Integrated Methods in Catchment Hydrology—Tracer, Remote Sensing and New Hydrometric Techniques
(Proceedings of IUGG 99 Symposium HS4, Birmingham, July 1999). IAHS Publ. no. 258, 1999.

Isotope hydrological study of mean transit times and related hydrogeological conditions in Pyrenean experimental basins (Vallcebre, Catalonia)

ANDREAS HERRMANN, SUSANNE BAHLS
*Institute for Geography and Geoecology, Technical University Braunschweig,
Langer Kamp 19c, D-38106 Braunschweig, Germany*
e-mail: a.herrmann@tu-bs.de

WILLIBALD STICHLER
*Institute for Hydrology, Research Centre for Environment and Health (GSF),
Ingolstädter Landstrasse 1, D-85764 Neuherberg, Germany*

FRANCESC GALLART & JEROME LATRON
*CSIC Institute of Earth Sciences Jaume Almera, Lluis Solé Sabarís s/n, SP-08028 Barcelona,
Spain*

Abstract Measurements of tritium and oxygen-18 concentrations in water samples from streams at low discharge, wells, and permanent springs are used to provide insight into hydrogeological conditions, storage properties, runoff formation, and flow partitioning of Pyrenean experimental basins 100 km north of Barcelona. Transit times as derived from tritium range between 8–11.5 years for wells, 8.5–13.0 years for streams, to 10.5–13.5 years for springs. These results are twice the usual values which suggests low permeability of the bedrock formations. Minimum groundwater reserves can be determined from low discharge and mean transit times, and groundwater plays an important role in flood generation. Tritium is still found to be a useful tracer provided that transit times are high enough, and geological information is available.

INTRODUCTION

A worldwide compilation of isotope hydrological catchment studies by Herrmann (1997) together with a regional one for central Europe by Lepistö *et al.* (1997) conclude that experimental and modelling techniques are well developed but still greater regional diversification is needed. This is above all true for tritium in view of the diminishing concentrations at absolutely low levels for which the present study is a good example.

The isotope hydrological investigations in the Vallcebre study basins in the Pyrenees which were performed in a model validation project (Gallart *et al.*, 1998) aim at distinguishing origins (source areas) and ages of subsurface waters. For this purpose tritium and oxygen-18 measurements of stream, well, and springs water samples were used. The study is profiting from former experience in two research catchments in the Bavarian Alps, Germany, with mean transit times and volumes of mobile water in the subsurface system as the major hydraulic and hydrological target parameters, and similar complex hydrogeological conditions: Lainbachtal (Maloszewski *et al.*, 1983) and Wimbachtal (Maloszewski *et al.*, 1992).

However, both alpine study cases have benefited from additional stable isotope measurements, i.e. either deuterium (Lainbach) or oxygen-18 (Wimbach) which have confirmed hydraulic findings from tritium. Furthermore, the higher tritium content of precipitation of 130–140 TU for the annual means (mid seventies) in Lainbachtal, and even 20 TU at the end of the eighties for Wimbachtal allowed more significant isotope hydrological results than let expect actually 10 TU in Vallcebre. Therefore, a major question is whether these unfavourable conditions permit reasonable hydrological findings as well.

EXPERIMENTAL SITE

The Vallcebre study basins, which have been more intensively investigated since 1996 under the VAHMPIRE (for acronym see acknowledgement section below) project, are situated in the Catalonian Pyrenees about 100 km north of Barcelona. The basins range in area between 0.56 and 4.2 km^2 and in altitude between 960 and 2245 m a.m.s.l. The land use is grassland and crops on terraced land (10–52%), forests (17–47%) on formerly terraced agricultural land, (17–34%), sparse shrub vegetation (14–16%), and minor badlands (1–5%); with percentages varying for each basin. Silty-clayey brown to red soils prevail. The geology is characterized by four main units of the continental Palaeocene Tremp formation, Garumnian facies (Aepler, 1968; cf. Fig. 1): 100 m thick and slightly karstified Santa Magdalena Limestones (SML) on karstified Cal Parisa clays and with several springs at the base; 80 m La Barrumba clays (LBC) with some gypsum nodules, major mass movements and badlands phenomena; 70 m clayey La Call silts (LCS) which are fairly permeable and allow important springs; 15 m thick Cal Rodó limestones (CRL) on top. Limestones form distinct outcrops facing south.

