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Use of environmental tritium to study catchment dynamics: case study from the Danube River basin

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Abstract Use of environmental isotopes, particularly, oxygen (^{18}O) and hydrogen (^2H and ^3H) offers unique methodologies for investigations related to rainfall–runoff relationships and catchment dynamics. Using long-term tritium (^3H) data in the Danube River, observed temporal variations in the river water have been simulated through a compartmental (mixing cell) modelling approach to estimate the fluxes of surface flow and groundwater to total river discharge and to characterize the transit time distribution of these component flows. The findings of this approach are compared to the results of an earlier simulation model based on the Artificial Neural Network (ANN) approach using the same long-term tritium data. The two approaches provide comparable results for the characteristics travel time of the water in the basin providing improved confidence for the results.

INTRODUCTION

Fluxes of water through different pathways and their mixing dynamics; sources (genesis) and transit time of water for such component flows are of substantial significance in catchment hydrology and they are also controlling parameters for the quality of water.

Identification of partial contributions from component flows to total runoff is often posed as the problem of "hydrograph separation", for which hydrochemical and isotope data are usually employed (Freeze & Cherry, 1979; Turner *et al.*, 1987; Caine, 1989; Moore, 1989; Wels *et al.*, 1991; Eshleman *et al.*, 1993; Caissie *et al.*, 1996). The general approach is often restricted to two-component separation of total hydrographs into contributing flows from surface and groundwater components for individual storm events. When the solute (conservative chemical constituent or isotope) concentrations of each component flow are significantly different and constant during an individual storm event, mixing ratios of the two components throughout that event are calculated from the equations based on hydraulic continuity and simple mass balance considerations. The use of naturally occurring isotopes of ^{18}O, ^2H, and ^3H offers considerable advantage due to both the conservative nature (except radioactive decay for tritium which can be accounted for) of these isotopes, and the contrast often observed in isotope signatures of rainfall and pre-storm runoff.

Most of the published results on hydrograph separation deal with studies in relatively small (experimental/representative) basins. The purpose of this paper is to utilize long-term tritium data available for a large Danube River basin to identify the component fluxes of surface and subsurface flow to the average total river discharge, and to derive information on transit time distribution of water in the basin.

DANUBE RIVER BASIN AND AVAILABLE DATA

The River Danube is an international basin in Europe extending from the Schwarzwald Massif down to the Black Sea, with a total drainage area of 807 000 km^2. The data used in this study refer to long-term observations available on the isotope composition of the Danube River at Vienna, Austria, representing a drainage area of 101 700 km^2. The long-term mean discharge of the river at this site is 1943 m^3 s^{-1} , corresponding to 603 mm of average total runoff (Stancik & Jovanovic, 1988).

Tritium concentrations in the Danube River at Vienna, Austria, have been monitored monthly since 1968 (Rank *et al.*, 1998). Similar long-term monthly isotope data for precipitation are also available since 1961 at the meteorological station in Vienna, one of the stations included in the IAEA/WMO global network on isotope survey of precipitation (International Atomic Energy Agency, 1998). Tritium data available for river water and precipitation, as shown in Fig. 1, are used both to investigate the ratio of surface and subsurface water fluxes to total river flow and to derive transit time distribution of water through each of these main component flows as well as for the entire basin.

METHOD OF ANALYSES AND APPROACH

The approach used in the evaluations is to represent the flow system in the basin by two-component flow and simulate the observed tritium concentrations (in the time domain) of the river water using the compartmental (mixing cell) approach (Przewlocki & Yurtsever, 1974; Van Ommen, 1985; Yurtsever, 1995), for which the

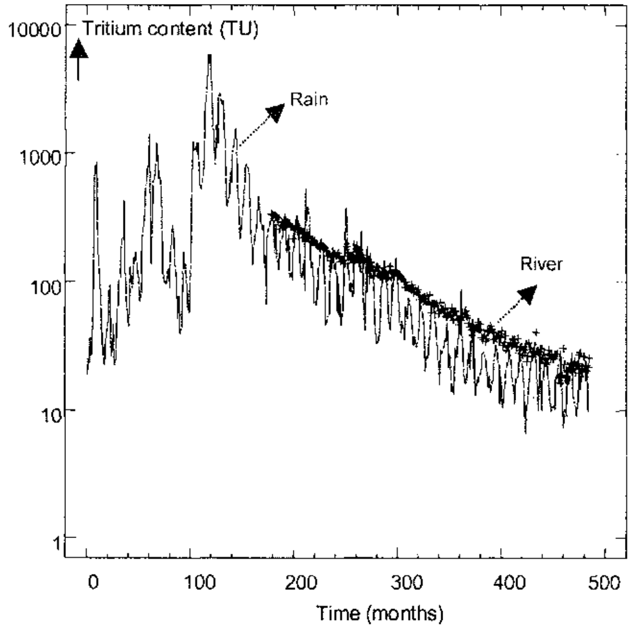

Fig. 1 Tritium concentration of precipitation and the Danube River , at Vienna.

