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Isotope Studies in Large River Basins: A New Global Research Focus

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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 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." This was 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.

The main objective of this article is to increase awareness of the potential value of incorporating isotope tracers in water cycle studies in large river basins, and thereby to promote new collaborative opportunities with researchers, managers, and scientific organizations with an interest in this area.

Large River Basins

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 also supports 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 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

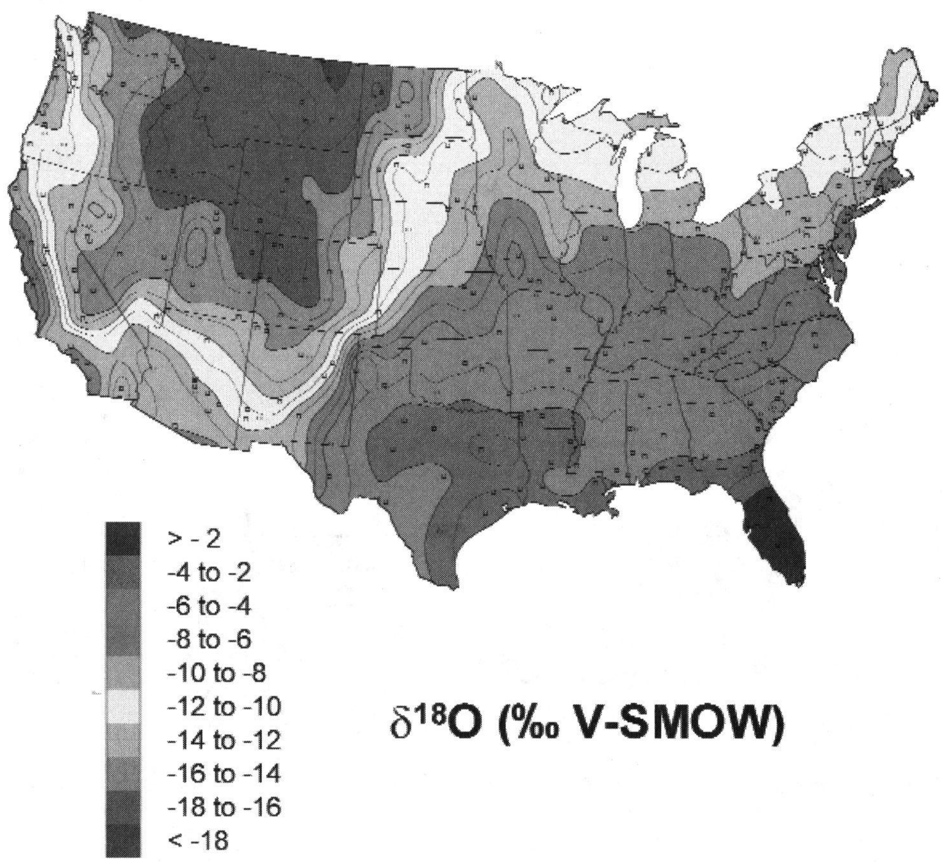

Fig. 1. Flux-weighted $\delta^{18}O$ (‰ V-SMOW) in discharge from sub-basins of less than 130,000 km^2 sampled across United States during the mid-1980s (modified from Kendall and Coplen, *2001). River isotope signals in this region predominantly reflect precipitation-controlled continental rain-out signals overprinted with only minor evaporative modification. Original color image appears at the back of this volume.*

