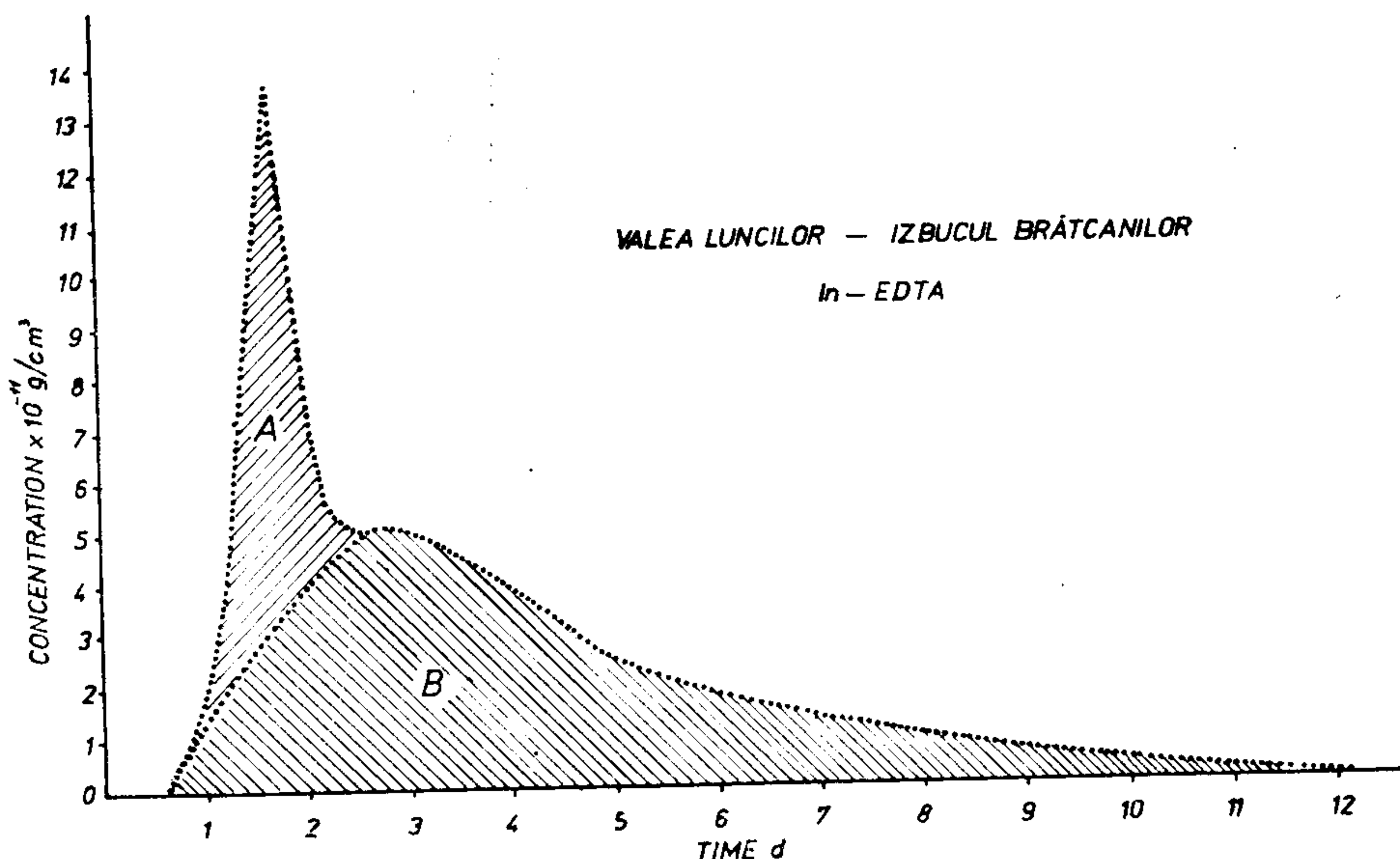


Fig. 28. The fast component of the flow may be assessed using the coefficient :

$$\beta = \frac{A + B}{A}$$

If the tracer occurred in several points, then the amount recovered will be :

$$M = \sum_{i=1}^n M_i$$

which, for an ideal tracer, in case of a steady-state flow throughout the duration of the experiment, must be equal to the injected amount, M_0 .

9. QUANTITATIVE DETERMINATIONS FROM TRACING EXPERIMENTS

Brown, Ford (1977) and Gașpar (1972) have shown that if the values of swallet discharge Q_0 , spring discharge Q , and recovered masses of tracer at spring are known, it is possible to determine one of five different types of flow networks to which the system may belong.

Let us give the schematic representation of a hydrokarstic structure characterized by an input, with the known discharge, Q_0 , and an output with discharge Q . This structure may be also supplied inside with a discharge :

$$Q_x = Q_{x_i}$$

and may discharge through several emergences :

$$Q_y = Q_{y_i}$$

which may have connections with discharge Q or not.

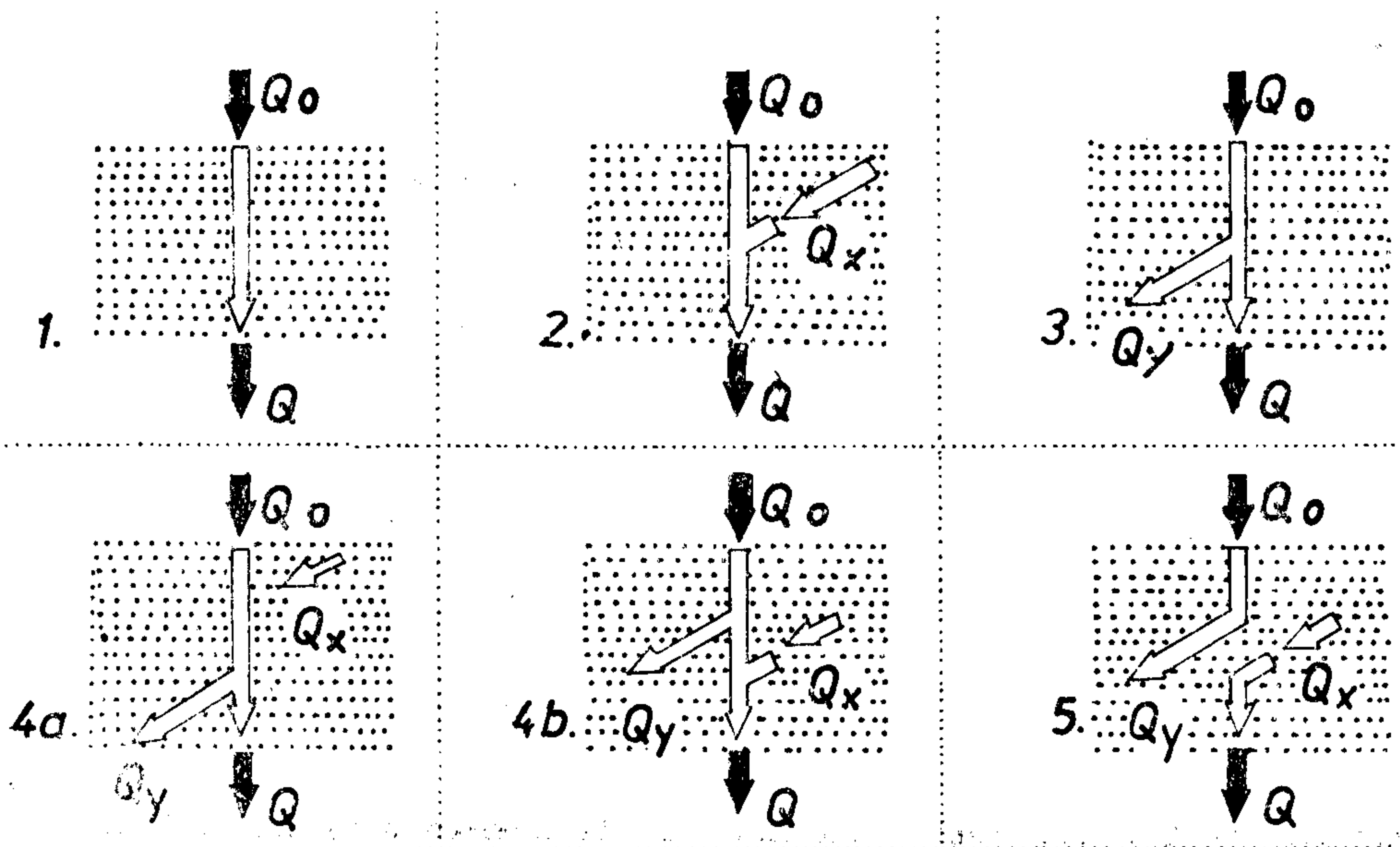


Fig. 29. Theoretical karstic flow networks.

With this image as a basis, hydrokarstic structures may be grouped in five types (fig. 29), according to the karstic networks crossing them :

- Type 1, a single input to a single output ;
- Type 2, additional, unknown input ;
- Type 3, additional, unknown output ;
- Type 4, additional inputs and outputs ;
- Type 5, an input which is not connected to the known output.

In certain circumstances, it is possible to assess the type of karstic network and the relative contributions of unknown inputs and outputs, when they exist, if all the information items available (hydrological, hydrochemical and isotopic pieces of information, investigations based on artificial tracers etc.) are processed. Let us make a brief survey :

Type 1 a of karstic network of flow corresponds to very recent karstic formations for which

$$Q_0 = Q \text{ and } M_0 = M$$

A variant of network type 1a is type 1b in which the tracer was detected in three outlets after having been injected in the inlet point A. If complete mixing has been achieved before point B it will be possible to evaluate the amounts of tracer M_1 , M_2 and M_3 emerging from the outlet points if the flow rates are measured in these points (Q_1 , Q_2 and Q_3).

In this case :

$$M_0 = M_1 + M_2 + M_3$$

and it will thus be possible to estimate the relative proportions of water at the outlet points originating from point A.

For a karstic network of type 2, it results that :

$$M_0 = M \text{ and } Q_0 < Q$$

In this case, the hydrochemical analyses and the data supplied by environmental isotopes may indicate the origin of the unknown discharge input. A complete study, however, calls for hydrogeological investigations through wells.

Type 3 refers to a karstic network in which :

$$Q_0 > Q \text{ and } M_0 > M$$

Therefore :

$$\frac{Q_0 - Q}{Q} = \frac{M_0 - M}{M_0}$$

In this case, other exurgences should be searched for, as they exist.

Type 4 corresponds to the situation in which the amount of recovered tracer is smaller than that injected and the discharge of the measured emergence may be smaller, equal to or larger than the discharge of the labelled insurgence :

$$\frac{Q_0 - Q}{Q} \neq \frac{M_0 - M}{M_0}$$

Very many hydrokarstic systems fall into this category. It presents only two special cases, 4a and 4b, where similar systems give different tracer budgets.

The most difficult to solve case is case 5. It represents a trap for tracer investigation for which we postulate that each labelling that does not lead to tracer occurrence in the measured emergences must not be taken as a proof of lack of hydraulic continuity. Only systematic hydrochemical analyses or the study of the variation of environmental isotopes will be able to accurately assess the origin of the waters of these emergences and the inexistence of a hydraulic link with the labelled ponor. Hydrogeological investigations through wells, as well as the use of additional geophysical methods complement the range of means which lead to an understanding of the intimate structure of the respective karst.

10. FLOW MODELS

The data obtained with the help of tracers may be used either directly or in association with flow models. Generally speaking, dispersion and mixing processes taking place during flow in a real hydrological system are far too complex to be entirely described by a mathematical relation; furthermore, it is difficult, if not downright impossible, to adapt a response function corresponding to the system under study. However, though idealized, the mathematical models and the digital simulation approach, which are currently used in hydrology (Dincer, Davis, 1967, Przewlocki, Yurtsever, 1974, Yurtsever, Payne, 1978, Bulgăr et al., 1984, Maloszewski, Zuber, 1984) may lead, in certain cases, to a convincing description of the dynamic behaviour of the aquifer. These models originate in two basic approaches, viz. the convolution approach and the quasi-physical models employing an interconnected array of mixing cells (compartmental models).