ISOTOPE DATA

Experimental data are available from 27 sampling sites for isotope analysis (Fig. 1 and Table 1) located at streams (15), wells (7), and springs (5) which have been sampled since July 1996 during low flow conditions, and analysed for ^3H and ^{18}O.

Concentrations of tritium are shown for sampling sites in Table 1, and of oxygen-18 in Fig. 3. Analytical results seem reasonable, however, differences between sampling sites and dates lie close to each other and within an analytical error of ±2 TU. Measuring accuracy for $\delta^{18}O$ is ±0.15‰.

Respective isotopic input functions which are needed for flow model application to tritium data and hydrological interpretation of oxygen-18 concentrations are available from GNIP (Global Network of Isotopes in Precipitations) stations. Most actual data have been received from the International Atomic Energy Agency (IAEA) directly. Since Barcelona ceased to supply IAEA with isotope data or samples of precipitation in 1992, comparisons with the closest GNIP stations in the western Mediterranean region, i.e. Faró (Portugal), Tunis (Tunisia), and Genoa (Italy) have shown that Genoa seems best for comparison with Barcelona; thus allowing the determination of the ^3H

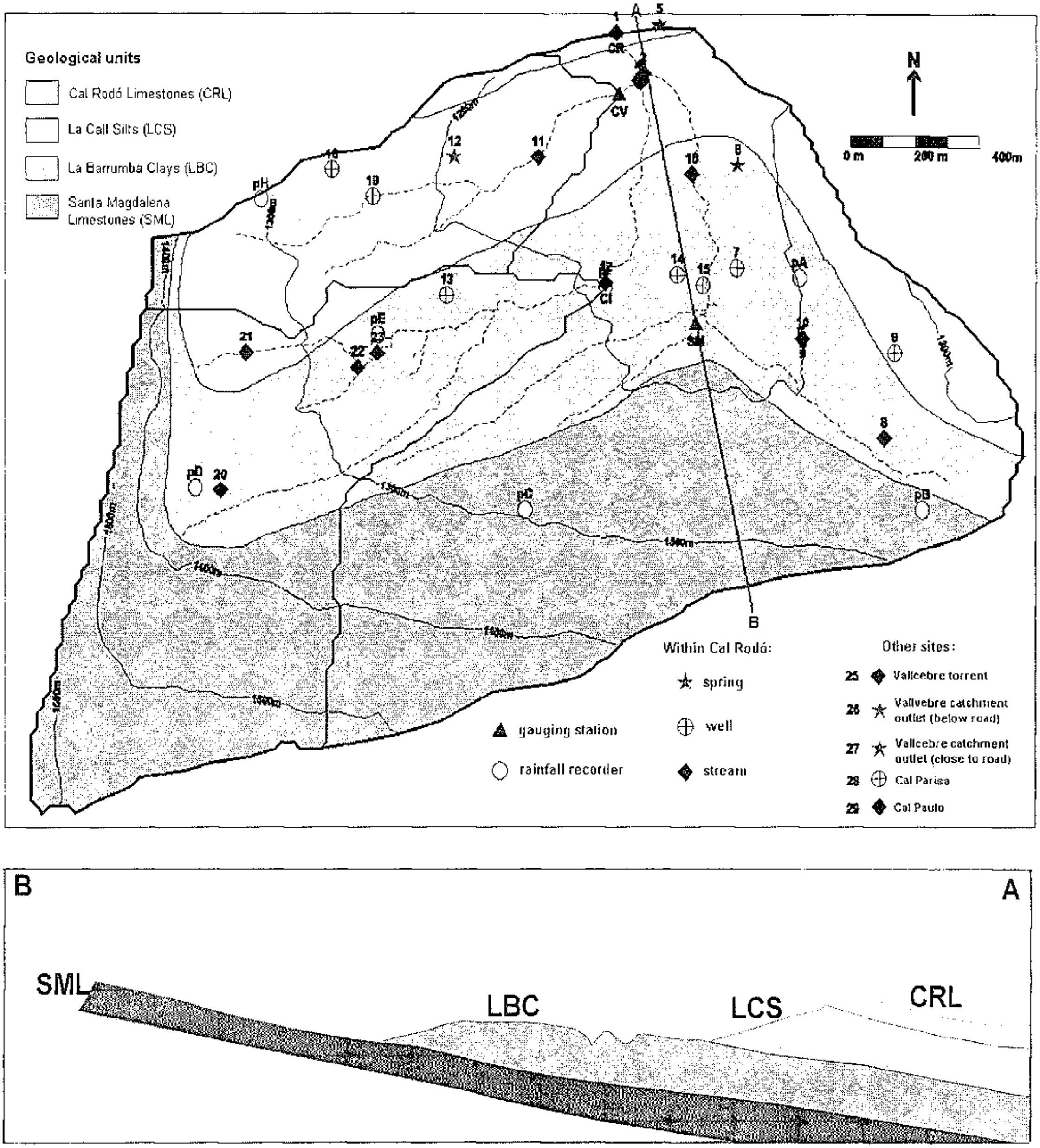

Fig. 1 Cal Rodó catchment and subcatchments with hydrological network, water sampling sites, major hydrogeological units, and isotopic hydrological results.

input function from these two stations. However, after 1995 isotope data were not available from Genoa. In Fig. 2 the ^3H content of spring, stream, and well water samples as measured for Vallcebre are compared to those for monthly precipitation in Barcelona and Genoa, respectively.

Table 1 Tritium content (TU) and average oxygen-18 concentration (δ‰) of water samples from the Vallcebre catchments (for locations see Fig. 1), and mean transit times (t_o) as calculated from EM and DM.

