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The Global Network of Isotopes in Rivers (GNIR): integration of water isotopes in watershed observation and riverine research

J. Halder, S. Terzer, L. I. Wassenaar, L. J. Araguás-Araguás, and P. K. Aggarwal

Isotope Hydrology Section, International Atomic Energy Agency, 1400 Vienna, Austria

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Correspondence to: J. Halder (j.halder@iaea.org)

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Abstract

We introduce a new online global database of riverine water stable isotopes (*Global Network of Isotopes in Rivers*) and evaluate its longer-term data holdings. Overall, 218 GNIR river stations were clustered into 3 different groups based on the seasonal variation in their isotopic composition, which was closely coupled to precipitation and snow-melt water run-off regimes. Sinusoidal fit functions revealed periodic phases within each grouping and deviations from the sinusoidal functions revealed important river alterations or hydrological processes in these watersheds. The seasonal isotopic amplitude of $\delta^{18}O$ in rivers averaged 2.5 ‰, and did not increase as a function of latitude, as it does for global precipitation. Low seasonal isotopic amplitudes in rivers suggest the prevalence of mixing and storage such as occurs via lakes, reservoirs, and groundwater. The application of a catchment-constrained regionalized cluster-based water isotope prediction model (CC-RCWIP) allowed direct comparison between the expected isotopic composition for the upstream catchment precipitation with the measured isotopic composition of river discharge at observation stations. The catchment-constrained model revealed a strong global isotopic correlation between average rainfall and river discharge ($R^2 = 0.88$) and the study demonstrated that the seasonal isotopic composition and variation of river water can be predicted. Deviations in data from model predicted values suggest there are important natural or anthropogenic catchment processes, like evaporation, damming, and water storage in the upstream catchment.

1 Introduction

Rivers play a crucial role in the earth's water cycle as watershed-integrating hydrological conduits for returning terrestrial precipitation back to the world's oceans. Despite comprising less than 0.1 % of the world's available surface freshwater, rivers are commonly linked to the largest freshwater reserves, like permafrost, glaciers, aquifers, as well as lake and wetland systems (e.g. Oki and Kanae, 2006). Recent estimates suggest that there are more than 58 000 dams sited on world rivers (ICOLD, 2015), with very few rivers left in a state of natural discharge regime (Dynesius and Nilsson, 1994). Riverine water quality degradation may be manifested by increasing downstream water pollution (chemicals that impact human consumption or recreational use), nutrient loadings, sedimentation, altered aquatic ecosystem function, or loss of biodiversity, and cultural eutrophication of estuarine and marine receiving environments (e.g. Gulf of Mexico "Dead Zone"). A survey of world rivers suggest that alterations have resulted in over 65 % of global rivers being in a state of moderate to high threat, with little evidence for turnaround with an ever increasing human population and rising water demands (Vörösmarty et al., 2010). Further, owing to the fact many important large rivers are transboundary; these threats have the potential to lead to conflict around freshwater security issues.

At any point along a river reach, water is ultimately derived from precipitation falling within its upstream catchment area. Depending on the size (ranging from a few km^2 to $> 5\,Mkm^2$) and geomorphological characteristics of the catchment, a variety of hydrological processes may affect the catchment and river water flow. The stable isotope ratios of the water molecule ($^{18}O/^{16}O$, $^{2}H/^{1}H$) are well-established powerful integrative recorders of key catchment processes (evaporation and transpiration, recycling, mixing), catchment water balance, as well as tracers of river recharge sources (direct precipitation, runoff, soil water, groundwater, lakes, snow and ice) (e.g. McDonnell et al., 1990; Kendall and McDonnell, 1998; Lambs, 2000; Gibson et al., 2005; Liu et al., 2008; Jasechko et al., 2013). Hydrological processes occurring between rainfall input and river discharge modify the stable isotopic composition of rivers including isotopic averaging during soil infiltration, runoff and damming (Ogrinc et al., 2008; Koeniger et al., 2009) and seasonally differential fractional inputs of water from surface and groundwater sources (Sklash, 1990; Buttle, 1994; Lambs, 2004); heavy isotope (^{2}H, ^{18}O) enrichment due to the effects of watershed evapotranspiration or in-stream evaporation (Simpson and Herczeg, 1991; Gremillion and Wanielista, 2000; Telmer and

Veizer, 2000) and isotopic fractionation of snowmelt (Taylor et al., 2002). All of these processes may result in markedly different average isotopic values in river discharge compared to precipitation, both in space and time (Dutton et al., 2005; Rock and Mayer, 2007).

Generally, a review of the literature shows that longitudinal $\delta^{18}O$ and $\delta^{2}H$ variations in a river strongly depend on the catchment elevation, since headwaters at high altitudes are generally depleted in ^{18}O and ^{2}H compared to lower elevation downstream regions (e.g. Longinelli and Edmond, 1983; Ramesh and Sarin, 1992; Pawellek et al., 2002; Winston and Criss, 2003; Rock and Mayer, 2007), except where high altitude tributaries merge into low elevation main stems (Yang et al., 1996; Yi et al., 2010). The cumulative effect of catchment scale evapotranspiration and instream evaporative processes may additionally increase $\delta^{18}O$ and $\delta^{2}H$ values in the downstream direction. Rivers that are hundreds of kilometres long may therefore have distinctive upstream vs. downstream isotopic patterns as they accumulate discharge and integrate various hydrological processes from contributing sub-catchments (Simpson and Herczeg, 1991; Gremillion and Wanielista, 2000; Ferguson et al., 2007). Alpine or high-latitude rivers may be ephemeral, driven mostly by isotopically depleted snow melt events (e.g. Friedman et al., 1992; Meier et al., 2013). Seasonal isotopic variations in rivers, nevertheless, can mirror annual variations in precipitation (e.g. Dalai et al., 2002; Lambs et al., 2005), but these variations are usually moderate compared to precipitation as a result of catchment buffering and the fact that the predominant source of riverine base flow often stems from relatively isotopic stable groundwater sources (Darling and Bath, 1988; Maloszewski et al., 1992; Kendall and Coplen, 2001; Dutton et al., 2005). Only a few systematic long-time series (> 5 yr) of monthly isotope sampling of rivers have been published. Those few which have been presented in detail (e.g. Danube River, Austria, 47 yr; Swiss and German Rivers, 30 to 36 yr; Parana River, Argentina, 5 yr) show great potential for identifying long-term hydrologic alterations and providing key scientific information for water resource assessments, since long-term isotope river data must ultimately record climatic trends and human impacts within a watershed.

