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Hydrologic Interpretation of the Environmental Isotope Data in the Eastern Styrian Basin

K. Przewlocki
IAEA
Section of Isotope Hydrology*

Content

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* Final report of the environmental isotope study in the northern part of the Styrian Basin, performed within the Austrian programme of the International Hydrological Decade by the International Atomic Energy Agency, Vienna, and the Vereinigung für hydrogeologische Forschungen in Graz, in 1969—1974.

1. Introduction

Within the Austrian programme of the International Hydrological Decade, the eastern part of the Styrian Basin is being included as a representative basin study. Concern resulting from some local decline in the artesian head in the eastern part of the Styrian Basin has resulted in a comprehensive investigation of groundwater resources by the VHFG (Vereinigung für hydrogeologische Forschungen in Graz; Prof. Dr. J. Zötl and Dr. H. Zojer). The IAEA (International Atomic Energy Agency) has been collaborating with the VHFG in isotope studies of groundwaters. This report summarizes most of the data and interpretations from these joint studies.

2. Hydrogeological Background (1)

Since more or less the beginning of the major uplift of the Alpine central core, a large subsiding sedimentary basin (including both the Pannonian and Styrian basins) occupied parts of Austria, Hungary and Yugoslavia. The Styrian Basin (Figure 1) is filled to a maximum depth of about 3000 meters with largely marine sediments — in the deeper parts and continental deposits nearer the surface but with some interfingering. It is underlain by crystalline and Paleozoic rocks, which also form the northern and western boundaries of the Basin. In the south

Fig. 1: Index map of Austria showing location of the Styrian basin and the area of this report.

Table 1: Generalized Table of Principle Water-Yielding Rock Units in the Hartberg/Grafendorf Basin.

Geologic Age		Rock Unit	Physical Characteristics	Water-Yielding Characteristics
Quaternary	Holocene	Surficial valley-fill deposits	Mostly clay, silt, and sand; absent in many places; generally some metres in thickness.	Not known to be significant as source of supply. Shallow groundwater of poor quality and small yield.
	Pleistocene	Unconsolidated terraces	Mostly clay, silt, sand and gravel; generally absent in most of the report area; terraces of a few metres thickness.	May yield small quantities of poor-quality water in places, but not a dependable source.
Tertiary	Pliocene	Pannonian formation	Layers of sand and gravel alternating with layers of silt and clay.	Water occurs in several layers under artesian pressure. Yields from wells are sufficiently large for domestic, farm. or small commercial supplies. Generally good quality water.
	Miocene	Sarmat formation	Sand, fine gravel, marl, and sandstone layers in lower part; coarse gravel, sand, marly sandstone, and limestone in the upper part.	Probably supplies most of the artesian wells in the report area. Water occurs in sand and gravel layers. Yields and quality-of-water are similar to Pannonian. Where it crops out, yields moderate amounts through springs. Limestone yields water readily.
Pre-Tertiary		Crystalline undifferentiated	Metamorphic rocks, mostly gneiss and schists.	Yields small quantities from cracks and joints, mostly to springs; adequate for farm and domestic supplies. Quality good.

and east the Styrian Basin extends into the Pannonian Basin but is differentiated from it by a ridge — the Südburgenländische Schwelle (shoal) — of the underlying crystalline and Paleozoic system. The rock units in the Styrian Basin of importance in this report are described briefly in Table 1. In much of the report area the Sarmat is exposed at the surface or lies beneath only a thin layer of Quaternary material. Many artesian wells obtain small yields from the permeable layers in this formation. Also a number of springs issue from the Sarmat and provide reliable yields of small to moderate amounts. The lower Sarmatian sediments are fine gravel, sand, marl and sandstone. The upper part of the formation includes coarse gravel covered by cyclic beds in ascending order, of clay, marl, fine gravel, sand, marly sandstone and locally limestone banks. As much as 800 meters of the Sarmat have been penetrated in a deep borehole near the centre of the Styrian Basin.

The Pannonian Formation, which covers the Sarmat — especially east of the report area — in the Styrian Basin, also yields artesian water supplies in certain localities. The Pannonian sedimentation began with layers of sand, clay and marl. The middle part of the formation contains layers or lenses of gravel, sand and clay that dip generally northeast and southeast. The gravel lenses occupy former channels whose northeast and east-flowing orientation lies at nearly right angles to the south and southeast flow direction of the present-day drainage. Gentle tectonic folding occurred immediately following the Pannonian deposition, but it has little effect on the occurrence of water in the formation.

The present-day geomorphology of the eastern part of the Styrian Basin consists largely of northwest—southeast tending ridges and stream valleys with local relief ranging up to about 150 meters. The ridges are composed mostly of Tertiary sediments but in places are covered by loam-covered Pleistocene terraces. The valleys are generally wide and subject to flooding so most of the settlements are on the low terraces. As the shallow groundwater of the valley is generally of poor quality — because of high iron content — the water supply mainly uses artesian aquifers. In the Austrian part of the Styrian Basin, over 1500 artesian wells have been drilled over the past century to provide domestic, stock and small industrial and municipal water supplies.

Due to the continuous increase of draft of the artesian system, a distinct decrease of the artesian head has been noted in several areas during the past few decades.

As the recharge area and water balance of the artesian aquifer are practically not known till now, an urgent need has arisen to obtain

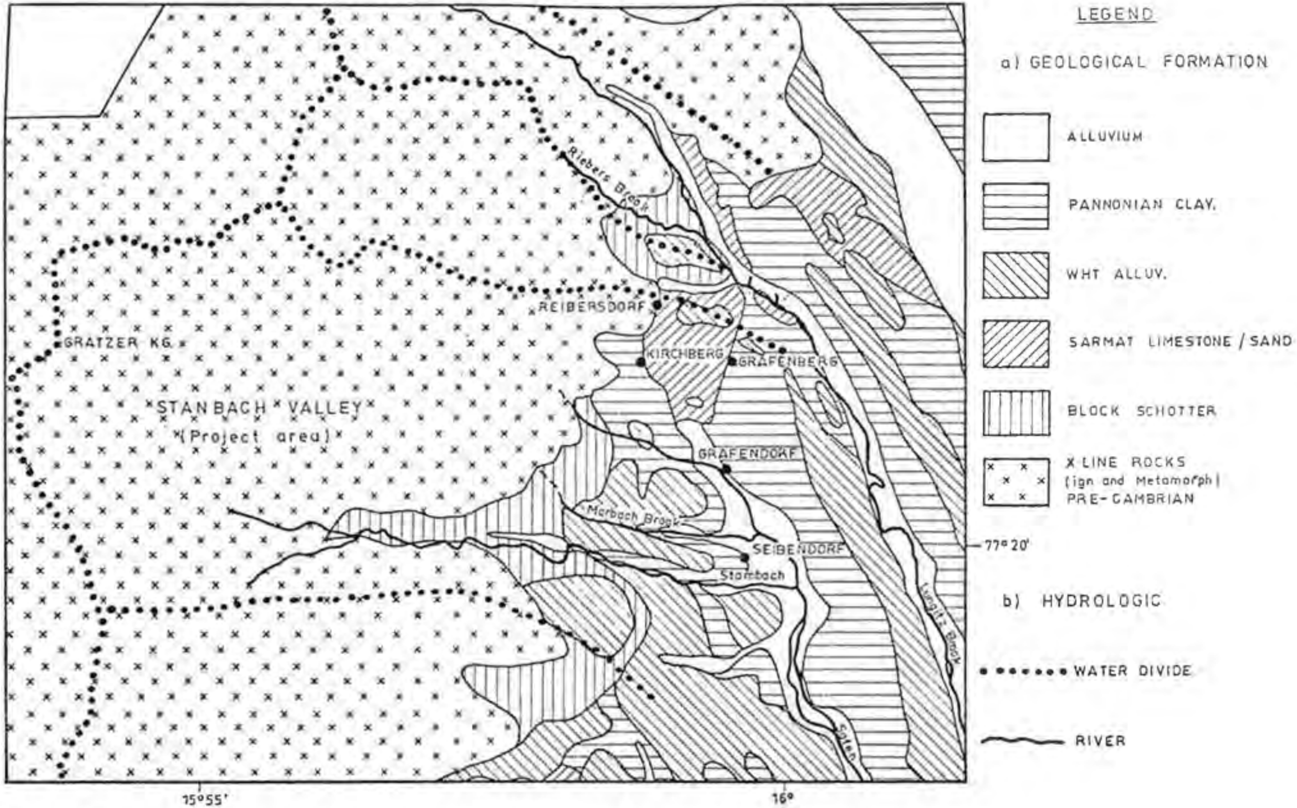

Fig. 2: Geological map of the area of investigation.

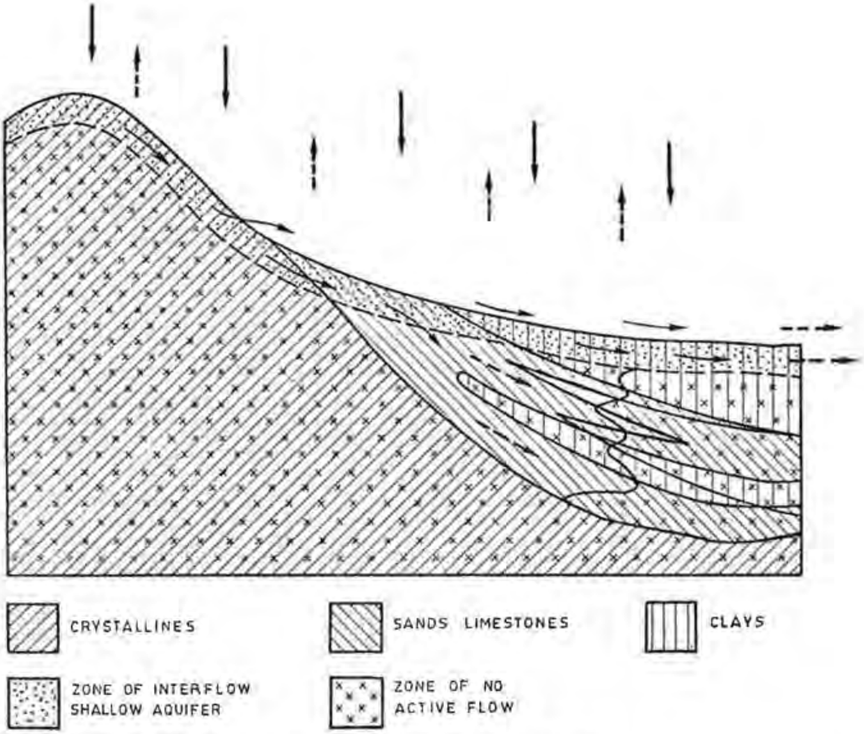

Fig. 3: Generalized cross section of the Hartberg basin.

more information concerning the internal dynamics of the total system.

Research described in this report was limited to the northern part of the Hartberg/Grafendorf Basin, which creates a separate smaller hydrological unit within the Styrian Basin (Figs. 2 and 3).

3. Climatic Conditions in the Hartberg Area

Within the Hartberg basin there exist three precipitation gauges: Hartberg (350 m above mean sea level), Kirchberg am Walde (452 m a. m. s. l.) and Masenberg (1250 m a. m. s. l.), two of them since a period of more than 60 years (Hartberg and Masenberg). The air temperature is only measured at Kirchberg am Walde (since 1951).

It is a local phenomenon caused by the lee-side of the mountain slopes which form the frame of the Hartberg basin that the normal increase of precipitation accompanying the increase of elevation does not occur. Table 2 shows nearly the same monthly depth of precipitation at Hartberg (350 m) and Masenberg (1250 m).

Table 2: Monthly average of precipitation (period 1901—1960) of Hartberg (350 m a. m. s. l.) and Masenberg (1250 m a. m. s. l.) in mm.

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Year
Hartberg	29	33	42	59	86	110	135	103	79	62	49	45	832
Masenberg	30	36	32	57	94	125	135	109	88	66	44	41	857

Compared with the 60 years average, the yearly accumulated precipitation of single years may strongly differ (from 1951—1960 the Hartberg station shows values from 669 to 941 mm, Masenberg from 666 to 1020 mm), and in this case Masenberg shows the larger amplitude.

Concerning the seasonal distribution of the precipitation, Table 2 shows that most of the precipitation falls in summer time (42% from June to August). The dryest months are January, February and March (12% of the yearly accumulated precipitation). This influences storage and groundwater enrichment, active mostly from fall to spring because of temperature and evapotranspiration in summer (Table 3). In this connection it is of interest that dry periods occur mainly in fall, winter and spring. In a 10-years average at least one period of 20 days without precipitation between October and March occurs, in a 5-years average at least one period of 16 days.

Table 3: Temperature at Kirchberg a. W. and Graz (period 1950—1960) in ° C.

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Year
Kirchberg a. W.	—1,4	—0,7	3,5	8,8	13,1	16,6	18,3	17,8	14,3	9,2	3,9	1,1	8,7
Graz	—3,8	—1,5	3,4	9,0	14,3	17,2	19,0	18,0	14,3	8,6	3,3	—1,3	8,3

the highest daily average: 28,4 (August 15, 1952)
the lowest daily average: —15,5 (February 2, 1956)
Maximum: 36,8 (July 4, 1950)
Minimum: —19,8 (February 2, 1956)

The period of snow cover depends much more on the elevation than the total sum of precipitation. From 1950 to 1960 the snow cover lasted on an average at Hartberg (350 m) from December 13 to March 15 = 42 days, at Masenberg (1250 m) from October 20 to April 4 = 102 days, and the winter cover (that means closed snow cover) on an average:

at Hartberg from January 21 to February 14 = 25 days
at Masenberg from January 2 to March 8 = 66 days.

