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A 50 Years' Isotope Record of the Danube River Water and Its Relevance for Hydrological, Climatological and Environmental Research

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Abstract: The isotope record of the Danube River water at Vienna station probably is the longest dataset of a large river worldwide: ^{3}H record since 1963, stable isotopes ^{2}H and ^{18}O records since 1968. From the ^{2}H-^{18}O relation ("deuterium excess") can be concluded that the isotopic composition in the Danube River water reflects mainly the isotopic relations in the precipitation in the catchment area with some delay due to the residence time of the precipitation water in the catchment. It allows drawing hydro-meteorological conclusions on a larger scale based on a relatively small number of measurements. The stable isotope time series shows significant changes on a decadal scale. Since 1952, the ^{3}H content in the precipitation and the Danube River water has been dominated by the ^{3}H releases of nuclear weapon tests. From this ^{3}H record a mean residence time of about three years of precipitation water in the Danube River catchment upstream of Vienna can be calculated (mainly base flow). A similar value can be found by using the climatologic signal of the stable isotope time series. Since about 1995 short-term ^{3}H elevations owing to releases from nuclear power plants have been detected. In order to obtain an isotopic database for the entire Danube River Basin, the Danube River water sampling at Tulcea (delta region) was carried out in 2009.

Key words: Isotope hydrology, climate change, Danube River, deuterium (^{2}H), tritium (^{3}H), oxygen-18 (^{18}O)

Introduction

The isotope ratios of hydrogen and oxygen in the Danube River water, at Vienna station, have been measured since 1963 for ^{3}H and since 1968 for stable isotopes ^{2}H and ^{18}O (Figs. 1 and 2). This is probably the worldwide longest isotope record of a large river (river km 1933, catchment area 103 000 km^{2}, mean annual discharge 1920 m^{3}/s). Upstream of Vienna the isotopic composition of the Danube River is strongly influenced by the discharge from the Isar, Inn, Traun and Enns alpine tributaries (Rank *et al.* 2012). From the ^{2}H-^{18}O relation (*i.e.* "deuterium excess") can be concluded that the isotopic signals of the precipitation water are transmitted through the whole catchment and that the isotope ratios in the Danube River water mainly reflect the isotopic relations in the precipitation within the drainage area with some delay due to the residence time of precipitation water in the catchment (*e.g.* Wyhlidal *et al.* 2014). The advantage of the sampling of river water in comparison to the precipitation sampling is that the isotopic composition in the river water represents the whole catchment area. It allows drawing hydro-meteorological conclusions on a larger scale based on a relatively small number of measurements.

The isotopic signature of a river is modified by several hydrological parameters and processes, such as delayed runoff of winter precipitation, residence time of the groundwater discharged to the river, confluence of tributaries and climatic changes (*e.g.* temperature changes, spatial and temporal change of precipitation distribution in the drainage area). Moreover, anthropogenic influences on the hydrological regime (*e.g.* the presence or construction of reservoirs, irrigation) can contribute to the isotopic variation. Releases from nuclear power plants directly influence the ^{3}H concentrations in the river water.

Rivers are an important linkage in the global hydrological cycle, returning about 35% of continental precipitation to the oceans. For the sustainable management of water supply, agriculture, flood-drought cycles, as well as for sustaining ecosystem and human health, there is a pressing need to improve the scientific understanding of water cycling processes in river basins and the ability to detect and predict impacts of climate change and water resources management. There are several examples on small scale in tracer-based studies; however their application in the research of water cycling processes in large river basins still remains a scientific frontier (Gibson *et al.* 2002, Iaea 2012). The International Atomic Energy Agency (Iaea) has launched a monitoring programme, the Global Network of Isotopes in Rivers (GNIR). It is aimed at regular analyses of the isotope composition of runoff in large rivers. This isotope monitoring network complements an earlier precipitation network, the Global Network of Isotopes in Precipitation (GNIP). Austria contributes to this global network with the long-term sampling and measuring series of the sampling site “Donau/Wien”. The existing sampling programme in Vienna comprises monthly grab samples.

Methods

Water samples for ^{3}H activity measurement were electrolytically enriched and analysed by low level liquid scintillation counting (LLSC, precision ±5%, 1 TU = 0.118 Bq/kg for water). All $\delta^{18}O$ results are reported as relative abundance in per mil (‰) with respect to the international standard VSMOW (Vienna Standard Mean Ocean Water). The accuracy of the measurements is better than ± 0.1‰. Since deuterium excess does not vary significantly in the water from the Danube River, conclusions drawn from $\delta^{18}O$ data in the following discussion are valid for $\delta^{2}H$ values of the Danube River water likewise (Wyhlidal *et al.* 2014).

