ISOTOPE STUDIES IN LARGE RIVER BASINS: A NEW GLOBAL RESEARCH FOCUS

In 2002, the International Atomic Energy Agency (IAEA), the United Nations organization responsible for promoting peaceful use of nuclear technology, 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". The project, implemented *via* a network of national research institutes and universities, supports sampling and isotope analysis of river discharge, and builds on complimentary 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.

Large river basins

Rivers are an important linkage in the global hydrological cycle, returning about 35% of continental precipitation to the oceans. Rivers are also the most important source of water for human use. Much of the world's population lives along large rivers, relying on them for trade, transportation, industry, agriculture and domestic water supplies. The resulting pressure has led to the extreme regulation of some river systems, and often a degradation of water quantity and quality. 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 recent years many international and national hydrology research programs have focused on the basin, continental and even global scale. One prominent example, the Global Energy and Water Cycle Experiment (GEWEX), is focusing on large river basins as an appropriate and overlapping scale for study of both atmospheric and hydrological processes and modeling. While GEWEX, and other international efforts, have extensively explored water and energy budget methods and modeling, they have not widely employed isotope tracer techniques, due largely to lack of available isotope data for major components of the continental hydrological cycle (notably river discharge), and uncertainty regarding the capability of the approach. Improvement of isotope monitoring will also support a wide range of multidisciplinary international programs such as the

International Geosphere Biosphere Programme's (IGBP) Food, Water and Carbon Commissions, and UNESCO's International Hydrological Programme (IHP). National level initiatives, such as the Water Cycle Dynamics and Prediction (WCDP) program of the U.S. Department of Energy, have promoted further interest in integration of isotope tracers for characterizing variability in the hydrological cycle, as a diagnostic tool for model development, and for discriminating between natural and anthropogenic variability in the water cycle (DOE, 2001).

Examples of tracer-based studies at the small scale are numerous (see Kendall and McDonnell, 1998), however their application in the study of water cycling processes in large river basins remains a virtual scientific frontier (GCIP, 1998). To improve the current situation, the IAEA project cooperatively supports development of both observational networks and methodology for applying isotope techniques to the study of hydrological processes at the large scale. The potential of isotope tracers to dissect the underlying causes of variability in the water cycle of large river basins can be demonstrated with a few outstanding datasets from basins within the IAEA project (Fig. 1A-E). These few examples suggest isotope signals in river discharge can provide additional insight into seasonal to decadal hydrological processes in large river basins.

Tracing hydrological processes

Isotopes of particular interest for hydrological studies include the stable isotopes of water (^{18}O, ^{2}H), which are incorporated within the water molecule ($H_2{}^{18}O$, $^{1}H^{2}H^{16}O$), and exhibit systematic variations in the water cycle (Fig. 1E inset) as a result of isotope fractionations that accompany phase changes and diffusion (see Gat, 1996). Precipitation variability is related mainly to air-mass source and evolution including temperature-dependant equilibrium fractionation effects. Evaporation results in a buildup of the heavy isotope species in surface waters due to additional kinetic isotope effects during diffusion through the atmospheric boundary layer (Gat, 1996), producing enrichment along evaporation lines below the meteoric water line (MWL). 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 river or contributing sources such as soil water, wetlands, lakes, and reservoirs. Coupled with measurement of isotopes in water sources, river discharge signatures can provide a clearer focus on groundwater recharge/discharge processes, water balance, and snow and glacier meltwater mixing. Radioactive tritium (^{3}H), another isotope

incorporated in the water molecule ($^{1}H^{3}H^{16}O$), has also proven useful for the study of river basin processes. Tritium concentrations in precipitation peaked in the 1960s in response to atmospheric nuclear weapons testing (Fig. 1B), creating an event marker that can be used to estimate water residence times. Although tritium levels have declined considerably in the past decade, recent advances have extended the usefulness of tritium by explicit measurement of the parent-daughter ratio of ^{3}H-^{3}He.