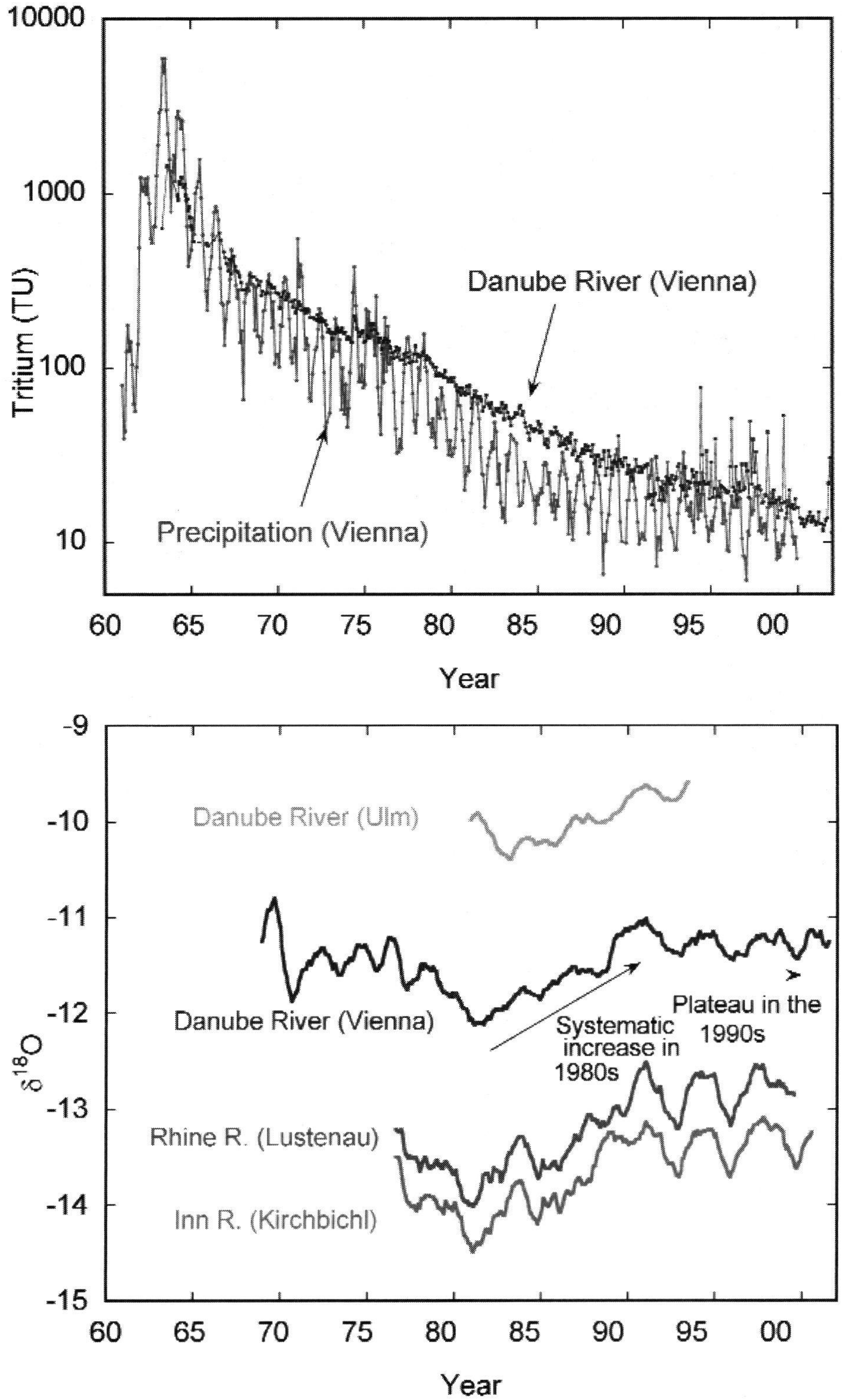

Fig. 2. (a) Time series of tritium (half-life = 12.32 years) in the Danube River and in precipitation at Vienna (modified from Rank et al., *1998). Temporal lag in tritium decay in river water versus precipitation following the mid-1960s peak from above-ground nuclear explosions provides a dynamic index of basin residence times, estimated to be close to 3 years. Periodically high tritium content in river water during the late 1990s may suggest new anthropogenic tritium sources; (b) Oxygen-18 time series (12-month running means of monthly grab samples) for stations on the Danube and Rhine rivers and selected tributaries illustrating similar decadal isotope variations among rivers across the Alps region of Europe. Note that T is Tritium Units where TU = 10^{-18} $^3H/^1H$ = 3.19 pCi/L or 0.118 Bq/L). Original color image appears at the back of this volume.*

[*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 data sets from basins within the IAEA project (Figures 1-3). 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 in general include the stable isotopes of water (^{18}O, ^{2}H), which are incorporated within the water molecule ($H_2{}^{18}O$, $^1H^2H^{16}O$), and exhibit systematic variations in the water cycle as a result of isotope fractionations that accompany phase changes and diffusion [*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 global meteoric water line.