Flow in karstic structures may be modelled if the input and the output functions are known. To obtain these functions is important as they provide for an assesement of the transfer function of the karstic system.

The input and the output functions may be the chronological series of precipitations on the one hand and the outflowing discharges on the other. The output function may correspond either to the chronological series of raw precipitations or to effective infiltrations when evapotranspiration is considered. A number of difficulties are encountered, namely that precipitations are known less accurately (as their special variability is substantial) and evapotranspiration is difficult to assess and the relations employed to compute it are not altogether satisfactory.

Other parameters (functions) related to water circulation may be considered: chemical concentrations, environmental isotope concentrations, thermal variations, solid discharge, the development of aqueous micro-fauna, as they all depend on the behaviour of the karst. For these functions to be considered and relevant, as long as possible chronological series are needed.

As they are used in the study of karst behaviour, artificial tracers may supply special information intems if successive labellings are performed in periods of low flow, of flood or in conditions of mean discharges. However, prior to applying transfer functions to the study of karst behaviour the system under investigation should be defined. There are

two methods whereby research aimed at defining a karstic system may be approached :

— knowledge of all losses and outflows from karst to establish whether it belongs to a system or not. This may be achieved through labellings within multitracings experiments ;

— research into the possibilities of existence of excess outlets (which are therefore operational only in cases of high discharges) or of uncontrolled inputs, starting from a surveillance of the main emergence of the system. This research work is conducted through both hydrological methods and labellings with tracers (which may show excess discharges, the discharges of epikarstic aquifers and the existence of karstic capture phenomena).

It is easy to determine the input function for labellings performed with the help of artificial tracers when injection is achieved through a pulse. In the case of diffuse losses through river beds or lake bottoms, a deconvolution operation is needed for the assessment of the input function.

There are large karstic systems which contain long solution channels and in this case water re-emerges to the surface either in intermediary points or in caves. The performance of labellings in such like karst takes long to obtain the complete tracer recovery curve at the karst outlet. In this interval, hydrological conditions may change substantially and discharges may vary from low flow to flood, which renders the RTD analysis in non-steady-state conditions extremely difficult (Molinari, 1976). The solution to the problem is the performance of simultaneous labellings in access points and the determination of tracer concentration distribution according to time, by sections. During data processing the RTD for the whole system may be obtained with the help of a convolution operation, which sensibly cuts the duration of investigations (fig. 30).

Water flow through a karstic system is far from ideal. Transfer functions may be interpreted and the age concept applied only in association with a flow pattern. The generally valid flow patterns cannot be defined as each karst boasts its own salient features and it is impossible to estimate all the parameters responsible for the behaviour of the respective karst.

These patterns are intended for understanding or simulation of the operation of the system. The lack of concordance between the results of observations and the pattern employed may be a consequence of a bad definition of the system, of an erroneous estimation of the input and output functions. If the flow pattern is appropriately selected then the experimental curves will superpose over the theoretical curves and all distribution parameters will be the same. In this situation, a series of important characteristics, such as static and dynamic reserve, the dispersivity of the aquifer, and, consequently, the vulnerability of the karst will be determined and, what is highly important, the behaviour of the karst in various hydrogeological conditions and its evolution predicted.

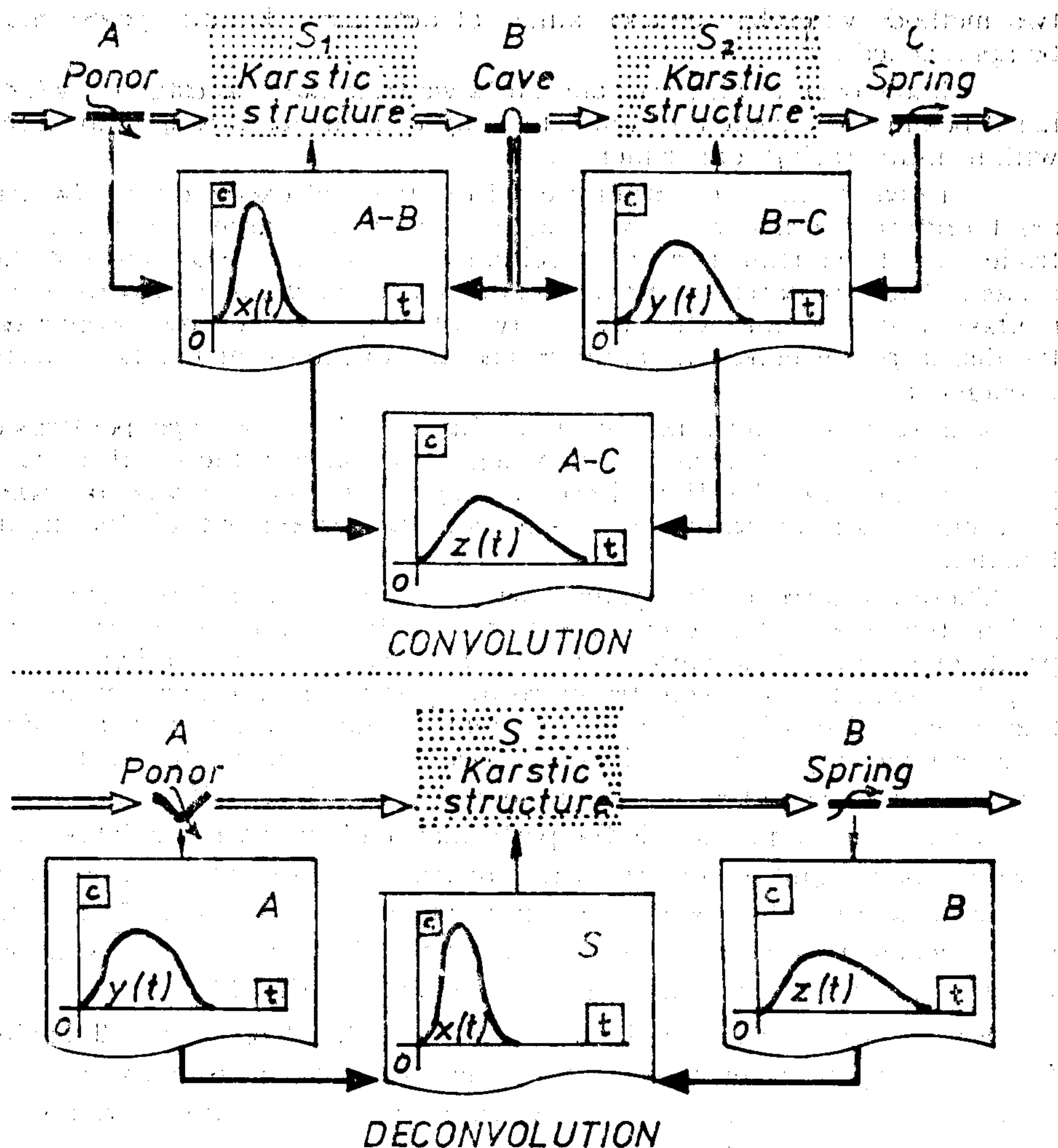


Fig. 30. Use of convolution and deconvolution for assessing an unknown component of the studied flow.

Correspondences with ideal flow models may be found in nature. A more frequently employed flow pattern is the hydrokarstic system well mixed represented by a connected group of basins. Thus, the model imagined in fig. 31 has a counterpart in reality and, with a slight deviation, represents a longitudinal section through Cueva de Boluga, Spain (Cox, 1971). The cave passage is assumed to consist of a sequence of well-stirred pools, each of volume w and a constant flow Q so that the concentration C of a solute in the water that leaves the n -th pool is the same with that of the water in the same pool. Connected basins represent a dispersion model with deviations from the piston flow (fig. 31).

The existence of a piston flow accompanied by dispersion and diffusion in the matrix (a convective-dispersive pattern) may be easily shown through a simultaneous labelling with particles (spores for instance) and a conservative hydrological tracer (either fluorescent or radioactive tracer). Thus, the outlet curve may feature a peak owing to the piston flow (materialized through spores) and a flat shape owing to the dispersion of the other tracer as in fig. 32.

In general, experimental data (repeated labellings, multitracing experiments) supply sufficient arguments for the selection of a flow pattern with total displacement drain or branches (short circuits, perfect-mixing zones (underground pools), stagnant zones (underground lakes, siphons), zones with dispersed, diffusion and exchange (auxiliary systems).

It should be pointed out, however, that the interpretations of flow patterns call for permanent hydraulic conditions, as two phenomena occur in this case — transport of masses of water, on the one hand, and tracer propagation on the other hand. The two phenomena are linked to each other through relations that are difficult to assess when discharge varies.

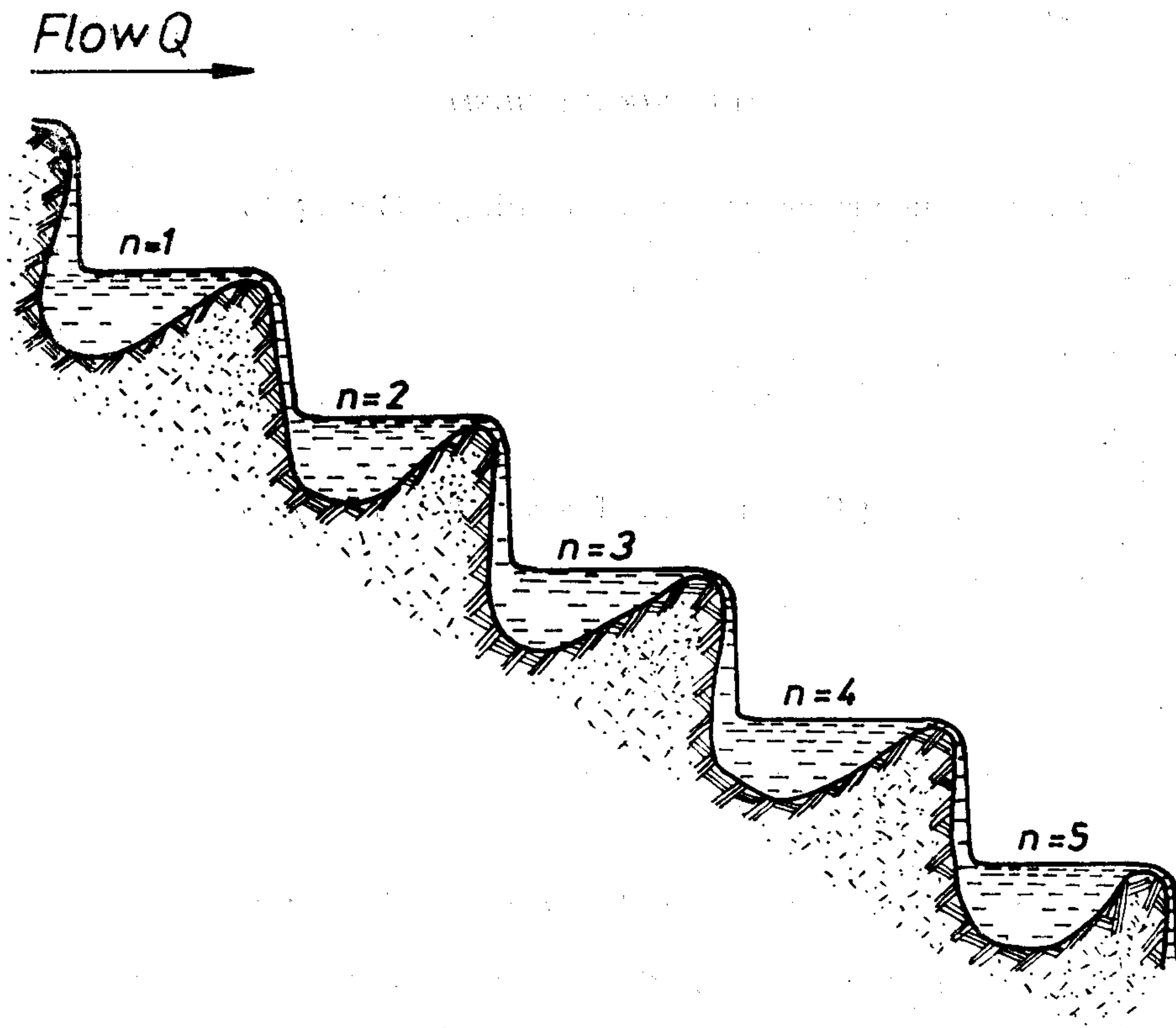


Fig. 31. Section through Cueva de Boluga, Spain (weil — stirred pools model).