In particular, differences in the timing and mixing of winter and summer precipitation runoff are observed in the variation of the river isotopic values over time. Moreover, dry and wet seasons as well as extreme precipitation events (Schotterer et al., 2010) or atmospheric oscillation cycles as the El Niño Southern Oscillation (ENSO) (Panarello and Dapeña, 2009) are revealed in riverine isotope records. In alpine catchments, the intensity and extension of hydropower reservoirs show important impacts on the natural seasonal isotopic amplitude, indicating e.g. the fluctuating mixing ratios of water sources due to reservoirs (Rank et al., 1998; Schotterer et al., 2010; Rank et al., 2014). Long-term patterns of isotopes in rivers generally correlate with that of precipitation, however the catchment signals may be delayed up to several years (Rank et al., 2014), or differ for rivers within a geographical region (Schotterer et al., 2010; Stumpp, 2015). Hence, long-term riverine isotopic series are key in providing scientific information for water managers and researchers to gain insights to study hydrological processes and better focus integrated water management strategies.

The isotopic composition of precipitation has been monitored for over 50 yr worldwide through the *Global Network of Isotopes in Precipitation (GNIP*), a joint initiative of the *International Atomic Energy Agency (IAEA)*, the *World Meteorological Organisation (WMO)*, and collaborating institutions as well as individuals (Rozanski et al., 1993; Aggarwal et al., 2010; IAEA/WMO, 2015). In order to fill isotopic data gaps between the well-known continental precipitation inputs to terrestrial landscapes and the aggregated and altered riverine discharges, a new Global Network of Isotopes in Rivers (GNIR) was initiated as part of the IAEA Water Resources Programme. GNIR began as a pilot project in 2002–2005, and focussed on the stable isotopes and tritium content of various world river catchments (Vitvar et al., 2007; Michel et al., 2014). The aim of the GNIR programme is to collect and disseminate time-series and synoptic collections of riverine isotope data from the world's rivers, and to inform a range of scientific disciplines including hydrology, meteorology and climatology, oceanography, limnology, and aquatic ecology.

HESSD
12, 4047–4079, 2015

The objective of this paper is two-fold: first, we formally introduce a new online database of riverine isotopes as the *Global Network of Isotopes in Rivers (GNIR)*, a publicly accessible database found at www.iaea.org/water (public release is under preparation). Second, having pre-populated the GNIR database with pilot, volunteered, and literature riverine isotopic data; we provide a first effort to analyse the spatial and isotopic patterns of GNIR sampling sites that are comprised of longer data series for δ^{18}O and δ^{2}H. This assessment will provide a first order global-scale perspective regarding (i) seasonal and local variations of the isotopic composition of river waters (ii) and to assess the comparative correlations and connectivity between the global isotopic variance in precipitation with that of river discharge.

Our meta-analyses provide a first overview of the potential for water stable isotopes to identify large-scale hydrologic processes in global rivers and to prove its application. With recent developments in low-cost laser spectroscopy techniques for conducting water isotope analysis, the widespread adoption of isotope tracers are now achievable in national river water quality monitoring programs (Kendall et al., 2010), as well as for aquatic ecological studies. We aim to demonstrate the benefits of routinely applying water stable isotopes as key tracers in evaluating hydrological processes in the worlds' rivers, and for the observation of short- as well as long-term climatic and human impacts.

2 Materials and methods

2.1 The GNIR database

GNIR relies upon voluntary partnerships with institutions and researchers for riverine sample collections and isotopic analyses, as well as upon contributions of published and unpublished data to the GNIR online database. The GNIR database comprises an electronic repository holding river water isotope and associated geographical and physio-chemical parameters, and is extended to include important water quality re-

HESSD
12, 4047–4079, 2015

lated isotopic parameters as well as other riverine isotopes. It is publicly accessible online through the web-based Water Isotope System for Data Analysis, Visualization and Electronic Retrieval (WISER) interface at www.iaea.org/water (public release is under preparation). For the inclusion of additional stations and technical details regarding GNIR catchment sampling and data structure, the reader is referred to the IAEA website.

2.2 Water isotope reporting

Stable isotopic analyses of river water samples were measured by the Isotope Hydrology Laboratory of the IAEA and a large number of external laboratories. Not all of the methodological procedures and metadata were recorded in the past, hence the reported analytical uncertainties for δ^2H and δ^{18}O were not always available. Because water samples were analysed by so many different laboratories, using different analytical methods over many years, analytical error can be assumed to be on the order of ±0.2 ‰ for δ^{18}O and ±2.0 ‰ for δ^2H. Nevertheless, all stable isotope measurements are expressed as δ value relative isotope-ratio differences, defined by the equation:

$$\delta X = [(R_A/R_{std}) - 1], \qquad (1)$$

where R_A and R_{std} are the isotope ratio of heavier and lighter isotope of the element X (e.g. ^{2}H/^{1}H, ^{18}O/^{16}O) in the sample and the international standard (Vienna Standard Mean Ocean Water, VSMOW), respectively. All water isotope δ values are reported in parts per thousand (‰) deviations from the international VSMOW standard.

2.3 Seasonal and local variations in the isotopic composition in river waters

We extracted and tabulated the δ^{18}O (δ^2H is strongly correlated but less frequently measured historically) isotope data for river stations having close to 2 yr of monthly time series data (minimum 5 samples per year), or 1–2 yr for geographical regions having poor spatial data coverage. The river water isotopic data evaluated were obtained

HESSD
12, 4047–4079, 2015

between 1960 and 2012. A map of all long-term GNIR sampling sites and a complete data table, including reference list, of the selected GNIR river stations used in this study are shown in the Supplement.

All river time series stable isotope data were averaged to depict monthly mean values (not discharge weighted due to missing flux data) over the measured time period. The selected GNIR station data were clustered by the timing of minimum δ^{18}O values and latitude, according to the flowchart in Fig. 1 the aim was to isotopically distinguish snow and glacier run-off dominated systems from direct precipitation and run-off dominated systems. Rivers were then grouped by δ^{18}O minima in late spring and summer due to the delayed seasonal snow and glacier-melt at higher altitudes (e.g. Meier et al., 2013). A second grouping was clustered by higher latitudes (> 30° latitude) and δ^{18}O minima in the winter months during lowest air temperature (Dansgaard, 1964). The last group comprises GNIR stations within a 30° N/S latitude band. Those were filtered based on the phase difference between the two low-latitude zones (N–S), that was about six months, according to Feng et al. (2009). The variation of the isotopic composition of tropical precipitation between ∼ 30° N and 30° S is determined by air temperature and by atmospheric circulation as the Inter Tropical Convergence Zone (ITCZ) (e.g. Yoshimura et al., 2003). Consequently, a best-fit model of the six-month phase difference (January to June and June to December) was used. After clustering, a least-square fitted sinusoidal function was applied to evaluate the periodicity of the δ^{18}O variations for all groups using the equation:

$$\hat{\delta}^{18}O = A[\sin(2\pi t + \Theta)], \quad (2)$$

where A = amplitude, t = lag time in years, and Θ = phase angle.