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 (^3H), another isotope incorporated in the water molecule ($^1H^3H^{16}O$), 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, 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 $^3H/^3He$.

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 (Figure 1), 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

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	Basin area X 10^6 km^2	Climate zone*	Discharge X 10^4 m^3/s	Runoff mm	# Sampling stations	Isotopes
Amazon	4327	5.85	3h	20.8	1119	19	^2H, ^{18}O
Mississippi	4185	3.20	2	1.94	191	17	^2H, ^3H, ^{13}C, ^{15}N, ^{17}O, ^{18}O, ^{34}S
Parana	2748	2.66	2	1.69	201	3	^2H, ^3H, ^{18}O
Lena	4387	2.42	1	1.52	198	4	^2H, ^{18}O
Niger	3401	2.24	3a	0.893	126	2	^2H, ^{18}O
Zambezi	2541	1.99	3ade	0.900	143	tbd	^2H, ^{18}O
Yangtze	4734	1.79	2d	2.96	520	4	^2H, ^{18}O
Mackenzie	3679	1.71	1k	0.919	169	28	^2H, ^{18}O
Ganges	2221	1.63	3d	4.00	775	5	^2H, ^{13}C, ^{18}O
St. Lawrence	3175	1.27	2k	1.52	378	4	^2H, ^{13}C, ^{18}O
Indus	2382	1.14	2d	0.333	92	22	^2H, ^{13}C, ^{14}C, ^{18}O
Murray-Darling	1767	1.03	2ad	0.0256	8	6	^2H, ^{18}O
Orange	1840	0.944	2ad	0.0145	5	tbd	^2H, ^{18}O
Yukon	2716	0.852	1	0.643	238	5	^2H, ^3H, ^{18}O, ^{35}S
Colorado	1808	0.808	2d	0.0021	1	2	^2H, ^3H, ^{18}O
Rio Grande	2219	0.804	2ad	0.0120	5	13	^2H, ^{11}B, ^{18}O, ^{32}S, ^{36}Cl, $^{86}Sr/^{87}Sr$
Danube	2222	0.788	2	0.661	265	10	^2H, ^3H, ^{18}O
Columbia	1791	0.724	2	0.757	330	1	^2H, ^{18}O
Jordan	200	0.040	2ade	0.0015	12	9	^2H, ^{18}O
Rhine	1018	0.165	2	0.234	448	10	^2H, ^3H, ^{18}O
Yobe	---	0.084	3ac	---	---	2	^2H, ^{18}O

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

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

seasonal variations in tritium and stable isotope content are observed due to oscillations in mixing proportions of precipitation and shallow runoff with snow, glacial meltwater, and groundwater (Figure 2). Comparison of tritium in the Danube River with precipitation at Vienna (Figure 2a) 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 the 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; Figure 2b). 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.*, 2002).

Interannual variations in precipitation and runoff processes are reflected in the significant year-to-year differences in 12-month running means of oxygen-18 in river dis-charge, especially during the 1980s (Figure 2b). 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 (Figure 3a) 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.*, 2002] and the Amazon headwaters (Figure 3a). While total vapor 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 (Figure 3b).