In summer time in eastern Styria local thunderstorms occur very frequently, and in this connection a part of the rainfall comes down as "intensive rainfall". The intensity of rainfall is characterized by the Wussow-formula, $h = \sqrt{5t-(t/24)^2}$ respectively $h = \sqrt{5t}$ for short-termed rainfall. An "intensive rainfall" has at least 5 mm in 5 minutes, 10 mm in 20 minutes, 17.1 mm during 1 hour (h = rainfall depth in mm, t = duration in minutes).

For the station Vorau which is subject to the same conditions as Hartberg, an investigation on the intensity of rainfalls was done by

Dr. STRUSCHKA. It shows that heavy rainfalls with a yield of 31 to 70 mm per hour only occur in summer time. During the time of calculation (1907—1938, 1947—1965) there occurred 8 heavy rainfalls of 31—70 mm/h and a duration until 3 hours (June—July), 28 of 16—30 mm/h a duration until 6 hours (May—August) and about 80 until 15 mm/h and a duration until 12 hours (mainly May—August).

Since these heavy rainfalls first of all feed the runoff, floods also occur from time to time in usually small brooks.

Runoff measurements of brooks of the Hartberg basin were begun only in 1970. Two water stage recorders at the Reibersbach have been destroyed by heavy floods in August 1970 and were installed again in summer 1971.

4. Purpose and Scope of Investigation

The area of investigation, as selected by J. ZÖTL of VHFG, was the northern part of the Hartberg basin. Previous carbon-14 measurements completed in this area in 1968 by Davis et al. (3) indicated existence of the very slow internal circulation within the aquifer (age of water ca. 10,000 years).

This is due to the geological structure of the basin. Water-bearing Sarmatian strata here are covered by the thick layer of the Pannonian loamy formation which probably prevents direct recharge to the artesian aquifer.

This was a criterion for the selection of the Stambach valley and adjacent flange of the Hartberg basin with Grafendorf as project area (4). The basin itself contains a complex system of multiple artesian aquifers. However, private drilled wells existing in this area show very little usefulness for hydrological investigation. In most cases, hydrological and technical documentation for them does not exist. They mainly render two uppermost confined aquifers and probably create unintentional interconnections between them.

Thus four boreholes with known casing and screen characteristics were drilled by the local government at one location near Grafendorf. The wells have different total depths; each is screened at a different and separate horizon, and the piezometric head in each is different (Table 4).

Even though they give only information on the internal structure of the basin, hydrologists believe that those four water-bearing strata, separated from each other, have the characteristics of the regular aquifers extending over the large area, rather than being confined to the local small lenses. This being the case, hydrologists believe that

Table 4: Technical parameters of the VHFG test wells.

aquifer no.	position of the filter (m)	diameter of the filter pipe (mm)	pressure head at day surface (m H_2O)	aquifer pressure (atm)	type of aquifer rocky matrix
Graf 2	41.15—44.15	142	10	5.3	loose sand with thin cemented layers
Graf 1	51.90—54.90	142	16	7.0	loose sand with thin cemented layers
Graf 3	82.82—85.82	101	16.2	10.2	fine to medium gravel with larger stones and a clay layer
Graf 4	165.40—168.40	101	4	17.3	clay with gravel and brown loam; fine gravel and pebbles in sandy loam

heavy storms cause remarkable changes in the pressure head. Such an effect ought not to exist in the case of a local lens-shaped aquifer (2).

Nevertheless, point access to the aquifer exludes proper sampling directed at recognition of the internal dynamics of the aquifer; this would require a regular grid of wells over the whole project area. As a result, it was decided at the beginning to limit the project to the following points:

1. To estimate the amount of groundwater in storage within the crystalline area west of Grafendorf (Stambach valley catchment area).

2. To describe the dynamics of the groundwater at the point of contact with Tertiary sediments, at the outlet of the Stambach valley, with the crystalline rocks of the Alpine Central Zone.

3. To characterize waters of the separate aquifer systems.

The Stambach valley creates semi-closed catchment systems (as can be seen from Fig. 2) and is delineated by the water divide of the Stambach valley from N, W and S. From the eastern side it creates a semi-opened hydrological system, waters from which may flow to the northern flange of the Hartberg basin.

A few springs at different altitudes, which could be used to sample water for isotope analyses, are available in the Stambach valley. At the outlet of the valley, in the sedimentary formation, there are VHFG testing holes, a few springs discharging from the Sarmat, and brooks and private wells which could be there a source of water samples representative for the Hartberg/Grafendorf Basin.

In this situation a research programme, established in 1968 between the two cooperating institutions, foresaw the following activity on the part of both partners:

A. From the side of VHFG

1. To make an inventory of springs in the igneous/metamorphic recharge areas and select 3 to 6 typical springs for monthly sampling for environmental isotope analysis.

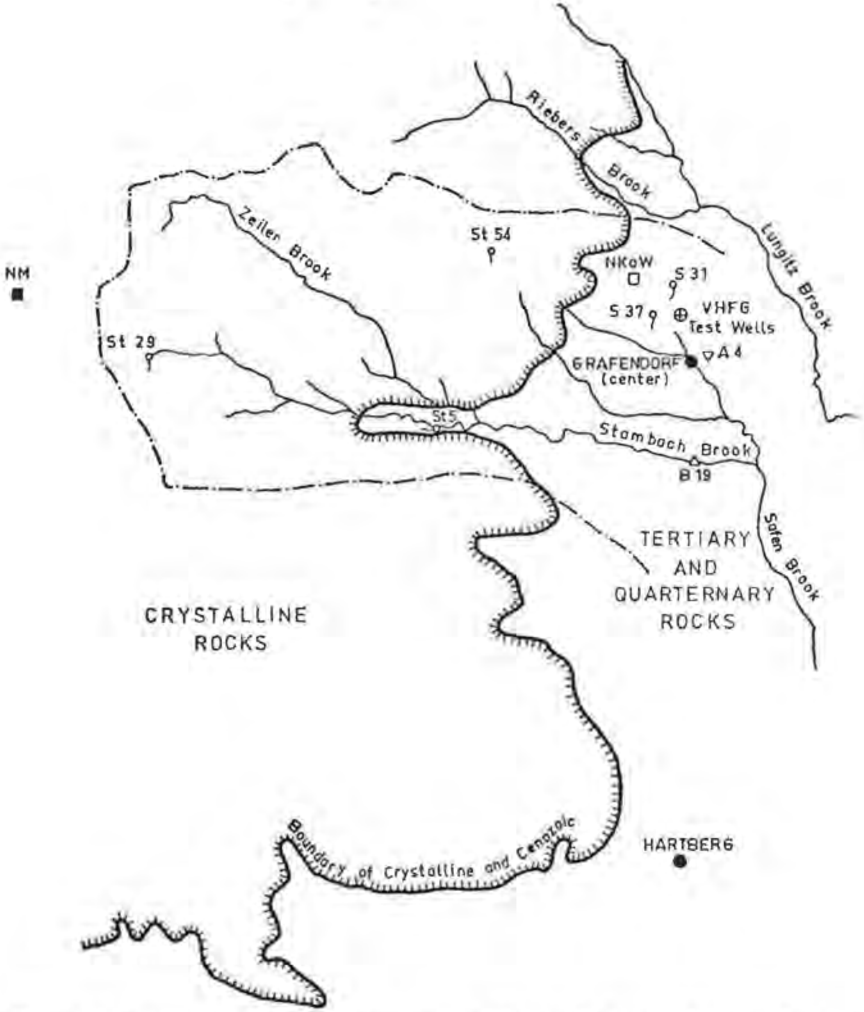

Fig. 4: Location of sampling points in the Grafendorf area, Eastern Styrian basin.

Table 5: Hydrologic and related data for sampling points in the Grafendorf/ Hartberg area.

Name of Sampling point	Type	Altitude (m. a. m. s. l.)	Geologic source	Yield or discharge (l/s)	Temperature (°C)	Other remarks, as depth for wells, etc.
Masenberg	Rainfall-station	1,250				
Kirchberg a. W.	Rainfall-station	457				
St 29	Spring	960	Crystalline rocks	0.5—5.0	6.1— 6.4	
St-54	Spring	610	Crystalline rocks	0.003—0.1	7.0—11.4	
St-5	Spring	535	Crystalline rocks	0.02—0.18	7.0—10.2	
S-31	Spring	418	Sarmat fm.	0.15—0.35	5.8—14.2	
S-37	Spring	410	Sarmat fm.	0.8—2.0	9.1—10.5	
R (Reibers B.)	Brook			*)		
A-1	Well	381	Sarmat fm.	~ 0.2		Total depth 30 m
B-19	Well		Quat.			~ 6 m

*) Average discharge at one of the former gauging sites

2. To establish flow gauging stations on the Reibersbach and Stambach rivers.

3. To conduct hydrologic tests and sampling for isotope analyses from the exploratory boreholes north of Grafendorf and from a few springs (Fig. 4, Table 5).

4. To collect monthly precipitation samples at Kirchberg/Walde and Masenberg (850 m higher than the average elevation of the Hartberg Basin).

B. From the side of IAEA

1. To analyse 3 to 7 samples monthly from springs in the Hartberg Basin for D, ^{18}O and T.

2. To analyse 4 samples monthly from streams of the Hartberg Basin for D, ^{18}O and T.

3. To analyse 4 samples a few times from the VHFG exploratory wells for D, ^{18}O, T, ^{14}C and ^{13}C.

4. To analyse monthly precipitation from 2 stations for D, ^{18}O and T. on a monthly basis in 1969, 1970 and then on a half-yearly basis in 1971—1974.

8 sampling points were selected, apart from two meteorological stations, for systematic isotopic analyses (see Fig. 4). They were analysed on a monthly basis in 1969, 1970 and then on a half-yearly basis in 1971—1974.

5. Environmental Isotopes

Tritium (T), carbon-14 (^{14}C), deuterium (D) and oxygen-18 (^{18}O) are the environmental isotopes used in this study. The spatial and time variability of input of these four isotopes in the hydrologic cycle, and the decay of the radioactive isotopes, are the key to their interpretation in hydrologic investigations. The trends of tritium and the stable isotopes in precipitation are now fairly well known, and with data from world network stations, input for given areas can be estimated with

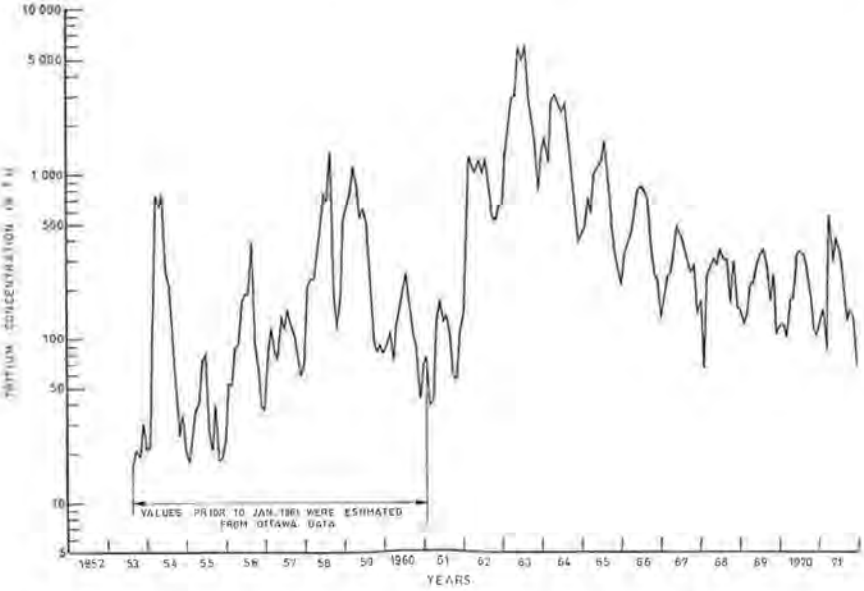

Fig. 5: Variation of tritium concentration in precipitation at Vienna.

reasonable precision, thus providing a starting point for local hydrologic interpretation of isotopic data (5).

Tritium (^3H) is the radioactive isotope of hydrogen with a half-life time $T_{1/2} = 12.26$ years, emitts soft beta radiation of the maximum energy 18 KeV. Its intensity may be measured by means of proportional counters, with internal filling, or by means of a liquid scintillation technique. In laboratory practice it is customary to determine tritium concentration in Tritium Units (T. U.). One T. U. is defined as one atom of ^3H per 10^{18} atoms of ^1H. It is equivalent to 0.12 dps per litre of water, or 3.2 pCi/l (7). The minimum tritium content which can be detected in a water sample is about 1 T. U.

Tritium in natural waters originates mainly from explosions of nuclear bombs. Fig. 5 shows as an example variations of the tritium concentration in precipitation for Vienna.

Carbon-14 (^{14}C) is the radioactive isotope of carbon, with a half-life of 5,730 years. (For hydrological purposes, however, it is customary to apply the value of 5,568 years, which corresponds to the old determination of ^{14}C half-life time.) It decays with β particle emission with the maximum energy of 156 KeV. The most efficient method of detection is also, as in the case of tritium, the liquid scintillation technique or proportional counter with internal filling. The ^{14}C concentration is generally expressed in % of the modern ^{14}C content of atmospheric CO_2 (excluding ^{14}C produced by thermonuclear explosions and the dilution with ^{14}C-free CO_2, due to the contribution of fossile oils and coals). It is continuously produced in the atmosphere as a result of interaction of neutrons from cosmic radiation with the atoms of nitrogen.