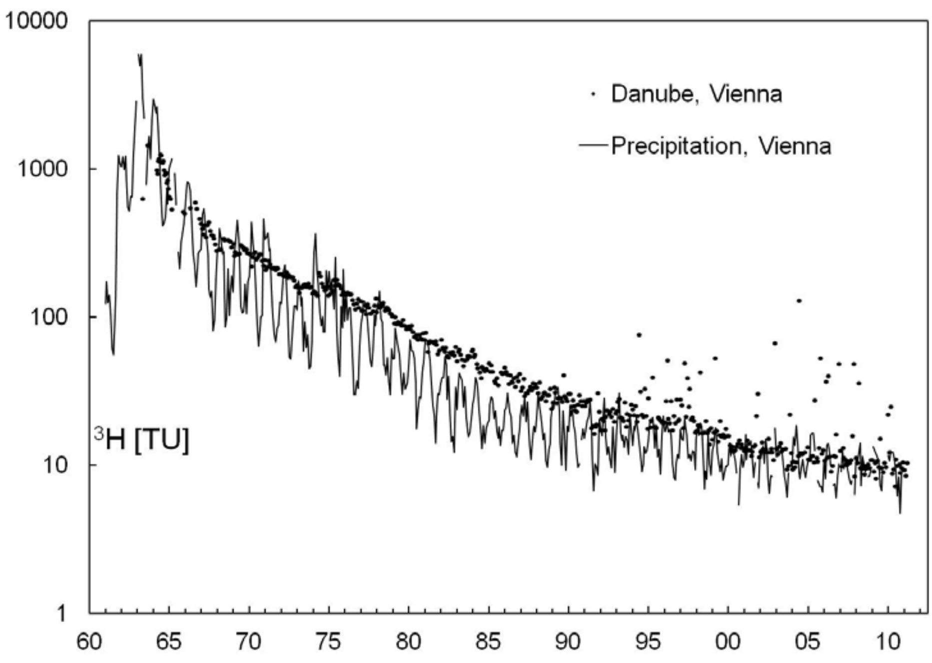

Fig. 1. Long-term ^{3}H time series of precipitation (monthly mean values) and the Danube River (monthly grab samples) at Vienna station (Rank *et al.* 2012, updated). The sometimes higher ^{3}H content of the Danube River water during the last 20 years is probably owing to releases from a nuclear power plant (NPP) some 400 km upstream of Vienna

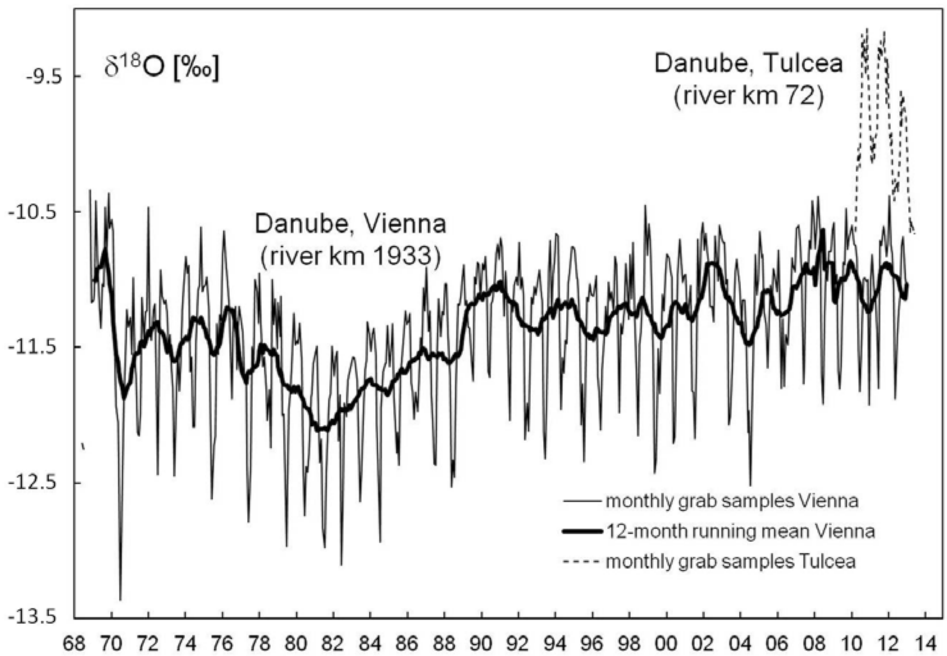

Fig. 2. $\delta^{18}O$ time series of the Danube River at Vienna station (monthly grab samples, 12- month running average, Rank *et al*. 2012, updated) and Tulcea (monthly grab samples). The $\delta^{18}O$ pattern reflects the general $\delta^{18}O$ trend of the precipitation in Central Europe (Rank, Papesch 2010)