2.4 Comparing the isotopic compositions of world rivers to precipitation

To compare the variance of δ^{18}O in river water to precipitation, riverine isotopic seasonality was compared with precipitation isotope data. GNIR stations that were obviously snow and glacier-run-off dominated were excluded from this comparison, in

HESSD
12, 4047–4079, 2015

order to compare the direct relationship between precipitation and river run-off. Feng et al. (2009) evaluated selected GNIP precipitation data using a similar approach, however, in the present study we used GNIP data updated to 2013. Then, 567 GNIP and 218 GNIR stations with averaged (amount-weighted for GNIP) monthly δ^{18}O values were used for a direct comparison.

One major challenge comparing terrestrial rainfall inputs with point-based river isotope locations is the fact there are usually few GNIP stations distributed across watersheds, and they are rarely in locations that may be considered representative of all precipitation in a watershed. Some have proposed a mathematical models to derive the comparability of the isotopic composition of rivers to rainfall, but these models rely on discrete but sparsely distributed GNIP station data (Landwehr and Coplen, 2006). To overcome this GNIP coverage limitation, we used a catchment-constrained version of the regionalized cluster-based water isotope prediction (RCWIP) model based on GNIP data (Terzer et al., 2013). This catchment constrained model modification (CC-RCWIP) was used to obtain and estimate of the average amount-weighted isotopic composition of rainfall, encompassing only the upstream catchment of any selected GNIR river station. The upstream catchment delineations were taken from the HYDRO1K basins geospatial dataset (data available from the US Geological Survey). Unfortunately, the application of the method was restricted by catchment delineation (30 arc second DEM) and/or minimum catchment sizes of about 500 km^2. The grid cell size was about 20 km and therefore only basins encompassing ≥ 4 grid cells were included. The δ^{18}O values for catchment-constrained precipitation were calculated as the amount-weighted mean of all RCWIP grid cells falling within the upstream catchment boundary polygon of a GNIR station, after pre-determining basin membership by spatial selection (ArcGIS 10.2.2, ESRI, Redlands CA), on a monthly or annual basis. The model error for derived δ^{18}O catchment precipitation input values was on average ±1.1 ‰. In total, the CC-RCWIP method was applied to 119 GNIR stations and catchments. The detailed results are shown in the Supplement. Data for detailed sub-catchment studies were kindly provided by: Helmholtz-Zentrum Munich, Germany; Environment Agency Austria; Federal Office for the Environment, Switzerland; and Centre for Isotope Research, University of Groningen, the Netherlands.

3 Results and discussion

3.1 GNIR water stable isotope data holdings

Currently, the GNIR database contains about 2730 sampling sites for water stable isotopes from 56 countries, and covering all continents. The GNIR database covers rivers of all lengths and sizes, including lakes and reservoirs falling within the course of rivers. A review of the GNIR data holdings showed that most of the sampling sites were a part of longitudinal or synoptic river studies, since 2000 out of the 2730 GNIR sampling sites record only one water isotope sample taken (Fig. 2). The evaluation showed also that most published isotopic river studies are generally focussed on smaller regional or sub-catchments of national or regional interest, either as one-time synoptic surveys, or as one-point measurements in larger watersheds. Fewer still, are integrated riverine isotopic studies aimed at quantifying major catchment scale processes, including targeted sampling across all hydrograph stages (and under ice). For the few remaining large scale isotopic studies, sampling locations were often opportunistically based upon existing water quality monitoring programs, river access, or are one-time efforts, and therefore less informed by hydrological considerations (Kendall and Coplen, 2001; Hélie and Hillaire-Marcel, 2006; Ferguson et al., 2007). Rarer yet were riverine isotopic studies that extended beyond a 1–2 year effort, or across major geopolitical boundaries, or those involving a larger suite of isotopic assays (Kendall et al., 2010). However 235 GNIR stations had ≥ 2 yr of systematic sampling records. Most of the isotope studies in GNIR do not include additional parameters such as discharge, water temperature, electrical conductivity or other water chemistry.

HESSD
12, 4047–4079, 2015

3.2 Seasonal and local patterns of $\delta^{18}O$ in global rivers

The 235 GNIR river station subset could be clustered into 3 major groupings on the basis of the seasonal variations in their oxygen (or hydrogen) isotopic composition (Fig. 3). Sinusoidal best fit functions (Fig. 3 and Supplement) revealed periodic phases within each of these groupings and their sub-groups. Because most GNIR stations happen to be located in latitudes above 30° N, and mainly in Central and Northern Europe as well as North America, the largest river grouping was comprised of winter snow melt dominated systems. This group (A) could be further divided into two subgroups; subgroup (A.1) included river stations which were most ^{18}O depleted circa April, which suggested winter precipitation runs off as the spring freshet. These river stations were generally located in lowlands with seasonal winter snow cover, or those in peri-alpine headwaters. The second subgroup (A.2) included river stations that were most depleted in ^{18}O between May and August, which indicated that infiltration and transport of winter precipitation to rivers was considerably delayed. These river stations were those with primarily alpine and montane headwaters, or were located in arctic regions. Subgroup (A.2) had, on average, the lowest seasonal $\delta^{18}O$ amplitude of 1.4 ‰ (expressed as the difference of the highest and lowest monthly mean value, Fig. 4), which may be related to the fact that many of the alpine rivers sampled have artificial reservoirs or lakes in their headwater catchments. Thus seasonal variations were diminished by reservoir storage and mixing. For example, the lowest seasonal amplitude in $\delta^{18}O$ (0.2 ‰) of all GNIR stations was observed in the Aare River at Thun, Switzerland, a river in an alpine catchment where the sampling station was located following the outlet of a lake system. Moreover, snowmelt and glacier-meltwater dominated contributions with negative $\delta^{18}O$ values mixing with enriched summer precipitation can also suppress seasonal isotope amplitudes. This may explain why river stations whose hydrographs were dominated by early snow-melt, by comparison, had higher average seasonal amplitudes in $\delta^{18}O$ on the order of 2.0 ‰. Therefore, it can be stated that low to negligible seasonal isotopic amplitudes in rivers do not necessarily mean that

HESSD
12, 4047–4079, 2015

isotopically invariant groundwater baseflow contribution is the predominant source of discharge.