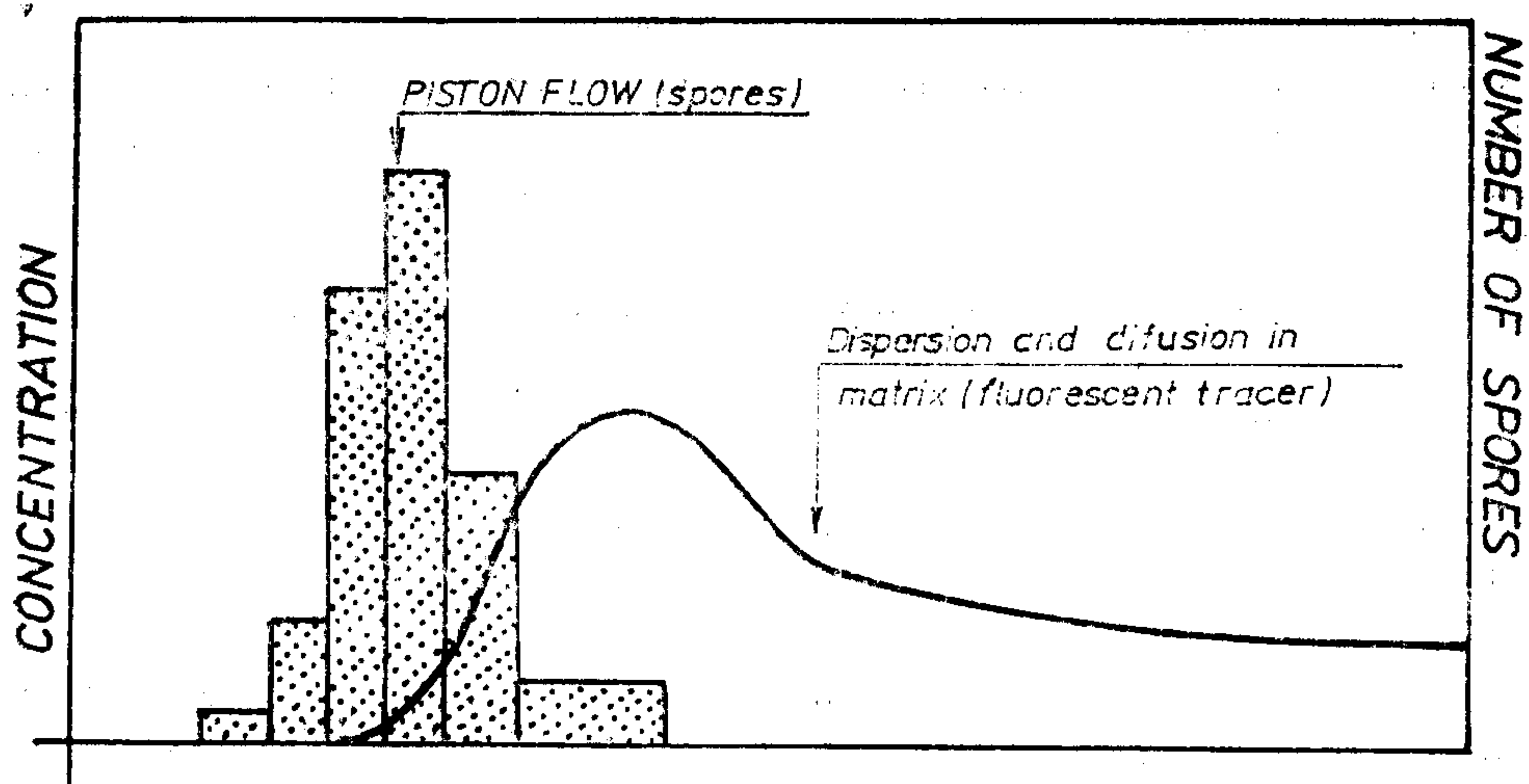


Fig. 32. A theoretical double labelling to assess the flow through fast channel (using *Lycopodium* spores as a tracer) and the contribution of slow channells, using fluorescent tracers.

11. MULTITRACING EXPERIMENTS IN ROMANIAN KARST

11.1. THE PROBLEM

Inespective of its qualities, a tracer is not sufficient and cannot be used for simultaneous or repeated labelling. Owing to the extremely different behaviour of the karst in between low flow and flood, important amounts of tracer may remain in its systems for a long time. Consequently, investigation of hydrokarstic structures should be performed through simultaneous labellings, with the help of different tracers: fluorescent dye tracers, chemical or activable tracers, radioactive or biological tracers.

Multitracing experiments are employed:

- for shortening the duration of research work by avoiding repeated trials;
- from the necessity to perform investigations in analogous hydraulic conditions;
- because of the fact that the main cost of a tracing in karst depends more often than not on the intervention of the personnel that take the samples. And the spending implied by this operation is independent from the number of labellings that are performed.

Labellings in karsts supply through knowledge of the karst, facilitate validation or nevalidation of hydraulic connexions, and provide for the discovery of new connexions. They are an ideal means of studying the vulnerability of the karst to pollutants. Labellings also allow of a verification of flow patterns of the hydrokarstic structure under investigation, the performance of methodological and comparative studies concerning the behaviour of other tracers.

On the other hand, the fact should be stressed that in multitracing operations artificial tracers cannot supply information on the slightly permeable sectors of karstic systems. Such pieces of information can be obtained if water chemism and environmental isotopes are associated.

For a better understanding of the goals of artificial labellings of hydrokarstic systems a number of case studies should be outlined.

11.2. LOCALIZATION OF GROUND WATER CATCHMENT AREAS

Differences in the D, T, ^{18}O and salt contents resulting from the local distribution pattern of these isotopic contents within the precipitations due to continenal, altitude and other isotopic effects have been successfully used for answering the question which catchment area belongs to a specific karstic system (fig. 33). Also, labelling experiments with intentionally added tracers contributed to the definition and delimitation of catchment areas in karstic aquifers.

In karst areas, the delineation of approximate groundwater catchment boundaries is the first step in any hydrogeological study. However, if it is always difficult to place the exact limits of an emergence in karstic areas in the absence of well defined geological boundaries. The topographic supply basin and the real drainage basin are seldom in concordance. The location of catchment areas may be identified by analysing

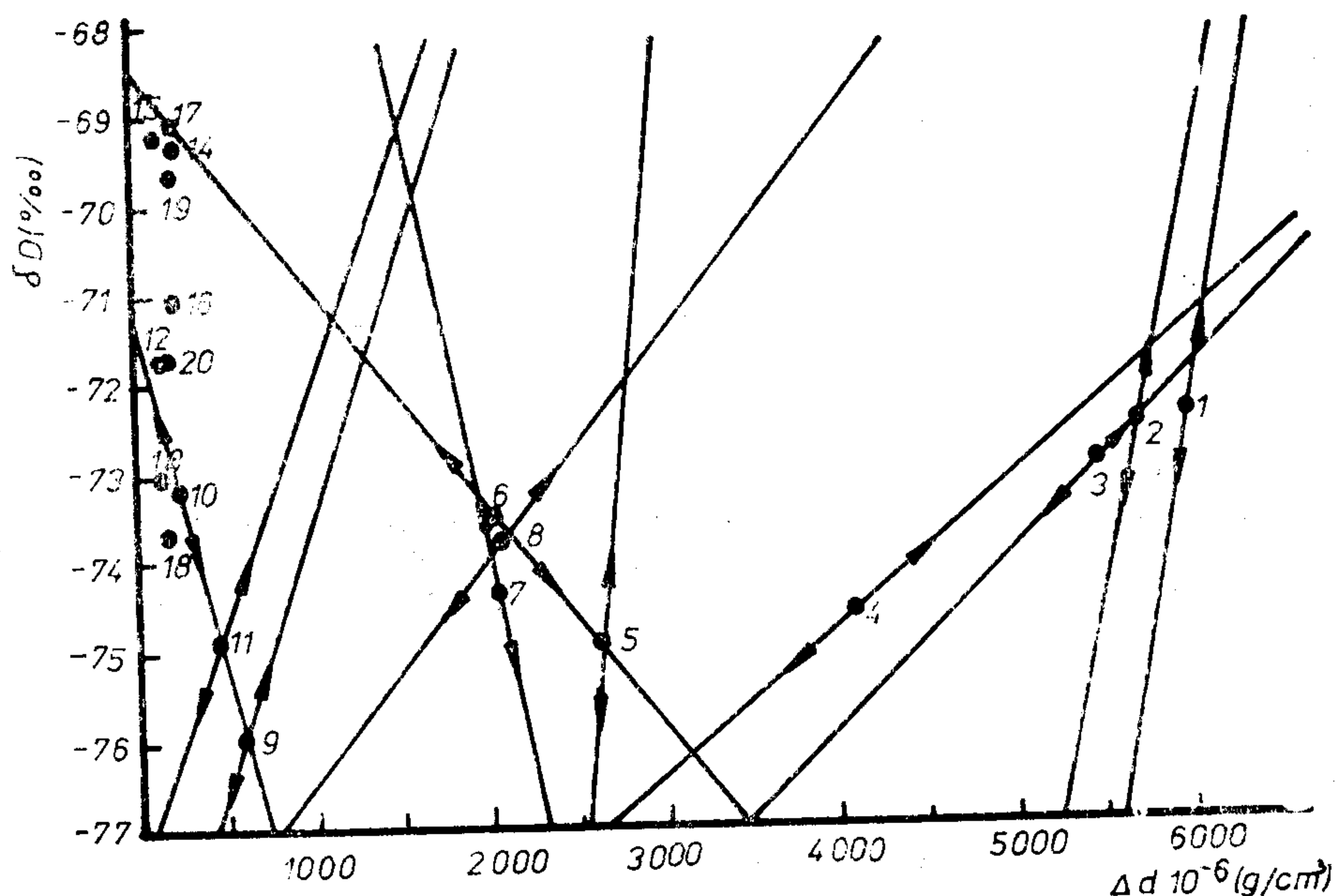


Fig. 33. Wandering lines of $\delta\text{D} - \Delta d$ values for geothermal water types and mean values δD and Δd for all water types taken into account in Băile Herculane area. 1 — Fabrica de var ; 2 — Decebal ; 3 — Traian ; 4 — Neptun ; 5 — Diana ; 6 — Apollo I ; 7 — Apollo II ; 8 — Hercules ; 9 — Scorillo ; 10 — Ghizela ; 11 — Șapte izvoare calde ; 12 — Șapte izvoare reci ; 13 — Cerna spring ; 14 — Topleț spring ; 15 — Poiana Beletina ; 16 — Izverna spring ; 17 — Pișetori ; 18 — Izvorul Alb ; 19 — Bîrza spring ; 20 — Ciocloare spring.