Results and Discussion

The impetus for starting isotope hydrological measurements and the setup of an isotope laboratory at the "Bundesversuchs- und Forschungsanstalt Arsenal (BVFA Arsenal)" in Vienna in the early sixties came from the marking of the atmosphere and therefore the precipitation water with tritium by the atmospheric nuclear weapons tests in the fifties and early sixties. Since 1952, the ^3H content in the precipitation has been dominated by the ^3H releases of nuclear weapons tests. As a consequence, the ^3H concentration of precipitation increased by about a factor 1000 in 1963, when it reached its maximum, followed by a continuous decrease. During the last two decades ^3H values have approached "pre-bomb" levels again (Fig. 1). The ^3H tracer went through all hydrological systems and allowed for decades to determine reliably the age or the mean residence time (MRT) of the water in a hydrological system (*e.g.* Mook 2000). The ^3H content of rivers follows with a certain delay on the ^3H content of precipitation, depending on the residence time of precipitation water in the catchment area. This delay in runoff leads also to an attenuation of seasonal fluctuations of the ^3H concentration.

Owing to the attenuation of the nuclear weapons ^3H activity in the environment local and regional ^3H releases have become more important and visible. Since 1994 some of the monthly grab samples of the Danube River water showed elevated ^3H content (Fig. 1), obviously owing to regional or local influences (mainly releases from nuclear power plants, Rank *et al.* 2000, Wyhlidal *et al.* 2014). All values exceeding about 12 TU are to be considered the consequence of anthropogenic activities. In most cases these contaminations show short-term characteristics. Such ^3H peaks were used at the Rhine River to determine travel time and dispersion of contamination pulses (*e.g.* Krause, Mundschenk 1994).

An attempt to model the ^3H data for the Danube River using a one-box exponential model revealed that although this approach might be useful to get general ideas about the magnitude of the mean residence time of the water in the system (best fit for 3 years, Fig. 3), particularly the base flow component, it does not adequately reflect all processes which might control the amount of ^3H in the system at any given time. It has been suggested that the buffering effect in aquifers operating in the catchment area of a river, which becomes important during periods of large fluctuations of discharge, may strongly influence the ^3H balance in the system, thus making predictions of the black-box steady state models unreliable (Rank *et al.* 1998). Since the results from this simple one-box exponential model are not satisfactory, a more complex model should be developed. Furthermore, the accuracy of the input data, *i.e.* precipitation, is problematic because of the lack of data from the early sixties. An additional possibility to improve the results is the selection of output data, the Danube River water, with respect to the discharge.

The long-term stable isotope records of precipitation water exhibit significant decadal changes in the isotopic composition (Rozanski, Gonfiantini 1990, Kaiser *et al*. 2002, Rank, Papesch 2010). As a consequence, also the stable isotope time series of rivers shows significant changes on a decadal scale, *e.g.* a remarkable increase of $\delta^{18}O$ in the 1980s mainly owing to the rising environmental temperature (Fig. 2). The long-term $\delta^{18}O$ trend of several Austrian rivers, such as the Danube River tributaries and the alpine section of the Rhine, is similar to that of the Danube River (Rank *et al*. 2012). Thus one can conclude that this trend in the order of decades represents a general climatic long-term isotopic signal – input from precipitation – in all hydrological systems. This suggests using this signal for the determination of water residence time (MRTs) in a similar way like ^3H input by nuclear weapons in the past.

As a first attempt we compared the $\delta^{18}O$ trends of precipitation and the Danube River water at Vienna station on the basis of ten-year averages (Fig. 4). We found that short-term and seasonal variations play only a minor role as short-term (event) $\delta^{18}O$ signals (maxima and minima) are eliminated by averaging. $\delta^{18}O$ time series of four precipitation stations of the Austrian Network for Isotopes in Precipitation (ANIP) were used for an average input signal: two lowland stations (Vienna station at 230 m a.s.l. and Bregenz station at 430 m a.s.l.), one medium-altitude station (Feuerkogel station at 1618 m a.s.l.) and one high-altitude station (Patscherkofel station at 2245 m a.s.l.). Absolute values and amplitudes of the average input signal are in agreement with those of the Danube River signal (Fig. 4).