The second group (B) (Fig. 3) included river stations that closely charted the seasonal temperature curve of the higher latitudes of the Northern (B.1) and Southern (B.2) Hemispheres (NH and SH), and along with that, the seasonal variation of the isotopic composition of precipitation. This subgroup showed the importance of direct surface-runoff, and/or fractions of infiltrated water with relatively short residence times as groundwater. However, GNIR river stations of the temperate and higher latitudes without stored winter precipitation in spring or summer had relatively low seasonal amplitudes in δ^{18}O on the order of 1.9 ‰ (Fig. 4), indicating also important groundwater baseflow contributions with well mixed summer and winter precipitation.

Finally, stations located between ~ 30° N and 30° S, group (C) (Fig. 3), could be divided into two sub groups, (C.1) and (C.2) based on a 6 month isotope phase deviation. In general, these river stations followed not only air temperature, but also the phase of atmospheric moisture cycling which is co-determining the isotopic composition of precipitation in those latitudes (Feng et al., 2009 and references there within). In comparison to groups A and B, GNIR stations between ~ 0 and 30° N (C.1) had the highest average seasonal isotopic amplitudes for δ^{18}O on the order of 3.9 ‰. Therefore, secondary processes have increased the isotopic enrichment and depletion, and this could be attributed to the fact that these catchments were strongly influenced by pronounced dry and wet seasons. For example, the highest seasonal isotopic amplitude in δ^{18}O (10.2 ‰) was observed in the Bani River at Douna, Mali. The highest δ^{18}O values in the Bani River corresponded to the end of the dry season in May with extremely low flow, indicating enrichment in ^{18}O due to in-stream and watershed evaporation. Conversely, the lowest δ^{18}O value was observed in the Bani River in August, and corresponded to the beginning of the rainy season and movement of the ITCZ. Relatively negative δ^{18}O values in river water in this zone correlated with rainy seasons, since rainfall from air mass circulation of the Inter Tropical Convergence Zone (ITCZ) are typically more depleted in ^{18}O (e.g. Feng. et al., 2009), and the high proportion of

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

HESSD

12, 4047–4079, 2015

The Global Network of Isotopes in Rivers (GNIR)

J. Halder et al.

direct surface-run-off is not allowing isotopic averaging in the soils and baseflow. GNIR stations located between ~ 0 and 30° S had somewhat lower seasonal amplitudes in $\delta^{18}O$ on the order of 2.4 ‰; however this may be spatially biased since this group contained more stations in South America, where the dry and wet seasons are less pronounced.

Some GNIR river systems could be assigned to several of the previous groupings, depending on the location of the river stations within a large catchment, and the type of hydrological alterations occurring within that watershed, hydrograph stage, as well as the sampling season. However, some GNIR stations showed seasonal isotopic variations that were typical of headwater latitudes, but not the latitude of the downstream sampling station (e.g. Paraná River, Argentina). Stations in highland headwaters vs. downstream reaches may not reflect the same time period (due to time of travel delays). In some cases, the seasonal variation in $\delta^{18}O$ at downstream stations could be influenced by tributaries having a vastly different water history or isotopic composition than the main stem (e.g. mid-reach Danube River in Austria (Rank et al., 1997, 2014), or where upstream damming altered natural run-off patterns (e.g. Oldman River, Canada, Rock and Mayer, 2007). Only 17 of the 235 GNIR stations examined could not be classified into one of these 3 riverine isotopic groupings. These included those river stations located at the outlet of large natural lakes or artificial reservoirs.

The results showed that the deviations of $\delta^{18}O$ values from the model sinusoidal curves (Fig. 5) give insights into important river alterations and processes, for example: the freezing of upstream surface water, which changes the river runoff components in winter (e.g. Torne River downstream of Lake Torneträsk, Sweden, Burgman et al., 1981); the averaging of different water sources due to cumulative dam systems (e.g. Euphrates River, Syrian Arab Republic, Kattan, 2012 and Waikato River, New Zealand, Mook, 1982); or the mixing of evaporated water and reverse seasonal flow from the outflow of regulated reservoirs having long water residence times (e.g. Zambezi River downstream of Cahora Bassa Dam, Mozambique, Talma et al., 2012).

HESSD
12, 4047–4079, 2015

The Global Network of Isotopes in Rivers (GNIR)

J. Halder et al.

Despite the caveats, most rivers still reflected the seasonal variation of δ^{18}O values in precipitaton that was expected based on the topography and latitude of the river basin, even though nearly all of the worlds' rivers flow through some form of artificial or natural reservoir. Because the GNIR data consisted only of monthly averaged δ^{18}O values, and most stations had no discharge data, it can be surmised that a monthly grab sampling approach is likely the minimum sufficient to isotopically characterize a watershed and record long-term changes in hydrological processes within the watershed over time. The sinusoidal model curves may help to compare and validate measured isotopic compositions of any seasonal river case study. Even if the isotopic composition and variability of a selected river is unknown, the model curves allow one to predict the seasonal variation of δ^{18}O in river water. As isotopic peaks might also be related to stochastic or climatic events, like as flooding or atmospheric circulation (e.g. movement of the ITCZ or ENSO), valuable information may also be gained by scheduling higher frequency campaigns (e.g. Wyhlidal et al., 2014) especially during extreme periods. In addition, the minima and maxima of river isotopic values may help to apply water isotopes as tracers to study infiltration of river water into isotopically averaged groundwater, and local case studies may be conducted during such predicted isotopic peaks.

3.3 Comparison of water stable isotopes in precipitation and rivers

A crossplot of mean and amount-weighted GNIP data vs. available GNIR samples (not averaged or discharge weighted) on a δ^{18}O vs. δ^{2}H diagram (Fig. 6) showed that precipitation and river samples all lie along one global meteroric water line that is well-established for water isotopes (Craig, 1961). The seasonal amplitude of δ^{18}O in global rivers did not increase as a function of latitude, as it does for precipitation (Fig. 4). Although some GNIR stations at high latitudes (e.g. Lena, Ob, and Yenisei River stations, Russian Federation (66.5 to 69.4° N)), had seasonal δ^{18}O amplitudes above average, other stations at similarly high latitudes (e.g. Mackenzie River and Yukon River,

HESSD
12, 4047–4079, 2015

Alaska (67.4 and 61.9° N, respectively)) exhibited relatively small amplitudes, or were below average. In summary, the average annual seasonal $\delta^{18}O$ amplitude was 2.5 ‰ for rivers compared to 7.5 ‰ for precipitation (Fig. 4). More than half of the evaluated 235 GNIR stations had a seasonal $\delta^{18}O$ amplitudes below 2 ‰. Catchment size or river length did not correlate with the isotopic amplitude. This global diminished riverine seasonal response, in comparison to precipitation, showed that additional hydrological processes, catchment storage and natural reservoir mixing (e.g. lakes, groundwater), or man-made alterations modified the expected seasonal amplitude of $\delta^{18}O$ in some rivers, as discussed above (Sect. 3.2). In any case, the seasonal amplitude of $\delta^{18}O$ can be used as a tracer of hydrologic processes.