Saturation of precipitation water occurs mainly during percolation through the unsaturated zone of soils where partial pressure of CO_2 is about 100 times higher than in the atmosphere, due to the biological decay of organic matter. CO_2 is dissolved and produces an acid solution, therefore $CaCO_3$ present in the soil can also be dissolved (9).

In order to take this into account, special corrections are made to estimate the contribution of non-radioactive carbon in groundwaters. This is commonly based on separate measurements of ^{13}C variations. The results of these measurements are related to the PDB interlaboratory standard (7).

The maximum age of water which can be determined by means of this method is 37,000 years. Standard deviation of measurements is about 10% relative (7).

Stable isotopes (D and ^{18}O). Hydrogen and oxygen, the two constituents of water, contain the following stable isotopes (in parantheses natural abundance in per cent):

^{1}H (99.985%), ^{2}H (0.015%), ^{16}O (99.76%), ^{17}O (0.04%), ^{18}O (0.2%).

The heaviest isotopes — deuterium and oxygen-18 — are considered as environmental isotopes (natural tracers).

A small water sample, ca. 25 ml, is required for the isotope laboratory analysis, performed by means of a mass spectrometer. Results are expressed in "δ" units in relation to the interlaboratory standard SMOW (Standard Mean Ocean Water) in per mills, according to the following relations:

$$\delta^{18}O = \frac{(^{18}O/^{16}O)\text{ sample} - (^{18}O/^{16}O)\text{ standard}}{(^{18}O/^{16}O)\text{ standard}} \times 1000$$

$$\delta D = \frac{(D/H)\text{ sample} - (D/H)\text{ standard}}{(D/H)\text{ standard}} \times 1000$$

The accuracy of ^{18}O measurements is 0.1‰ and for D measurements 1‰ SMOW.

When water evaporates from oceans, the vapour is depleted in heavy isotopes, because $H_2{}^{16}O$ is more volatile than $HD^{16}O$ and $H_2{}^{18}O$. The isotopic fractionation during the evaporation of water and its condensation during the hydrological cycle cause the different stable isotope composition of groundwaters. These effects can in many cases be used to determine the origin of groundwaters. The reader interested in a more detailed picture of the principles of isotope hydrology is referred to special literature on this topic (6, 7).

6. Experimental Data

Isotope analyse for selected sampling points (Table 5, Fig. 4) were performed in 1969 on a monthly basis and in 1970—1974 less regularly, approximately on a half-yearly basis. Results are presented in Table 6.

As VHFG testing wells made tritium-free artesian water accessible, a set of measurements of ^{14}C was performed on these wells, in 1970—1973 for the well in Grafendorf as well as for three other wells located nearby at Seibersdorf. The location of these last VHFG testing wells can be found in Fig. 2.

Results of the tritium, carbon-14 and oxygen-18 analyses of these waters are presented in Table 7.

Finally, on 22 August 1973, special sampling was made in the Grafendorf area, both for environmental isotopes and chemical analyses.

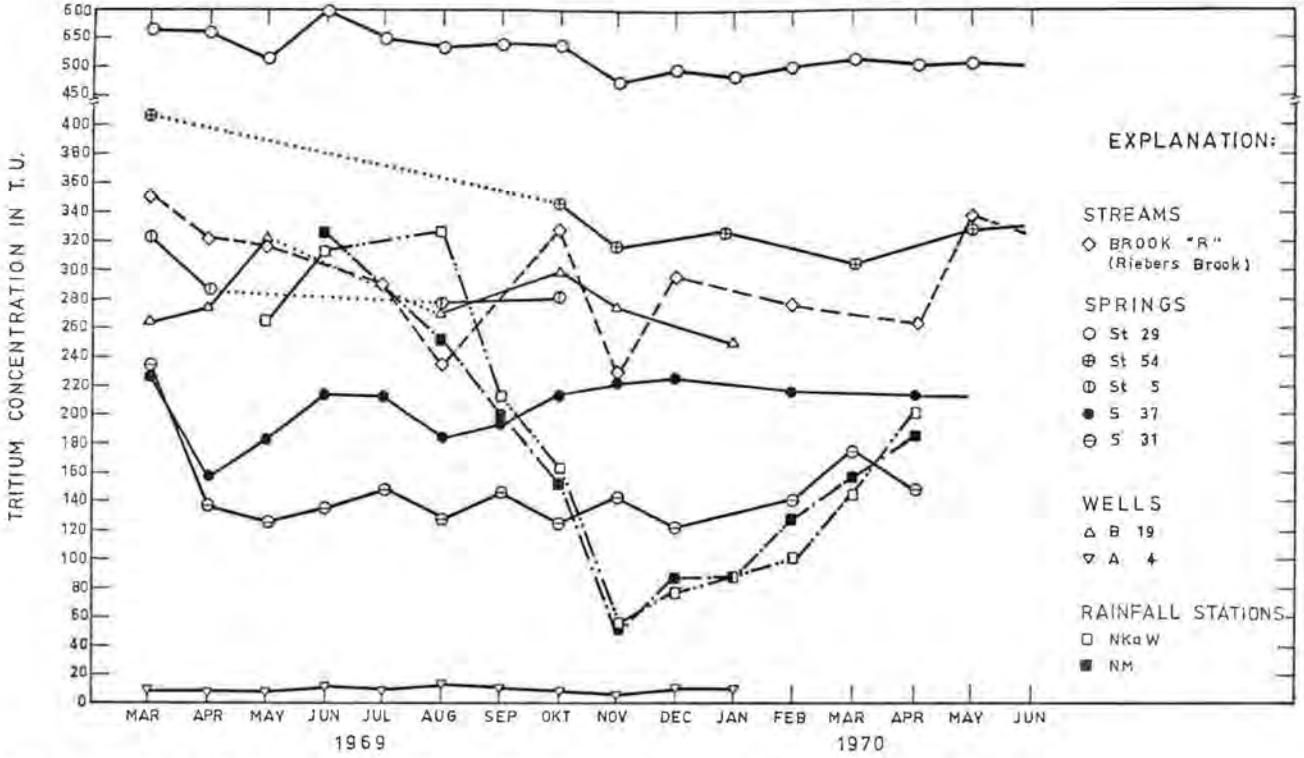

Fig. 6: Variation of tritium concentration with time in the Grafendorf area Eastern Styrian basin.

Chemical analyses were made by the Geochemical Laboratory of the Upper Silesian Station of the Geological Institute, Sosnowiec, Poland. Results are presented in Table 9.

7. Tritium Data

From the tritium data one can expect to be able to distinguish between waters at least 40 years old, if they are tritium-free and tritium-containing contemporary waters for which mean residence time is of the order of a few years to a few decades.

On the basis of this criterion, a first inspection of the data from Table 7 shows that the artesian waters from Grafendorf are old in the sense of tritium age.

In Table 7 one can admittedly find a few results where the tritium content exceeds the standard error of the background by slightly more than three times. These data do not indicate, at least in our case, the presence of tritium. In order to prove a small tritium content almost at the threshold of detection, one would require a set of measurements

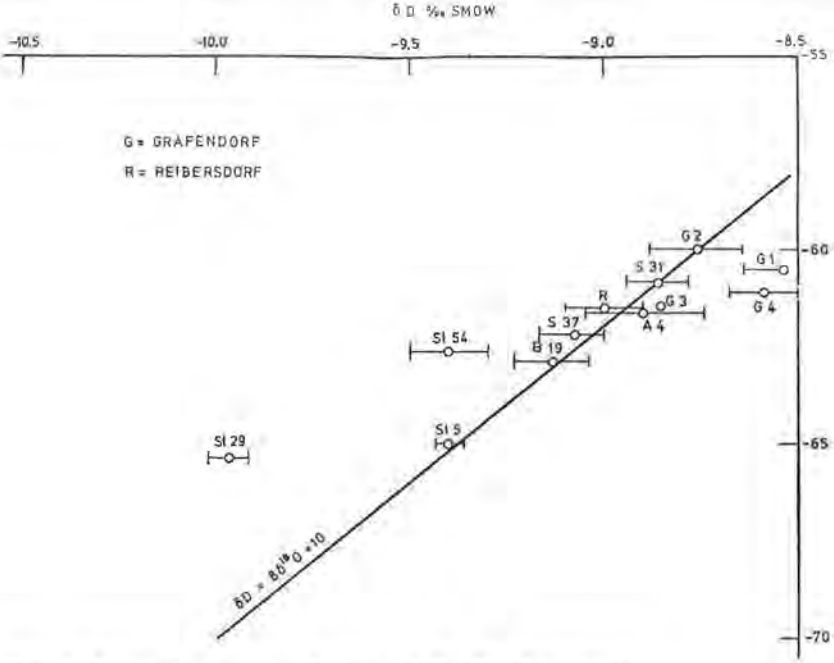

Fig. 7: Deuterium-oxygen diagram of the Hartberg basin.

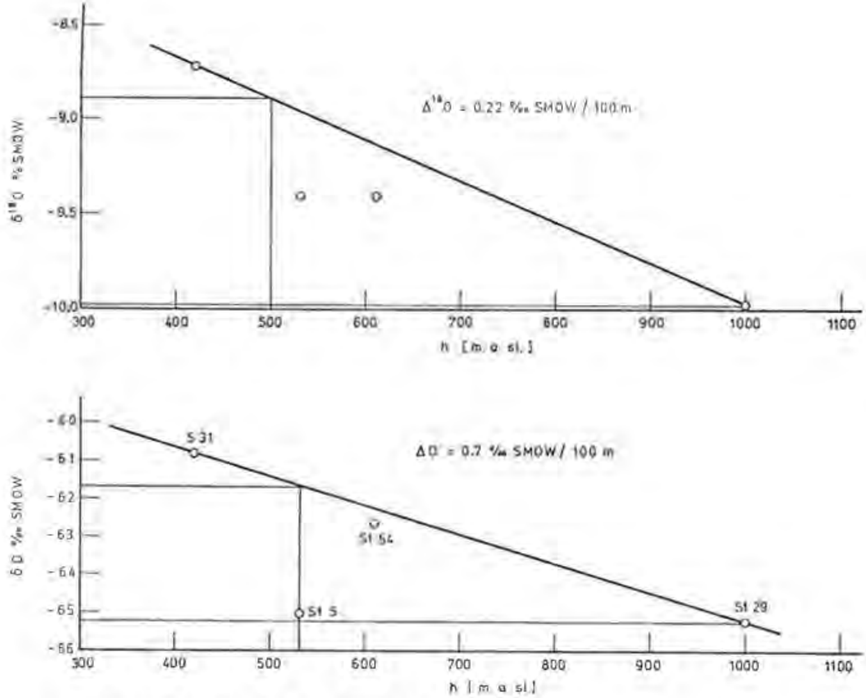

Fig. 8: Altitude effect in the Stambach valley.

systematically indicating increased activity at the level of confidence of at least 99/100th error (18). In Table 7, moreover, the slightly increased tritium activity correlates itself with a certain sampling date: 14 July 1972. This, however, suggests a slight contamination of the flasks used for sampling, or of the counting equipment in the laboratory during the period of counting. This conclusion also coincides with another observation; two other independent measurements of the same water, sampled on 26 August 1970 and 20 September 1972, show no tritium content.

Samples from the Stambach valley taken from springs, brooks and shallow wells (Figs. 6, 8 and Table 6) all indicate a presence of tritium. They belong, therefore, to the hydrological zone of relatively fast replenishment. Graphical presentation of the tritium data from Table 6 for 1969 illustrates Fig. 6.

The sudden decrease of tritium content in precipitation during the winter of 1969 reflects seasonal variations. This regularity was observed many times at different places throughout the world (8).

Table 6: Isotope data in the Grafendorf/Hartberg area.