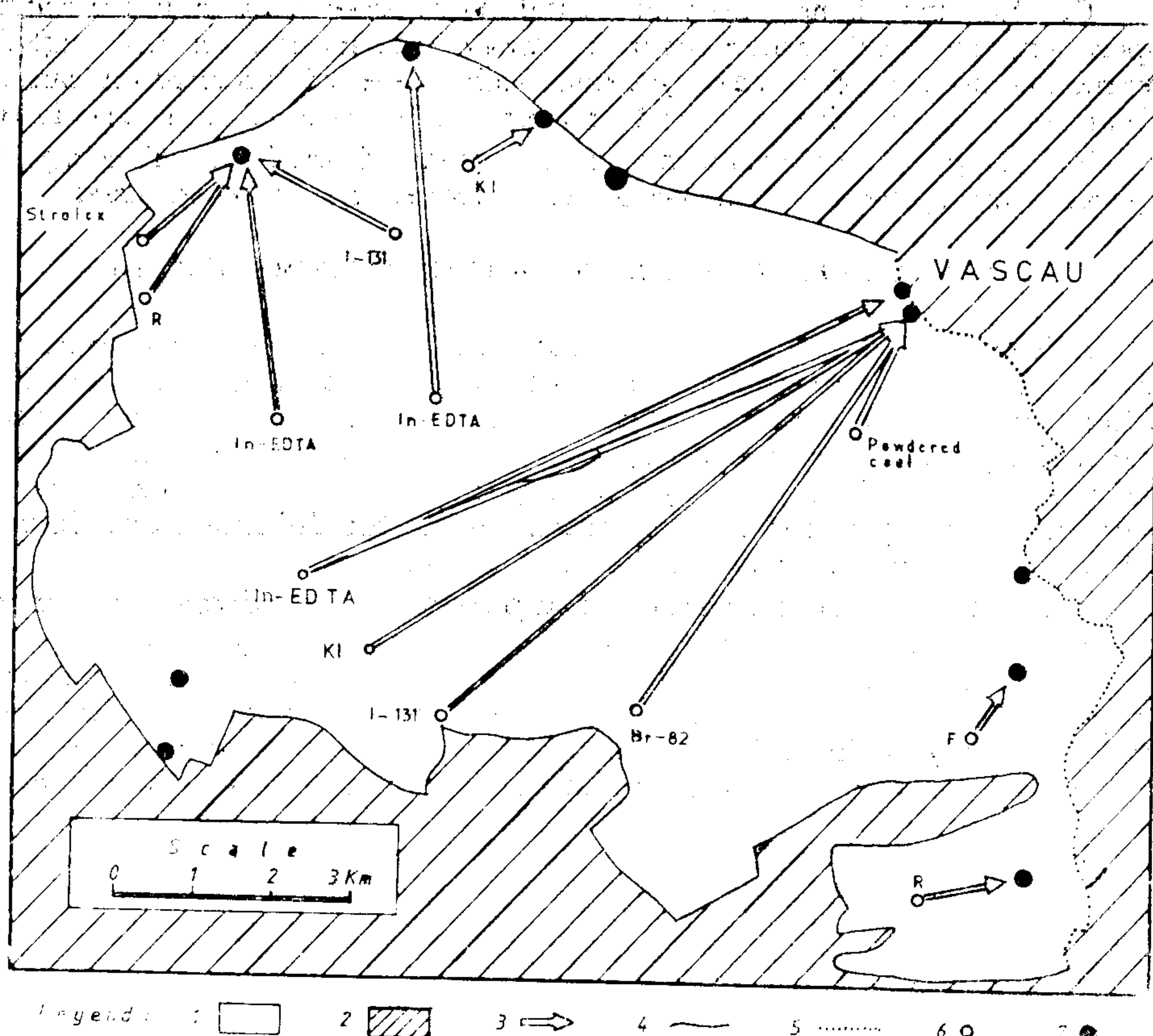


Fig. 34. Main spring and underground flow direction in Vașcău karstic plateau. 1 — Karstic terrains. 2 — Non karstic terrains. 3 — Underground routes. 4 — Secondary barrier. 5 — Permeable border. 6 — Ponor. 7 — Spring.

hydric balance in correlation with the results of the labellings performed with the help of artificial tracers (Quinlan, 1982).

In the wake of labellings convergent and divergent flow routes result. Figure 34 shows the delineation of karstic area and drainage divides with the help of convergent labellings in Vașcău karstic Plateau (Orășeanu, 1985), and fig. 35, the extension of drainage area of „Peștera cu apă de la Bulz” (Rusu, 1981; Orășeanu and Jurkiewicz, 1982).

11.3. HIGHLIGHTING OF PARTIAL CAPTURES AND DIFFLUENCE SURFACES

Phenomena of stream water piracy are specific to karstic areas; they are characterized by the fact that the water infiltrated into a hydrographic basin and having covered a certain underground route is to be found again in a source that appears in another hydrographic basin (fig. 36).

In order to individualize the surface of the hydrographic basin upstream of the partial capture in terms of hydrogeology, the notion of difffluence surface was suggested, while to designate the phenomenon,

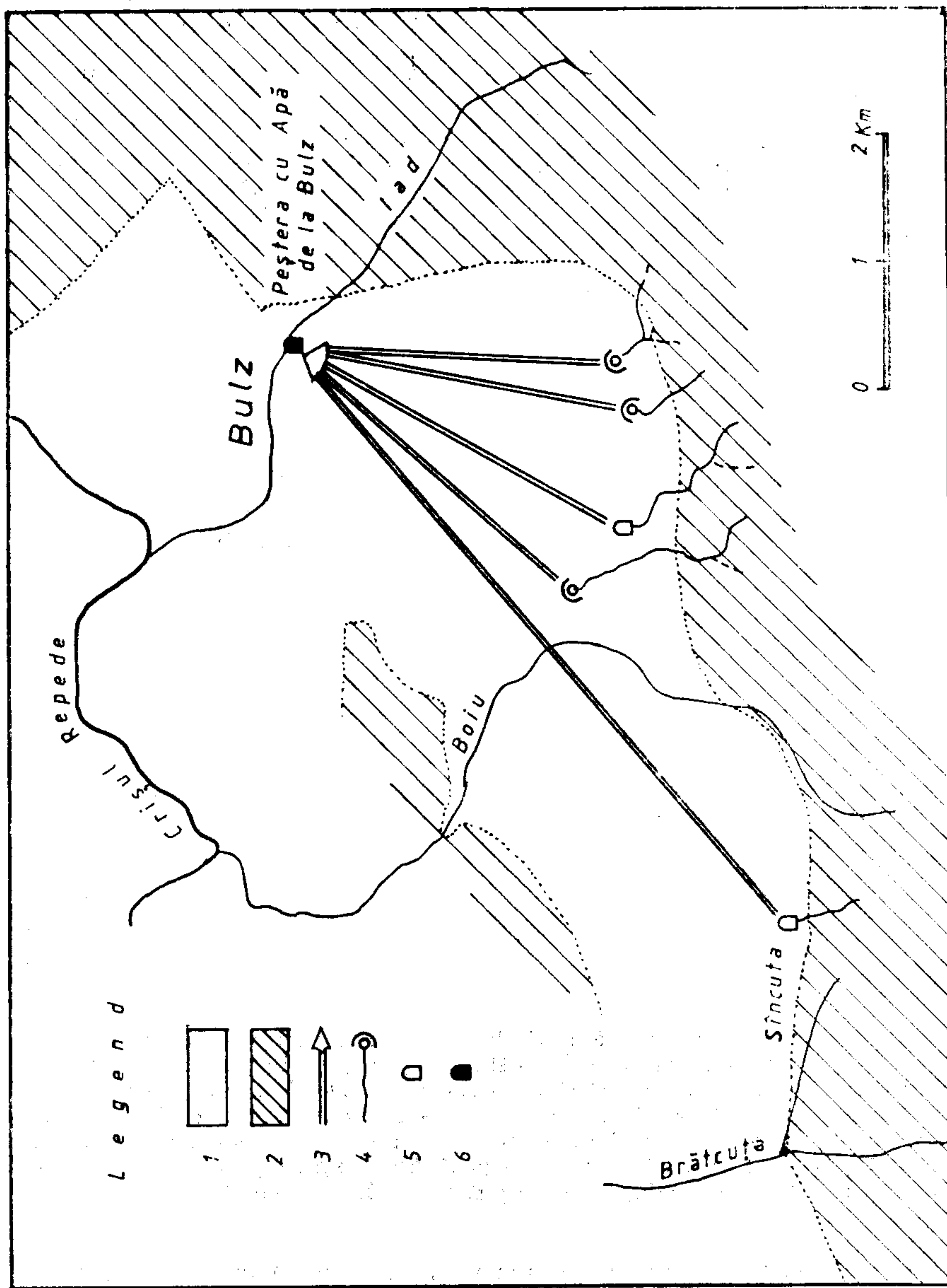


Fig. 35. Drainage area of Peștera cu Apă de la Bulz cave. 1 — Karstic terrains. 2 — Non karstic terrains. 3 — Underground routes. 4 — Ponor. 5 — Inflow cave. 6 — Outflow cave.

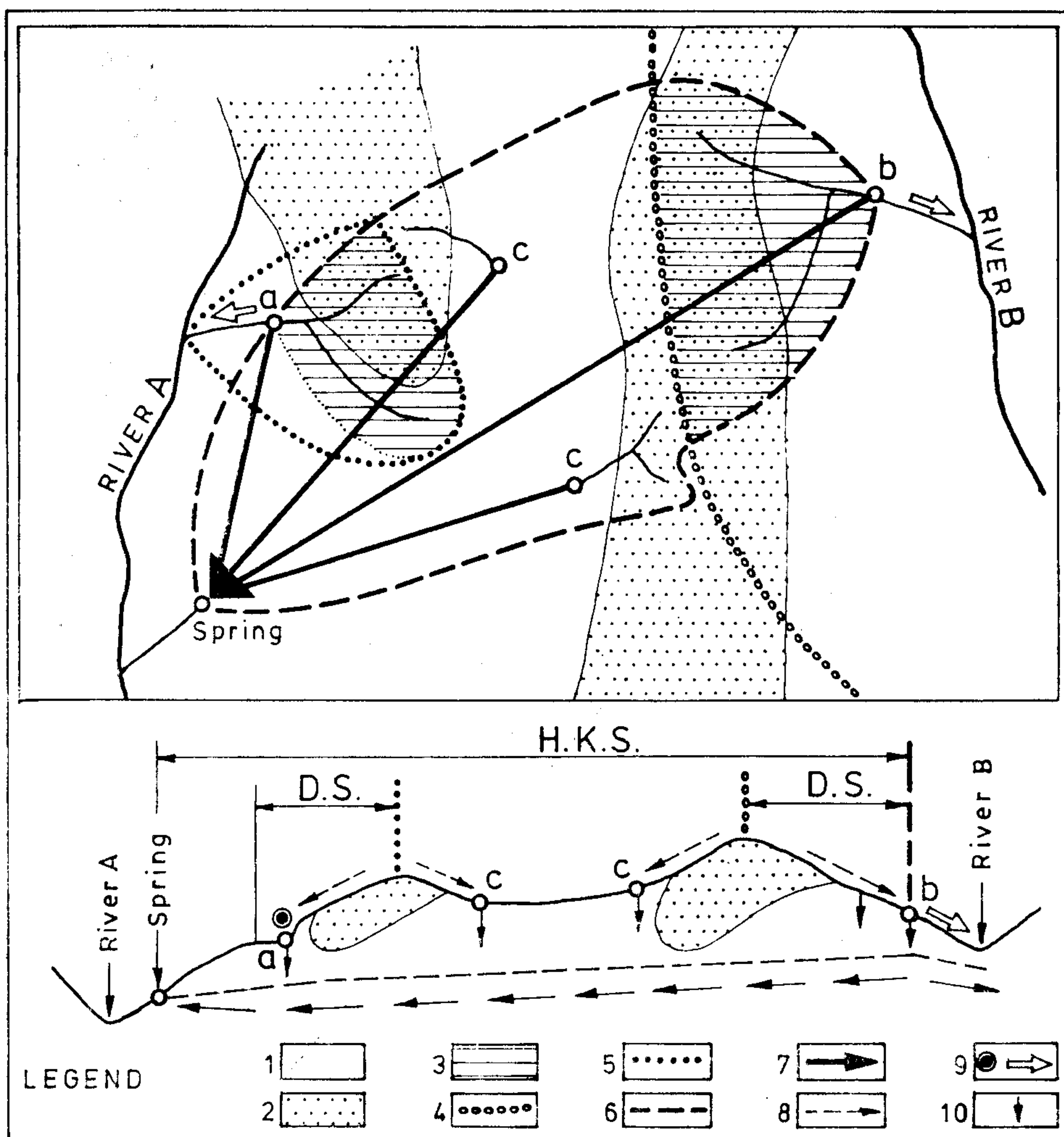


Fig. 36. Partial captures and position of the diffiurface surfaces (after Orășeanu, 1985 b). a — Cohydrographic capture, b — Heterohydrographic partial capture, c — Endohydrographic (total) capture; H.K.S. — Hydrogeological karst system, D.S. — Diffiurface surface; 1 — Karstifiable rocks, 2 — Nonkarstifiable rocks, 3 — Diffiurface surface, 4 — Superficial watershed between rivers, 5 — Superficial watershed between brooks, 6 — Limit of hydrogeological karst system, 7 — Underground flow direction, 8 — Efficient rain, 9 — Output from the system, 10 — Infiltrations.

the concept of basin karstic diffiurface was set forth (Orășeanu and Jurkiewicz, 1982).