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; Figure 3a). 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 (Figure 3a; 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, sulfur, chloride) are potentially useful for labeling solute and pollution sources, and for study of hydrological and biogeochemical controls on water quality [*Phillips et al.*, 2002]. Of particular interest are ^{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;

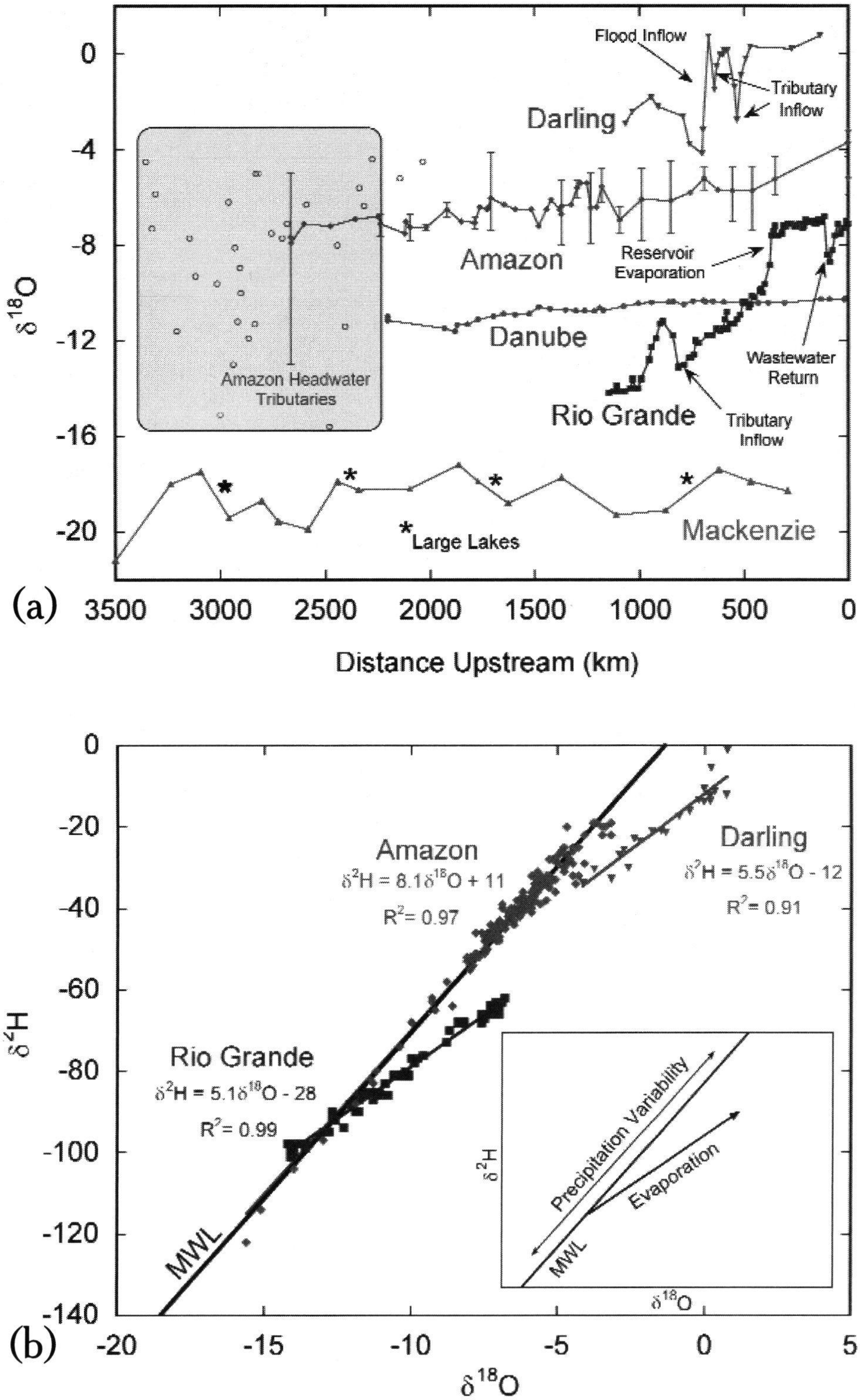

Fig. 3. (a) Synoptic sampling campaigns on the Amazon (September 1971 to December 1972; Matsui et al., *1980), Rio Grande (August 2001;* Phillips et al., *2002), Mackenzie (3-week summer period 1969;* Hitchon and Krouse, *1972), Danube (March 1988;* Rank et al., *1990), and Darling rivers. (Herczeg et al., unpublished data, 2002). Rio Grande and Darling scales refer to distances upstream from U.S.-Mexico border and confluence with Murray River, respectively. Important shifts and related causes are shown. (b) Oxygen-18 and deuterium relationships for the Amazon* [Matsui et al. 1980], *Rio Grande* [Phillips et al., *2002*], *and Darling rivers, with inset showing schematic of major controls on variability of oxygen-18 and deuterium relationships in large rivers. Trends are linked to precipitation variability (i.e., air-mass source and evolution, including temperature-dependent equilibrium fractionation effects) and evaporation loss, the latter of which produces distinctive enrichment along evaporation lines at a lower slope than the global meteoric water line (MWL). Original color image appears at the back of this volume.*

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 programs, 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 analyzed in selected large river basins where long-term data sets 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, 19–23 May 2003. Details can be found at www.iaea.org/programmes/ripc/ih.

A follow-on workshop on "Isotope Tracers in Water Cycle Models" will be held in conjunction with the IAHS Meeting in Sapporo, 7–9 July 2003. For details, see the Web site: http://www.cig.ensmp.fr/%7Eiahs/sapporo/HW06.htm.

Authors

John J. Gibson, Pradeep Aggarwal, James Hogan, Carol Kendall, Luiz A. Martinelli, Willi Stichler, Dieter Rank, Ibrahim Goni, Manzoor Choudhry, Joel Gat, Sourendra Bhattacharya, Atsuko Sugimoto, Balazs Fekete, Alain Pietroniro, Thomas Maurer, Hector Panarello, David Stone, Patrick Seyler, Laurence Maurice-Bourgoin, and *Andrew Herczeg*