	NM (1250m)			N K a W (457 m)			St-29 (960 m)			S-31 (418 m)			S-37 (410 m)		
Samplg. Date	Tritium T.U.	$\delta^{18}O$ ‰ (SMOW)	δD ‰ (SMOW)	Tritium T.U.	$\delta^{18}O$ ‰ (SMOW)	δD ‰ (SMOW)	Tritium T.U.	$\delta^{18}O$ ‰ (SMOW)	δD ‰ (SMOW)	Tritium T.U.	$\delta^{18}O$ ‰ (SMOW)	δD ‰ (SMOW)	Tritium T.U.	$\delta^{18}O$ ‰ (SMOW)	δD ‰ (SMOW)
1969															
29. 3.							565±16		—65.4	233±9		—61.6	227±7		—62.1
23. 4.	190			261±24			559±24	—10.1	—66.3	139±5		—60.8	158±29	—9.2	—62.9
5.	210			263±34		—54.6	510±32	—10.1	—65.3	127±8		—61.7	182±19	—9.1	—62.2
30. 6.	320±22	—11.8	—79.0	310±16	—9.2	—62.6	595±22	—9.8	—64.2	136±8		—60.7	212±17	—9.1	—62.7
31. 7.			—62.2			—48.4	542±30	—10.0	—64.3	150±13	—8.6	—60.5	211±20	—9.1	—63.0
28. 8.	253±15		—48.5	322±23	—6.6	—41.5	528±20	—9.8	—65.6	129±10	—8.6	—60.1	182±10	—9.0	—61.8
30. 9.	195±15	—8.4	—51.5	211±15	—7.5	—45.3	537±20	—10.0	—65.3	148±19	—8.5	—60.2	193±17	—9.0	—63.0
30. 10.	152±6			161±7		—62.8	541±18	—9.7	—64.0	126±11	—8.8	—63.7	213±14	—9.0	—63.1
30. 11.	51±5.8			53.4±7.7		—62.4	476±11		—66.0	143±7		—60.3	222±10		—60.8
30. 12.	86.1±5.5	—16.1	—108.3	75.1±9.7	—15.8	—106.8	505±25	—10.0	—65.8	123±24		—59.3	224±10	—9.1	—60.6
1970															
27. 1.	87.4±3.4	—9.8	—72.1			—98.3	484±18	—10.0	—65.6			—60.5			—61.6
27. 2.	127±11	—11.8	—103.6	98.6±10.1		—102.4	502±15		—65.2	143±8	—8.7	—59.7	217±12		—62.7
31. 3.	163±7			140±8			522±19			179±8	—8.7				
30. 4.	188±10			218±7			490±12			142±11			210±10		
31. 5.							499±15								
11. 12.	73.4±3.4	—13.0		293±13	—7.0		420±15	—10.2		167±16	—9.1		201±15	—9.2	
1972															
9. 11.							359±16						166±11		
1973															
23. 1.							312±10			157±5			154±6		
15. 5.							311±11			141±5			143±6		
22. 8.							286±8	—9.83	—66.2	128±5	—8.7	—61.2	163±5	—8.86	—62.6

Samplg. Date	R 6			A 4 (381 m)			B 19 (380 m)			St-54 (610 m)			St-5 (535 m)		
	Tritium T.U.	δ^{18}O‰ (SMOW)	δD‰ (SMOW)	Tritium T.U.	δ^{18}O‰ (SMOW)	δD‰ (SMOW)	Tritium T.U.	δ^{18}O‰ (SMOW)	δD‰ (SMOW)	Tritium T.U.	δ^{18}O‰ (SMOW)	δD‰ (SMOW)	Tritium T.U.	δ^{18}O‰ (SMOW)	δD‰ (SMOW)
1969															
29. 3.	352±9		—63.9	8.1±0.7		—60.2	264±17		—61.5	416±11		—63.0	324±11		—66.4
23. 4.	323±10		—62.9	9.1±0.7		—62.6	274±10		—63.3			—62.2	286±10		—65.8
5.	318±11		—62.3	9.0±0.6		—61.9	320±11		—63.7			—62.3	254±9		—64.5
30. 6.	338±11		—61.9	11.5±0.7		—60.7			—64.3			—60.8			—64.1
31. 7.	291±12	—8.9	—60.4	10.1±0.7		—60.7			—63.6			—62.1			—64.5
28. 8.	236±10	—8.7	—59.2	11.6±0.8	—8.8	—61.1	271±10	—9.1	—64.0			—62.3	276±10		—65.3
30. 9.			—59.7	11.1±0.8	—8.8	—61.1			—61.3			—62.0			—63.8
30. 10.	328±14	—8.9	—62.3	9.4±0.6	—8.9	—63.7	298±10	—9.1	—65.5	347±15	—9.3	—62.2	281±11	—9.4	—63.1
30. 11.	228±7		—61.9	8.4±0.8		—61.9	275±8		—60.8	316±9		—63.9	261±9		—64.2
30. 12.	295±10	—9.2	—60.4	10.4±7	—9.7	—61.4		—9.1	—60.1			—63.3			—64.5
1970															
27. 1.			—60.9	11.4±0.6	—9.1	—62.0	250±8	—9.2	—62.6	337±12		—63.3			—65.6
27. 2.	276±10	—9.4	—61.9	0		—61.8	271±12	—9.5	—63.4			—64.3			—66.5
31. 3.				11.9±0.5						309±15			291±15		
30. 4.	258±8			11.2±0.7			284±15						298±14		
31. 5.	356±17			10.6±0.6			295±15			349±18			281±12		
11. 12.	280±13	—8.9		7.3±0.7	—9.0		276±21	—8.8		307±21	—9.7				
1973															
23. 1.	274±21			15.8±3.5			226±13			252±13					
15. 5.							160±6							dried	
22. 8.	179±6	—8.6	—59.0				141±5	—8.6	—59.8						

Table 7: VHFG Grafendorf wells, environmental isotope data.

Well	Date of sampling	Tritium	$\delta^{18}O$‰ SMOW	δD‰ SMOW	Temp.	measured $\delta^{13}C$ ‰ (PDB)	measured ^{14}C % modern	pH	HCO_3 (ppm)	^{14}C initial (%)	Adj. age (years)	Stand dev. ± δ	Mean adj. age (years)	Apparent (uncorr.) age (years)	Remarks
Graf 1	26. 8. 70	0.6±0.5	—8.5			—11.30	41.8±2.1			65.4	3700				
	14. 7. 72	1.5±0.2			12.5	—11.11	44.3±1.2	7.26		64.1	3100^{1})				^{1}) laboratory error?
	20. 9. 72	0.4±0.4	—8.23		10.9	—11.58	41.5±1.0	7.43		70.0	4300				
	9. 11. 72		—8.67		10.7	—11.11	41.4±1.0	7.43	293	69.9	4000	250	4080	7000	
	15. 5. 73	0.4±0.2					40.6±1.1			68.2	4100		±110		
	22. 8. 73		—8.54	—60.9			39.6±1.0			66.9	4300				
	8. 2. 74		—8.76	—60.0											
Graf 2	26. 8. 70	0±0.4	—8.6			—11.70	40.0±1.1			69.4	4800				
	14. 7. 72	1.8±0.2			12.1	—11.38	40.4±1.2	7.35		67.3	4200				
	20. 9. 72	0.6±0.3	—9.24		11.7	—10.59	42.3±1.2	7.60		64.9	3500				
	9. 11. 72		—8.73		11.6	—11.96	41.3±1.1	7.30	285	70.5	4400	380	4200	7200	
	15. 5. 73	0.3±0.2				—11.90	41.3±1.1			70.1	4400		±160		
	22. 8. 73		—8.58	—59.2		—11.69	41.3±1.1			68.8	4200				
	8. 2. 74		—8.68	—60.6											
Graf 3	26. 8. 70	0.7±0.5	—8.70			—11.20	30.6±1.0			64.5	6200				
	14. 7. 72	1.4±0.2			13.5	—11.47	43.9±1.2	7.24		65.9	3400^{2})				^{2}) results with laboratory mistakes or invasion of younger water
	20. 9. 72	0.6±0.2	—8.90		12.2	—11.13	31.3±1.0	7.62		68.4	6500				
	9. 11. 72				11.7	—10.58	31.1±1.1	7.40	281	62.8	5800	290		9500	
	9. 11. 72		—8.94		11.7	—10.56		7.40	281				6150		
	9. 11. 72				11.7	—10.58	29.9±0.9	7.40	281	62.8	6100		±150		
	15. 5. 73	0.1±0.2				—11.71	41.5±1.0			70.0	4300^{2})				
	22. 8. 73	0.1±0.3	—8.72	—61.5		—11.60	43.1±1.0			69.5	3900^{2})				
	8. 2. 74		—9.06	—61.6		— 4.86	31.5			25.3					$\delta^{13}C$ unrealistically low

Well	Date of sampling	Tritium	$\delta^{18}O$‰ SMOW	δD‰ SMOW	Temp.	measured $\delta^{13}C$ ‰ (PDB)	 ^{14}C % modern	pH	HCO_3 (ppm)	^{14}C initial (%)	Adj. age (years)	Stand dev. ± δ	Mean adj. age (years)	Apparent (uncorr.) age (years)	Remarks
Graf 4	26. 8. 70	0.5±0.5	−8.70			− 9.50	35.3±1.0			55.9	3800				
	16. 10. 71					−10.68	34.4±1.1			63.6	5100				
	14. 7. 72	1.5±0.3			14.5	−10.73	34.4±1.0	7.42		63.2	5000				
	20. 9. 72	0.3±0.2	−8.28		11.1	− 8.65	38.0±1.1	7.50		51.4	2500[3]				[3] invasion of younger water
	9. 11. 72		−8.78		12.3	− 8.60	35.4±1.1	7.15	193	45.8	2100[3]		4700	8500	
	15. 5. 73	0.3±0.2				−11.19	36.2±1.0			63.8	4600	460	±170		
	15. 5. 73					−11.34	36.6±0.9			63.8	4600				
	15. 5. 73					−11.45	35.7±0.9			64.5	4900				
	22. 8. 73		−8.56	−61.0		−11.40	34.5±1.0			64.2	5100				
	8. 2. 74		−8.65	−61.1		− 4.66	36.7±1.0			18.65					$\delta^{13}C$ unrealistically low
Seib 1	14. 7. 72	0.9±0.2	−8.64		11.8	−14.14	41.5±1.8	7.25		85.7	6000				
	9. 11. 72		−8.64		11.5	−13.59	39.4±1.3	7.15		78.8	5700	350	6000	7300	
	15. 5. 73	0.1±0.2				− 9.48	23.7±0.6			51.7	6400		±200		
Seib 2	14. 7. 72	2.3±0.2			10.2	−17.48	66.6±2.7	7.20		100	3800				
	9. 11. 72		−9.12			−16.92	68.1±3.2	8.00	124	100	3900	600	4200	3200	
	15. 5. 73	1.3±0.2				−17.50	62.2±1.5			100	4900		±350		
Seib 3	9. 11. 72		−8.64		10.5	−14.35	44.0±2.0	8.0	131	92	6100		6100	6600	[4] rejected from calculation of mean value on the basis of the Chauvenet criterion
	15. 5. 73					−12.17	19.0±0.7			78	11000[4]				

Table 8: Mean values of the stable isotope data obtained for the Hartberg-Grafendorf Basin.

Sampling point	$\overline{\delta^{18}\mathrm{O}}$ ‰ SMOW	$\overline{\delta \mathrm{D}}$ ‰ SMOW
S-31	−8.71±0.07	−60.8±0.3
Reibersbach	−9.00±0.10	−61.5±0.4
A4	−8.90±0.16	−61.6±0.3
S-37	−9.08±0.10	−62.2±0.3
B-19	−9.13±0.09	−62.8±0.5
St-5	−9.40±0.03	−65.0±0.3
St-29	−9.97±0.05	−65.3±0.2
St-54	−9.40±0.10	−62.6±0.3
Graf 1	−8.54±0.09	−60.4±0.5
Graf 2	−8.77±0.12	−59.9±0.7
Graf 3	−8.86±0.07	−61.6±0.5
Graf 4	−8.59±0.09	−61.1±0.5

In the Grafendorf area, both local meteorological stations (Masenberg and Kirchberg a. W.) show similar tritium content with an average in 1969 of ca. 200 T. U. From Fig. 6 it can be seen that most of the springs discharge water with a tritium content close to this value, which indicates relatively recent precipitation water. The exceptions are waters from well A-4, yielding much lower values for tritium content, and St-29, showing much higher tritium content. On the basis of tritium alone one can draw the following conclusions:

A-4 — Private artesian drilled well. Shows some admixture of contemporary water. Most probably this well penetrates the uppermost

Table 9: Temperature of springs in the Hartberg area, sampled for environmental isotope analysis (in °C).

Spring Code	1969										1970	
	March 27/29	April 23/25	May 29/30	June 29/30	July 30/31	Aug. 27/28	Sept. 29/30	Oct. 30	Nov. 26	Dec.	Jan.	Feb.
St-5	8.7	8.2	8.9	9.2	10.2	10.0	9.6	9.3	8.7	7.0	7.1	7.6
St-29	6.1	6.2	6.2	6.3	6.4	6.4	6.4	6.3	6.3	6.3	6.2	6.2
St-54	7.9	—	9.0	10.2	11.1	10.7	10.5	11.4	8.9	7.1	7.2	7.0
S-31	6.2	8.0	11.5	12.0	14.2	14.2	13.6	11.9	9.7	7.3	6.3	5.8
S-37	—	—	9.1	9.3	9.7	9.8	10.5	9.8	9.3	—	—	—

Table 10: Results of the chemical analyses of waters in the Hartberg/Grafendorf Basin.

No.	Ref.	Samplg. Date	Temp. °C	Field pH	Ion Composition (mg/l)							Sum of Constituents (mg/l)	SIC	P CO_2 10^2 atm.
					cations				anions					
					Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{--}			
1	G 1	22. 8. 73	10.9	7.3	86.3	1.8	7.5	2.6	307.7	1.8	9.9	417	0.0+	1.2
2	G 2	22. 8. 73	11.7	7.5	85.5	5.1	6.6	2.3	291.8	2.8	16.9	411	+0.1	0.7
3	G 3	22. 8. 73	12.2	7.4	78.6	6.0	8.0	2.3	292.5	1.2	9.0	398	0.0	0.9
4	G 4	22. 8. 73	12.0	7.3	80.3	2.8	10.2	2.3	295.2	1.4	5.8	398	0.0	1.1
5	B 19	22. 8. 73	10—15*	7.2	95.1	3.2	15.0	1.6	298.7	17.6	22.2	453	—0.1	1.5
6	Reib.	22. 8. 73	10—15*	7.4	28.9	5.9	6.7	3.4	99.8	10.3	14.4	170	—0.9	0.3
7	St-29	22. 8. 73	6.4	6.6	3.0	0.7	3.8	1.2	17.2	0.5	4.5	31	—3.4	0.3
8	S-31	22. 8. 73	14.2	7.2	103.7	9.5	11.7	1.4	271.9	50.0	23.0	471	—0.1	1.4
9	S-37	22. 8. 73	9.8	7.2	79.8	4.0	7.7	4.1	210.0	22.0	24.3	352	—0.4	1.0

*) range of values

Methods of determination: Ca, Mg — complexometrically; Na, K — flame photometer; Cl — argentometrically; SO_4 — by weight; HCO_3— by titration (H_2SO_4 0.05N against methyl-orange)

Table 11: Discharge of springs in the Hartberg area, sampled for environmental isotope analysis (l/s).