The best agreement between the two $\delta^{18}O$ trend curves could be achieved with a shift of the precipitation curve (input) by about three years (Fig. 4). In a simple model concept this corresponds to a MRT of the water in the drainage area of about three years. The smoother signal in the Danube River reflects the age distribution of the river water. As mentioned before, short-term influences were eliminated by ten-year averaging, thus the calculated MRT of about three years represents mainly the baseflow from the Upper Danube River Basin. The MRT of about three years found out from $\delta^{18}O$ time series corresponds well with the value calculated from tritium time series of the river water. This agreement confirms that reasonable MRT values can be achieved by using long-term $\delta^{18}O$ signals.

Furthermore, in addition the fast component of flow can be determined from a comparison of the

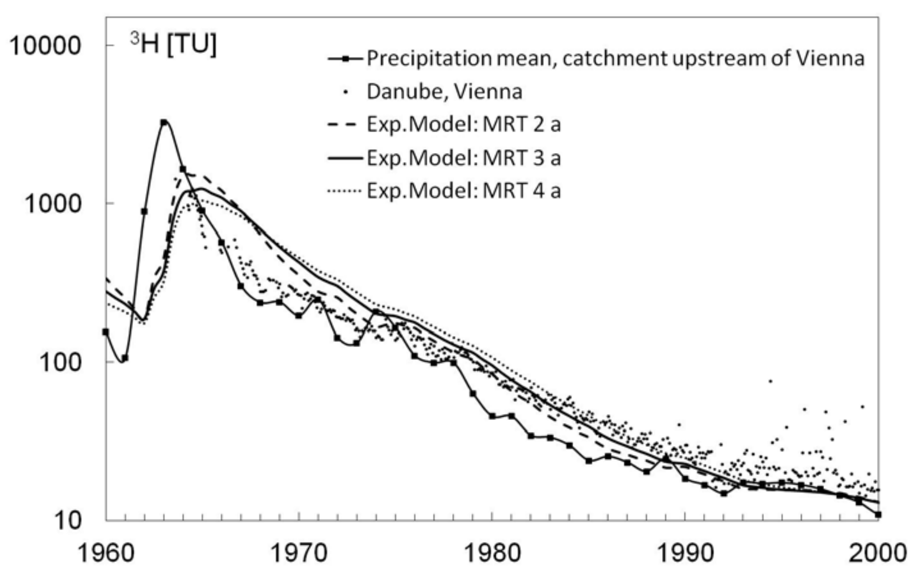

Fig. 3. Comparison of measured and modelled 3H contents of the Danube River water at Vienna (1960-2000) using the one-box exponential model (US- Geological Survey: http://ca.water.usgs.gov/user_projects/TracerLPM/). Precipitation 3H data are average values of 10 stations of the Austrian Network of Isotopes in Precipitation (ANIP)

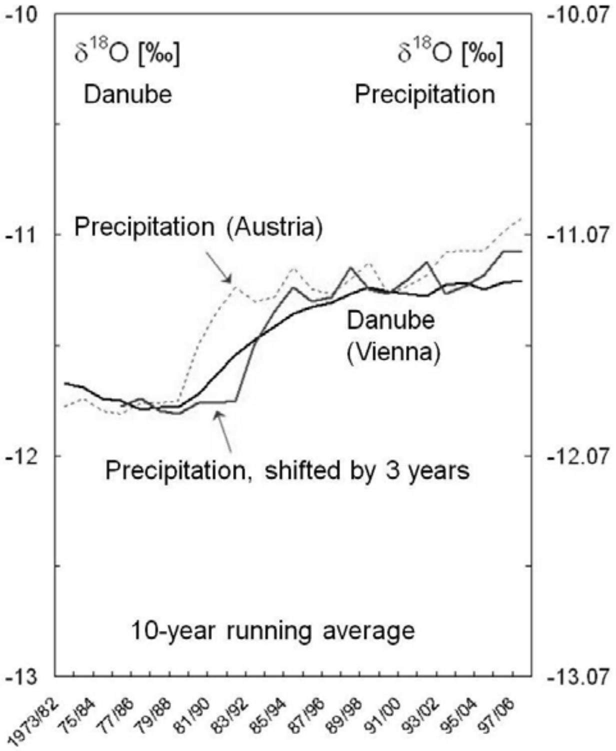

Fig. 4. Comparison of δ18O long-term trends in precipitation in Central Europe and in the Danube River water at Vienna (Rank, Papesch 2010)

long-term trend curves of $\delta^{18}O$ for the Danube River and for precipitation (RANK *et al*. 1998). From these trend curves a transit time around one year can be derived for the fast flow component of the Danube River at Vienna.