Hydrogeological investigations carried out in the northern part of the karstic area of Pădurea Craiului Mountains showed major developing capture phenomena, that induce a diversion in the epigean hydrographic network of karstic terrains. Fig. 37 shows the areas of karstic diffiurface

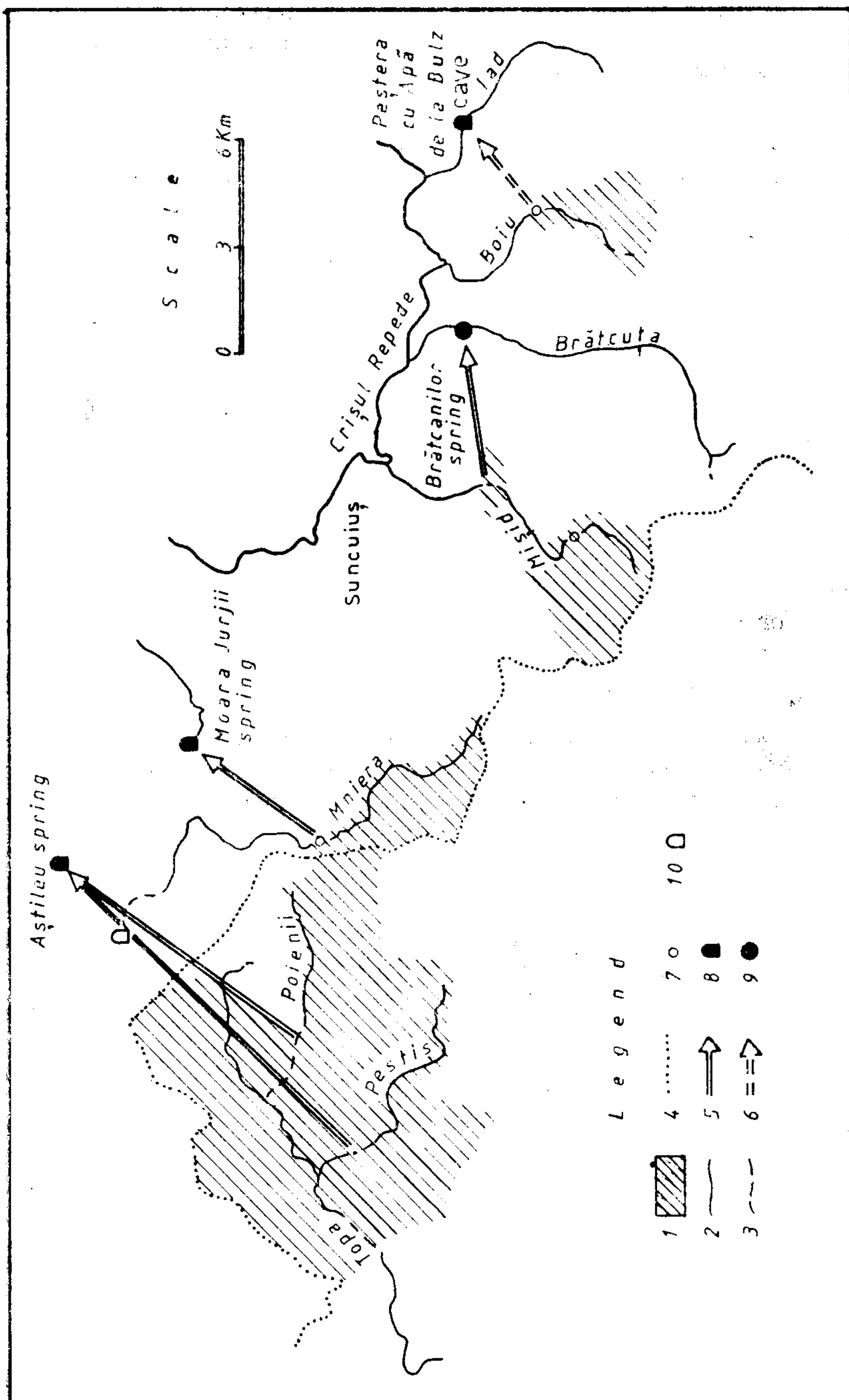


Fig. 37. Partial captures and diffidence surfaces in northern part of Pădurea Craiului Mountains (after Orășeanu, 1985 b).
 1 — Diffidence surface, 2 — Perennial river, 3 — Temporary river, 4 — Superficial watershed between Crișul Repede and Crișul Negru river; 5 — Underground connection established by tracing method, 6 — Underflow connection established by budget method, 7 — Perennial partial capture, 8 — Outflow cave, 9 — Spring, 10 — Inflow cave.

set through multitracing experiments using fluorescein, rhodamine B, Iodine-131, Cl^- and In-EDTA as tracers, in the karstic area of the Pădurea Craiului Mountains (Orășeanu 1985).

11.4. USE OF DEUTERIUM, ARTIFICIAL TRACERS AND HYDROCHEMICAL DATA TO STUDY RECHARGE AND GENESIS OF THERMAL WATERS

Geological and hydrogeological research carried out within the Cerna river basin indicated the deposit structural general model as well as another model concerning underground waters origin, thermal capacity, mineralization and dynamics (Simion, 1985). These models were checked by isotopic techniques, deuterium concentrations analysis, radioactive and stable tracers.

The analysis of deuterium concentrations and salt content of shallow and underground waters was performed during the 1979–1982 period by L. Blaga. The δD -time variation curves, drawn for all thermomineral sources, show that maximum or minimum deuterium concentrations reveal almost simultaneously. This fact indicates a rapid underground circulation, allowing thus the waters refreshing within the active areas of each source.

Typical for Herculane area is δD and Δ_{dens} value alignment a δD - Δ_{dens} diagram (average values) along the mixing straight line

$$\delta\text{D} = 448,41 \Delta_{\text{dens}} - 75,45 \quad (r = 0,82)$$

This fact may be considered as a unique mixing water system, generating the thermo-mineral waters in the area. So, the δD -time variations and δD average values in Cerna Valley indicate a meteoric origin of these waters (fig. 38).

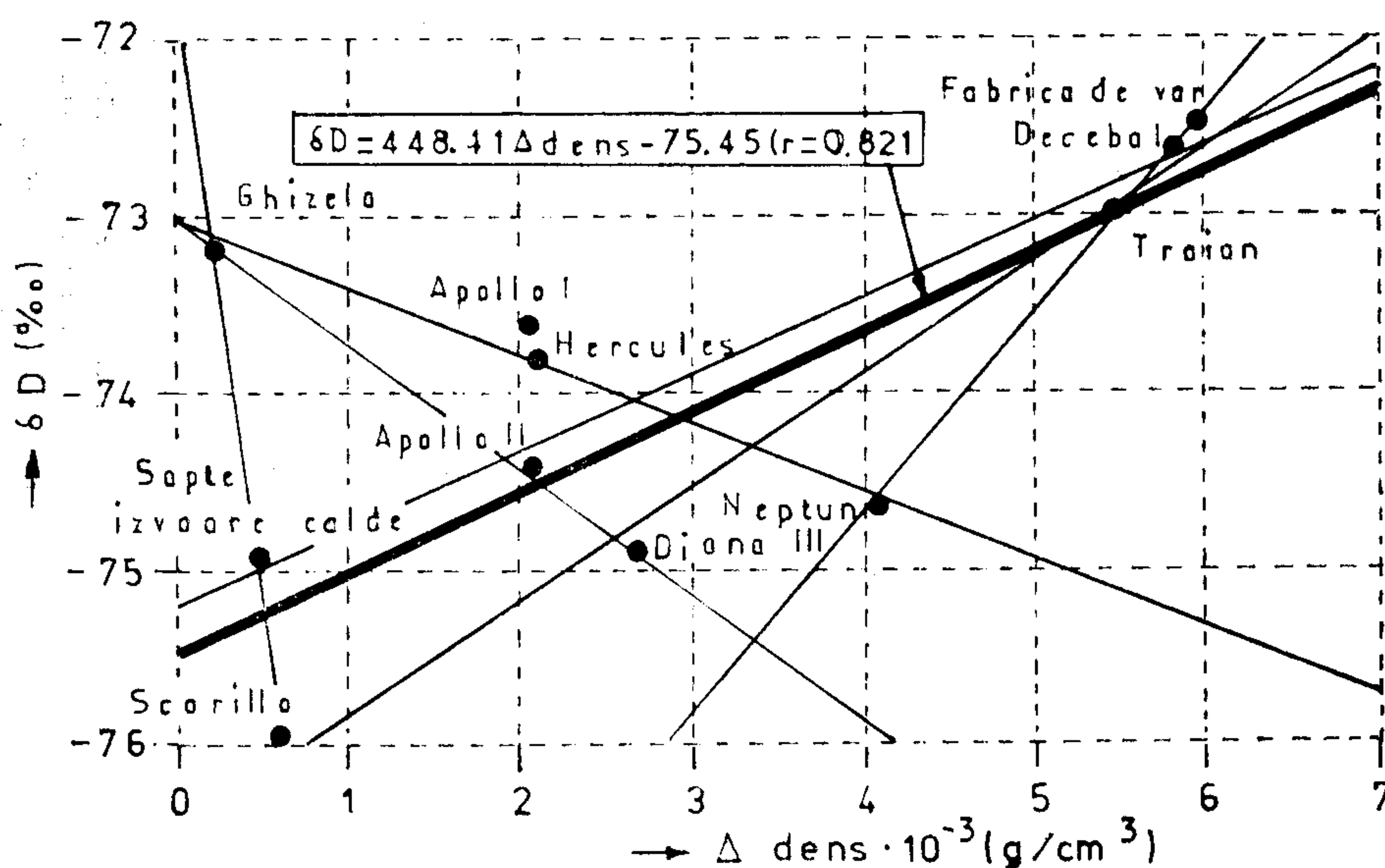


Fig. 38. Diagram of δD -time variation and δD -average values in Cerna Valley (after Blaga, 1979).

Direct investigations were carried on, labelling about 30 sinkholes and swallowholes located in the geothermal deposit recharge areas, using ^{82}Br , ^{131}I , ^{198}Au , ^{35}S as radioactive tracers as well as In-EDTA, fluorescein and other dyes.

As a result of geological, hydrogeological, hydrochemical, isotopic correlated determinations, performed also by tracers, the geothermal deposit of Băile Herculane may be considered as having an exclusively meteoric origin, with a recharge area that covers almost the entire hydrographic basin of Cerna river.

11.5. DETERMINATION OF REGIONAL GEOLOGICAL STRUCTURES

In certain hydrogeological conditions, labellings with artificial tracers may bring valuable contributions to the knowledge on the tectonic structure of certain regions, and at a low cost too.

Thus tracers investigations performed in the Motru Sec — Baia de Aramă area established a continuity of the limestone in the Danubian unit under the crystalline schists. These labellings proved through a hydrogeological method the existence of the Getic Nappe in this area. The hydrogeological relation between the waters infiltrated into the basin of the Gorgan brook and the springs in Baia de Aramă were highlighted with the help of ^{131}I and the relations between the diffuse losses from the Motru Sec river and the same springs with the help of In-EDTA. Figure 39 shows the two divergent labellings which contributed to the knowledge on the tectonic structure of the region (Slăvoacă, et al., 1985).