Origin	Site	26 July 1996	12 May 1997	25 June 1998	Mean transit time from EM (years)	Mean transit time from DM (for D/vx = 0.15) (years)	$\delta^{18}O$(‰)
springs	V5	10.0	10.3	9.4	10.5	10.5	−7.78
	V6	14.5	12.6	12.7	15.5	13.5	−7.84
	V12	10.6	9.9	9	10.5	10.5	−8.19
	V26	-	10.8	9.3	12.0	11.5	−8.23
	V27	-	10.7	9.4	12.0	11.5	−7.96
streams	V1	9.3	10.5	9.4	10.5	10.5	−7.58
	V2	12.3	11.9	10.6	13.0	12.0	−7.69
	V3	10.3	9.8	8.9	10.5	10.5	−6.97
	V4	11.0	9.9	8.3	10.5	10.5	−7.87
	V8	10.8	10.5	10.6	11.5	11.5	−7.31
	V10	-	12.5	11	15.0	13.0	−7.90
	V11	9.8	-	10.2	11.0	10.5	−8.05
	V16	-	8.9	6.8	9.0	9.5	−7.91
	V17	9.4	9.2	9	10.0	10.0	−7.11
	V20	-	-	-	-	-	−8.30
	V21	7.9	-	-	7.0	8.0	−7.90
	V22	10.1	10.2	6.8	9.5	10.0	−7.90
	V23	10.4	9.0	8	10.0	10.0	−7.79
	V25	-	7.9	6.6	8.5	8.5	−7.79
	V29	-	-	8	10.0	10.0	−9.64
wells	V7	8.5	7.1	6.9	8.0	8.5	−7.91
	V9	11.5	10.6	10.5	12.0	11.5	−7.81
	V13	6.6	8.5	7	7.5	8.0	−7.66
	V14	9.4	7.2	8.1	8.5	9.0	−7.53
	V15	8.7	–	-	8.0	9.0	−6.98
	V18	8.7	7.7	6.8	8.0	8.5	−7.88
	V28	-	8.5	8.6	10.0	10.0	-

FLOW MODELLING

To get the desired hydraulic and hydrological information from environmental isotopes, a convolution integral is normally applied to the isotopic input and output functions of the system under investigation, with $g(t)$ as the weighting function which corresponds to the basin response function or flow model, and determines the time distribution of the tracer at the outlet of the system. A common hydraulic parameter of flow models like the frequently used one-parameter exponential (EM) or two-parameter dispersive models (DM; Zuber, 1986) is the mean transit time of water (t_o) or even tracer (t_t) only in the case of DM and double porosity with diffusion as the second physical process besides dispersion which means that $t_t > t_o$.