Start of a long-term isotope monitoring of the Danube River water at Tulcea in 2009

No similar long-term isotope record exists for the Lower Danube River. Therefore a representative isotope monitoring near the Danube River Delta was initiated in 2009 to collect isotope-hydrological information about the entire Danube River Basin (drainage area ca 800 000 km^2, average discharge ca 6500 m^3 s^{-1}). A simple extrapolation from the Upper Danube River data to the whole catchment is not possible because of the different morphological, hydrological and climatic conditions.

As a result from a preliminary investigation (cooperation between the AIT and the Danube River Delta National Institute for Research and Development), we can conclude that it is possible to achieve a representative long-term isotope record for the whole Danube River Basin by sampling at only one suitable location in the pre-delta section (Tulcea region, RANK *et al.* 2013). Routine sampling twice a month began at Tulcea in November 2009. The first results showed seasonal variations of $\delta^{18}O$ values of the Danube River water at Tulcea of about 1.5‰ between November 2009 and May 2013 (Fig. 5). The values are generally higher than those from the Danube River at Vienna, due to the major contribution of water from lower parts of the Danube River Basin. While the $\delta^{18}O$ time series of Vienna station is characterised by a sharp negative peak in summer (snowmelt in the Alps), the $\delta^{18}O$ values of the Danube River at Tulcea show a more sinusoidal course with a minimum in late spring/ early summer (as an influence of the winter precipitation) and a maximum in autumn (as a result of the amount of the precipitation during the summer). A longer observation period and the inclusion of discharge and precipitation data in the interpretation of isotopic composition of river water will give a more detailed insight into the isotopic behaviour of the Danube River water in the delta region.

Generally, much more of the ^3H values of the Danube River water samples from the delta region exceed the "environmental" level of about 10 TU (Fig. 6, Danube Tulcea) in comparison with the samples from the Upper Danube River (Danube/ Vienna). This is owing to the increasing number of nuclear installations along the river course. Therefore, for the lower section of the Danube River it is more difficult to identify the source because all NPPs upstream of the sampling point are possible candidates.

Conclusions and Outlook

The isotope record "Donau/ Wien" (the Danube River at Vienna station) is a unique database for hydrological and hydroclimatic modelling. The isotopic composition of the Danube River water is mainly governed by the isotopic composition of the precipitation water in the catchment area, while the evaporation effects play only a minor role. Short-term and long-term isotope signals of the precipitation water are thus transmitted through the whole catchment. Therefore, the isotopic composition of the Danube River water provides an integrated isotope signal for climatic and hydrological conditions and changes in the Upper Danube River Basin.

The transient pulse of ^3H in global precipitation derived from thermonuclear tests during the late 1950s and early 1960s offered a unique possibility

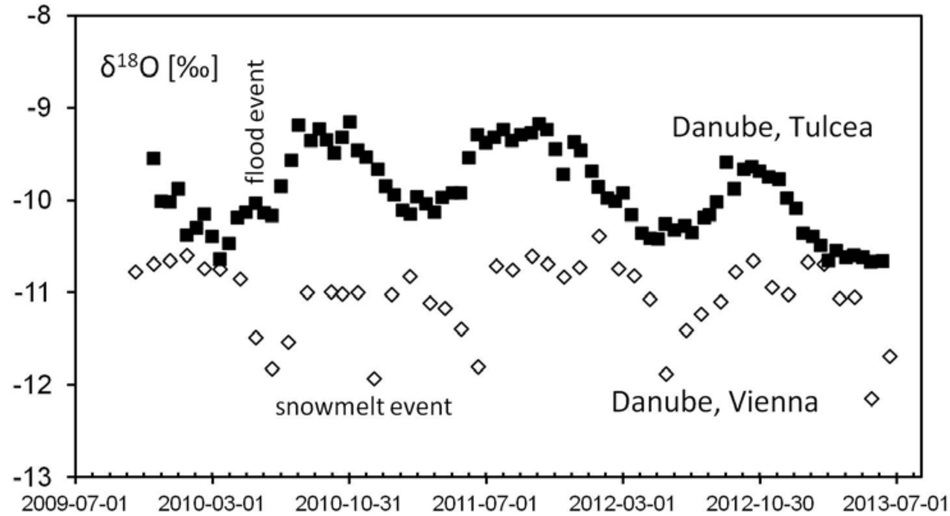

Fig. 5. δ18O time series of the Danube River at Tulcea (black squares) and Vienna (open diamonds) stations from 16.11.2009 to 15.05.2013