Correspondence should be addressed to: Pradeep Aggarwal, Head, Isotope Hydrology Section, International Atomic Energy Agency, P.O. Box 100, Wagramer Strasse 5, A-1400 Vienna, Austria; E-mail: p.aggarwal@iaea.org

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Mixed Prognosis for Coral Reefs

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A new report on the global state of coral reefs indicates that there is "strong evidence that the corner is being turned" in the ability to stop reef decline.

However, attempts to manage coral reefs to arrest their decline still lag behind the increasing rate of reef degradation, according to the report, "Status of Coral Reefs of the World 2002," issued on 10 December. The report is produced biennially by the Global Coral Reef Monitoring Network (GCRMN).

The report notes that in addition to climate change and El Niño events, threats to coral reefs include sewage pollution and sedimentation, overfishing and destructive fishing practices which use dynamite and toxins, diseases, and collapses in coral recruitment to reefs. Also, many countries with coral reefs lack effective protection programs and monitoring plans, and often are not aware of the extent of damage to their reefs, according to the report.

Some of the most seriously threatened coral reefs are located off the coasts of East Africa, Indonesia, The Philippines, southern China, Haiti, and the U.S. Virgin Islands. Reefs in good condition include the Great Barrier Reef and some mid-Pacific Ocean reefs.

"We are sitting on a knife's edge" between making or losing ground in reef conservation, said GCRMN coordinator Clive Wilkinson, principal research scientist with the Australian Institute of Marine Science in Queensland. Wilkinson said that while there is much work ahead, some management efforts are proving effective in protecting what he called "these cute, cuddly, charismatic ecosystems."

There are encouraging signs that marine protected areas can help to reverse reef decline. Another successful management effort is increased scientific monitoring.

Tracking reef conditions "demonstrates the power of having global observing systems in place regularly collecting data," said Conrad Lautenbacher, administrator of the U.S. National Oceanic and Atmospheric Administration. The agency, which is one of the principal financial supporters for the GCRMN, provides satellite mapping and other tools to monitor reefs.