tritium concentration of precipitation is used as the input. In the approach, the mixing and dispersion processes involved in the tracer transport are represented by the use of interconnected compartments (volume elements). Mass balance considerations over discrete time intervals for each compartment and for the assigned flow pattern, enable the mass transport through the system to be simulated by assuming each compartment to be a well mixed cell. Mass balance considerations for such a well mixed compartment during a time increment (between $n-1$ and n) result in the following equation linking the tracer input and output concentrations (Fig. 2):

$$C_{Qn} = C_{Vn} = \left(\frac{V_{n-1}C_{Vn-1} + I_n C_{In}}{V_n + Q_n} \right) \exp(-\lambda \Delta t)$$

It is assumed that the tritium content of precipitation, as observed at the Vienna station, is representative for the entire basin. The conceptual compartmental model is shown in Fig. 2. The input–output simulations over the time period 1953–1993 are carried out on discrete monthly intervals for steady-state flow conditions using equations of continuity and mass balance, as given above, for each compartment. Monthly tritium concentrations of Vienna precipitation for the period prior to 1968 are estimated through correlation with the Ottawa station which has a complete record for the period 1953–1993 (International Atomic Energy Agency, 1998).

The mean residence time for each compartment and the ratio of flux between the two main component flow systems are the parameters varied to obtain simulation of the output (river) tritium concentration. The root-mean-squared (RMS) error between

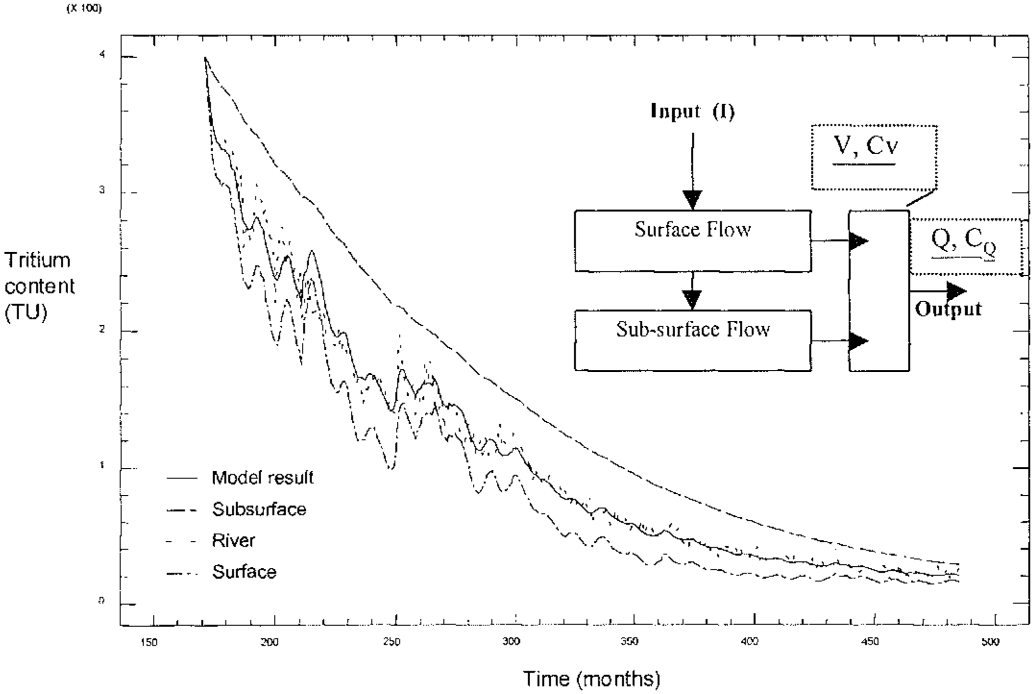

Fig. 2 Compartmental model simulated concentrations and actual observed tritium concentrations for the Danube River.

the observed and simulated tritium output concentrations is used as the decision criterion for model performance and to arrive at the best estimate of the above parameters.

