Investigation of the isotopic composition of Danube water as indicator for hydroclimatic changes in the Danube basin. Establishment of a representative isotope monitoring near the mouth of the river

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Keywords: Danube, isotope hydrology, climatic change, deuterium (^{2}H), oxygen 18 (^{18}O)

1 Introduction

Isotopes of particular interest for hydrological studies generally include the stable isotopes ^{2}H and ^{18}O. They are incorporated within the water molecule and exhibit systematic variations in the water cycle as a result of isotope fractionation linked with phase changes and diffusion. Precipitation variability is related mainly to air-mass source and evolution including temperature-dependant equilibrium fractionation effects (e.g. Mook 2000). River discharge signatures provide insight into the basin-integrated hydroclimate forcings on water cycling such as precipitation variability (e.g. changes in condensation temperature, latitude/altitude of precipitation, air mass mixing and recycling, distance from ocean source, and seasonality) and evaporation from the catchment by rivers, soil water, wetlands, lakes, and reservoirs. Since evaporation has little effects on the isotopic composition of river water within the Danube Basin, the isotopic composition in Danube water reflects mainly the isotopic composition of precipitation in the whole basin and so provides an integrated isotope signal for climatic/hydrological conditions and changes in the catchment (Rank et al. 2009).

Rivers are an important part of the global hydrological cycle, returning about 35 % of continental precipitation to the oceans. For sustainable management of water supply, agriculture, flood-drought cycles, and ecosystem and human health, there is a basic need for improving the scientific understanding of water cycling processes in river basins and the ability to detect and predict impacts of climate change and water resources development. In 2002 the International Atomic Energy Agency (IAEA) launched a coordinated research project on “Isotope tracing of hydrological processes in large river basins” aimed at developing and testing isotope methods for quantitative analysis of water balance and related processes, tracing environmental changes, and ultimately establishing an operational “Global Network for Isotopes in Rivers” (http://isohis.iaea.org). This network builds on complementary monitoring of the IAEA/WMO Global Network of Isotopes in Precipitation (GNIP), a cooperative program for analysis of monthly isotope composition of precipitation at over 500 stations worldwide, operated since 1961. In recent years many international and national hydrology research programs have focused on the basin, continental and even global scale. Examples of tracer-based studies at the small scale are numerous, however their application in the study of water cycling processes in large river basins remains a virtual scientific frontier (Gibson et al. 2002).

The worldwide longest isotope record of a large river exists for the Upper Danube at Vienna (drainage area 102,000 km^2, average discharge 1915 m^3/s). The results suggest that isotope signals in river discharge can provide additional insight into seasonal to decadal hydrological processes in large river basins and reflect hydroclimatic changes (Figure 1, Rozanski & Gonfiantini 1990, Rank et al. 1998, Kaiser et al. 2001, Rank &

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Papesch 2005). Isotope records from some other river stations of the Austrian isotope network on Danube tributaries (Figure 2) show the same trend (Rank & Papesch 1996). No similar records exist for the Lower Danube. Therefore a representative isotope monitoring near the Danube Delta should be established to achieve isotope-hydrological information about the entire Danube Basin (drainage area ca 800,000 km^2, average discharge ca 6.500 m^3/s, Lászlóffy 1967). A simple extrapolation from the Upper Danube data to the whole catchment is not possible because of different morphologic, hydrological and climatic conditions within the catchment.

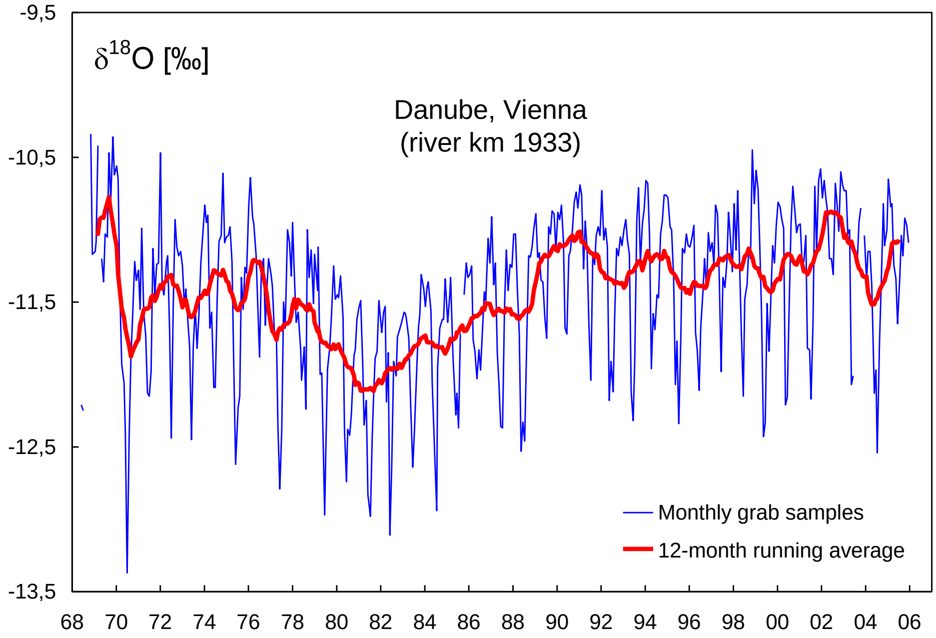

Figure 1. *δ^{18}O time series of the Danube at Vienna (monthly grab samples, 12-month running average) (Rank & Papesch 1996, updated). The δ^{18}O pattern reflects the general δ^{18}O trend of precipitation in Central Europe (Rank & Papesch 2010).*