As for the Bavarian Alps (Maloszewski *et al.*, 1983, 1992), both models apply here, too, with the transit times agreeing quite well. However, best fits are obtained when taking for DM a dispersion parameter (D/vx; with D/v as the dispersion constant, and x the length of recharge zones measured along the stream lines) of 0.15 (cf. Table 1). Using additionally 0.1 and 0.2 means that transit times lessen and rise, respectively, by approximately one year only as compared to those found from 0.15 in

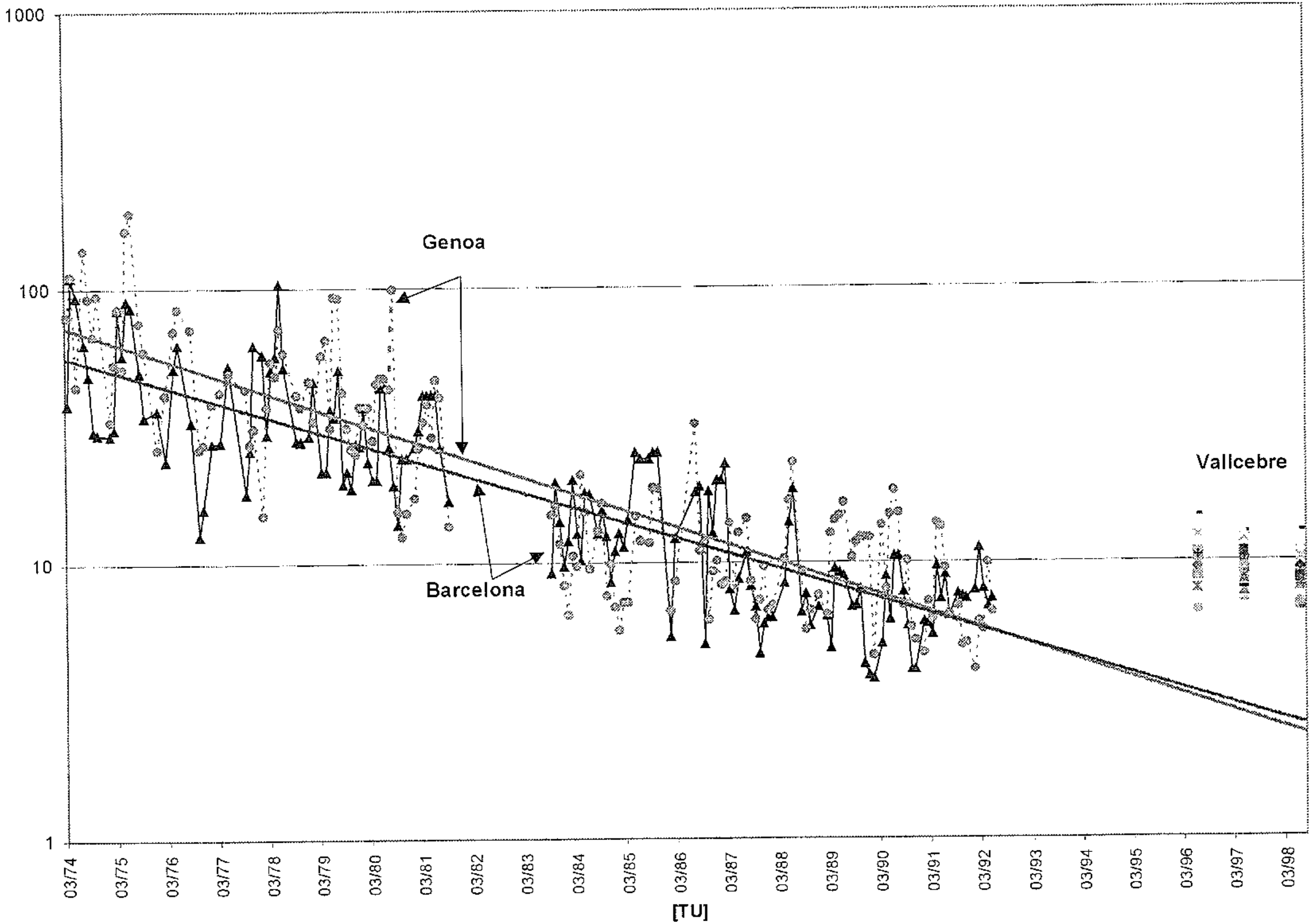

Fig. 2 Monthly tritium concentrations for precipitation at Barcelona and Genoa with trend lines (source: GNIP; IAEA) and tritium contents at Vallcebre sampling sites.

Table 1. However, one should also notice that for computation of t_o, which is the overall hydraulic target parameter, the exact isotopic input function is a most crucial point. But once reliable t_o values are derived it is possible to assess the volume of mobile water in the system: $V_m = t_o\, Q$ where Q is the flow rate. To calculate t_o from t_t the retardation factor (R_p) as a result of tracer diffusion to the matrix is needed ($t_o = t_t/R_p$) but is difficult to approximate: $R_p \approx 1 + (n_p/n_f)$ where n_p is matrix or micro-porosity, and n_f fracture or macro-porosity.