Spring Code	1969										1970	
	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.
St-5	—	0.06	0.04	0.05	0.03	0.02	—	0.05	0.07	0.02	0.06	0.18
St-29	1.2	3.0	2.5	5.0	1.6	1.1	1.7	1.4	1.1	0.5	0.7	0.8
St-54	0.1	0.02	0.03	0.01	0.08	0.06	0.05	0.06	0.03	0.03	0.04	0.06
S-31	0.15	0.16	0.16	0.16	0.27	0.2	0.23	0.35	0.17	0.2	0.35	—
S-37	1.0	0.35	1.3	0.8	—	—	—	—	—	—	—	—

artesian aquifer, but due to the inadequate insulation during drilling, or due to the bad present technical state of the casing, some interconnection with the shallow groundwater was created, and the water yielded by this well is a mixture of water from these two sources.

St-29 — High altitude spring (960 m a. m. s. l.). Shows exceptionally high tritium content, much higher than in contemporary precipitation (factor 2.5). The only explanation is to assume that the spring discharges water recharged around 1963, the time of the maximum tritium content in precipitation.

In addition to sampling in 1969, the VHFG performed measurements of temperature and discharge of the same springs. Relevant data are presented in Tables 10 and 11. Two conclusions can be drawn from these tables. First: the low and stable temperature, over the whole year, of St-29 spring water suggests rather a deep aquifer. Second: an examination of the discharge function of the spring reveals great seasonal variations (Table 11). At the same time, there is almost no variation in the tritium content over the year. This precludes the hypothesis that some precipitation close to the topographical spring location is contributing significantly, causing seasonal variations of discharge. This would also require significant variations in the tritium content, which is not the case. The main aquifer is probably situated at the top of the mountain. This qualitative recognition of the internal dynamics of the aquifer and the favourable topographic situation of this spring, permitting a precise delineation of the catchment area, may be treated as a starting point for making a quantitative approach to the water storage in the Stambach valley.

St-54 — Spring discharging from crystalline rocks at an altitude of 610 m, discharging, as can be seen from Table 6 and Fig. 6, in 1969 and 1970 water with an increased tritium content. The internal mechanism of the aquifer is probably similar to that proposed for spring St-29. Small discharge, relatively high variation of temperature, and distant water divide with a relatively high mean residence time, may indicate that the water was tapped at higher altitudes than the actual location of the spring.

St-5 — Spring discharging from crystalline rocks at an altitude of 535 m, increased tritium content, relative to precipitation. Mechanism of recharge probably similar to that assumed for St-54. As can be seen later from the stable isotope data, they indicate an even higher altitude of recharge for spring St-5 than for the above-mentioned St-54; even the location of that spring is higher. Lower value of tritium content than in the two upper springs shows lower mean residence time, and hence faster replenishment of the hydraulic system to which spring St-5 belongs.

S-37 — Spring discharging from the Sarmat formation at an altitude of 410 m. Average tritium content for 1969 is very close to the average tritium content in precipitation.

S-31 — Spring discharging from the Sarmat formation at an altitude of 418 m. Shows lower tritium content than the local precipitation. Water shows identical stable isotope composition as for the artesian aquifer. It is possible to expect, therefore, that the spring discharges old artesian water diluted by local precipitation.

Reibersbach — The brook is draining next to the north catchment area. Tritium content higher than in precipitation. This may be explained by the fact that the brook draining the whole catchment area contains also high altitude springs of the type of the above-described St-29 spring, characterizing themselves by the high tritium content. Some connection can be observed between tritium content and precipitation. Yearly precipitation in Hartberg is presented in Table 12. One can notice that the periods of higher precipitation, e. g. July, August, November 1969 and April 1970, correlate with the lower tritium content. As can be seen from the examples quoted above, there is very little seasonal variation in the tritium content of high altitude springs discharging in 1969 water with a high tritium content. Thus precipitation with a small average tritium content dilutes water caught from the springs. Exceptions to this correlation in June 1969 (Table 12) may be explained by the exceptionally high tritium content (equal to the tritium concentration in the brook) of precipitation during this month (Table 6).

B-19 — Shallow groundwater, sampled from a private well, at an altitude of 380 m, in the vicinity of the four testing VHFG boreholes in Grafendorf. Water shows relatively small variations in tritium content. Mean tritium content for years 1969 and 1970 yields correspondingly $\overline{X}_{1969} = 284$ T. U. and $\overline{X}_{1970} = 275$ T. U. Tritium measurements from the local meteorological stations are not properly representative from the statistical point of view, as they do not cover the full year, indicating at the same time great seasonal variability. The most abundant data, available for the meteorological station Kirchberg (NKaW, Table 6) in 1969, yields for the unweighted mean a value of 207 T. U. Weighted mean of the tritium content in 1969 for the nearest other meteorological station is available for Vienna (station Hohe Warte). This value is $\overline{X}_{HW} = 218.77$ T. U.

Both mean values therefore are smaller than the tritium content in the B-19 sampling point. This might suggest that the phreatic aquifer in the Grafendorf/Hartberg basin is mainly recharged by the underground flow from crystalline rocks, or by surface runoff. (Average tritium content for Reibersbach brook for 1969 is equal to 301 T. U. and is close to similar values in the phreatic aquifer — 284 T. U.).

Table 12: Monthly precipitation in Hartberg.*

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Annual
1951	57	42	83	40	110	132	118	56	60	8	106	29	
1952	44	60	29	16	70	78	58	62	119	98	16	48	698
1953	26	14	18	20	89	158	138	86	86	54	18	15	722
1954	46	11	40	45	129	164	144	89	95	26	69	83	941
1955	11	44	46	18	91	76	224	109	81	71	29	19	819
1956	5	27	30	79	106	104	149	92	4	85	53	33	767
1957	16	45	37	70	67	47	196	86	52	13	28	12	669
1958	25	53	68	31	41	90	111	168	85	74	37	50	833
1959	8	8	51	90	59	194	130	109	30	24	49	83	835
1960	16	34	53	38	55	50	105	102	84	102	39	50	728
1961	15	6	20	42	152	131	98	65	42	115	82	41	809
1962	35	21	57	14	109	57	90	88	74	48	152	19	764
1963	45	24	47	66	102	135	45	209	47	22	75	32	849
1964	0	8	39	71	82	62	68	78	53	190	17	41	709
1965	18	5	32	213	139	158	285	104	105	0	73	29	
1966	8	19	22	66	47	151	148	133	54	119	52	40	
1967	9	18	65	29	122	42	69	55	117	58	58	15	
1968	15	5	7	31	62	109	92	204	62	31	39	34	
1969	47	61	51	24	38	159	98	140	79	26	71	38	
1970	14	33	55	114	76	142	115	137	39	45	73	22	
1971	13	9	39	51	43	78							

*) from the Hydrographisches Zentralbüro in the Bundesministerium für Land und Forstwirtschaft, Wien

8. Stable Isotope Data

The stable isotope data obtained for springs and shallow wells are listed in Table 6, for artesian aquifers in Table 7. Table 8 shows the mean values of the stable isotope content, on which the oxygen-deuterium diagram presented in Fig. 7, was based.

It should be noted that most experimental points within the limit of the error fit the meteoric line described by the equation

$$\delta D = 8\,\delta^{18}O + 10$$

The kind of correlation between the deuterium and oxygen content described by the above equation proves, in general, that precipitation was not subject to significant evaporation on the surface before recharge took place.

The only source of water which obviously does not coincide with the above deuterium/oxygen-18 correlation is the high altitude spring St-29, which shows excess of deuterium.

The statistical material on which the calculations of the mean stable isotope content were based, and the coherency of all other data with the general meteoric line, rather eliminate the possibility of a systematic error involved in the measuring procedure. On the other hand, until now does not exist any physical model explaining such a phenomenon in literature, although similar local enrichments in deuterium were observed by some authors (20, 21).

A first survey of the stable isotope data reveals two main features, on which a further detailed interpretation can be based:

1. The artesian aquifer shows the lower values in deuterium and oxygen-18 content, compared to the values observed in the Stambach valley springs.

2. The oxygen-18 data from the uppermost sampling point, spring St-29 (960 m a. m. s. l.) and from spring S-31 (418 m a. m. s. l.) show a significant difference in the isotopic composition, on the basis of which the local altitude effect may be quantitatively estimated.

Fig. 8 illustrates the way of determination of the altitude effect in the Hartberg/Grafendorf basin. The line is mainly based on two experimental points: St-29 and S-31 springs. The origin of these waters is assumed to be known: for St-29 the top of the Waldseppl area (1164 m a. m. s. l.) (22), and for S-31 an elevation of the outcrop of the Sarmatian formation northwest from Grafendorf (415 m a. m. s. l., the supposed recharge area for the artesian aquifer). This reasoning gives an increment of $/\delta^{18}O/_{100\,m} = /0.22‰\ SMOW/_{100\,m}$ for oxygen-18. A similar procedure for deuterium will yield $/\delta D/_{100\,m} = /0.70‰\ SMOW/_{100\,m}$ (Fig. 8).

For oxygen-18 this is only slightly less than the average value of the altitudinal isotopic increment, the mean value of which is, in literature, assumed to be $/0.3‰\ SMOW/_{100\,m}$, and significantly less for deuterium, where the average altitudinal increment is estimated at 2.5‰ SMOW/100 m (19).

On the basis of these general features, the following conclusions can be formulated for these particular sampling points.

St-29 shows relatively small seasonal variations in the stable isotope composition whith the $\delta^{18}O$ mean value averaged for the period 1969 till 1970 and equal to $-9.97 \pm 0.05‰$ SMOW. It discharges water caught at the top of Waldseppl. There is a plateau of the size of a few hectars with a smooth westward slope, probably highly weathered, creating a local aquifer.

NM and NKaW meteorological stations, located at the top of the Masenberg and in Kirchberg. The stable isotope content in precipitation shows significant variations. Such seasonal variations of precipitation are observed everywhere and must be considered as a normal phenomenon. Concerning hydrology, however, the most significant is the mean yearly value of a particular stable isotope content, weighted for the amount of precipitation in each month.

With the few data available at the same time for both isotopes, it is impossible to calculate the yearly weighted mean value; and these data will not be used for further interpretations.

A-4 private drilled well. The tritium data suggest a mixture of contemporary water with old artesian water.

St-54 — The spring is located at an altitude of 610 m a. m. s. l. The oxygen-18 data available are limited to the results of two measurements (in 1970 the spring dried out). When considering the straight line at Fig. 8 as a curve properly interpolating the oxygen content for different altitudes, one must consider that the spring discharged water of local origin, characteristic for the altitude of the spring's location. This conclusion would also coincide with the observed significant yearly variations of temperature (Table 5) which indicate a shallow and rather small aquifer.

St-5 — Spring discharging from the crystalline rock, located at an altitude of 535 m a. m. s. l. As the isotopic composition is the same as for spring St-54, it has to be assumed that the water discharged by spring St-5 is also locally recharged.

S-37 — Spring at an altitude of 410 m. Despite the fact that the spring discharges from the Sarmat formation, the stable isotope composition shows that the water was probably tapped at higher altitudes, than the location of the spring itself. Its isotopic composition is quite stable in time, differs significantly from the isotopic composition characteristic for the artesian aquifer confined deeper in the same geological formation, and is similar to that of the phreatic aquifer. In using Fig. 8 to estimate the source of origin of this water, one can assume that the average altitude at which the water is tapped is appr. 600 m a. m. s. l. There is only one later measurement available of water sampled from this spring on 23. 1. 1973, showing an oxygen content of $\delta^{18}O = -8.61‰$ SMOW.

S-31 — Spring at an altitude of 418 m a. m. s. l. discharging from the Sarmat formation. Both oxygen and deuterium contents are low and show that the water was collected at lower altitudes (probably local recharge).

Reibersbach brook — Both, the mean values of $\delta^{18}O$ and δD indicate that the isotopic composition of the water from this brook is more depleted in these stable isotopes than the precipitation characteristic for these altitudes. The brook drains next to Stambach valley, with many high altitude springs. This conclusion again coincides with the observed increased tritium content in this brook; as is shown for spring St-29, this phenomenon was characteristic for high altitude springs in the project area in 1969/70.

B-19 shallow groundwater well at an elevation of 380 m a. m. s. l. It indicates an increased absolute value of $\delta^{18}O$ and δD, even more so than Reibersbach brook. According to Fig. 8, the mean altitude at which water was tapped has to be appr. 700 m a. m. s. l. This suggests that at least the main part of the water in the phreatic aquifer originates from higher elevations, was then conducted down as a subsurface flow through the uppermost weathered part of the crystalline rock and recharged the phreatic aquifer.

After completing this review of particular sites, the following general conclusions can be drawn from the stable isotope data:

1. The water from the artesian confined aquifer has a different stable isotope composition from that of local surface runoff and the phreatic aquifer. This is in agreement with the hypothesis that the local recharge of the artesian aquifer probably occurs through existing Sarmat outcrops.

2. The underground flow through the slopes of the neighbouring mountains and valleys continuously recharges the Hartberg/Grafendorf basin; the phreatic aquifer is mainly recharged by this flow.

9. Carbon-14 Data

Four artesian VHFG test wells in Grafendorf were the subject of systematic measurements and, sporadically, three artesian aquifers in Seibersdorf.

The results of the measurements of stable isotopes and tritium content, of temperature, pH, carbonate content and ^{14}C age, are presented in Table 7.