As noted, GNIR stations are clustered by a strong correlation between seasonal isotopic variability of $\delta^{18}O$ in precipitation and river water as a function of latitude (groups B and C). Feng et al. (2009) previously evaluated seasonal variation of GNIP precipitation data based on the timing of maximum isotopic values in relation to latitude. A comparison of the GNIR river data to updated GNIP precipitaton data (Fig. 7) affirmed their finding that there appear to be "four world zones of isotopic seasonality" which can be applied equally to rivers as to precipitation. Further, the latitudinal precipitation groupings around the equator, as well as ~ 30° N and S were observed in rivers and precipitation. This suggests that despite the fact that GNIR and GNIP data are only point measurements and originate from different time periods, the main seasonal signals of precipitation are reasonably well preserved and are visible in most river systems, even though the world's rivers are extensively modified by human impacts or impoundments.

While GNIP stations represent the isotopic composition of precipitation at a specific point location, GNIR stations integrate the cumulative hydrological processes of the upstream catchment. The application of CC-RCWIP allowed for the comparison of modelled amount-weighted isotopic precipitation inputs for upstream catchment precipitation ($\hat{\delta}^{18}O_P$) to measured riverine (not discharge weighted) isotopic compositions at the GNIR observation stations ($\overline{\delta}^{18}O_R$). The catchment-constrained model comparison revealed a strong correlation (R^2 = 0.88) across the world catchments between amount-weighted mean precipitation ($\hat{\delta}^{18}O_P$) and river water discharge ($\overline{\delta}^{18}O_R$) (Fig. 8). Of 119 GNIR river stations assessed, only 19 had $\overline{\delta}^{18}O_R$ and $\hat{\delta}^{18}O_P$ that deviated beyond the predicted CC-RCWIP model and analytical error (1.3 ‰). Of these, in 15 stations the CC-RCWIP predicted river discharge was more depleted in ^{18}O than was observed. The largest model vs. observed mean difference was 4 ‰ for the Salinas River catchment in Southern California, USA. For river stations where CC-RCWIP predicted $\delta^{18}O$ values that were more negative than observed, all were from arid regions, such as Western and South Africa, and the south-western USA. River water from two stations in Canada and Sweden located downstream of large lakes were also more enriched in ^{18}O than modelled precipitation for the upstream catchment. This analysis showed that direct comparison of CC-RCWIP modelled catchment inputs with measured riverine isotope data helps to reveal the important evaporation and hydrologic alterations within a catchment than can be accomplished by comparison with discrete GNIP stations, or mathematical models. GNIR stations for which CC-RCWIP predicted overly positive $\delta^{18}O$ values included mainly the alpine basins, such as rivers within the Indus watershed, the Rhône River, Switzerland, or arctic watersheds as the Lena River, Russian Federation. This indicates that stored water sources from permafrost, snow, and glacier melt-water, are comparatively important long-term contributors to the river-runoff in these catchments.

Finally, also the CC-RCWIP modelled seasonal amplitude of $\hat{\delta}^{18}O_P$ was not correlated to the seasonal amplitude of $\overline{\delta}^{18}O_R$, which confirmed the results from the direct comparison of GNIP and GNIR station data (Fig. 4).

3.4 GNIR data to calibrate isotope precipitation model(s)

To test the CC-RCWIP model as a tool to predict the expected isotopic composition of riverine discharges, the model was applied to regional and smaller water catchments that had exceptionally high GNIR and GNIP station isotopic data density, com-

HESSD
12, 4047–4079, 2015

pared to the overall global dataset (Fig. 9). In this example, two major European river catchments (Rhine and upper Danube River, Switzerland, Germany, and Austria) were selected. The results showed that CC-RCWIP correctly predicted the δ^{18}O isotopic composition of river discharge for all 12 GNIR river stations within a model and analytical error range of 1.3 ‰. The best fits (within 0.17–0.21 ‰ modelled vs. predicted deviation) were for 4 river stations located in peri-alpine and foreland sub-catchments. The CC-RCWIP model predicted slightly negative δ^{18}O values in the northern lowlands rivers (except station Rhine-Lobith) and slightly positive δ^{18}O values for most alpine headwaters and close after their confluence into main streams. This finding suggested isotope enrichment processes occurring due to evaporation in the lowlands, but greater contributions of stored glacier melt-water to the alpine catchments. However, the comparison of CC-RCWIP model to riverine results may allow us also to improve and validate the CC-RCWIP model calibration, since model vs. observed differences can also arise due to the underestimation of local atmospheric circulation effects (e.g. influence of the Gulf Stream or ITCZ) by the model. Moreover, CC-RCWIP grid is 10 arc minutes, which means the model spatial resolution may smooth out extreme elevations in the terrain models, which would potentially bias the prediction of towards positive δ^{18}O values in alpine watersheds. Such effects were e.g. observed by Kern et al. (2014).

In general, the CC-RCWIP model results showed that averaged δ^{18}O values in river water samples were strongly correlated with amount averaged precipitation in the upstream catchment of a river station. This finding underscores that the average isotopic composition of river water reflects amount averaged rainwater on a global scale. These model comparisons provide a comparative tool whereby isotopic deviations of rivers from average precipitation reveal natural or anthropogenic catchment impact effects. A comparison of modelled and measured data may also indicate the relative importance of stored watershed resources as ice, glaciers, old groundwater, or other important basin scale evaporation processes.

4 Conclusions

An evaluation of the IAEA GNIR database holdings of water isotopes in rivers revealed that seasonal variations in the stable isotopic composition of rivers are closely coupled to precipitation and to snow-melt water run-off on a global scale. This finding underscores the importance and advantages of combining long-term riverine isotope and precipitation data networks (GNIR and GNIP) to assess global and catchment water cycles as well as important environmental and human impacts. The results suggest that long-term observational time series in combination with modelling provide key scientific information for water managers and researchers to better study hydrological processes and impacts. Because the seasonal isotopic variability in river water is lower than that of precipitation, it can be stated that the isotopic composition of river water is likely more representative of the water used by plants and organisms within the watershed. The GNIR database may therefore become an additional valuable scientific resource, not only for hydrology, but also related disciplines focusing on isotope applications e.g. for ecological and paleoenvironmental studies. With the recent development of laser spectroscopy technologies for water stable isotope analysis, the approaches presented here are likely to be integrated within river quality, water quantity, and ecological studies. An increase in the number and spatial coverage of both GNIP and GNIR stations in areas of low spatial data coverage, and the downscaling of the IAEA CC-RCWIP model (or others) would also allow applying the presented methods to smaller local catchments within the future.

