To the editor:

All changes which were addressed and suggested were done and are tracked in the revised manuscript. Additional typing and grammar errors were corrected. Answers regarding the editor's comments, below.

Anonymous Referee #1

We thank the referee for the comments. Please find our answers below:

General comment and comment 2: The GNIR groups were clustered by the timing of minimum δ18O values and latitude (see p. 4054L6-9). The sinusoidal function was applied after the clustering in order to evaluate correlation and periodicity within each group (see p. 4054L19-21). Snow cover, air temperature or atmospheric circulation was not analysed. We have later given the groups a classification title, which refers to the major process determining its seasonal isotopic variation (See p. 4057 L8-10, 14-15; p. 4058L3-6, 12-16). We agree the titles may be confusing, especially in the method section, and we delete the titles from the flow chart and Fig.3. We will evaluate the phase/angle cross plot as suggested.

Comment 3: We will evaluate the suggested function. We have not observed such a bimodal seasonality in any of the data series we evaluated.

To the editor: We have waited for the editor comments to revise/evaluate certain issues. Please find the answers regarding the editor comments below:

It was evaluated that the application of different sinus functions can slightly increase or decrease the fitting of the function. However, these changes are insignificant and in this case the objective was only to demonstrate that a sinus function can be applied and illustrates the periodicity. We decided therefore to keep our approach as it serves mainly for illustration.

In this study we did not evaluate in depth, how far the delay between maxima and minima d18O (phase shifts) values provides information of groundwater residence time, transport delay, travel time etc. in an individual system. We consider that a more detailed evaluation of certain systems with long and coherent time series may provide insights. In this case a phase/angle plot may provide also additional information. We consider making a further separate study going here in more detail of selected case studies. In reference to the current study we have already evaluated the amplitude of the systems (Fig. 4) as well as the timing of maxima d18O values (Fig. 7). A phase/angle plot of the applied functions shows no correlation and does not add more information.

Specific points:

P4048L6: deleted periodic

P4053L25: There are geographical regions like the USA and Central Europe where there is a dense coverage of long data series. Here, it is permissible to exclude data series, which show gaps or are relatively short and work with the best available datasets. In regions like South America, Asia, and Africa isotopic measurements are very rare and rivers may carry even no water in the dry season.

Here it deems necessary to work with all available time series to perform a global assessment. We added ”…geographical regions having poor spatial data coverage (South America, Africa, and Asia).”

P4054L4-19: See answer for general comment and comment 2.

P4054L12: The occurrence of minimum and maximum δ18O in relation to temperature is well understood for precipitation. We refer here to existing knowledge and publications and a general approach. Temperature data were not analysed.

P4054L19-23: We do not use the phase to cluster and subset the data, only the timing of minimum δ18O values and latitude (See also answer for general comment and comment 2.). The analysis of the amplitude confirms later that the different groups have also distinguished amplitudes.

P4054L25: By “seasonality” we refer to the variation of monthly means (1 to 12) at a GNIR station. We will define seasonality as “variation of monthly mean values” in the text.

To the editor: Done

P4054L27: The occurrence of minimum δ18O values in summer is generally known to be related to snow and glacier melt water run-off (p. 4050L16-18; 4054L9-11). It could be also delayed winter precipitation run-off due to residence time in groundwater but we verified that all those stations are located in catchments with significant snow cover in winter.

P4055L19: The limiting factor in terms of the grid cell size is the RCWIP isoscape resolution (which is 10 arc minutes, roughly translated into ca. 20 km at the equator [and of course less with increasing latitude]) – i.e. the space between 4 grid cell centerpoints is already 400 km2. We found it fairly misleading to derive predictions from the iscoscape on a number of cells smaller than that; hence the threshold of 500 km2 is certainly arbitrary. We will rephrase this accordingly. As for the HYDRO1K dataset, we don’t question its spatial resolution but we found its object attributive granularity (i.e. the subcatchment levels available) quite variant. In any case, the catchments excluded from this analysis were rather small.