The basic equation for the carbon age determination is (23):

$$t = \frac{5730}{\ln 2} \ln \frac{^{14}C \text{ initial}}{^{14}C \text{ measured}}$$

However, as was mentioned previously, the value of the initial carbon-14 content must be estimated separately, taking into account that after saturation with modern ^{14}C in the unsaturated zone the following additional effects can occur in the aquifer:

1. further dissolution of carbonates;

2. addition of bicarbonate from the oxidation of organic matter.

The pH and ^{13}C content can serve as a basis for estimating the initial fraction of the dissolved carbonates; the initial δ^{13}C value for the Grafendorf/Hartberg basin (moderate climate) was assumed to be — 25‰ PDB.

G. SAUZAY (23) worked out a procedure taking all these effects into account. It was used to process the experimental data gathered in Table 7 for estimating the ^{14}C age of waters in the confined Grafendorf/Hartberg aquifer.

A first inspection of these data showed that the age of the confined aquifer is of the order of 5000 years.

The first three aquifers show a relatively stable chemical composition. The precision of the age determination is also good at a level of 5%. The sharp changes in the ^{14}C content from sampling to sampling, observed in aquifer 3, seem to show an interconnection between aquifers 1 and 3. Aquifers 2 and 3 in Seibersdorf (5 km from Hartberg) were sampled three times, aquifer No. 1 only twice.

The results quoted in Table 7 show that the age of the water is comparable to that determined in Grafendorf.

As the confined aquifer in the Grafendorf/Hartberg basin is assessed for carbon-14 only in one place by means of the testing wells, nothing more can be said about the internal dynamics of the aquifer on the basis of the measurements performed.

10. Chemical Data*

The chemical analysis results are presented in Table 10. The sum of the ionic species of the four artesian aquifer samples (no. 1 to 4) ranges between 400 and 450 ppm. The Sarmat springs and the brook (no. 6, 8, 9) are also in the same order of values, but the high altitude spring St-29 (no. 7) holds 10 times less dissolved solids and the river (no. 6) appears also to be significantly different.

The graphical representation of the water quality using the PIPER (25) and SCHOELLER (24) diagrams (Figs. 9 and 10) shows that all the waters are of the calcium bicarbonate type, with the exception of St-29, where the relative proportion of alkaline ions is much higher. Both the weak mineralization and the different ionic proportions for St-29 are due to the nature of the water-bearing formation: the high altitude spring originates from crystalline rock (in which the alkaline elements are predominant and the rate of weathering lower) while all other groundwater samples are from sedimentary rocks.

The anion distribution indicates a difference between the four deep

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* This chapter was prepared by G. GALLO, IAEA, Isotope Hydrology Section.

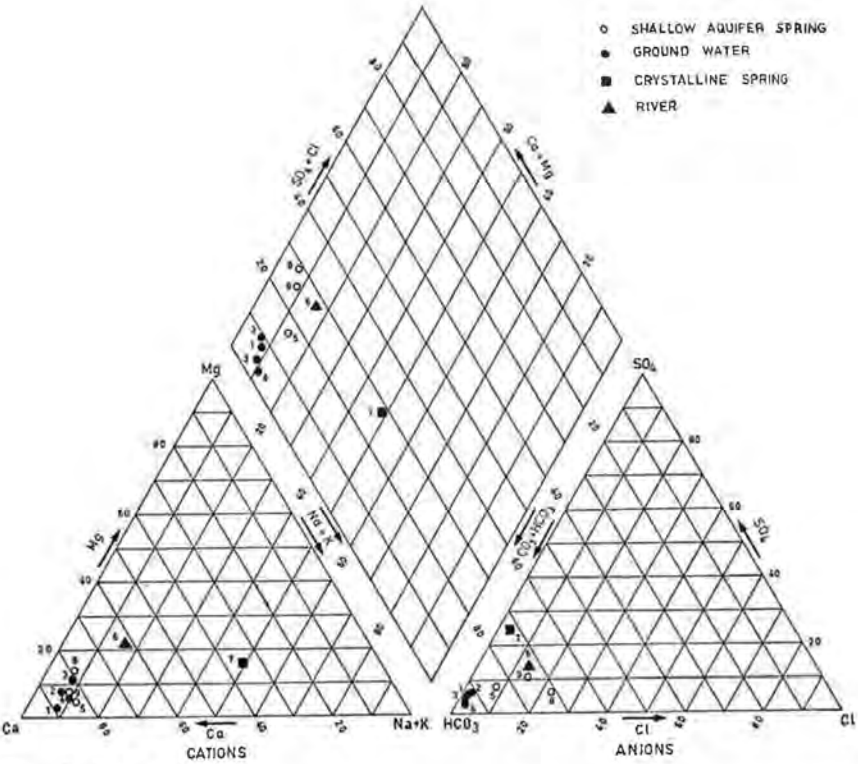

Fig. 9: Piper diagram.

groundwater samples where HCO_3^- exceeds 90% and all other samples in which the Cl^- and SO_4^{--} concentration is relative higher. For the shallow groundwater (B-19) and springs (S-31 and S-37) r Cl is even higher than r SO_4^{--} and exceeds largely the normal level of content in precipitation. These high values of Cl^- may be due to agricultural activity in the area.

The two last columns of Table 10 give the values of the saturation index versus calcite (26), and the partial pressure of CO_2 in equilibrium with the water (27). These two parameters are computed considering the three phases thermodynamical equilibrium:

$$\begin{array}{c} CO_2\ \text{(gaseous)} \\ \uparrow\downarrow \\ CO_2 + H_2O \rightleftarrows HCO_3^{--} \rightleftarrows CO_3^{-} \\ \downarrow\uparrow \\ \text{(solid)}\ CaCO_3 \end{array}$$

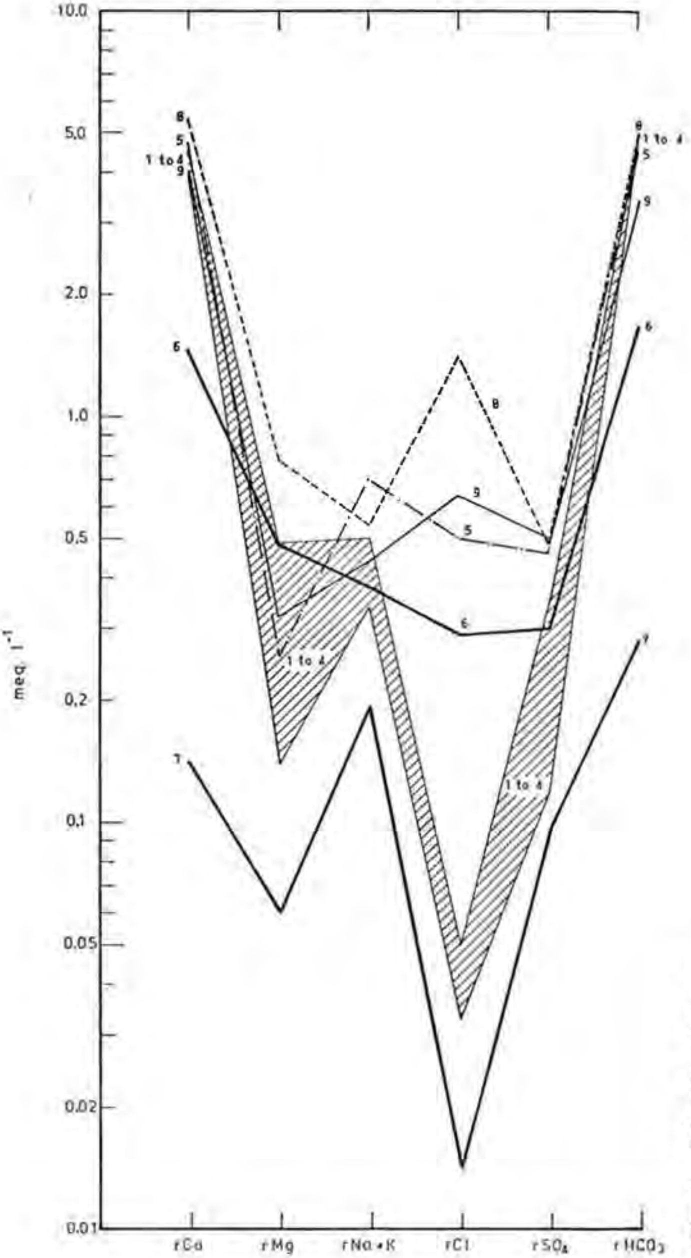

Fig. 10: Schoeller diagram.

The saturation index is defined by:

$$SIC = \log \frac{a_{Ca^{2+}} \cdot a_{CO_3^{--}}}{K_c}$$

$SIC \rangle 0$ indicates supersaturation; $SIC = 0$: equilibrium; $SIC \langle 0$: undersaturation. The partial pressure of CO_2 has the value:

$$P_{CO_2} = \frac{10^{-pH} \cdot a_{HCO_3^-}}{K_H \cdot K_1}$$

In the above two equations a_i represents the molar activities of the ionic species i. By definition $a_i = \gamma_i\, m_i$, where m_i is the molality and γ_i the activity coefficient calculated by the Debye-Huckel equation with the ionic strength of the solution. $a_{CO_3^-}$ is calculated considering the second dissociation of H_2CO_3. K_c is the solubility product of calcite, K_H the HENRY's constant, K_1 the first dissociation constant of H_2CO_3. Their values at 25° C were taken according to GARRELS and CHRIST (28): $pK_C = 8{,}35$, $pK_H = 1{,}47$, $pK_1 = 6{,}35$, $pK_2 = 10{,}33$. For temperatures other than 25° C, the numerical values are computed by the VAN'T HOFF equation using the values at 25° C and the free enthalpies of formation of each ionic species determined from the data of WHEAST (29).

The main error in SIC and Pco_2 is due to the pH measurement. The accuracy is not better than the first decimal in field measurements. Then the value of SIC is accurate to ± 0,1 unit and Pco_2 at 10—15%. For samples no. 5 and 6 for which the water temperature was not available, the computed values of SIC and Pco_2 at 10 and 15° C range in the order of precision of these parameters.

The results for SIC show that the four groundwater samples are in equilibrium versus calcite. The high altitude spring is highly undersaturated and the brook is in an intermediate state between the previous spring and the two Sarmat springs, which are near equilibrium.

The mean partial pressure of CO_2 in equilibrium with these waters is about 10^{-2} atm. This figure can be considered as the average of Pco_2 of the soil air in the area and is about 30 times the atmospheric Pco_2 (6). The figure is much lower for the high altitude spring and the river.

In conclusion, the geochemical study shows the main differences between the high altitude spring, the river and the groundwater samples. For this last category of waters one can also differentiate between the deep groundwaters (nos. 1 to 4) in equilibrium with calcite after a long contact time between rocks and water and the shallow aquifer springs (nos. 5, 8, 9) not yet saturated with calcite even if they have already a higher total mineralization, probably because of their evolution in an open system in the unsaturated zone of the soil with a constant partial pressure of CO_2.

These conclusions, although only indicative distinguishing between types of water (high altitude spring, Sarmat springs and confined aquifers) find full confirmation in the environmental isotope data.

In the case of the Sarmat springs and the high altitude spring, the mean residence time of water computed by tritium data give information on the kinetics of the two different geochemical systems: evolution faster in superficial formation (higher mineralization, waters near equilibrium versus calcite) than in crystalline rocks (low mineralization, waters highly undersaturated).

11. $^{234}U/^{238}U$ Measurements

Independent of the main systematic isotope analysis programme in the Grafendorf area, additional sampling for uranium disequilibrium analysis was performed in 1974. The intention of this sampling campaign was mainly to check the method of measurements and to record the differentiation of the $^{234}U/^{238}U$ ratio in groundwaters in the project area.

Six water samples of a volume of approximately 25 litres each were collected in the field. The laboratory preconcentration method, proposed by J. VESELSKY (30), was used to separate uranium*.

Only samples Graf-1 and St-29 were processed by another method proposed by J. A. S. ADAMS and J. KRONFELD (31).

Alpha spectrometric measurements were performed at the IAEA laboratory in Seibersdorf** by means of the silicon gold drifted barrier solid state detector. The results of the measurements are shown in Table 13. All that can be said on the basis of these few results is, that the investigated samples of the groundwater from the project area show an increased value of $^{234}U/^{238}U$ ratio, similar to that observed by other authors (14—17). The results of the measurements, however, are yet subject to a relatively large error, excluding at this stage the possibility of any quantitative interpretation.

In possible future research, spring St-29 may be of particular value.

As will be shown later, the mean residence time for that aquifer may be determined with relatively high accuracy using tritium data (Chapter 13); the value is 7 ± 1 years.

Water from spring St-29 and possibly from a well specially drilled at the top of Waldseppl, may be used to investigate the source of

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* The ^{233}U spike donated by Prof. J. K. OSMOND of the Florida State University at Tallahassee was used as an internal standard for uranium concentration measurements.

** The measurements were performed by Mrs. M. NEDBALEK and Mr. J. VESELSKY.

uranium in the groundwaters. If in the unsaturated zone it is organic material which is mainly responsible for the initial $^{234}U/^{238}U$ ratio in the groundwaters, then the water sampled at the top of Waldseppl must have the same uranium isotope ratio as that of the spring. If, however, this ratio is formed mainly through the contact of water molecules with the surface of the aquifer rocks, then the value of the uranium disequilibrium measured in the spring 200 m below, must be higher than that at the top of the Waldseppl massif. In this case, the value of the uranium isotopes ratio (2.34 ± 0.68) recorded for the spring would be due to the contact of the aquifer water with the crystalline rocky matrix during the first 7 years.

Table 13: Uranium isotope disequilibrium in water samples from the East-Styrian Basin.