RESULTS AND DISCUSSIONS

Results from the compartmental simulation approach

The best estimates for the three main parameters from the calibrated simulation model using tritium data are:

Mean transit time of water for fast component (surface flow):	10 months
Mean transit time of water for slow component (subsurface flow):	140 months
Fraction of water contribution from subsurface flow:	36%

The RMS error of fit between observed and simulated tritium output curves for different trial values of the subsurface flow contribution is shown in Table 1. This parameter is not too sensitive within the range 36–40%, and the error terms in this range would be comparable (Table 1). The observed and simulated tritium output concentration curves for the above cited best estimates of the three parameters are given in Fig. 2, where similar curves for each component flow are also shown. Thus, the model performs a forward simulation of the tritium input–output relationship through the two-component flow system. The observed temporal variations of the river concentrations are the result of mixing (at an average ratio of 36% from subsurface flow and 64% from surface flow) of these component flows. The tritium output concentration of each component flow is governed by their specific response (transit) times as given above. The shape of the transit time distribution of water for each flow component and for the total flow (entire basin) derived from the compartmental model is shown in Fig. 3. The average travel time (flux weighted mean transit time) of the water in the whole basin is about 57 months. The transit time distribution functions derived for each component flow and the estimated average transit time of water in the system are important features directly related to the rainfall–runoff relationships and flow dynamics in the catchment basin.

The estimated subsurface flow contribution of 36% agrees quite well with the observed flow regime of the river. The mean low discharge of the Danube River at Vienna, Austria, is 804 $m^3 s^{-1}$ (Stancik & Jovanovic, 1988) and compared to the earlier mentioned average flow of 1943 $m^3 s^{-1}$, 41.4% of the river flow, as the long-term average, would be expected to originate from groundwater.

Table 1 Error (RMS) of fit for compartmental model.

Fraction of subsurface flow	RMS error (TU)
0.30	19.7
0.36	17.40
0.40	**17.45**
0.45	18.7
0.50	21.1
0.60	26.7

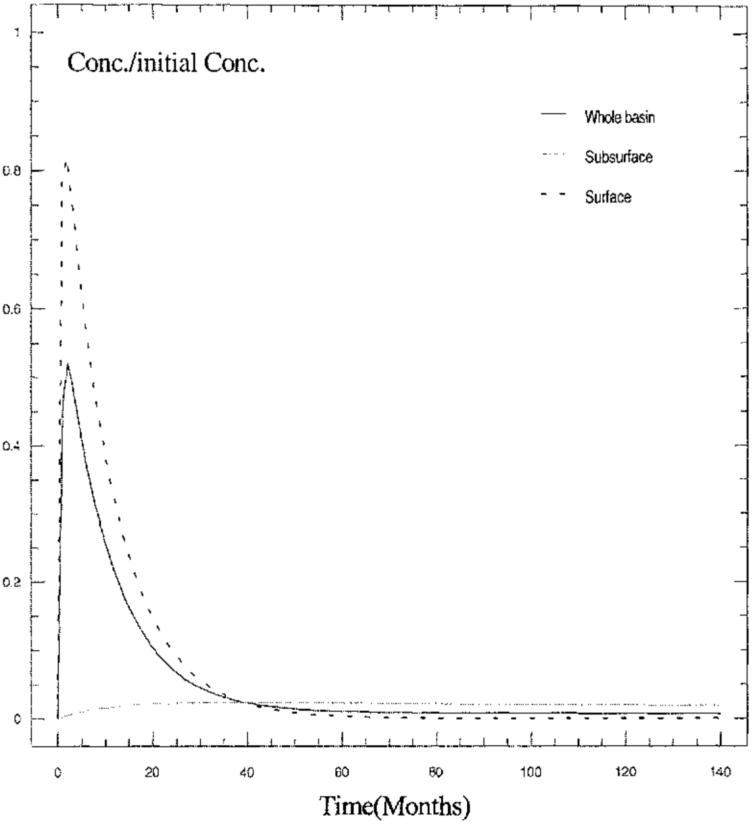

Fig. 3 Shape of the transit time distribution of water in the basin derived from the compartmental model.

Comparison with earlier results obtained by neural model

The same data set related to temporal variations of tritium concentration in the Danube River was earlier simulated through application of the Artificial Neural Network approach and the results were published (Yurtsever & Yurtsever, 1997). The main concern of this neural approach was modelling the relationship between the precipitation concentration and the concentration in the river discharge in a general multivariate input–output functional relationship, as given below:

$$y_t = f(x_t, x_{t-1}, x_{t-2}, \ldots, x_{t-n})$$

For this purpose a standard multilayer feedforward perceptron (MLP) configuration with n inputs and a single output was used (Hornik *et al.*, 1989). The MLP was trained using a backpropagation algorithm to fit the data. The training was monitored by using a fixed cross-validation set of randomly selected samples, about one-fifth the size of the data set to avoid overfitting. Simulations were performed by using networks with multiples of 12 inputs up to 120 inputs, and with up to two hidden units (Fig. 5); the software environment ECANSE developed by Siemens AG, Austria, was used for this purpose (Thurner & Yurtsever, 1995). The performance of the models were assessed by RMS error.

Table 2 Error (RMS) for MLP models in Tritium Units (Yurtsever & Yurtsever, 1997).