The previous GCRMN report in 2000 was "all doom and gloom," according to Wilkinson. That report followed the 1997-1998 El Niño and the resulting bleaching, which devastated about 16% of coral reefs globally. Four years later, about 8% of those reefs are showing encouraging recovery, though improvement of some other reefs is being slowed by stresses of pollution and overfishing, he said.

The new report also notes that countries and institutions are becoming more aware of the economic value of coral reefs; the value of associated goods and services is estimated $375 billion annually

The report is available online at the following Web site: http://www.aims.gov.au/pages/research/coral-bleaching/scr2002/scr-00.html.

Randy Showstack, Staff Writer

U.S. Climate Science Conference Examines Strategic Plan

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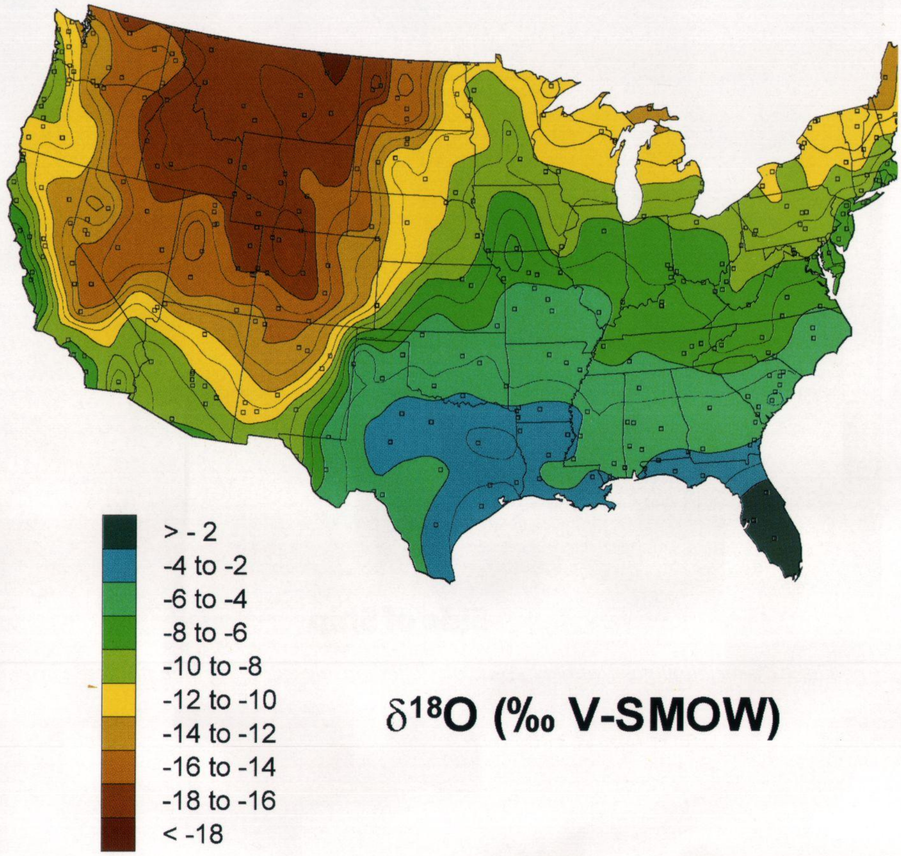
A major Bush administration conference on climate change science was widely praised for its efforts to help formulate a good research agenda pursuant to producing a final U.S. government science strategic plan by April 2003; and for promises to seriously consider suggestions from the scientific community about climate research priorities.

However, a number of scientists at the U.S. Climate Change Science Program workshop, which took place 3–5 December, said they are concerned about how the administration will eventually select priorities from among a broad array of climate research topics that some said resembled a "Santa's wish list;" and whether sufficient funding will be allocated in the present difficult budgetary environment.

Some of the 1500 attendees at the Washington, D.C. event also questioned whether the government's emphasis on further research to reduce uncertainties about climate change amounts to delaying taking action on the issue.