Sampling place	$^{234}U/^{238}U$ activity ratio	Method of Pre-concentration A*, V**	Recovery %	U Concentration μg/l
Graf 1	1.83 ± 0.29	V	54	0.109 ± 0.14
Graf 2	2.68 ± 0.44	V	53	0.193 ± 0.03
Graf 3	2.64 ± 0.58	A	7	—
Graf 4	1.52 ± 0.47	V	89	0.046 ± 0.01
St-29	2.34 ± 0.68	A	26	0.088 ± 0.02
S-31	1.69 ± 0.17	V	47	0.060 ± 0.01

*) Method proposed by J. A. S. Adams (31)
**) Method proposed by J. Veselsky, IAEA, Seibersdorf Laboratory

12. Simulation of the Water Balance of St-29

The availability of long tritium records for some springs in the Stambach valley creates a favourable situation for a quantitative approach to the local hydrological situation. This is due to the clearly defined borders of the local catchment area for these particular springs. Of special interest is the high altitude spring St-29, discharging in 1969 and 1970 water with a tritium content much higher than in the precipitation at that time. This leads to the logical conclusion that the spring must discharge water gathered 6 to 7 years ago during the most intensive bomb tests in the atmosphere. It became possible to apply, in this case, some mathematical models and, by means of the simulation technique, to recognize the internal dynamics of groundwater in the Stambach valley.

Mathematical models based on the transport phenomena and population balance principle were used to simulate the real world situation (32).

Fig. 11 shows the idea of a model of the six interconnected mixing cells, which was used to represent St-29 spring dynamics (33). The reader can find a more detailed description of the model making in the paper. Minicomputer WANG 720 was used to perform simulation experiments.

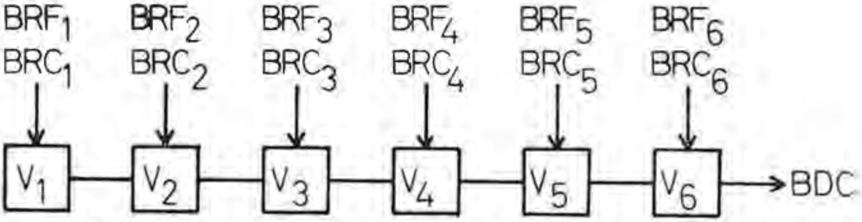

Fig. 11: One dimensional model of 6 mixing cells.
BRF = Boundary recharge fraction
BDC = Boundary discharge concentration
BRC = Boundary recharge concentration
V = Volume

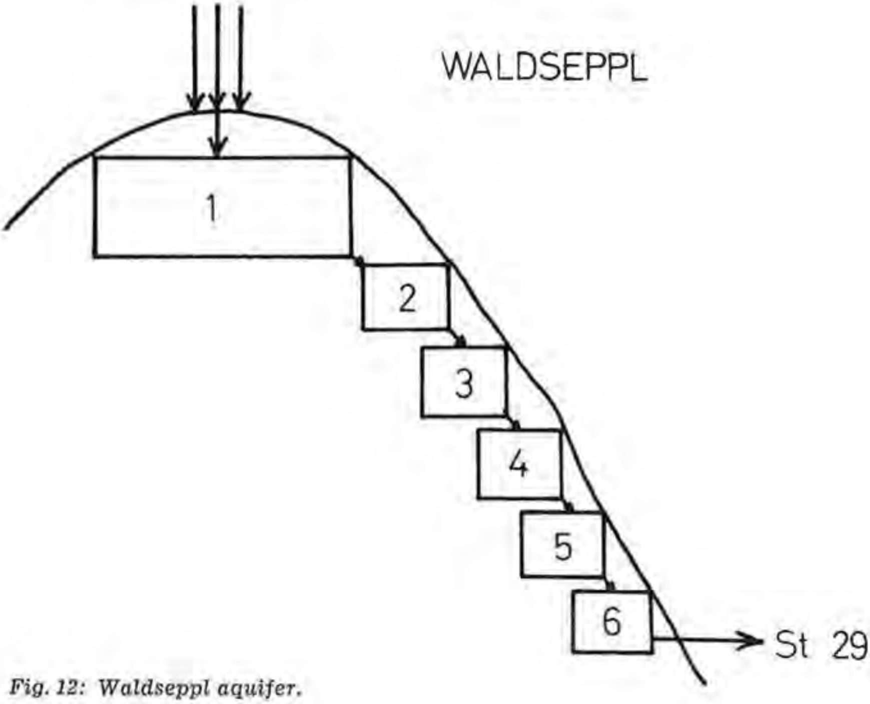

Fig. 12: Waldseppl aquifer.

A conceptual model was based on the assumption that on the flat top of Waldseppl (plateau ca. 4 ha) there is a main recharge area for the high altitude aquifer. The slopes are probably less weathered than the top and serve as a conductor for the stratified flow to the point of discharge. Fig. 12 presents this concept.

To be able to perform a simulation experiment for the Waldseppl aquifer, the so-called „input function", representing yearly tritium concentration in the local precipitation, must be known.

Such a record since 1953 is available for Vienna (part of the data being obtained as a result of correlation studies between Vienna and Ottawa, Canada, to extend the data between 1953 and 1961). These data are quoted in T. U. in Table 14, in the upper row. As the distance between Hartberg and Vienna along a straight line does not exceed 100 km, it was possible to assume that the Vienna tritium record is also representative for the whole East Styrian Basin (Table 12). Not all precipitation, however, recharges aquifers; part of it is lost due to evaporation, particularly in the summer months. It is customary, therefore, in the interpretation of tritium data, to correct results because of this loss. THORNSWAITE's empirical formula (34) was used, therefore, to calculate potential evapotranspiration.

$$U = 1.6 \left(\frac{10\ t}{J}\right)^{a}$$

where $a = 6.75 \cdot 10^{-7} J^{3} - 7.71 \cdot 10^{-5} J^{2} + 1.79 \cdot 10^{-2} J + 0.49$, and
U = evapotranspiration for the given period (in cm)
J = THORNSWAITE's „temperature-efficiency index", being equal to the sum of 12 monthly values of „heat index" $i = \left(\frac{t}{5}\right)^{1514}$, where t is the mean monthly temperature in °C.

In order to compute the „heat index", mean monthly temperatures were taken, as for Graz, from Table 3. All precipitation data from Table 12 are processed this way, and the results are shown in Table 14 in the lower row. The last two columns of this table represent the annual tritium and precipitation input. Calculated in this way, the annual tritium input was used then as an „input function" during the further simulation experiment. It was also assumed that during a one-year period, four recharges (representing quarters of the year) with a tritium content characteristic for that year and a constant rate, took place (4 iterations).

Each year a certain portion of water entered the first cell of the model (cell No. 1 of relatively large volume). From this main cell (representing the top of the Waldseppl), the water, after mixing, is then

Table 14: Tritium input function for the Waldseppl aquifer.

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Annual Trit. Input (T. U.)	Annual Prec. Input (mm)
1953								15	19 13	17 13	29 4	19 12	292	237
1954	21 46	— 11	670 24	580 —	740 46	235 56	180 23	105 —	49 22	24 —	31 55	19 80	29	384
1955	17 11	25 44	34 30	37 30	68 8	75 —	27 103	19 1	36 8	16 30	16 15	22 16	77	397
1956	49 5	47 27	83 14	84 31	155 23	180 —	180 28	360 —	87 —	62 44	37 39	33 30	85	292
1957	75 16	108 45	75 21	70 22	— —	— —	140 75	115 —	100 —	— —	54 14	64 9	437	203
1958	190 25	215 53	215 52	310 —	460 —	700 —	650 —	1200 50	260 12	108 33	180 23	485 47	552	304
1959	570 8	720 8	1050 35	800 42	530 —	570 86	460 9	205 1	— —	75 —	83 35	75 80	80	202
1960	85 16	100 34	70 37	110 —	142 —	200 —	230 —	145 —	105 11	77 61	39 25	62 47	100	261
1961	73 15	39 6	43 4	123 —	174 69	125 23	140 —	104 —	61 —	56 74	101 68	136 38	442	303
1962	460 35	1232 21	1078 41	1032 —	1210 26	990 —	1228 —	870 —	550 1	521 7	647 138	648 16	2070	409

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Annual Trit. Input (T. U.)	Annual Prec. Input (mm)
1963	1265 45	1900 24	2900 31	— 18	5930 19	4960 27	5950 —	3010 101	2200 —	1470 —	788 61	1334 29	1581	144
1964	1664 0	1171 8	2745 23	2973 23	2686 —	2365 —	2610 —	1783 —	1073 —	649 149	384 3	432 38	868	664
1965	475 18	719 5	582 16	1003 165	1080 56	1173 50	950 164	941 —	578 32	— —	275 59	213 26	524	261
1966	322 8	368 19	432 4	578 18	780 —	835 43	792 27	703 25	373 —	235 78	229 38	134 37	255	268
1967	189 9	236 18	241 49	323 —	475 39	423 —	359 —	299 —	252 44	280 17	139 44	162 12	236	234
1968	65 15	237 5	266 —	302 —	277 —	349 1	301 —	299 96	164 —	289 —	153 25	150 31	194	282
1969	123 47	140 61	211 35	213 —	270 —	315 51	342 —	267 32	169 6	240 —	105 57	119 35	171	313
1970	120 14	101 33	176 39	172 66	310 —	333 34	319 —	266 29	191 —	114 4	106 59	124 19	194	130
1971	147 13	84 9	551 23	292 3	390 —	333 —	216 —	127 —	146 —	134 —	68 —	— —	200	

1. Figures in upper row indicate tritium data

2. Figures in lower row indicate tritium data corrected for evaporation and weighted for the amount of precipitation

discharged to the five next cells which are of a smaller volume and connected in series, in which mixing is much less (representing the slopes of the Waldseppl), and flows closer to the „piston flow".

Values of the discharge concentration of tritium from the last cell of this model were compared with the average yearly values measured for the same period, in the field, for spring St-29. The original print of the simulation experiment, showing the best coincidence of the simulated and experimental data, is shown in Table 15. The state of the system after each iteration was automatically corrected for radioactive delay by the proper adjustment of the programme. Simulation was started for the water year 1952—53 (beginning September, ending August of the next year). The second column of Table 15 shows the number of iterations performed from the beginning, as four iterations were used for a one-year period. The best fit was obtained with the following assumed parameters for the model: 6.5 relative volume units (r. v. u.) interconnected, as at Fig. 13, for the total volume of the system, and a total discharge (BRF) that equals 0.8 r. v. u. per year. Dividing one of these figures into the other yields for the turnover time of the system 8.1 years.

There is also the possibility of determining a total storage capacity of the real aquifer, based on the results obtained by simulation.

Since:

$$\bar{T} = \frac{V_{\text{model}}}{\text{BRF}} = \frac{V_{\text{real}}}{\Theta}$$

where: $\bar{T}$ = hydrological turnover time

V_{model} = total volume of the cells in the model

BRF = boundary recharge fraction

V_{real} = volume of water in the real aquifer (storage capacity)

Θ = yearly average spring discharge measured

it is possible to estimate V_{real} from the above equation. In the case of spring St-29, average yearly discharge may be assumed to be $2.75 \cdot 10^{-3}$ m^3/s (Table 5). Hence the total storage capacity of the aquifer is ca. 7.10^5 m^3.

The last question which may be put forward is — how accurately results of simulation represent the real world situation. Models used here are deterministic ones and do not permit correction of the error, even if uncertainty of determination of the input function is known.

The answer to this question may, however, be found in an indirect way. Some more simulation experiments can be made with the aim of finding the divergence between the best fit curve and the generated output function at the level of three standard deviations from the experimental data.

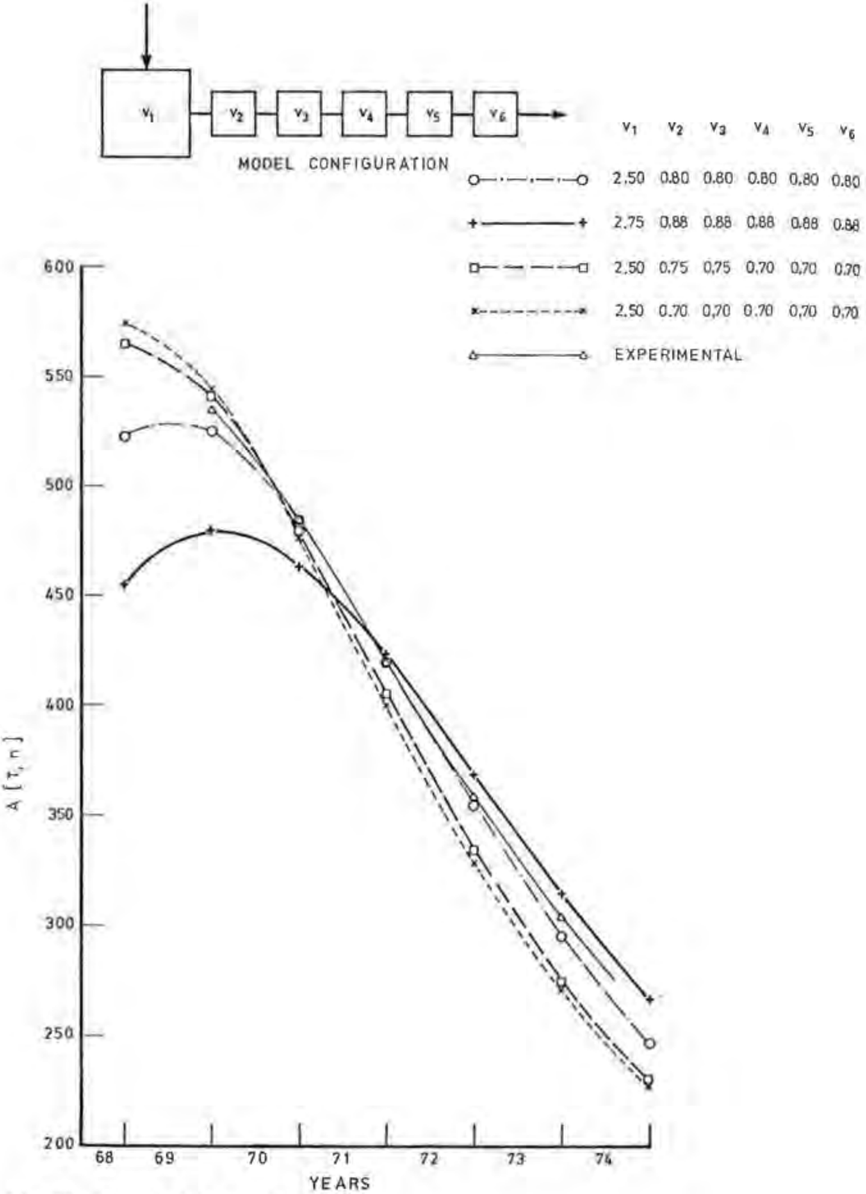

Fig. 13: Simulation experiments.