Number of inputs	Hidden 1	Layers 2
12	17.0	15.6
36	13.2	13.2
60	9.5	9.2
84	9.2	9.5
120	**7.5**	**7.5**
144	**7.5**	**7.5**

The performance of some of the models on the validation set are given in Table 2, where the error values indicate that the last 60 values mainly contribute to the output as well as some values between the last 84 and 144. The results of sensitivity analysis performed on the MLP model, as shown in Fig. 4, clearly indicate that the main time span influencing the output concentration in the Danube River basin is around 60 months. These earlier reported results also confirm the findings of the compartmental simulation model. As can be seen from the transit time distribution function derived from the compartmental model (Fig. 3), the time span mainly affecting the output concentration is about 60 months, with a (weighted) mean transit time value of about 57 months. The shape of the curve for sensitivity analysis of the MLP model, given in Fig. 4, can also be considered to represent the transit time distribution of the water in the basin. The peak values observed at different times are most probably related to the individual time-parameters of transport in different tributaries of the Danube River. Obviously, the neural MLP model is capable of producing the transfer function between the input and the output at much higher resolution than the compartmental model. Actual observed and MLP model simulated tritium concentrations of the river water are shown in Fig. 5. The RMS error of fit for the MLP model is 7.5 TU as compared to that of 17.4 TU for the compartmental model. The performance of the

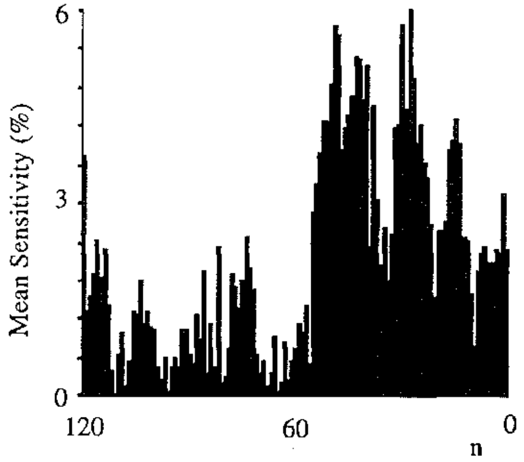

Fig. 4 Sensitivity of MLP network model output to inputs (Yurtsever & Yurtsever, 1997).

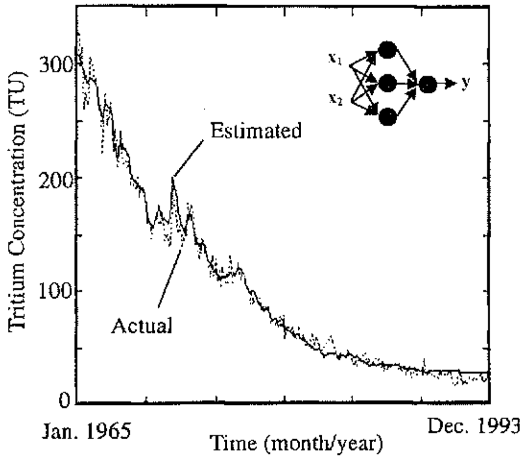

Fig. 5 MLP simulated and observed tritium concentrations in the Danube River (Yurtsever & Yurtsever, 1997).

MLP model in simulating the temporal variations observed in the output is more satisfactory than the compartmental model. However, the results obtained from both approaches provide comparable values for the transit time of water in the basin, which is one of the most important physical parameter related to catchment dynamics.

CONCLUSIVE REMARKS

The use of the natural tritium isotope in watershed hydrology, even for large basins, offers a unique opportunity for the derivation of the relevant physical information about rainfall–runoff relationships. The modelling approach based on compartmental simulation of the tracer input–output relationships for the Danube basin indicates that the flux of water contributing to the total river flow through subsurface pathways is about 36–40% of the total average flow, with a mean transit time of about 140 months. The fast component surface flow has a mean transit time of about 10 months. The findings of the compartmental model adopted for the Danube basin are also confirmed by the MLP model based on the Artificial Neural Network approach.

Use of both compartmental and neural model approaches offer considerable advantage to the study of tracer input–output relationships in hydrological systems as a means for inferring physical catchment dynamics. The neural models may also have the advantages of simulating nonlinear processes with higher precision and facilitating better insight into the processes involved. On the other hand, they have the disadvantages of non-transparency and difficulty in incorporating prior knowledge into the modelling process. Furthermore, their long-term data requirements for simulations in the time-domain may be a limitation for their use in isotope hydrology. The compartmental simulation approach facilitates a flexible methodology to incorporate basic physical knowledge into modelling of tracer input–output relationships and they can be extended to represent the hydrological system as a distributed parameter model both for steady and non-steady flow.

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