A second example is outlined in fig. 40 the area under study being located in the western part of the Bihor Mountains.

As can be seen in the section of fig. 40, a thick bridge of sandstone, conglomerates and permian shales rests discordantly over the limestone and dolomite attributed to the Autochthonous of Bihor and the Văleni overthrust. The diffuse losses in Seaca valley, a tributary of Galbena valley originating the Ruginoasa hole situated on the northern flank of the Tapu top, were labelled with In-EDTA. The presence of the tracer was detected on the southern slope on the mountain in the Criș spring; in this way, the overthrust position of the permian rocks was established through a hydrogeological method.

11.6. IDENTIFICATION OF SUB-AQUATIC SPRINGS

This is an difficult experiment which may, however, direct to quantitative results. Two types of tracers were found to have a number of applications: fluorescent dye tracers, that, more often than not can be detected with the naked eye, and radioactive tracers, which can be detected *in situ*.

Such a spring was identified under the Cerna river waters in the Piatra Pușcată point, with the help of ammonium dichromate and ^{192}Au , used as tracers. The tracers were injected in the Iuta valley whose confluence with the Cerna river is situated downstream of the aforesaid spring (Gaspar and Simion, 1985).

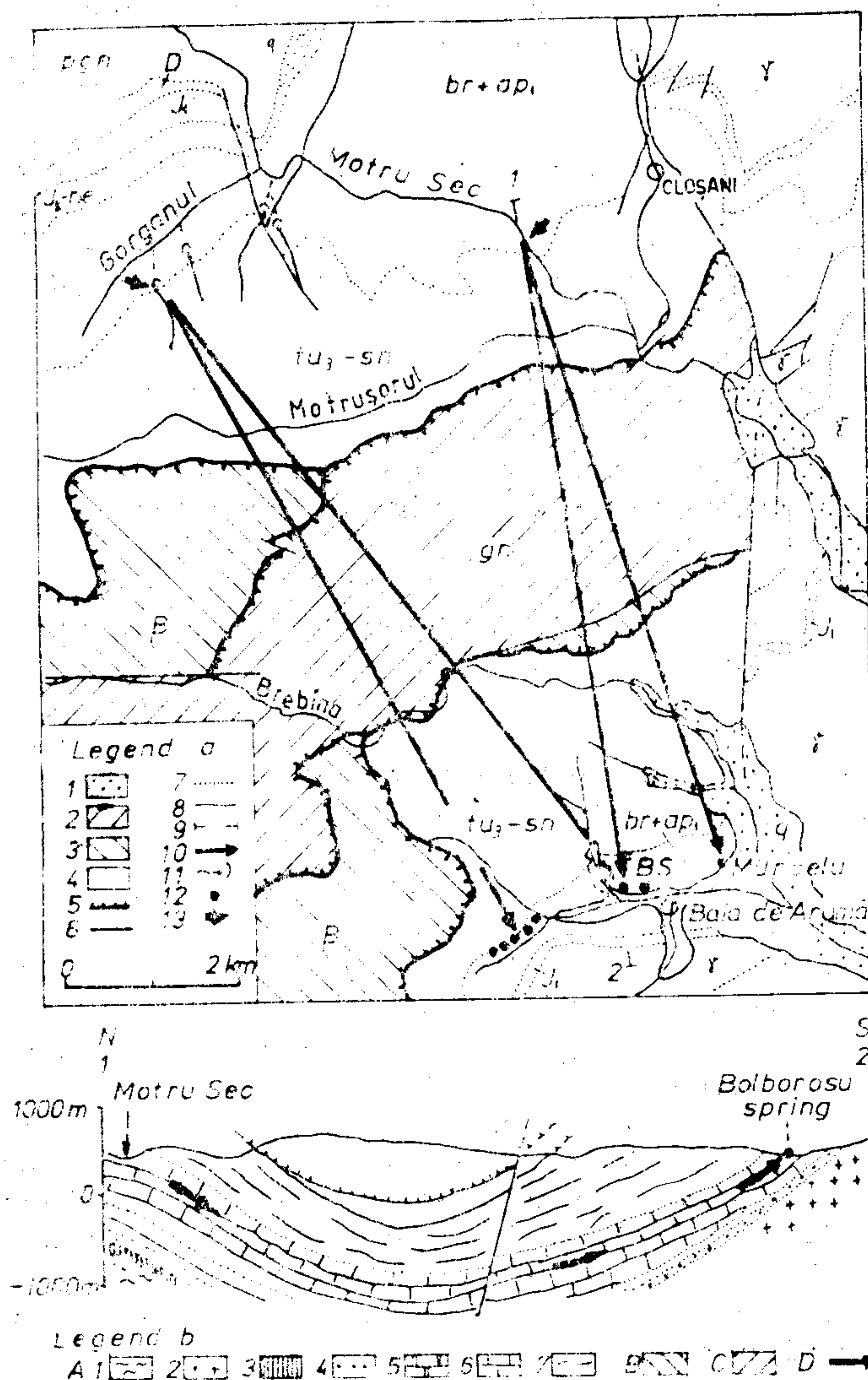


Fig. 39. Main underground drainage direction established by a multitracing experiment in Motru Sec — Baia de Aramă area. Legend a: 1 — Quaternary; 2 — Getic Nappe; 3 — Severin Nappe; 4 — Danubian Unit; 5 — Overthrust front; 6 — Geological boundary; 7 — Fault; 8 — Boundary of Quaternary formations; 9 — Geological cross section; 10 — Underground flow direction established by tracer experiments; 11 — swallet; 12 — Spring; 13 — Injection point. Legend b: A — Danubian Unit; A₁ — paragneiss; A₂ — Granite; A₃ — Chlorite shists (Devonian); A₄ — Conglomerates, sandstones (lower Jurassic); A₅ — Limestones (upper Jurassic-Neocomian); A₆ — Limestones (Barremian — lower Aptian); A₇ — Wildflysch formation; B — Severin Nappe; C — Getic Nappe.

Another labelling that led to the establishment of a karstic difffluence was performed with the help of ⁸²Br. In labelling the Kara Oban insurge, part of the tracer was guided towards the mezothermal spring of Mangalia and an other part towards the gulf bearing the same name in the Black Sea (fig. 41). It is worth noting that the sinkhole was labelled with a tracer constant discharge. The shape of curve C(t) is probably due to the marine currents which prevented the maintenance of a constant measuring geometry, throughout the duration of the determinations.

11.7. THE INFLUENCE OF WATER-DEVELOPMENT OPERATION ON WATER CAPTURES IN THE KARST

When waterflows originating in non-karstic areas cross karstified calcareous rocks, water losses may be refound downstream in the form

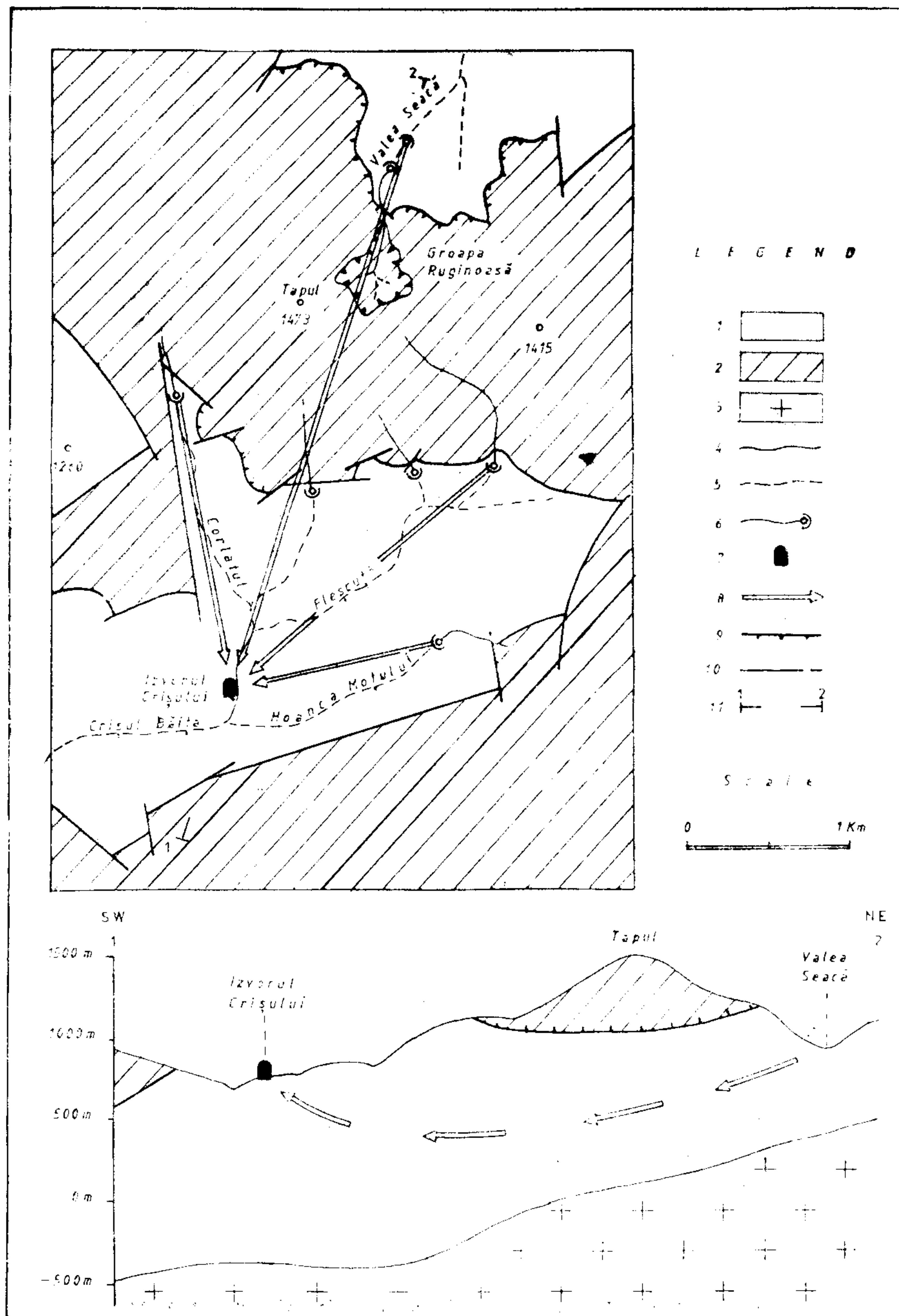


Fig. 40

Fig. 40. Extension of Izvorul Crișului catchment area in Valea Seacă basin (geological data after Borcea et al., 1975) 1 — Bihor Unit; 2 — Arieșeni Nappe; 3 — Magmatites; 4 — Perennial course; 5 — Temporary course; 6 — Ponor; 7 — Outflow cave; 8 — Underground routes; 9 — Overthrust front; 10 — Fault; 11 — Direction of geological cross section.