RESULTS

From tritium measurements: mean transit times

By applying EM and DM to the (theoretical) tritium input function and measured ^{3}H output data the mean transit times in Table 1 have been calculated. Accordingly, both models yield similar results. However, one should consider that EM represents a well-mixed reservoir which is not the case in reality, and DM representing t_t rather than t_o. Similar agreement was reported by Maloszewski *et al.* (1983, 1992).

Mean transit times in Vallcebre catchments range between 8.0 and 13.5 years. On average, wells are found to have the youngest waters (9.1 years), followed by 10.5 years for stream waters at low flow conditions, and spring waters at 11.5 years. Differences between the last two averages are statistically significant at the 5% level, but the two others are not. Geological assignment of probable source areas of sampled water is also possible.

There is good agreement between mean transit times for baseflow components and assumed average length of subsurface flow paths with the least ages found in small sub-basins. Similar findings are found for springs located at the outlets of subsurface reservoirs. Unlike these system outlets, samples which were taken at the water tables of wells represent specific internal aquifer travel time conditions and, therefore, the youngest subsurface components in the study area. Therefore, the oldest spring and well waters were sampled in LBC clays (cf. Fig. 1) which is not a surprise.

Another conclusion from Table 1 is that all transit times are two to three times the usual values obtained for other wet medium-alpine hydrological systems (Herrmann, 1997). A main reason could be the extended thick clayey substrates of low hydraulic conductivity. Accordingly, subsurface flow flux rates are extremely small.

From oxygen-18 measurements: origin of water

Oxygen-18 can be used to trace the origin of water, i.e. whether it was taken from streams, springs, or wells (Fig. 3). Figure 3 also shows the annual variation which one can expect for the weighted mean monthly ^{18}O input at Vallcebre, but which should be approximately established at an isotopically lighter level by 2‰ δ^{18}O as compared to Barcelona because of the altitude effect (Fritz & Fontes, 1980). Compared with the typical sinusoidal input function, the subsurface reservoirs confirm the expectation of a distinct damping of the ^{18}O input signal depending on the magnitude of mean transit times.

Although ^{18}O measurements were not an initial objective of the study, the analytical results do to some extent support the mean transit times found from tritium. The findings in Fig. 3 confirm the ^{3}H data given above, i.e. highest $\delta^{18}O$ variation