The CC-RCWIP model presented in this study allows a priori prediction of the seasonal variability as well as the average isotopic composition of stable isotopes in rivers. This predictive model capacity will help to improve and inform existing and new river sampling strategies, and help to validate and interpret riverine isotope data, and identify important catchment processes. Hence, the IAEA promotes and supports long-term hydrological isotope observation networks and the application of isotope studies complementary with conventional hydrological, water quality, and ecological studies.

HESSD
12, 4047–4079, 2015

We propose the GNIR database be further expanded using volunteer efforts to disseminate contributed and published time-series of riverine isotope data, which can eventually include a far broader suite of isotopic variables involving not only water, but a potential suite of water quality isotopic parameters such as dissolved constituents (e.g. ^{13}C-DIC/DOC), nutrients (e.g. ^{15}N and ^{18}O in NO_3), radioisotopes (e.g. ^{3}H, U), and sediments (e.g. ^{7}Li).

The Supplement related to this article is available online at doi:10.5194/hessd-12-4047-2015-supplement.

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HESSD
12, 4047–4079, 2015

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HESSD
12, 4047–4079, 2015

The Global Network of Isotopes in Rivers (GNIR)

J. Halder et al.

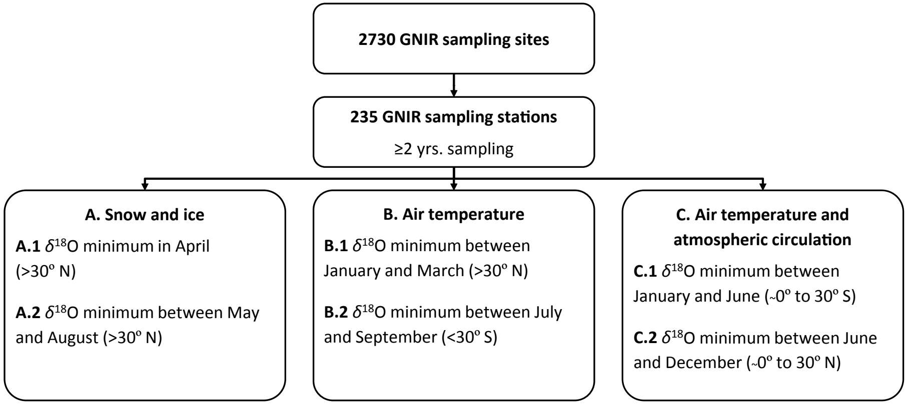

Figure 1. Flowchart of river grouping. The diagram illustrates the criteria used to cluster long-term GNIR stations (> 2 yr) into 3 major and 3 sub-groups, based on their stable isotopic patterns.

HESSD
12, 4047–4079, 2015
The Global Network of Isotopes in Rivers (GNIR)
J. Halder et al.

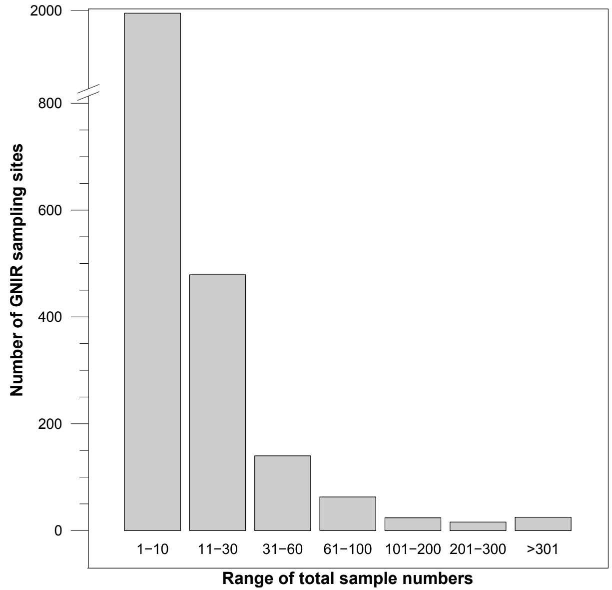

Figure 2. GNIR station and sample statistics. Frequency histogram of GNIR sampling sites (*y* axis) (1960–2012), and the number of water isotope samples per sampling site (*x* axis).

HESSD
12, 4047–4079, 2015

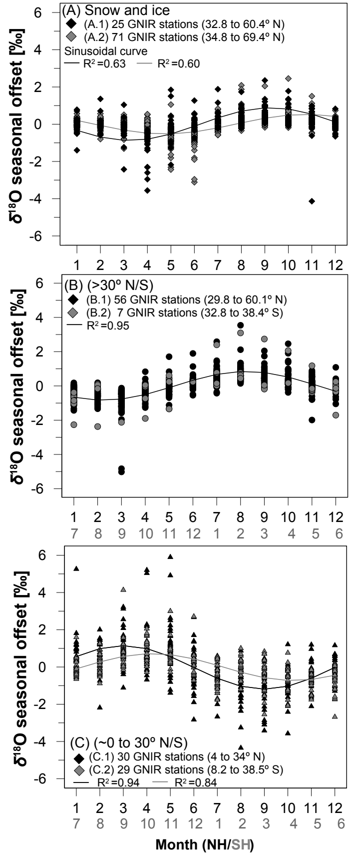

Figure 3. Seasonality of $\delta^{18}O$ in different river systems. Seasonality clustering, based on the isotopic data, showed that stations could be divided into 3 major and 3 sub-groups. To normalize $\delta^{18}O$ values, the seasonal variations were plotted as the offset from the mean annual value (zero ‰) for each station. A sinusoidal fit function was applied to the river stations within each sub-group. No sinusoidal curve was calculated for the small group (B.2).