In humid basins, precipitation processes are typically the primary signal traced by river discharge. The spatial variation of oxygen-18 in river discharge across many parts of the contiguous United States (Fig. 1A), which is strongly correlated with air mass sources, altitude, and continentality gradients, reflects progressive depletion in heavy isotope content in precipitation by fractionation during rainout and moisture recycling over the North American continent. The isotopic composition of river discharge is not static. Pronounced seasonal variations in stable isotope content are observed due to oscillations in mixing proportions of precipitation and shallow runoff with snow, glacial meltwater and groundwater; these processes are also is traced by tritium (Fig. 1B). Comparison of tritium in the Danube River with precipitation at Vienna (Fig. 1B) reveals a stronger seasonality signal in precipitation due to the buffering effect of groundwater and glacial meltwater mixing on the river signatures. A persistent lag in tritium decay in Danube river reflects a mean basin residence time estimated to be close to 3 years with significant interannual variability (Rank et al., 1998). Evidence that stable isotope signatures of precipitation input are not static is found from long-term isotope records of the European rivers (Rhine, Danube and tributaries; Fig. 1C). In general, the alpine headwater rivers, Inn (tributary to Danube) and Rhine at Kirchbichl are depleted in heavy isotopes relative to the Danube (at Vienna and Ulm) due to higher mean precipitation altitude (a.k.a the isotope-altitude effect; see Dalai et al. in press). Interannual variations in precipitation and runoff processes is reflected in the significant year-to-year differences in 12-month running means of oxygen-18 in river discharge, especially during the 1980s (Fig. 1C). This striking 1980s shift, contemporaneously attributed to potentially alarming rates of anthropogenic climate warming (Rozanski et al., 1993), did not continue through the 1990s revealing the inherent decadal variability of precipitation processes in the Alps region of Europe.

Synoptic surveys along the main stem of large rivers (Fig. 1D) are useful for estimating the contribution and mixing of tributary sources, the influx of irrigation or wastewater return and for identifying the location and patterns of evaporation (Simpson and Herczeg, 1991). Synoptic

results from humid region rivers, such as the Amazon and the Danube, often identify a small upstream depletion due to the precipitation-altitude effect. More pronounced altitude effects are noted for the Himalayas (Dalai et al., in press) and the Amazon headwaters (Fig 1D). While total vapour fluxes from humid basins such as the Amazon can be much larger than evaporation from arid zone rivers due to unrestricted moisture supply, plant-mediated transpiration is generally isotopically non-fractionating (see Gat, 1996) and, in contrast to arid zone rivers, does not result in evaporative enrichment of water along lower slope evaporation lines (Fig. 1E). In arid or semi-arid regions, the evaporative enrichment of stable isotopes can be used to gauge the progressive downstream water loss by evaporation (see Darling and Rio Grande; Fig. 1D). In basins with substantial contributions from both evaporation and transpiration (e.g. Canadian and Scandinavian Shields) it is also possible to monitor partitioning of these fluxes in the basin integrated discharge signals (Gibson and Edwards, 2002). A synoptic survey along the main stem of the Mackenzie-Athabasca River system (compiled from Hitchon and Krouse, 1972) reveals fluctuating oxygen-18 signatures from headwaters to mouth due to interaction of tributaries draining both western alpine regions (with depleted isotope signatures) and eastern lowlands (with enriched isotope signatures) and the storage effect of several large lakes (e.g. Great Slave Lake, Great Bear Lake).

Synoptic and time-series sampling of solute isotope systems (e.g. carbon, nitrogen, strontium, boron, sulphur, chloride) are potentially useful for labeling solute and pollution sources, and for study of hydrological and biogeochemical controls on water quality (Phillips et al., in press). Of particular interest is ^{15}N and ^{18}O of nitrate, which can be very different for pollution originating from fertilizers, animal/human waste, and automobile exhaust, and which transform predictably by assimilation and denitrification during transport in large rivers (Battaglin et al., 2001).

Organization

The research project involves participation of 17 research groups who, in cooperation with IAEA, have developed field programs to collect water samples from large rivers and to perform a range of isotopic analyses. Data collected at over 150 river stations, organized in nested networks within some of the largest rivers in the world, will form the basis of the study (Table 1). Hydrological regimes under investigation include arctic, temperate and tropical areas, the arid zone, lowland and alpine drainages, and hyporeic and endoreic drainages. Initially, the project includes monitoring of isotope signals in runoff from 22% of the continental land surface,

accounting for approximately 33% of the global river discharge. Where possible, studies are linked to existing research programmes, including several GEWEX CSEs (Continental Scale Experiments). The common intersection of interest of the participants is application of the stable isotopes of water to trace hydrological processes and water balance. Tritium is also being applied in selected large river basins where long-term datasets exist or where tritium concentrations in river water are found to be substantially different than present levels in local precipitation. In addition to collectively improving global capability for isotope hydrology studies, and closing the continental isotope mass balance, researchers involved in the project are motivated by diverse special interests in understanding linkages between water and nutrient cycling, pollution sources, salinity controls and other water quality issues, as well as climate and environmental change detection, particularly where long-term data sets are available. Where possible, water samples are being archived to promote and expand future collaborative opportunities to include other isotope and geochemical parameters. This research project, one of several being led by the IAEA Isotope Hydrology Section, endeavors to develop and test the application and transferability of isotope techniques in a wide range of hydrological settings over the next 5 years. This initiative will expectedly contribute to better scientific understanding of water cycling processes at the large scale, and seeks to clarify the potential value and limitations of incorporating isotope techniques in a global river network.