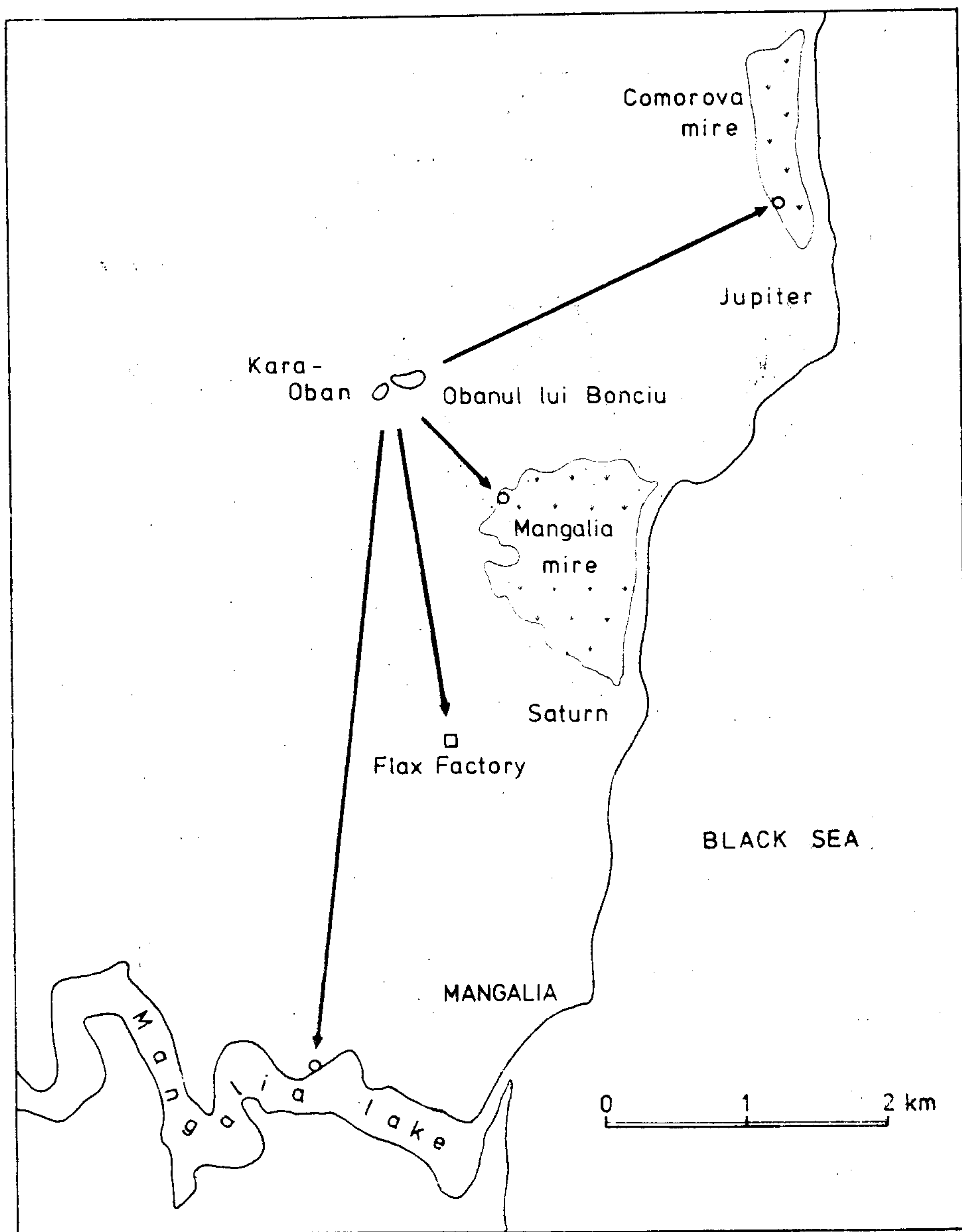


Fig. 41. Groundwater flow directions in Mangalia area.

of permanent springs. Such a group of springs, the Izvarna, with an average discharge of more than $2 \text{ m}^3/\text{s}$, was partially captured to provide for the water supply of the town of Craiova. The construction works on an elaborate hydropower complex in the area, which implied the building of dams to create storage lakes with waters from the rivers that cross the

zone, posed the problem of the influence these retentions exert on capture. Consequently, water losses from seven rivers in the region were detected in the captured springs (fig. 42). Therefore, as the damming of waterflows entails a diminution of the capture discharge, engineering solutions should be found to the problem. (Rădulescu et al., 1987).

11.8. ASSESSMENT OF SEEPAGE RISK IN THE CASE OF WATER RETENTION

If the waters of a storage lake may cover calcareous areas where karstification processes developed, it is highly important to know the relationships between surface and underground waters in the floodable area. The establishment of the loss areas represents a wide-scope tracer experiment which may assess real sizes of loss and existing risk of failure (Özis and Yurtsever, 1982). In Romania, damming of river Cerna posed

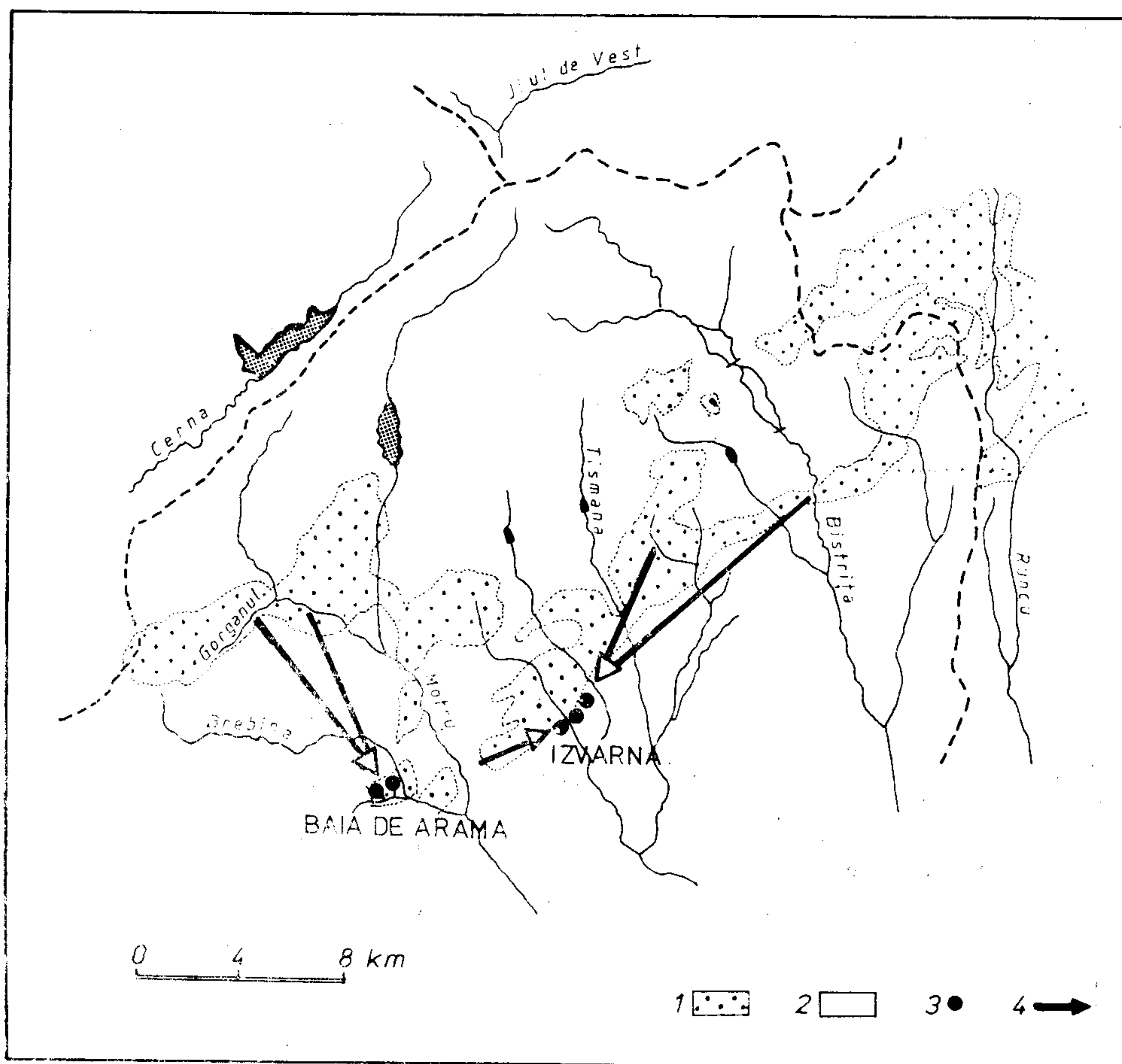


Fig. 42. Underground drainage directions in Baia de Aramă and Izvarna areas. 1 — Karstic terrains; 2 — Nonkarstic terrains; 3 — spring; 4 — Underground flow direction established by tracer experiments.

7 — Theoretical

a number of problems related to the possible water loss from the storage lake along some karstic routes. They were clarified with the help of multi-tracing experiments.

11.9. MINE DRAINAGE IN KARST

The Răcaş-Sclavul Pleş Karstic plateau in the Pădurea Craiului mountains consists of lower tithonian and cretaceous limestone. The geological research conducted here highlighted lens-shaped accumulations of bauxite in the depressions of the paleokarst developed on tithonian limestone.

The plateau has no surface streams and the waterflows formed by the precipitations on the eastern, non-calcareous side of the plateau infiltrate into the underground through numerous ponors at the entering point in the karstic area.

Following the artificial-tracer labellings in the ponors, it was established that the underground waters moving towards Topliţa de Vida resurgence intersect the mining operations to open the deposit and substantially enhance the hydrogeological risk in the digging works (Fig. 43).

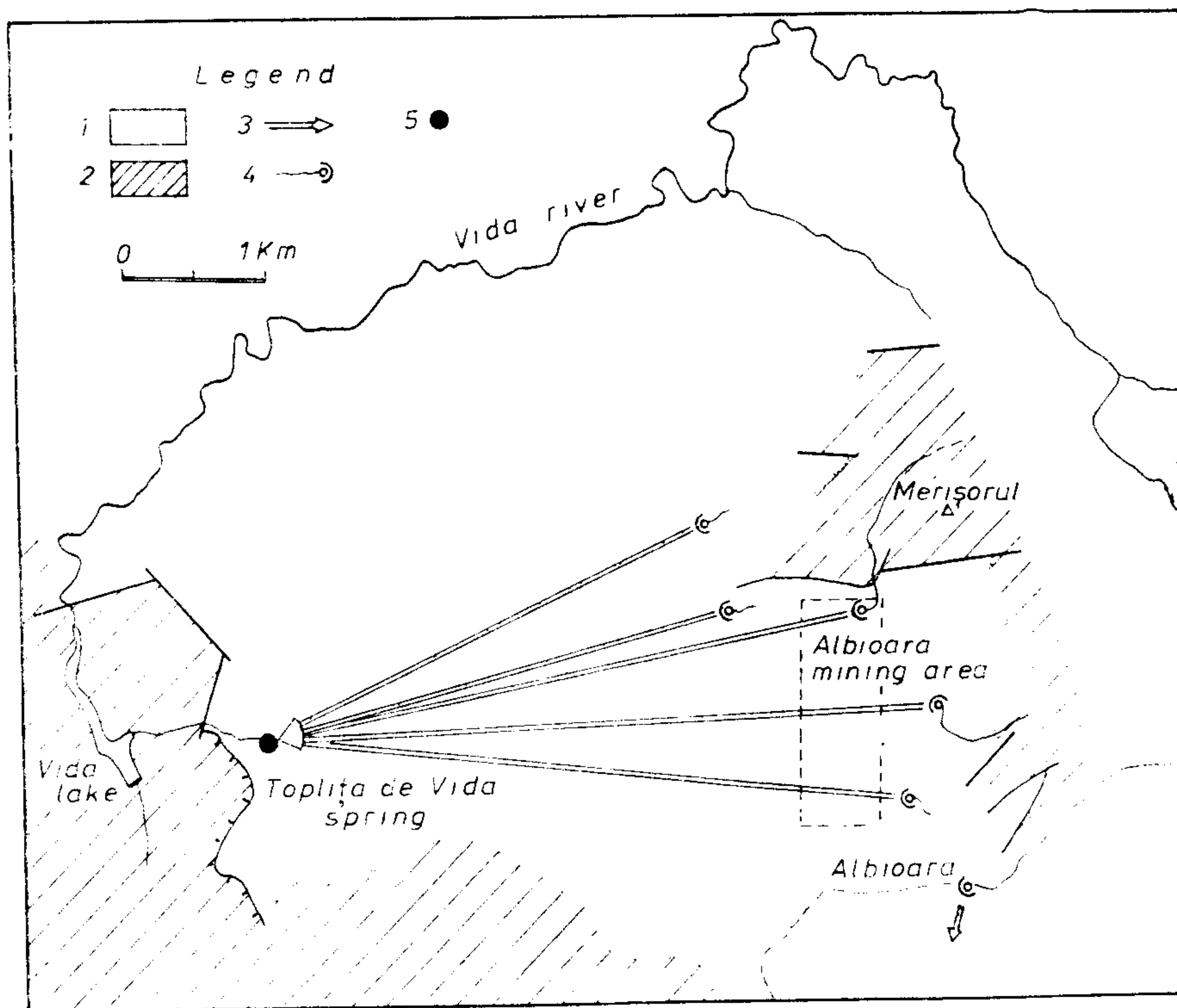


Fig. 43. Underground flow directions in Albioara mining area (after Orăşeanu et al., 1984). 1 — Karstic terrains; 2 — Nonkarstic terrains; 3 — Underground flow direction established by tracer experiments; 4 — Ponor; 5 — Spring.