Figure 2. *The Danube Basin river system with indication of the two proposed sampling points at the Iron Gate and Tulcea as well as the sampling points of the Austrian network for isotopes in river water, where long-term isotope records are available (based on ESRI ArcGIS 9.3).*

2 Preliminary isotope survey on the Lower Danube (Iron Gate, Delta) in order to find suitable sampling points for a long-term isotope monitoring of river water

Representative isotope monitoring on a river requires a careful selection of sampling site(s) and sampling frequency. The sample(s) should be representative for the entire cross-section of the river and thus for the whole catchment and not be influenced by side effects (e.g. inflow of tributaries, channels, municipal wastewater outlets etc.). In case of totally mixed rivers, one single sampling location would be enough for a routine sampling program.

The spatial isotopic variation of Danube water in the pre-delta region was investigated in two cross-sections at the bifurcations of the Danube Delta arms in October 2009 (Figure 3) within a bilateral Austrian-Romanian cooperation between Austrian Institute of Technology - AIT, Seibersdorf and National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca. A few samples were taken also in the Iron Gate section of the Danube and at Braila.

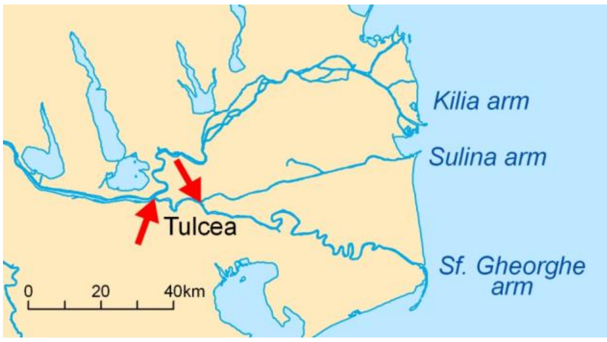

Figure 3. *Sampling sites for stable isotope cross-sections at the bifurcations of Kilia/Tulcea arm and Sulina/Sf. Gheorghe arm, respectively.*

Table 1. *Results of a preliminary isotope survey of the Lower Danube (Iron Gate, Braila, Danube Delta) in October 2009 (d = deuterium excess, calculated from d = δ^2H - 8.$\delta^{18}O$).*

Sampling point	River km	Date of sampling	δ^2H [‰]	$\delta^{18}O$ [‰]	d [‰]
Dubova, left bank	969	2009-10-06 09:00	-68.2	-9.71	9.5
Iron Gate 1, downstream of dam, left bank	943	2009-10-06 10:30	-67.6	-9.61	9.3
Drobeta, left bank	927	2009-10-06 11:00	-68.1	-9.65	9.1
Braila, ferry, right bank	167	2009-10-08 10:00	-68.1	-9.65	9.1
Cross section bifurcation Kilia/Tulcea arm					
1 Middle of the river		2009-10-07 10:30	-68.2	-9.62	8.8
2 10 m from right bank		2009-10-07 10:45	-68.7	-9.68	8.7
Cross section bifurcation Sulina/Sf. Gh. arm					
1 15 m from left bank		2009-10-07 10:00	-68.8	-9.65	8.4
2		2009-10-07	-67.5	-9.67	9.9
3		2009-10-07	-69.0	-9.68	8.4
4		2009-10-07	-68.2	-9.68	9.2
5		2009-10-07	-67.9	-9.64	9.2
6		2009-10-07	-68.0	-9.66	9.3

7	2009-10-07	-68.9	-9.67	8.5
8	2009-10-07	-67.5	-9.67	9.9
9 15 m from right bank	2009-10-07	-67.6	-9.67	9.8

Uncertainty of measurement: below ± 1.0 ‰ and ± 0.1 ‰ for $\delta^{2}H$ and $\delta^{18}O$, respectively. Samples 1-9 were taken in equal distances.

The results (Table 1) do not show any significant isotopic variations within the cross-sections in the pre-delta region. So the Danube River was isotopically totally mixed at the time of sampling (the flow rate was near mean discharge). Also the isotope values of the samples from the Iron Gate section and Braila did not exhibit variations exceeding the uncertainty of measurement.

As a result from this preliminary investigation we can conclude that it will be possible to achieve a representative long-term isotope record of the whole Danube Basin by sampling at only one suitable location.

3 Conclusions and outlook

Since evaporation has only little effects on the isotopic composition of river water within the Danube Basin, the isotopic composition of Danube water near the mouth in the Black Sea reflects mainly the isotopic composition of precipitation in the whole basin and so provides an integrated isotope signal for climatic/hydrological conditions and changes in the whole catchment.

A preliminary investigation of the isotopic composition of Danube water in cross-sections in the Tulcea region showed that the Danube River is isotopically totally mixed at the bifurcation of the Danube Delta arms. Therefore routine sampling at only one location in the pre-delta region seems to be sufficient to get a representative isotope record for the whole Danube Basin. This result should be checked by repeating the investigation at different hydrological conditions to elucidate seasonal and inter-annual variation.

Routine sampling at Tulcea twice a month was started in November 2009. A sampling program at the Iron Gate (rkm 944) is in preparation.

The Danube water isotope time series will serve as a basic data set for hydrological investigations as well as for assessing future impacts within the Danube Basin. This includes climatic/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).

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