Future Meetings

The coordinated research project will run through 2006. Research groups who would like to participate are encouraged to contact the IAEA Isotope Hydrology Section. An informal workshop and special session on large river basins will be held at the upcoming 40th Anniversary Isotope Hydrology Symposium in Vienna, Austria during 19-23 May 2003. Details can be found at www.iaea.org/programmes/ripc/ih.

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Table 1. Large River Basins Being Studied Within the IAEA coordinated research project. Statistics based on UNH-GRDC runoff fields v. 1.0 (Fekete et al.., 1999).

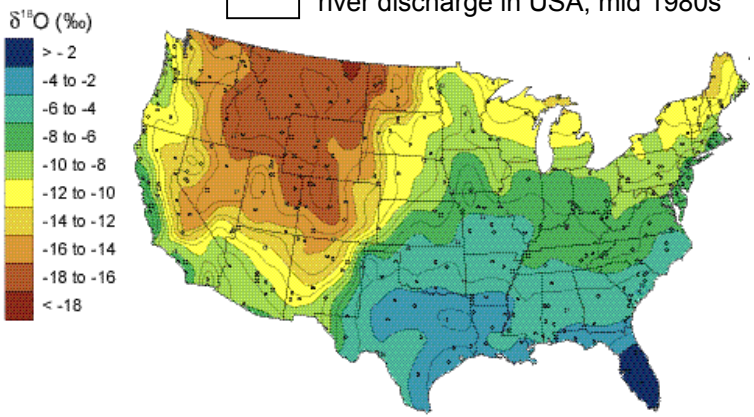
Name	*Basin Length km*	*BasinArea km^2*	*Climate Zone**	*Discharge m^3/s*	*Runoff mm*	*# Sampling Stations*	*Isotopes*
Amazon	4327	5853804	3h	207682	1119	19	^{2}H, ^{18}O
Mississippi	4185	3202959	2	19396	191	17	^{2}H, ^{3}H, ^{13}C, ^{15}N, ^{17}O,^{18}O,^{34}S
Parana	2748	2661392	2	16936	201	3	^{2}H, ^{3}H,^{18}O
Lena	4387	2417937	1	15210	198	4	^{2}H, ^{18}O
Niger	3401	2240019	3a	8925	126	12	^{2}H, ^{18}O
Zambezi	2541	1988756	3ade	9005	143	tbd	^{2}H, ^{18}O
Yangtze	4734	1794243	2d	29583	520	4	^{2}H, ^{18}O
Mackenzie	3679	1712738	1k	9192	169	28	^{2}H, ^{18}O
Ganges	2221	1628405	3d	40025	775	5	^{2}H, ^{18}O, ^{13}C
St. Lawrence	3175	1266642	2k	15156	378	4	^{2}H, ^{18}O, ^{13}C
Indus	2382	1143101	2d	3332	92	22	^{2}H, ^{13}C, ^{14}C,^{18}O
Murray-Darling	1767	1031512	2ad	256	8	6	^{2}H,^{18}O
Orange	1840	943577	2ad	145	5	tbd	^{2}H, ^{18}O
Yukon	2716	852029	1	6425	238	5	^{2}H, ^{3}H,^{18}O, ^{35}S
Colorado (US)	1808	807573	2d	21	1	2	^{2}H, ^{3}H, ^{18}O
Rio Grande (US)	2219	804791	2ad	120	5	13	^{2}H, ^{11}B, ^{18}O, ^{32}S, ^{36}Cl, $^{86}Sr/^{87}Sr$
Danube	2222	788002	2	6612	265	10	^{2}H, ^{3}H, ^{18}O
Columbia (US)	1791	724025	2	7570	330	1	^{2}H,^{18}O
Jordan	200	40000	2ade	15	12	9	^{2}H,^{18}O
Rhine	1018	165058	2	2345	448	10	^{2}H, ^{3}H, ^{18}O
Yobe	---	84138	3ae	---	---	1	^{2}H,^{18}O

* 1 –Arctic, 2- Temperate, 3-Tropics, Distinct features: a-arid, h-humid, d- relatively high degree of water development, e-internal (endoreic) drainage, k-large lakes,; tbd – # sampling stations to be determined.