To the editor: Rephrased: Unfortunately, the application of the method was restricted by the resolution of the RCWIP grid (cell size of 10 arc minutes, ca. 20 km at the equator). As a minimum, albeit arbitrary threshold catchment size, we defined 500 km2 or ≥ 4 grid cells.

P4055L26: The model error is not relative to GNIP but the error includes also analytical errors of GNIP data.

P4057L10: We have no GNIR stations in the SH, which have an alpine or arctic catchment. We expect the same or similar variations.

P4058L3: We want to underline here that the seasonal curve progression of temperature and the isotopic composition are nearly identical.

P4058L4: We refer here to a generally well known average temperature curve in the discussed latitudes.

P4058L10: Yes, we meant here “by comparison” (see 4057L26)

P4060L10: We mean here that the sinusoidal curve, calculated on existing data from several rivers of similar latitudes, can help to predict or verify the seasonal variation (e.g. approximate timing of minimum and maximum δ18O values; magnitude) in any river of similar latitude or topography.

P4060L20: We will rephrase to: "A δ18O vs. δ2H diagram comparing GNIP data (mean and amount-weighted isotopic values) and GNIR samples (not averaged or discharge weighted) showed…"

To the editor: Done

P4060L24: We will calculate and include r2 (correlation of latitude vs. amplitude) for GNIP and GNIR

To the editor: Done. No mathematical correlation found. Rephrased: Although there was no coherent correlation, the seasonal amplitude of δ18O in global rivers did not increase with latitude, as it was in average observed for precipitation (Fig. 4). This was related to the different spatial distribution of precipitation and river observation stations (coastal/continental), but also hydrological processes.

P4061L11: We agree that in principle it would be desirable to correlate variations over time in the isotopic composition of precipitation and rivers. However, this approach demands spatially and temporally coherent GNIP and GNIR datasets; a known generic issue of past isotopic data records. For this reason we chose a rather simplified approach, last but not least to outline this deficit.

P4071F1: (see answer for general comment and comment 2)

P4072F2: We show a range not a number. Measurement is not correct, as one sample could be measured several times. We suggest rephrasing to "sample per site".

P4073F3: We have not evaluated sinusoidal functions for GNIP as this has been evaluated in detail by others (e.g. Feng et al., 2009).

P4077F7 and P4078F8: We use the same symbol for GNIP (grey cross) in Fig 4 and 7. We used a different symbol for GNIR in Fig. 6 and 7 to better point out the results. Fig. 8 we plot a new correlation not addressed before. However we will assess whether the reviewer's suggestions enhance clarity for Fig. 7.

To the editor: Done. Symbols were changed and unified.

Anonymous referee #2

We thank referee for the review and comments. Please find our answers below:

Specific comments 1: The objective was to analyse the variation of water isotopes in rivers and to compare its variation to isotopes in precipitation. The variation of water isotopes in precipitation is well understood and described in several publications, whereas river water isotope data have not been analysed on a global scale; this is novel. We refer to the Feng et al. study, as that study focuses on local and seasonal variation on a global scale and we did not want to repeat GNIP interpretations. Any data and interpretation of the Feng. et al. study used in our publication is cited.

We added “It was assumed that the seasonal and local variation of the isotopic composition of river water is closely coupled to the well understood regional and continental isotopic variance in precipitation (Rozanski et al., 1982; Rozanski et al. 1993; Rozanski et al. 1996; Araguás-Araguás et al., 1998; Bowen and Wilkinson, 2001; Feng et al., 2009).”

Specific comment 2: The database and its structure are further explained on the IAEA WISER website. We will consider giving an overview about the detailed data structure in the supplemental materials.

To the editor: Rephrased and added: The GNIR database is structured as a relational database allowing to query on a number of attributes, particularly on spatial and temporal attributes. All data for GNIP and GNIR can be downloaded in CSV or Microsoft Excel ® flat files, cost-free, to registered users. For the inclusion of additional stations and technical details regarding GNIR catchment sampling, and data structure, and quality assessment of data, the reader is referred to the IAEA website (www.iaea.org/water).