Table 15: Results of the simulation experiment.

FSM/1*6/MMCaut
rd .986000000

CELL		1	2	3	4	5	6	BDC	Experimental value T. U.	Hydrologic year
VOL		2.5000	.8000	.8000	.8000	.8000	.8000			
So		12.000	3.000	3.000	3.000	3.000	3.000			
BRF		.000	.000	.000	.000	.000	.000			
BRC		.0	.0	.0	.0	.0	.0			
C		4.8	3.7	3.7	3.7	3.7	3.7	.0		
BRF		.200	.000	.000	.000	.000	.000			
BRC		10.0	.0	.0	.0	.0	.0			
C	4	5.9	4.7	3.8	3.6	3.5	3.5	3.5		52-53
BRF		.200	.000	.000	.000	.000	.000			
BRC		292.0	.0	.0	.0	.0	.0			
C	8	84.1	31.3	9.1	4.1	3.5	3.3	3.4		53-54
BRF		.200	.000	.000	.000	.000	.000			
BRC		29.0	.0	.0	.0	.0	.0			
C	12	64.9	58.7	35.1	15.1	6.2	3.7	3.4		54-55
BRF		.200	.000	.000	.000	.000	.000			
BRC		77.0	.0	.0	.0	.0	.0			
C	16	65.0	60.6	50.2	33.3	17.7	8.4	6.6		55-56
BRF		.200	.000	.000	.000	.000	.000			
BRC		85.0	.0	.0	.0	.0	.0			
C	20	67.3	62.0	55.6	45.2	31.5	18.7	15.8		56-57
BRF		.200	.000	.000	.000	.000	.000			
BRC		437.0	.0	.0	.0	.0	.0			
C	24	165.4	95.8	64.0	51.7	41.5	29.8	27.2		57-58

BRF		.200	.000	.000	.000	.000	.000		
BRC		552.0	.0	.0	.0	.0	.0		
C	28	263.3	170.9	104.5	68.5	50.7	39.0	36.8	58-59
BRF		.200	.000	.000	.000	.000	.000		
BRC		80.0	.0	.0	.0	.0	.0		
C	32	200.2	204.8	161.6	108.7	71.8	50.8	47.0	59-60
BRF		.200	.000	.000	.000	.000	.000		
BRC		100.0	.0	.0	.0	.0	.0		
C	36	163.0	181.7	177.9	147.2	106.8	73.4	66.6	60-61
BRF		.200	.000	.000	.000	.000	.000		
BRC		442.0	.0	.0	.0	.0	.0		
C	40	231.6	185.2	170.5	159.3	134.8	102.5	95.4	61-62
BRF		.200	.000	.000	.000	.000	.000		
BRC		2070.0	.0	.0	.0	.0	.0		
C	44	724	372.8	212.0	165.8	146.9	124.4	120.0	62-63
BRF		.200	.000	.000	.000	.000	.000		
BRC		1581.0	.0	.0	.0	.0	.0		
C	48	924.0	658.3	405.2	244.2	171.5	139.6	135.2	63-64
BRF		.200	.000	.000	.000	.000	.000		
BRC		868.0	.0	.0	.0	.0	.0		
C	52	863.7	789.7	611.4	410.1	262.0	179.2	164.8	64-65
BRF		.200	.000	.000	.000	.000	.000		
BRC		524.0	.0	.0	.0	.0	.0		
C	56	728.5	764.1	705.9	564.9	402.0	269.8	242.9	65-66
BRF		.200	.000	.000	.000	.000	.000		
BRC		255.0	.0	.0	.0	.0	.0		
C	60	563.2	656.7	688.3	637.2	522.7	387.7	358.4	66-67
BRF		.200	.000	.000	.000	.000	.000		
BRC		236.0	.0	.0	.0	.0	.0		
C	64	446.0	531.0	601.8	622.6	578.8	484.3	464.4	67-68

Continuation of Table 15

BRF		.200	.000	.000	.000	.000	.000			
BRC		194.0	.0	.0	.0	.0	.0			
C	68	355.2	424.4	498.0	553.1	566.5	528.4	522.9		68-69
BRF		.200	.000	.000	.000	.000	.000			
BRC		171.0	.0	.0	.0	.0	.0			
C	72	287.4	340.0	403.1	465.4	509.4	517.8	524.8	536	69/70
BRF		.200	.000	.000	.000	.000	.000			
BRC		194.0	.0	.0	.0	.0	.0			
C	76	274.8	279.1	325.7	381.4	434.4	469.9	484.2	486	70/71
BRF		.200	.000	.000	.000	.000	.000			
BRC		200.0	.0	.0	.0	.0	.0			
C	80	222.6	239.4	269.2	311.4	360.2	405.2	422.0	420	71/72
BRF		.200	.000	.000	.000	.000	.000			
BRC		200.0	.0	.0	.0	.0	.0			
C	84	205.5	213.6	230.7	258.9	297.0	339.7	355.5	359	72/73
BRF		.200	.000	.000	.000	.000	.000			
BRC		200.0	.0	.0	.0	.0	.0			
C	88	194.0	196.4	204.9	221.8	248.2	282.2	295.8	305	73/74
BRF		.200	.000	.000	.000	.000	.000			
BRC		200.0	.0	.0	.0	.0	.0			
C	92	186.2	184.8	187.7	196.5	213.0	237.5	247.7		74/75
BRF		.200	.000	.000	.000	.000	.000			
BRC		200.0	.0	.0	.0	.0	.0			
C	96	180.9	177.0	176.1	179.4	188.3	204.1	211.5		75/76
BRF		.200	.000	.000	.000	.000	.000			
BRC		200.0	.0	.0	.0	.0	.0			
C	100	177.3	171.7	168.3	167.9	171.5	180.4	185.5		76/77
BRF		.200	.000	.000	.000	.000	.000			
BRC										

The results of such a simulation experiment with the volume of each cell increased by 10%, if compared with the best parameters found, are presented on Table 15. As can be seen, the above assumption significantly changes the shape of the output curve, particulary for the years 1969 and 1970. Divergence between the experimental and the generated output curve is more than three standard deviations, in this case. Such a curve cannot be considered, in interpretation, as the one fitting the experimental points. It can be stated, therefore, that the mean residence time for the Waldseppl aquifer is determined, in our case, with an accuracy of no less than 8.1 ± 0.8 years. One more parameter, namely flow rate of underground flow, may be determined from knowledge of mean residence time. As the distance between the spring and the summit of the Waldseppl is ca. 500 m, it must be travelled with a mean velocity of ca. 2.10^{-6} m/s to fit the value of the mean residence time (63 m/y).

13. Mechanism of Recharge in the Hartberg/Grafendorf Basin

Enviromental isotope data permit the establishment of a qualitative picture of the internal dynamics of the East Styrian Basin. This idea is presented in Fig. 14.

The Stambach valley creates a semi-closed catchment area. Rainwater recharges the uppermost weathered part of the crystallinic formation. The storage capacity is greatest at the top of the surrounding mountains, where the weathering processes penetrate deeper, and

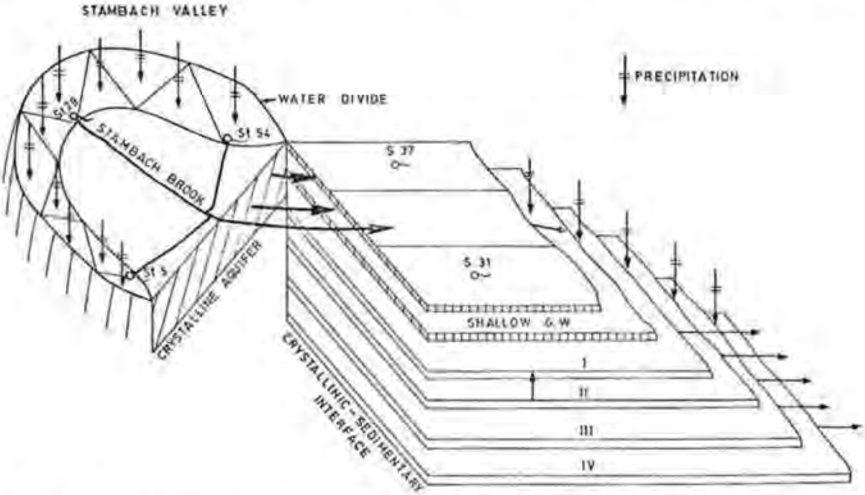

Fig. 14: Hypothetical internal dynamics of the Eastern Styrian basin.

smaller on the slopes. The slopes then serve as **sui generis** conduits for the water flow moving downwards due to gravitational force.

Further evidence of the existence of the stratified flow down along the slopes in the Stambach valley is shown by the results of the simulation experiment described in the preceding chapter.

Therefore, down at the interface between the crystalline and sedimentary formation at the outlet of the Stambach valley, one can expect that a flux of the groundwater flow formed the Grafendorf/Hartberg basin. Similar tritium data as that for spring St-29 are not available for the other parts of the valley. This would enable a quantitative approach to the recognition of dynamics in the whole valley, even allowing an appropriate mathematical model to be constructed*.

The stable isotope composition of the water in the confined aquifer is different from the water discharged by high altitude springs. One can expect there an oxygen-18 content at the level of — 9.1‰ SMOW, being the average of the ^{18}O content in all the springs discharging in the valley, whereas in the confined aquifer the average oxygen content is at the level of — 8.6‰ SMOW.

On the other hand, the stable isotope composition of the shallow groundwater and surface runoff coincides quite well with the stable isotope composition characteristic for the water gathered at higher altitudes, and yields accordingly (— 9.0 ± 0.1)‰ SMOW for the Reibersbach brook and (— 9.13 ± 0.09)‰ SMOW for the shallow groundwater (B-19). One has to assume, therefore, that the underground flow of the interface recharges mainly the phreatic aquifer. This conclusion does not exclude possible hydraulic interconnections between the surface runoff and the shallow groundwater.

Concerning water in the confined aquifer, different stable isotope composition suggests a local recharge. Spring S-31, showing similar stable isotope composition may be considered as natural seepage from the aquifer. This would support the assumption made by J. Zötl (4) that the confined aquifer is recharged through the nearby outcropping Sarmat formation.

It has to be emphasized that the observed differences in the stable isotope composition of groundwaters in the project area were rather small. An interpretation of the stable isotope data may, therefore, not suggest a higher degree of confidence than that offered by the experimental data.

It must be clearly said that in the case of the Hartberg/Grafendorf project, the results of the environmental isotope study should not be considered separately, but have to be used jointly with other results of hydrological measurements as supporting material.

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* 3-dimensional models of the Stambach valley were constructed by Mr. Peter Siwy, from the IAEA Computing Centre in 1973, but not verified because of the lack of experimental data.

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Summary

Results of environmental isotope studies performed in the northern part of the Hartberg Basin are presented in the report.

Results of isotope analyses of water samples from 10 different locations on tritium, deuterium, oxygen-18 and carbon-14, complemented by some chemical data and $^{234}U/^{238}U$ ratio measurements, are quoted.

As a result suggestions concerning the mechanism of recharge of the confined aquifer are given for the Hartberg Basin.

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Zusammenfassung

Der Bericht faßt die Resultate von hydrologischen Studien mittels der Umweltisotope im nördlichen Teil des Hartberg-Grafendorfer Beckens zusammen.

An zehn verschiedenen Wasseraustritten bzw. Entnahmestellen wurden von der Section of Isotope Hydrology der IAEA in Wien Tritium-, Deuterium-, Oxygen-18- und Carbon-14-Untersuchungen durchgeführt, ergänzt durch chemische Analysen und Messungen des $^{234}U/^{238}U$-Verhältnisses. Die Auswertung der Daten unter Berücksichtigung der hydrometeorologischen Gegebenheiten und der Anwendung von Computer-Modellen erbrachte eine weitgehende Klärung des verschiedenen Wasserhaushaltes der Quellen im kristallinen Grundgebirge, des seichtliegenden ungespannten Grundwassers, der Sarmatquellen und der gespannten artesischen Wässer in diesem Gebiet. Für die Genehmigung der Veröffentlichung des Berichtes ist dem Leiter der Sektion für Isotopenhydrologie in der IAEA, Herrn Dr. Bryan R. Payne, bestens zu danken.

Anschrift des Verfassers: Dr. K. Przewlocki, ul. Staszczyka 3 m 20,
30-123 Krakow, Polen