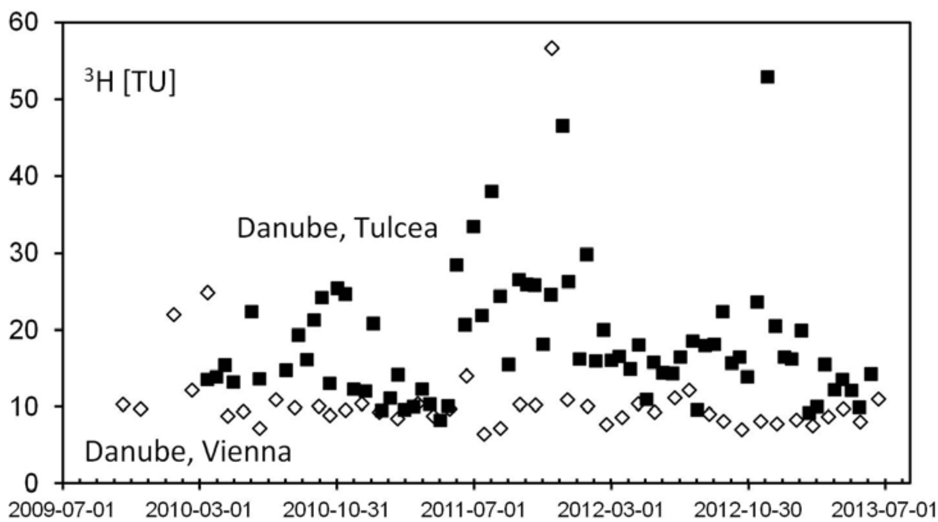

Fig. 6. 3H time series of the Danube River at Tulcea (black squares) and Vienna (open diamonds) stations from 15.03.2010 to 15.05.2013

to gain a closer insight into the dynamics of water transport in the catchment areas of large river systems. A mean residence time (MRT) of about three years (mainly base flow) can be calculated for the Upper Danube Basin by using a one-box exponential model. The results are not yet satisfactory and therefore the modelling has to be improved.

Long-term records of stable isotopes in the precipitation exhibit significant decadal climatic signals (more pronounced in mountainous regions). These signals are reflected in the isotope records of hydrological systems, if other influences like evaporation effects have minor influence on the isotopic composition. This is the case for most parts of the river system in the Danube River Basin.

The temporal shift of significant sections in the isotope records of hydrological systems can be used to determine the MRT (age) of water in the system. The initial evaluations show a shift of about three years for the climatic signal in the Danube River water at Vienna station, most probably the MRT of baseflow water (groundwater discharge to the river) in the Upper Danube River Basin. A MRT around one year can be derived from the long-term $\delta^{18}O$ record for the fast flow component of the Danube River at Vienna station.

Decadal stable isotope signals may be used to determine MRTs of rivers and groundwaters by model calculations in a similar way like the use of the ^{3}H input by nuclear weapons tests in the past. Such applications require long-term isotope records for the investigated water bodies. In this respect, the ongoing activities of the Section of Hydrology of the IAEA to establish a global network for isotopes in rivers (GNIR) are an interesting initiative that will make more long-term isotope records of river water available. The hydrological use of climatic signals is a strong argument to run networks of isotopes in precipitation and hydrological systems also in the future.

The Danube River water's isotope time series could serve as a basic data set for hydrological investigations, as well as for assessing future impacts within the Danube River Basin. This includes climatic and hydrological changes (*e.g.* temperature changes, change of precipitation distribution), as well as anthropogenic impacts on the hydrological regime (*e.g.* reservoirs, change in land use). All these changes will be reflected to different extent in the isotopic composition of the river water.

The tritium results clearly exhibit the influence of short-term contaminations owing to human activities. These ^{3}H releases from nuclear power plants can be used for studying the travel time and dispersion of contamination pulses in the Danube River. This could be a basis for the development of emergency measurements in case of pollution accidents in the catchment area.

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