Specific comment 3: Repetition was reduced.

Specific comment 4: in the abstract around page 4055, we do not address the difficulties of the dataset (not resolvable since many data were contributed) but the challenge was to compare the GNIP and GNIR datasets (See p. 4055L6-9). This explains why catchment constrained modelling was applied.

Specific comment 5: The study included watersheds of all sizes. A correlation between catchment size and e.g. d18O amplitude was not found. We agree long-term studies can also help to evaluate transit times or estimate baseflow contributions. Evaluation of transit and residence time is beyond the scope of this publication, due to the spatially and temporally heterogeneous data situation.

Technical comment 1: We will increase the font size – suggest tackling this issue during editing for the final HESS paper.

To the editor: Done

Technical comment 2: Revised.

Technical comment 3: Replaced “analyses” with “compositions”

Technical comment 4: Delete the “a” mathematical models.

Technical comment 5: The sentence was shortened: “This catchment constrained model modification (CC-RCWIP) was used to estimate the average amount-weighted isotopic composition of rainfall in the upstream catchment of a selected GNIR station”.

Technical comment 6: Rephrased to “Moreover, snowmelt and glacier-meltwater dominated contributions with relatively negative 18O values, mixing with enriched summer precipitation, can also suppress seasonal isotope amplitudes.”

Referee G. Bowen

We would thank Gabriel Bowen for the review and comments. Please find our answers below:

General comment: Additional important publications, which were pointed out and contributed to the existing knowledge as well as methods were added.

Specific comments:

4050L3-4: Added

4052L1-4: The database now publicly released (web link provided).

4060L14: Added

4061L3-4: Changed

4061L12: Changed

4062L15-20: We agree that lower measured d18O values in comparison to modelled d18O values do not necessarily require contributions from ice as of the problematic of model calibration. This is discussed p.4063L15-19. However, glacier melt water and permafrost are well known contributors in alpine and arctic rivers and therefore we expect such a signal in the isotopic composition of those river systems. We added: “The importance of glacier meltwater in those river systems was also evaluated by non-isotopic studies (e.g. Immerzeel et al., 2010; Huss et al., 2011). Especially in ungauged catchments but also in addition to quantitative studies this method may therefore be applied to evaluate glacier or permafrost contributions or observe winter/summer runoff ratios, as proposed by Bowen et al. (2011)”.

Moreover, also long-term GNIR stations with automated discharge weighted sampling (The Swiss dataset from BAFU, e.g. Rhone River), for which we can exclude the problematic of runoff ratios, showed such results. Moreover, for the RCWIP prediction, precipitation amount weighting functions (for each month of the year as well as for the grid cell) were used.

4063L11: See answer above.

4063L22-23: We rephrased to: “This finding underscores that the average isotopic composition of river water reflects amount averaged rainwater on a global scale, as it has been evaluated regionally for the United States by Fekete et al. (2006) and Bowen et al. (2011)”.

The differences between modelled and measured isotope composition pointed out by Bowen et al. (2011) is primarily related to the sampling frequency, averaging, and errors in the modelling component, not to the fact that the averaged isotopic composition of river water is in general significantly different to that of averaged amount weighted upstream precipitation.

4063L26-28: Added

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

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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 δ^{18}O in rivers averaged 2.5 ‰, and did not increase as a function of latitude, like~~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 compositions 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 human 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 >5M km^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 ($^{18}O/^{16}O$, $^2H/^1H$) 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 (^2H, ^{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 reveals ~~shows~~ that longitudinal δ^{18}O and δ^{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 δ^{18}O and δ^{2}H values in the downstream direction. Rivers that are hundreds of kilometres long may therefore have distinctive upstream versus 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; Bowen et al., 2011). Alpine or high-latitude rivers may be ephemeral, dominated~~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 y) of monthly isotope sampling of rivers have ever been published. Those few which have been presented in detail (e.g. Danube River, Austria, 47 yrs; Swiss and German Rivers, 30 to 36 yrs; Parana River, Argentina, 5 yrs) 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 for example~~e.g.~~ the fluctuating mixing ratios of water sources due to reservoir storage and release~~s~~ (Rank et al., 1998; Schotterer et al., 2010; Rank et al., 2014). Long-term patterns of isotopes in rivers generally correlate with that of local 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 time series are key to~~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 years 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 to the sea, 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.