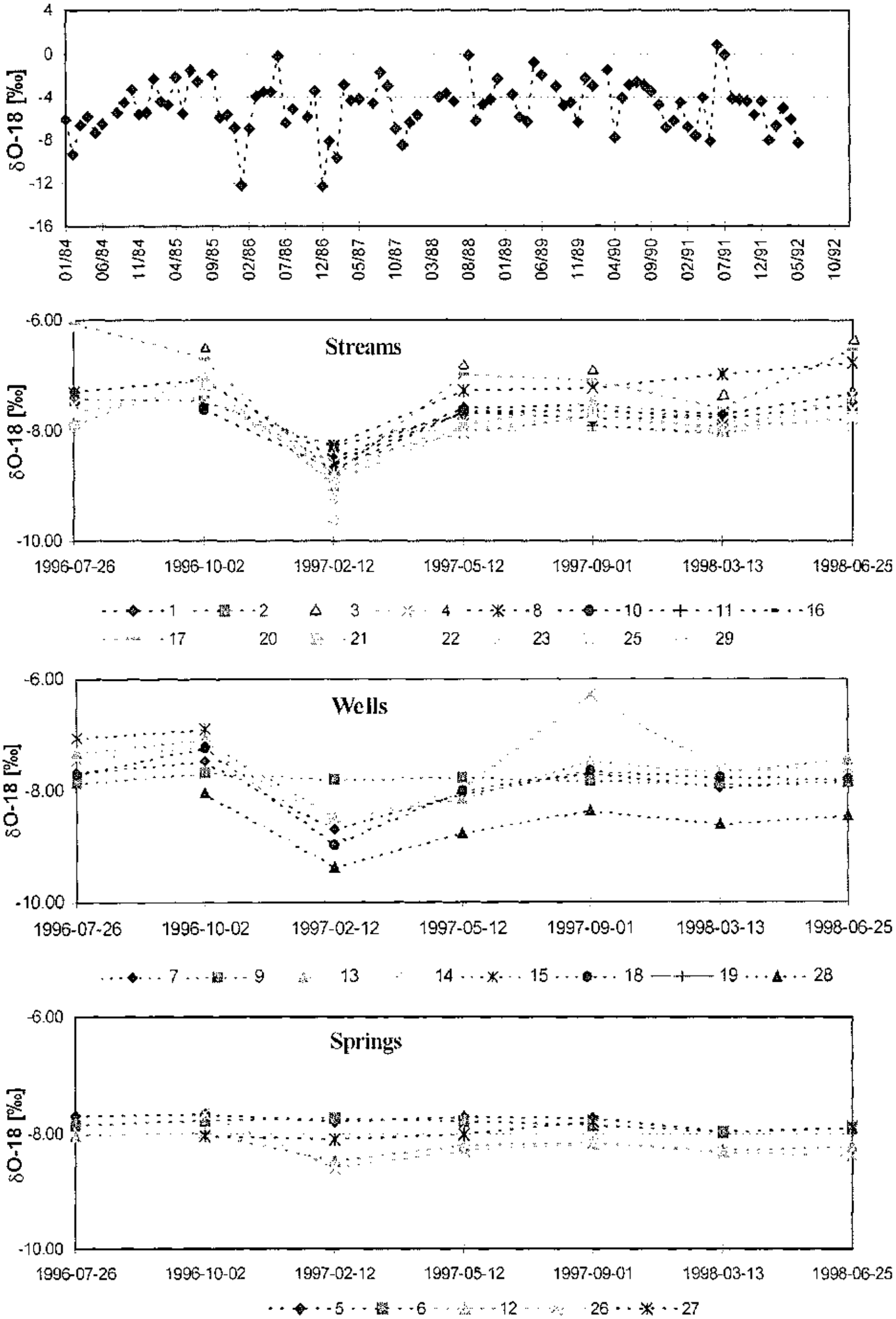

Fig. 3 Oxygen-18 concentrations for monthly precipitation at Barcelona (Source: GNIP; IAEA) and for stream, well and spring waters from Vallcebre catchments (numbers correspond to sampling sites in Fig. 1).

ranges for wells and streams having average δ-values of –7.63‰ and –7.71‰, and least for springs (–7.94). The lowest ^{18}O content in winter (February) at most locations means that some winter precipitation is leaving the reservoir at once. Respective wells and stream water sampling sites are characterized by smallest mean transit times whereas waters of more or less constant ^{18}O concentrations like at well V9 and spring V6 have relatively high ages, up to 13.5 years (cf. Table 1). Furthermore, catchment areas of springs seem to incorporate higher locations on average compared to well and stream waters if we attribute isotopic depletion to an increase in altitude. However, the differences between isotopic mean values are statistically not significant.

Hydrogeology and subsurface storage volumes

Isotope hydrological results as assembled in Fig. 1 allow at least some hydrogeological conclusions. Accordingly, spring and well waters, and headwater streams as well are to some extent older and isotopically heavier in La Barrumba clay unit (LBC) compared to La Call silts (LCS) which overlie them, and are more permeable.

For determining subsurface storage volumes from mean transit times and discharges a main restriction was the limited hydrological data series of just one and a half years. A first approximation was made by taking discharge measured at times of water sampling as a basis which reflects seasonal low flow conditions. As a result, the Cal Rodó study catchment of 4.17 km^2, $t_o \sim 10.5$ years and 2.1–3.9 $l\ s^{-1}$ has a minimum groundwater reserve of $0.69–1.29 \cdot 10^6\ m^3$ or 160–310 mm WC; Ca l'Isard subcatchment of 1.32 km^2, $t_o \sim 10.0$ years, and 0.7–3.2 $l\ s^{-1}$ a base reserve of $0.22–1.01 \cdot 10^6\ m^3$ or 160–765 mm; and smallest Can Vila subcatchment of 0.56 km^2, $t_o \sim 10.5$ years, and 0.6–2.6 $l\ s^{-1}$ of $0.2–0.86 \cdot 10^6\ m^3$ or 355–1535 mm. Errors for storage volumes might be ±20%.

Can Vila subcatchment's subsurface minimum water reserve which is located in relatively permeable LSC silts is at least double that for the other catchments. On the other hand, the smallest storage volumes determined for both Cal Rodó and Ca l'Isard catchments are almost identical.