Critique of Draft Plan

The conference examined the draft strategic plan for the U.S. Climate Change Science Program (CCSP). That document, released in November, provides a broad overview of climate change and identifies key outstanding research questions. It also reviews two components of the CCSP. One of these is the administration's Climate Change Research Initiative, whose purpose is to study areas of



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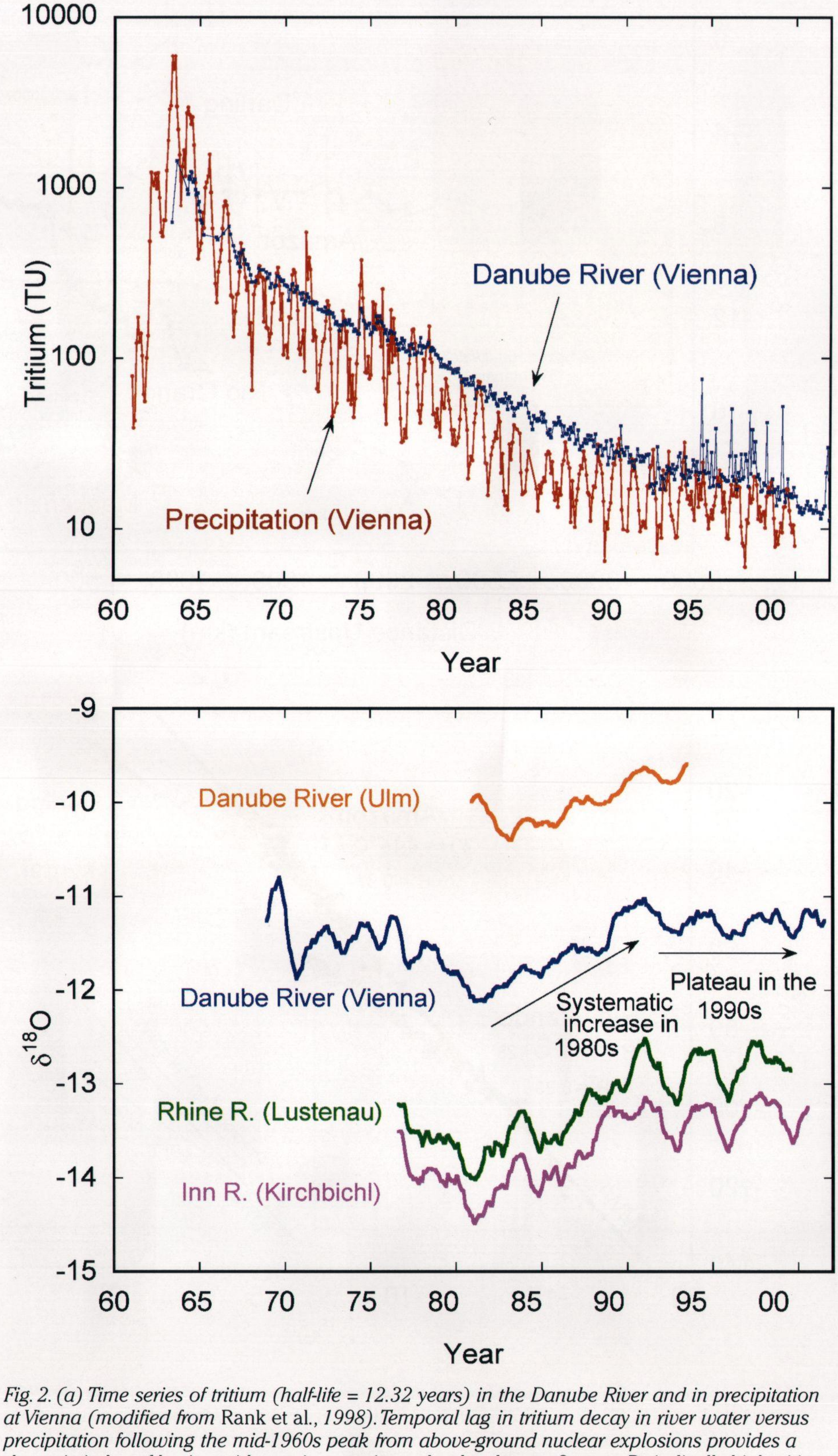