HESSD
12, 4047–4079, 2015

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀◀ ▶▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

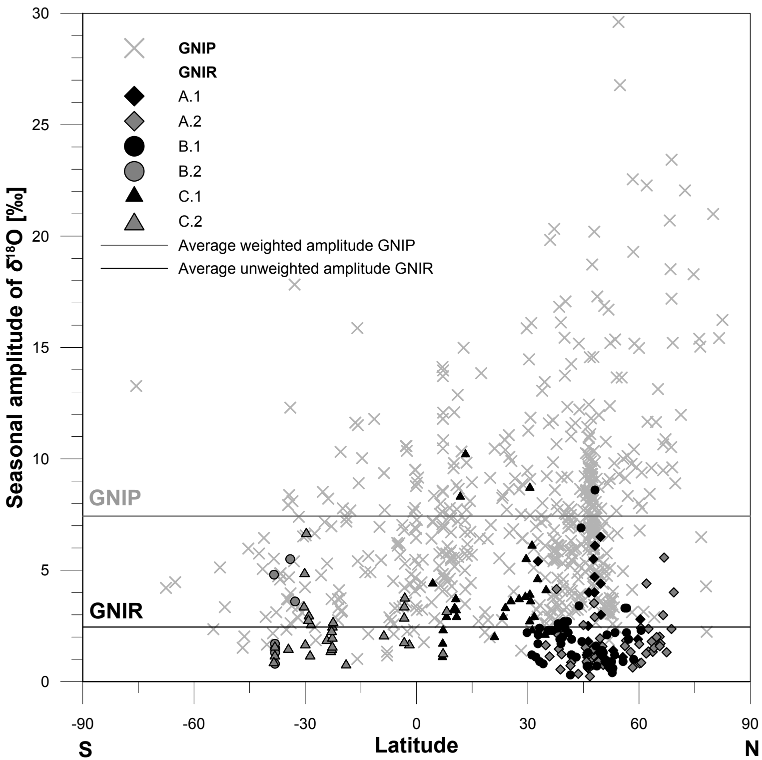

Figure 4. Seasonal amplitude of δ^{18}O in rivers. The seasonal isotopic amplitude, expressed as the difference of the highest and lowest monthly mean value, against the latitude of the river station, for GNIR river groups (diamond, circle and triangle symbols) and for precipitation (GNIP, cross symbol).

HESSD
12, 4047–4079, 2015

The Global Network of Isotopes in Rivers (GNIR)

J. Halder et al.

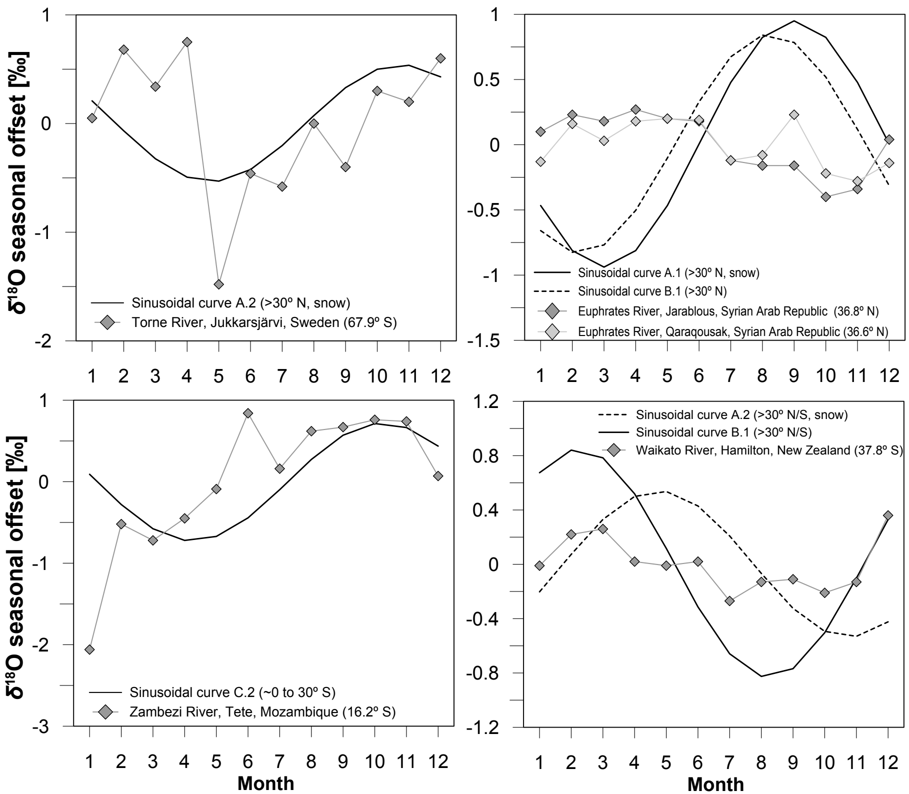

Figure 5. Seasonality of $\delta^{18}O$ in reservoir influenced river systems. Hydrologic alterations and natural lakes affected the predicted seasonality of $\delta^{18}O$ in different river systems. The figure shows examples of GNIR stations for which seasonality of $\delta^{18}O$ deviated significantly from the sinusoidal curve expected based upon the station latitude and topography. Case study data were taken from Burgman et al. (1981) (Torne River); Kattan (2012) (Euphrates River); Talma et al. (2012) (Zambezi River); Mook (1982) (Waikato River).

HESSD
12, 4047–4079, 2015

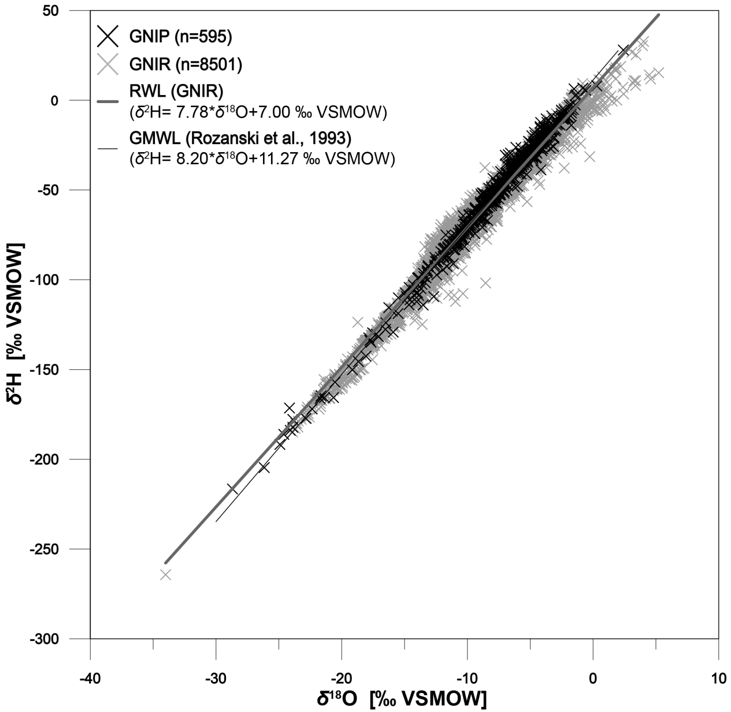

Figure 6. GNIR vs. GNIP. Comparison of all available GNIR water samples (un-weighted, grey crosses) and amount-weighted average GNIP data (black crosses).

HESSD
12, 4047–4079, 2015

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J. Halder et al.