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 https://nucleus.iaea.org/wiser ~~www.iaea.org /water (NOTE: THIS SERVER IS NOT YET ENABLED PENDING REVIEW)~~. 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~~ provides a first order global-scale perspective regarding i) seasonal (variation of monthly mean values) 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. It was assumed that the seasonal and local variation of the isotopic composition of river water would be closely coupled to the isotopic variance in precipitation.

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 stable isotope tracers are now achievable in many national river water quality monitoring programs (Kendall et al., 2010), as well as in~~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

The 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 was recently~~is~~ extended to include important water quality related isotopic parameters as well as other riverine isotopes. GNIR~~It~~ is publicly accessible online through the web-based Water Isotope System for Data Analysis, Visualization and Electronic Retrieval (WISER) interface at https://nucleus.iaea.org/wiser~~www.iaea.org/water~~. ~~(NOTE: THIS IS NOT YET ENABLED PENDING REVIEW).~~ The GNIR database is structured as a relational database allowing to query on a number of attributes, particularly on spatial and temporal attributes. All data for GNIP and GNIR can be downloaded in CSV or Microsoft Excel ® flat files, cost-free, to registered users. For the inclusion of additional stations and technical details regarding GNIR catchment sampling, ~~and~~ data structure, and quality assessment of data, the reader is referred to the IAEA website (www.iaea.org/water).

2.2 Water Isotope Reporting

Stable isotopic compositions~~analyses~~ of river water samples were measured at~~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 at~~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 years of monthly time series data (minimum 5 samples per year), or 1-2 years for geographical regions having poor spatial data coverage (e.g. South America, Africa, and Asia). The river water isotopic data evaluated were measured~~obtained~~ 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 Supporting Information.

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. It was assumed that seasonal and local variations of the isotopic composition of river water were closely coupled to the well understood regional and continental isotopic variance in precipitation (Rozanski et al., 1982; Rozanski et al. 1993; Rozanski et al. 1996; Araguás-Araguás et al., 1998; Bowen and Wilkinson, 2001; Feng et al., 2009). The first aim, however, 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 comprised~~s~~ 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 was~~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:

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

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 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. Subsequently~~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 was~~is~~ the fact there were~~are~~ usually few GNIP stations distributed across watersheds, and they were~~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 or were applied regional (Landwehr and Coplen, 2006; Bowen et al., 2011). 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 estimate~~obtain and estimate of~~ the average amount-weighted isotopic composition of rainfall in the upstream catchment of a selected GNIR station~~, 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 U.S. Geological Survey).~~ Unfortunately, the application of the method was restricted by catchment delineation (30arc second DEM) and/or minimum catchment sizes of about 500 km^2.~~ Unfortunately, the application of the method was restricted by the resolution of the RCWIP grid (cell size of 10 arc minutes, ca. 20 km at the equator). As a minimum, albeit arbitrary threshold catchment size, we defined 500 km2 or ≥ 4 grid cells. ~~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 successfully applied to 119 GNIR stations and catchments. The detailed results are tabulated~~shown~~ in the Supporting Information. Data for the 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, 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 recorded only one water isotope sample taken (Fig. 2). The evaluation showed also that most published isotopic river studies were~~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, were~~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 yrs of systematic sampling records. Most of the isotope studies in GNIR did~~o~~ not include additional parameters such as discharge, water temperature, electrical conductivity or other water chemistry.