The average transit velocities assessed with the help of the afore-said tracers vary from 3.9 m/h to 20.6 m/h; these values were used in designing the drainage gallery for the opening of the mine (Orăşeanu et al., 1984).

11.10. CAVE STREAM INVESTIGATIONS

This is the oldest form of hydrological research and it probably dates back to the paleolithic. At present, it has broad-scale applications. Here is, for example, an experiment with radioactive tracers which highlighted the contribution of a surface stream to the supply of the underground waterflow in the Wind Cave. The respective cave has an extent of 3,000 m and its terminus is located at the confluence between the Sesii and Mişid valleys.

An important contribution to the underground stream in the Wind Cave is made by the waters infiltrated from the Recea ponor, situated at a horizontal distance of 3,185 m from the cave entrance. The labelling of this ponor with Na ^{131}I provided for the identification of the tracer in the cave with the help of ion-exchanger filters. Figure 44 shows the diagram of ^{131}I variation at the point where the underground stream in the wind cave emerges to the surface (Orăşeanu and Gaspar, 1981).

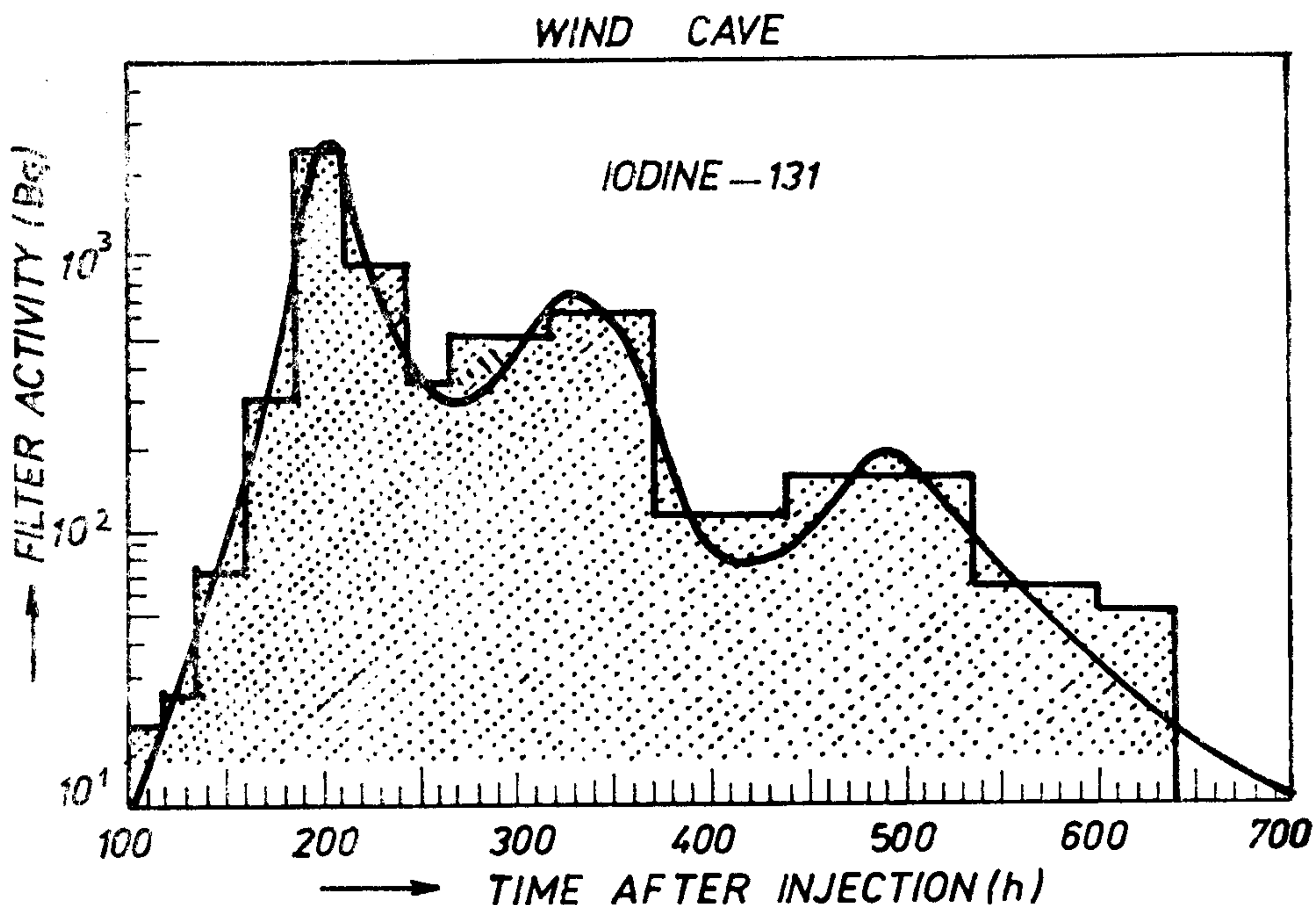


Fig. 44. The diagram of ^{131}I variation at the point where the underground course in the Vind Cave emerges to the surface.

11.11. INVESTIGATION OF GEOTHERMAL WATERS

The use of artificial tracers to investigate geothermal waters stored in limestones and dolomites was performed in various karstic zones. Thus, to determine the origin of Seven Warm Sources from Cerna Valley (55°C) the Tesna ponor was labelled with ^{131}I (Gaspar and Simion, 1985). The geothermal waters from South Dobrogea was investigated with ^{82}Br . The tracer injected in Kara Oban appeared in IAS-Mangalia (23°C) mez-zothermal spring, and in the thermal submarine spring from Mangalia gulf (Gaspar, 1972). In the Codru Moma karstic zone, a labelling performed with Indium-EDTA in Brătcoia ponor was localized the water divide line and proved a great karstic diffuence and the origin of the mez-zothermal waters from Moneasa spa. The tracer appeared in Feredeau and in the geothermal wells from Moneasa (Fig. 45, after Orășeanu, 1987).

In the geothermal field from Borș (Oradea) and in Iratoș (Arad) the tracer techniques has been particularly useful in hot water (130°C) re-injection investigations for detecting the invasion of reinjected water into the production zone, using ^{131}I as a tracer.

12. CONCLUSION

The intensive exploitation of aquiferous resources stored in karstic zones, water-development works and the location of various mining, industrial and farming units and of towns, and various ecological aspects call for a massive research work into karstic structures. The methods with artificial tracers, in association with geophysical, hydrochemical, hydrobiological and isotopic methods, are conventional methods (Gaspar, 1987).

The need for a simultaneous investigation under similar hydrogeological conditions, of all the inlets and outlets of a karstic structure through multi-tracing operations and by pluridisciplinary teams will lead to complex studies of karst area, conducted with concentrated forces, sometimes through international cooperation. Recent research, under way in various laboratories, will encourage the use of tracer methods in karst.

Tracer determinations are a common technique for the investigation of flow through karstic conduits and solution channels; however in present no adequate models are available to describe tracer breakthrough curves in terms of hydraulics of conduit flow, turbulent dispersion and exchange with the fissure system (auxiliary system).

The future development of the application of tracers in karst hydrology will follow two directions. It will be aimed at improving the hydrogeological interpretation of tracer data and isotopic contents and at searching for new tracers (activable and fluorescent dye tracers, environmental isotopes other than D, T, ^{14}C and ^{18}O) permitting new hydrological findings.

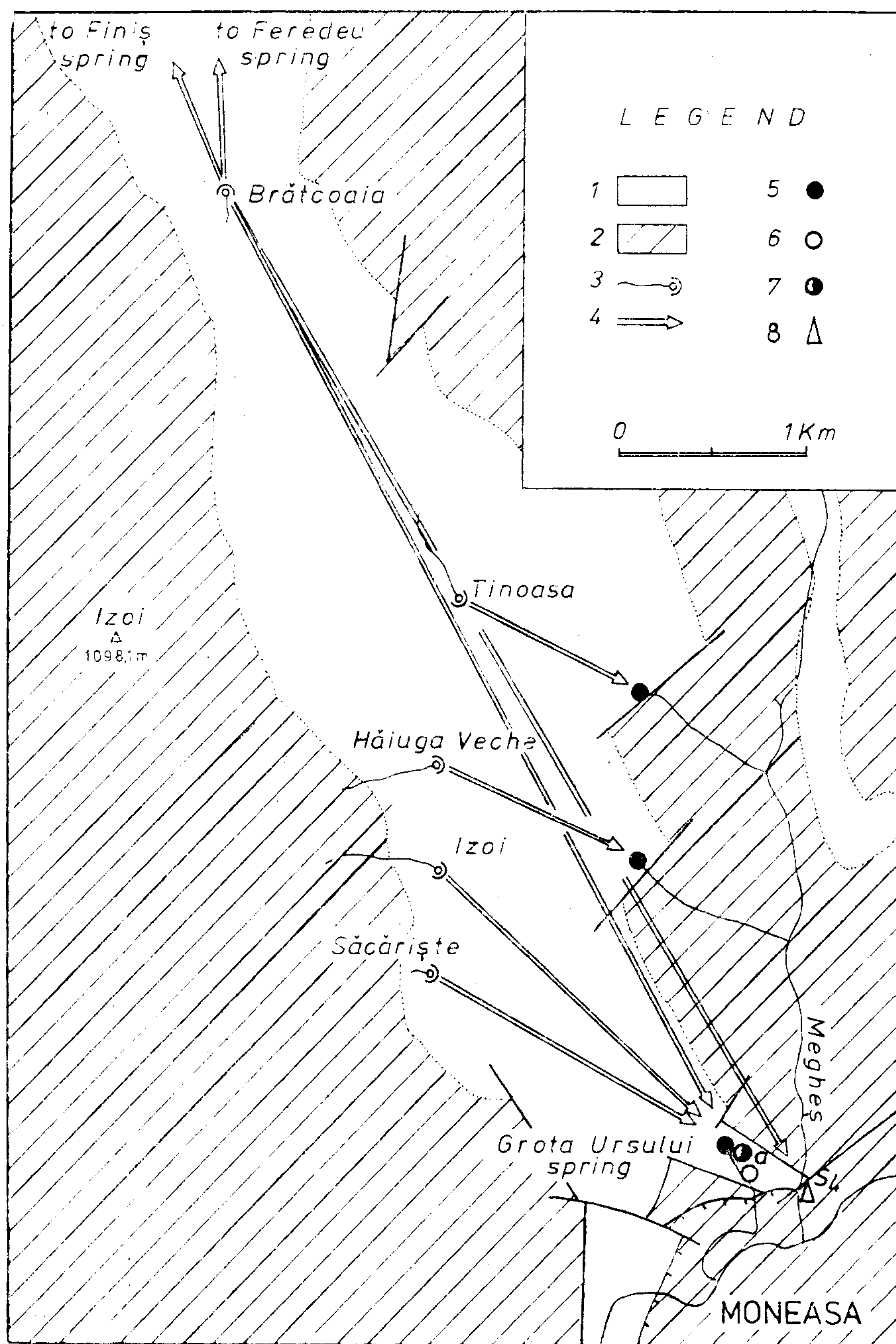


Fig. 45. Underground drainages in Moneasa area. 1 — Karstic terrains; 2 — Non-karstic terrains; 3 — Ponor 4 — Underground flow direction established by tracer experiments; 5 — Cold spring; 6 — Thermal spring; 7 — Subthermal spring; 8 — Hydrogeological well.

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