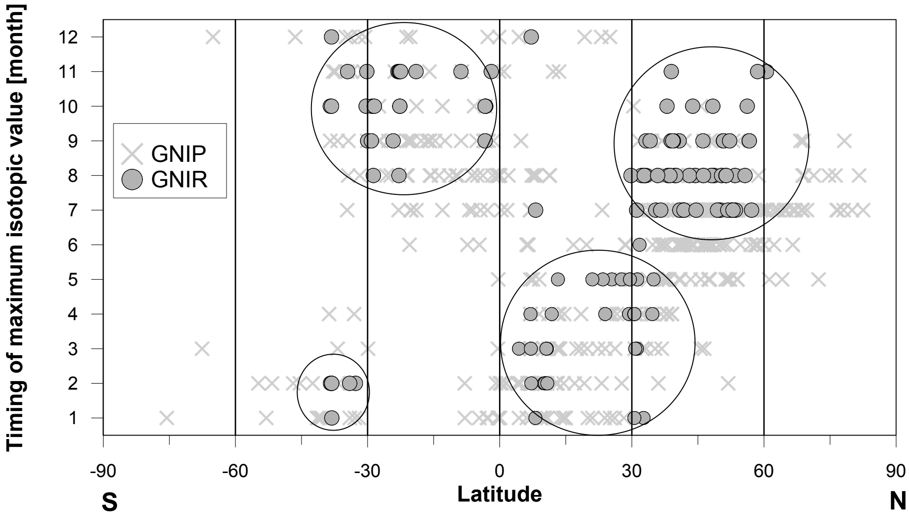

Figure 7. Isotopic seasonality of GNIR compared to GNIP stations. 567 GNIP and 218 GNIR stations with averaged (amount-weighted for GNIP) monthly δ^{18}O values used for a direct comparison of latitude (x axis) and timing of maximum isotopic value (y axis), revealing "four world zones (large circles) of isotopic seasonality".

HESSD
12, 4047–4079, 2015

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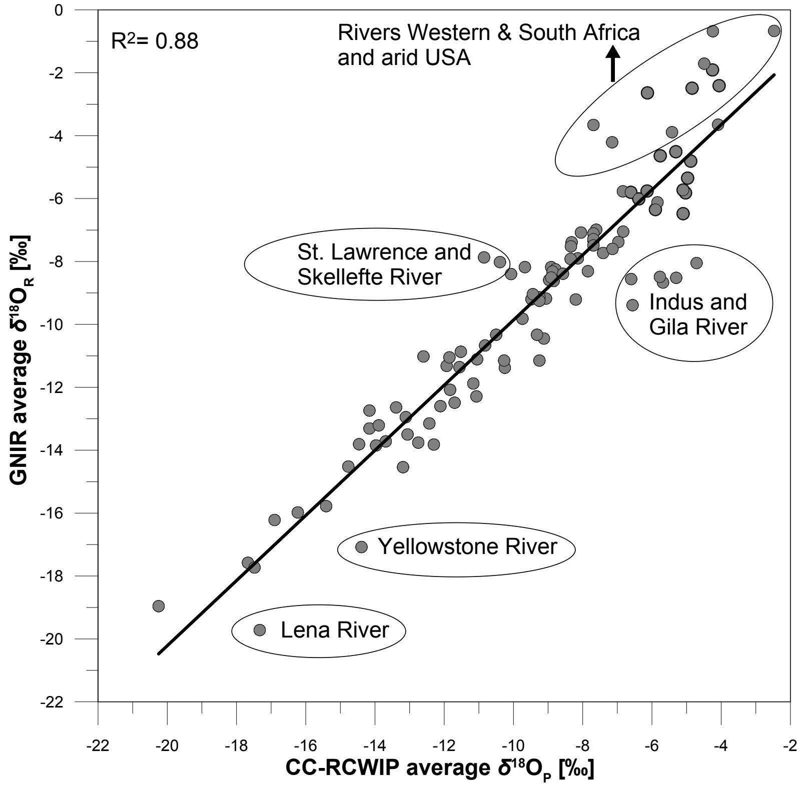

Figure 8. Comparison CC-RCWIP model and GNIR data. This figure depicts the comparison between the predicted amount-weighted upstream catchment precipitation ($\hat{\delta}^{18}O_P$) against measured (un-weighted) isotopic composition at the GNIR river observation stations ($\overline{\delta}^{18}O_R$).

HESSD
12, 4047–4079, 2015

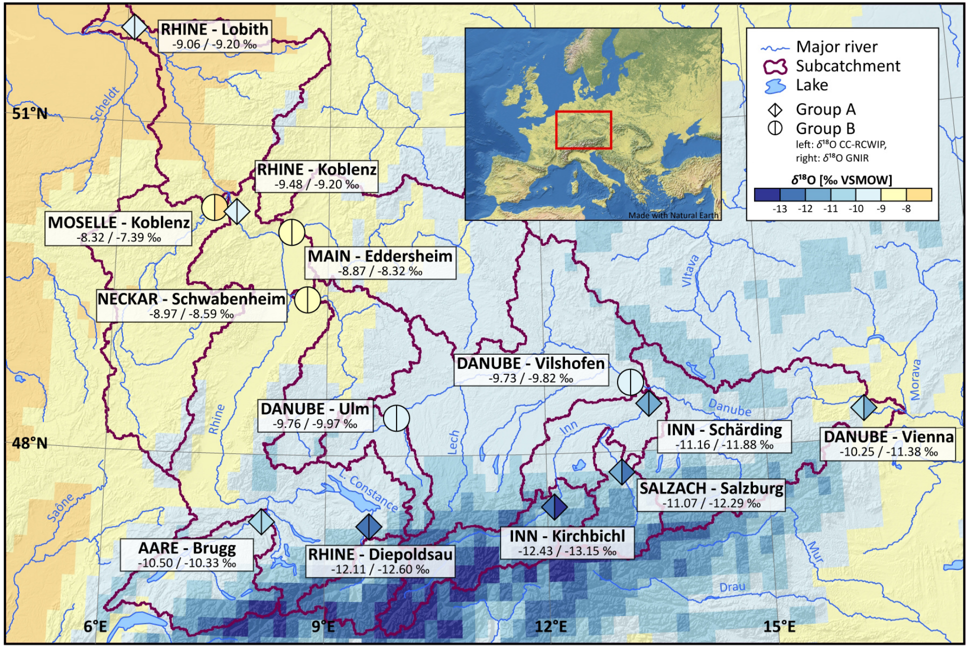

Figure 9. Catchment Isoscapes for the Rhine and upper Danube River. This figure compares the modelled and amount-weighted isotopic input contributions of the entire upstream catchment precipitation to measured (un-weighted) isotopic compositions at the GNIR river observation stations. Case study data were kindly provided by: Helmholtz-Zentrum Munich, Germany; Environment Agency Austria; Federal Office for the Environment, Switzerland; and Centre for Isotope Research, University of Groningen, the Netherlands.