3.2 Seasonal and local patterns of δ^{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 Supporting Information) revealed periodic phases within each of these groupings and their sub-groups. Because most GNIR stations happened 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 δ^{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 discharge controlled~~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 δ^{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 relatively negative δ^{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 on ~~higher~~ average higher seasonal amplitudes in δ^{18}O on the order of 2.0 ‰. Therefore, it can be stated that low to negligible seasonal isotopic amplitudes in rivers did~~o~~ not necessarily mean that isotopically invariant groundwater baseflow contribution was~~is~~ a~~the~~ predominant source of discharge, as is often assumed.

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

Some GNIR river systems could be assigned to several of the previous groupings, depending on the location of the river station~~s~~ within a larger 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 versus downstream reaches may not reflect the same time period (due to time of travel delays). In some cases, the seasonal variation in δ^{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; Rank et al. 2014), or where upstream damming had 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 beyond~~at~~ the outlet of large natural lakes or artificial reservoirs.

The results showed that the deviations of δ^{18}O values from the model sinusoidal curves (Fig. 5) ga~~i~~ve 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).

Despite all of the above 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 flowed 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 could~~an~~ be surmised that a monthly grab sampling approach is likely the minimum sufficient to isotopically characterize a watershed and to 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 were~~is~~ unknown, the model curves could 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 of targeted higher frequency campaigns (e.g. Berman et al., 2009; 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 the 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 δ^{18}O vs δ^{2}H diagram (Fig.6) comparing GNIP data (mean and amount-weighted isotopic values) and GNIR samples (not averaged or discharge weighted) showed ~~A crossplot of mean and amount-weighted GNIP data versus 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). Although there was no coherent correlation, t~~T~~he seasonal amplitude of δ^{18}O in global rivers did not increase with ~~as a function of~~ latitude, as ~~it~~ in average observed~~does~~ for precipitation (Fig. 4). This was related to the different spatial distribution of precipitation and river observation stations (coastal/continental), but also hydrological processes. For example, a~~A~~lthough 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, Alaska (67.4 and 61.9° N, respectively) exhibited relatively small amplitudes, or were below average. In summary, the average annual seasonal δ^{18}O amplitude was 2.5 ‰ for rivers compared to 7.5

‰ for precipitation (Fig. 4). More than half of the 235 evaluated ~~235~~ GNIR stations had ~~a~~ seasonal δ^{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 δ^{18}O in some rivers, as discussed above (3.2). In any case, the seasonal amplitude of δ^{18}O can clearly be used as a tracer of watershed hydrologic processes.

As noted, GNIR stations were~~are~~ clustered by a strong correlation between seasonal isotopic variation~~bility~~ of δ^{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 precipitation data (Fig. 7) affirmed their finding that there appears to be “four world zones of isotopic seasonality” which could~~an~~ 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 suggested~~s~~ 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 so 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 precipitation input and 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 ($\bar{\delta}^{18}O_R$). 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 ($\bar{\delta}^{18}O_R$) (Figure 8). Of 119 GNIR river stations assessed, only 19 had $\bar{\delta}^{18}O_R$ 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 versus observed mean difference was 4 ‰ for the Salinas River catchment in Southern California, USA. For river stations where CC-RCWIP predicted δ^{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 a direct comparison of CC-RCWIP modelled catchment inputs with measured riverine isotope data further helps to reveal ~~the~~ important evaporation and hydrologic alterations within a catchment than can be accomplished by comparison with discrete GNIP stations, or by mathematical models. GNIR stations for which CC-RCWIP predicted overly positive δ^{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 indicated~~s~~ that stored water sources from permafrost, snow, and glacier melt-water, were~~are~~ comparatively important long-term contributors to the river-runoff in these catchments. The importance of glacier meltwater in those river systems was also affirmed by non-isotopic studies (e.g. Immerzeel et al., 2010; Huss et al., 2011). Especially in ungauged catchments, but also in addition to quantitative studies, this method may be applied to evaluate glacier or permafrost contributions, or observe winter/summer runoff ratios, as proposed by Bowen et al. (2011).