Runoff formation

As to runoff formation, there are several hydrological, hydraulic, and isotopic indications that in Vallcebre groundwater is not always a major component in flood hydrograph generation as in many study catchments of the world (Herrmann, 1997). Subsurface storage volumes from low discharge and high mean transit times support this fact, as do tensiometric and piezometric results by Latron *et al.* (1999). However, in autumn and spring floods which are typical in Mediterranean environments, groundwater seems to contribute considerably more to hydrograph formation which will now better agree with the same processes described by Herrmann (1994) for central European conditions: (a) infiltration with initial saturation; (b) rise of hydraulic head through pulse pressure transmission; and (c) groundwater exfiltration increase which might cause considerable groundwater recharge rates to compensate for the losses.

CONCLUSION

The results demonstrate that mean transit times of water found from tritium data and flow modelling increase from wells, followed by streams and permanent springs. The transit times found here are more than twice the usual values obtained for other wet mountain areas, and suggest a delayed contribution from groundwater as a result of dry conditions and low permeability of bedrock.

Even for low tritium concentrations, discrimination of hydrological systems is possible on a small basin scale, thus completing and supporting findings from traditional water balance investigations. Oxygen-18 measurements may roughly back tritium age intervals as demonstrated here, but they are not really necessary. On the other hand, errors and uncertainties of hydraulic and hydrological results are high but still acceptable considering the beneficial aspects of the isotope technique for the complex environmental system under investigation, the short hydrological data series, and also slight hydrogeological knowledge.

Acknowledgement This work has been carried out under the VAHMPIRE (**Va**lidating **H**ydrological **M**odels using **P**rocess studies and **I**nternal data from **Re**search basins) research project funded by the EC under contract no. ENV4-CT95-0134.

REFERENCES

Aepler, R. (1968) Das Garumnium der Mulde von Vallcebre und ihre Tektonik (Spanien, Provinz Barcelona) (The Garumnium of the Vallcebre syncline and its tectonics [Spain, Province of Barcelona]). Diploma Thesis, Scientific Faculty, Free University Berlin.

Fritz, P. & Fontes, J. C. (eds) (1980) *Handbook of Environmental Isotope Geochemistry*, vol. 1: *The Terrestrial Environment.* Elsevier, Amsterdam.

Gallart, F., Latron, J., Llorens, P. & Rabadà, D. (1998) Hydrological functioning of Mediterranean mountain basins in Vallcebre, Catalonia: some challenges for hydrological modelling. *Hydrol. Processes* **11**, 1263–1272.

Herrmann, A. (1994) Ecohydrological research on a small basin scale: scientific approach of the runoff formation key process. *Beiträge zur Hydrologie der Schweiz* **35**, 83–95.

Herrmann, A. (1997) Global review of isotopes hydrological investigations. In: *FRIEND 3^{rd} Report 1994–1997* (ed. by G. Oberlin), 307–316. Cemagref, Antony, France.

Latron, J., Gallart, F. & Salvany, C. (1999) Analysing the role of phreatic level dynamics on the streamflow response in a Mediterranean mountainous experimental catchment (Vallcebre, Catalonia). In: *Catchment Hydrological and Biogeochemical Processes in a Changing Environment* (ed. by I. Littlewood & V. Elias) (Proc. ERB Liblice Conf., September 1998). Technical Documents in Hydrology, UNESCO, Paris (in preparation).

Lepistö, A., Andersson, L., Herrmann, A. & Holko, L. (1997) Hydrological processes in forested catchments. In: *FRIEND 3^{rd} Report 1994–1997* (ed. by G. Oberlin), 317–329. Cemagref, Antony, France.

Maloszewski, P., Rauert, W., Stichler, W. & Herrmann, A. (1983) Application of flow models in an alpine catchment area using tritium and deuterium data. *J. Hydrol.* **66**, 319–330.

Maloszewski, P., Rauert, W., Trimborn, P., Herrmann, A. & Rau, R. (1992) Isotope hydrological study of mean transit times in an alpine basin (Wimbachtal, Germany). *J. Hydrol.* **149**, 343–360.

Zuber, A. (1986) Mathematical models for the interpretation of environmental radioisotopes in groundwater systems. In: *Handbook of Environmental Isotope Geochemistry* (ed. by P. Fritz & J. C. Fontes), vol. 1, 1–59. The Terrestrial Environment, B. Elsevier, Amsterdam.