** - supplementary dataset provided by C. Hillaire-Marcel, GEOTOP, UQAM, Montreal, Canada.

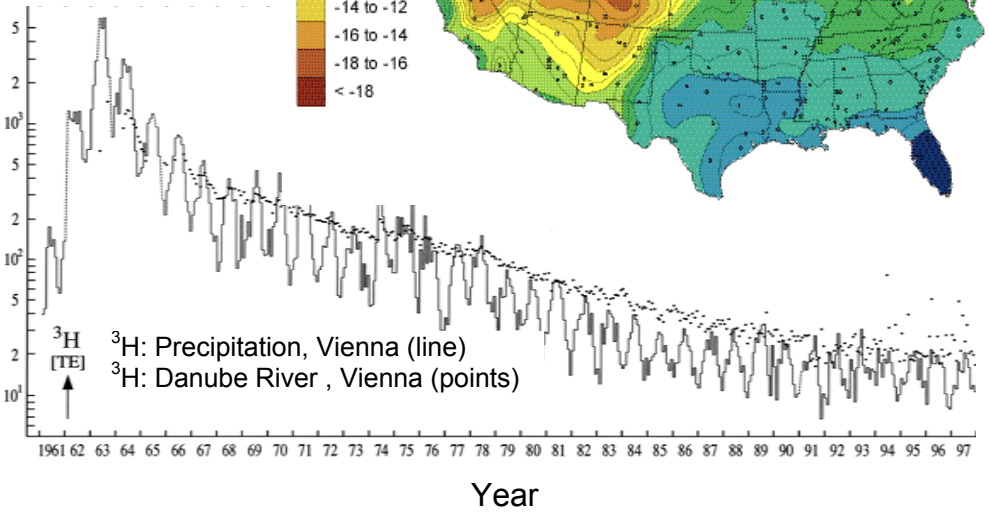
A

Oxygen-18 in flux-weighted river discharge in USA, mid 1980s



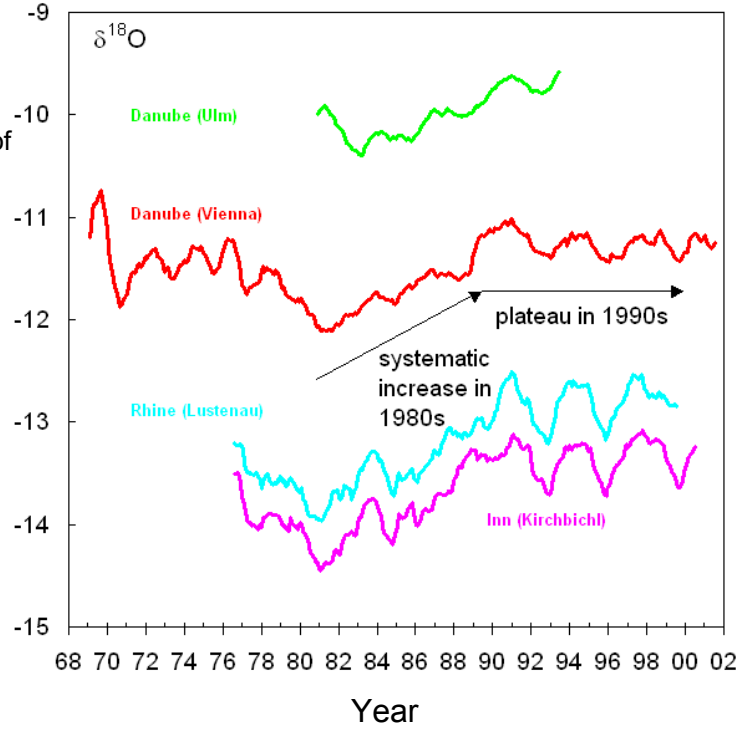
B

Time-series of tritium content in Danube R and precipitation



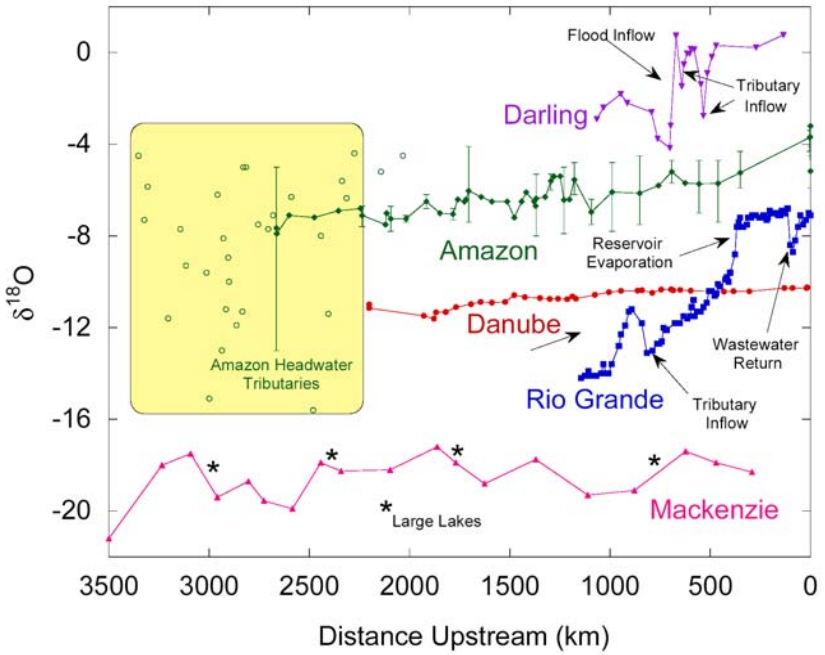
C

Time-series of oxygen-18 in European rivers (12-month running means)



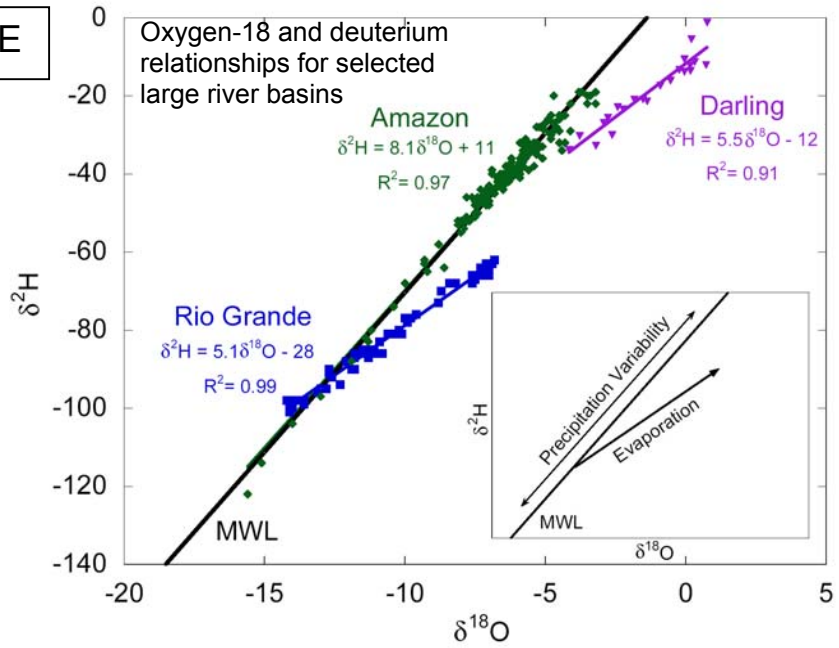
D

Synoptic trends in oxygen-18 content in large rivers identifying some important shifts



E

Oxygen-18 and deuterium relationships for selected large river basins



Caption:

Fig. 1. Examples of existing isotope datasets from large river basins to be augmented within the IAEA project: (a) discharge-weighted $\delta^{18}O$ from sub-basins of less than 130,000 km^2 (after Kendall and Coplen 2001); (b) time-series of tritium in Danube River and precipitation at Vienna (after Rank et al. 1998), (c) oxygen-18 time-series (12-month running means of monthly grab samples) for stations on the Danube and Rhine rivers and selected tributaries, (c) synoptic sampling campaigns on the Amazon (September 1971 to December 1972; Matsui et al., 1980), Rio Grande (August 2001; Phillips et al., in press), Mackenzie (3-week summer period 1969; Hitchon and Krouse, 1972), Danube (March 1988; Rank et al. 1990), and Darling R. (Herczeg et al., unpublished data). Rio Grande and Darling refer to distances upstream from US/Mexico border and confluence with Murray River, respectively, (d) oxygen-18 and deuterium relationships for the Amazon (Matsui et al. 1980), Rio Grande, and Darling Rivers with inset showing schematic of major controls on variability of oxygen-18 and deuterium relationships in large rivers. Precipitation variability is related mainly to air-mass source and evolution including temperature-dependent equilibrium fractionation effects. Evaporation produces distinctive enrichment along evaporation lines at a lower slope than the meteoric water line (MWL). See text for further discussion.