Finally, ~~also~~ the CC-RCWIP modelled seasonal amplitude of $\hat{\delta}^{18}O_P$ was not correlated to the seasonal amplitude of $\bar{\delta}^{18}O_R$, 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 an exceptionally high GNIR and GNIP station isotopic data density, compared to the overall global dataset (Fig. 9). For~~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 occurred~~ing~~ 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 prediction to riverine results may allow us ~~also~~ to improve and validate the CC-RCWIP model calibration, since model versus 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, the 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, for example,~~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 underscored~~s~~ that the average isotopic composition of river water reflected~~s~~ amount averaged rainwater on a global scale, as was also observed regionally evaluated also regional for the United States by Fekete et al. (2006) and Bowen et al. (2011). These model comparisons provided a comparative tool whereby isotopic deviations of rivers from average precipitation revealed natural or anthropogenic catchment impact effects. In general, a~~A~~ comparison of modelled and measured data may ~~also~~ indicate the relative importance of stored watershed resources as ice, glaciers, old groundwater, or as demonstrated by Jasechko et al. (2013) ~~other~~ important basin scale evaporation and transpiration 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 were~~are~~ closely coupled to precipitation and to snow-melt water run-off on a global scale. This finding underscoreds~~s~~ 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 suggested 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 was~~is~~ lower than that of precipitation, it can be stated that the isotopic composition of river water was~~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 increasingly 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 these ~~presented~~ methods to smaller local catchments ~~with~~in the future.

The CC-RCWIP model presented in this study allows for an *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 aid in identifying 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. 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).

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Figures

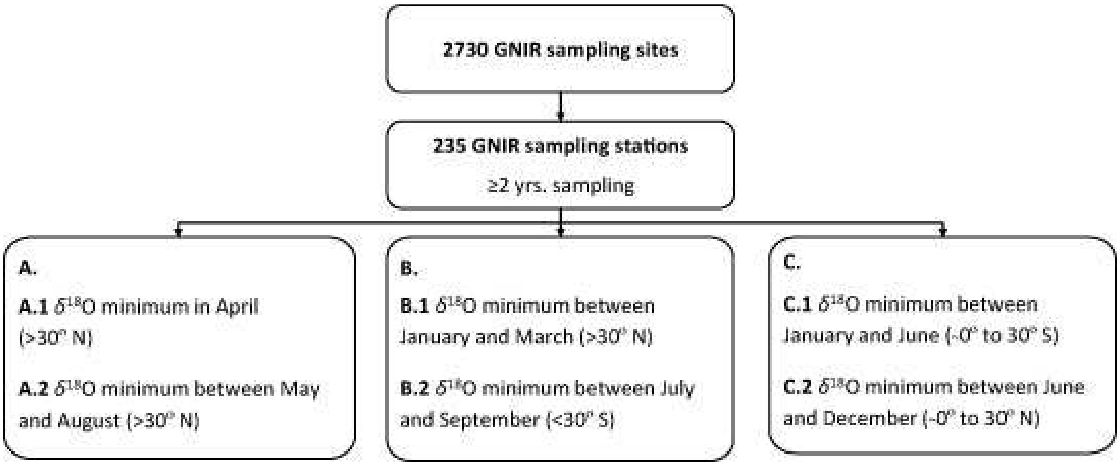

Fig. 1 Flow chart of river grouping

The diagram illustrateds the criteria used to cluster long-term GNIR stations (>2 yrs) into 3 major and 3 sub-groups, based on their stable isotopic patterns.