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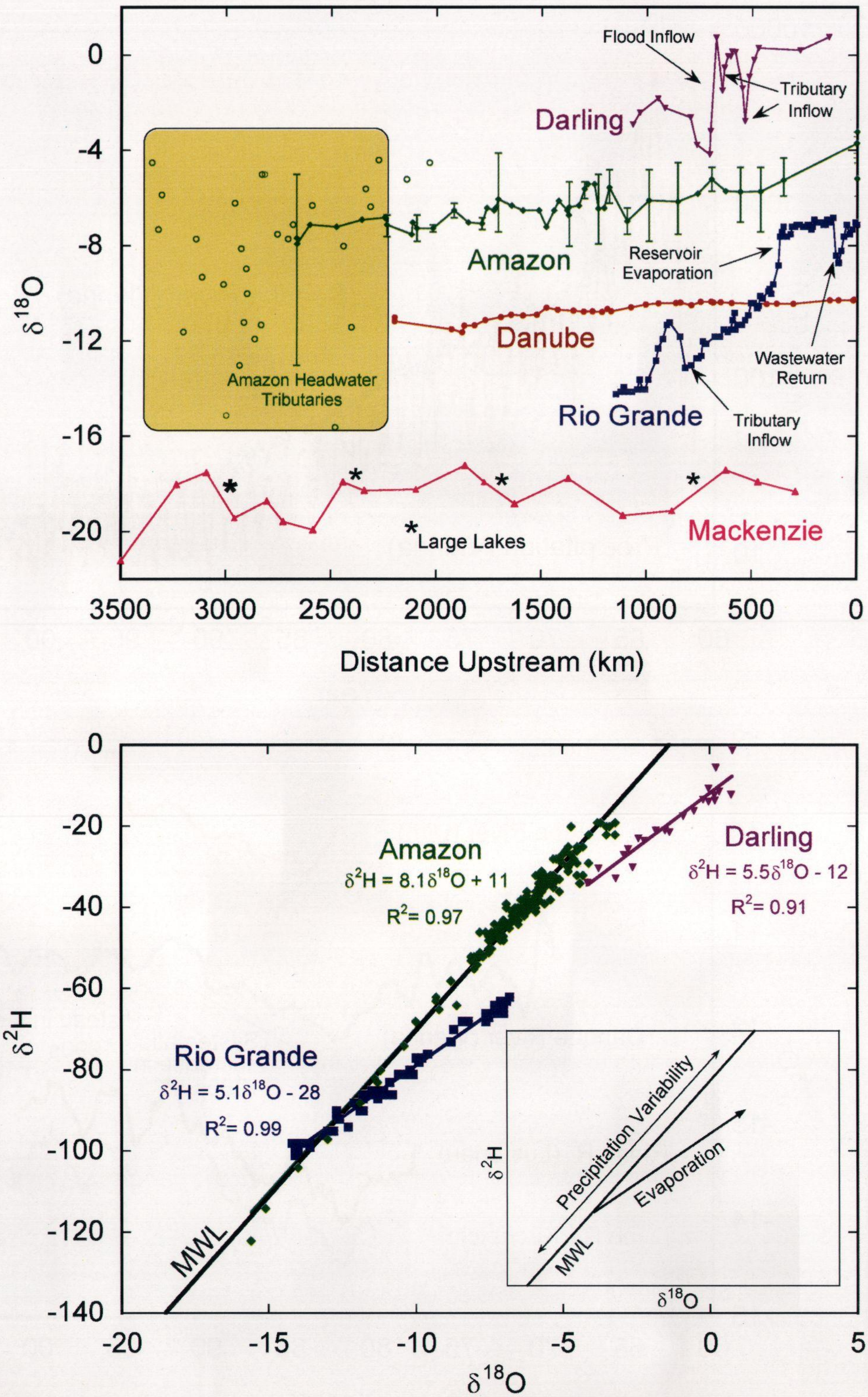

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