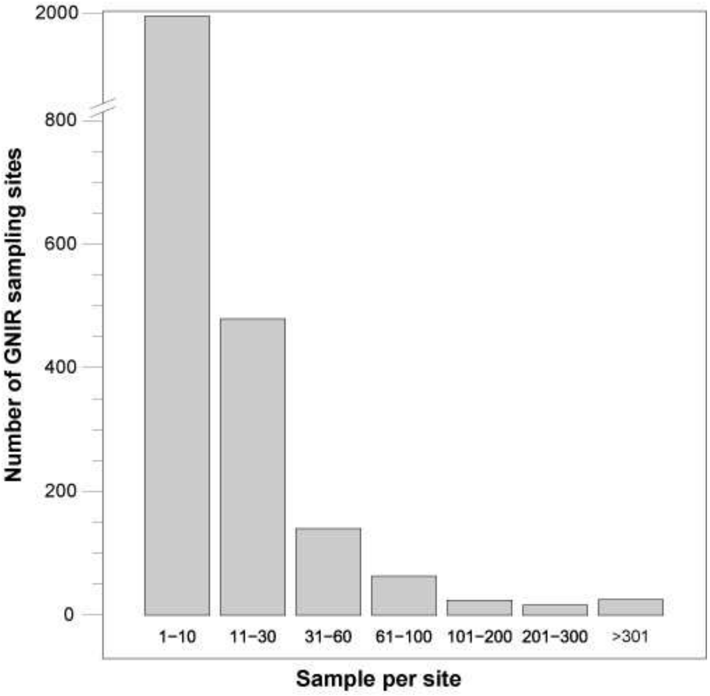

Fig. 2 GNIR station and sample statistics.

Frequency histogram of GNIR sampling sites (y-axis) (1960-2012), and the number of water isotope samples per sampling site (x-axis).

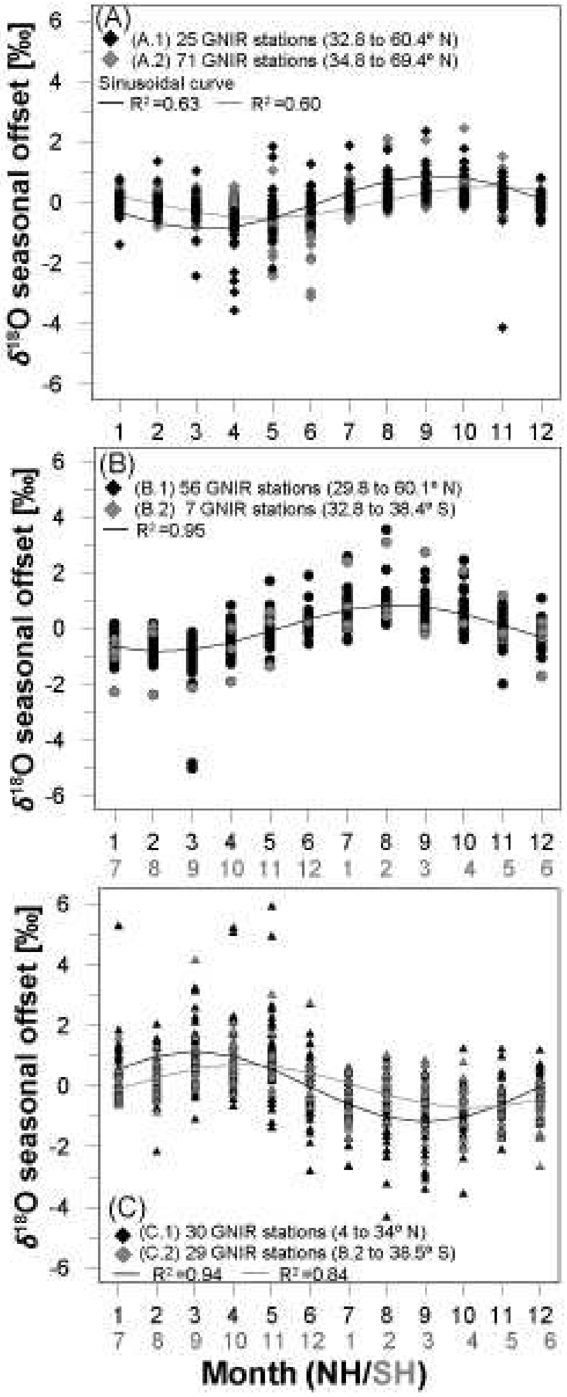

Fig. 3 Seasonality of δ^{18}O in different river systems

Seasonality clustering, based on the isotopic data, showed that stations could be divided into 3 major and 3 sub-groups. To normalize δ^{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).

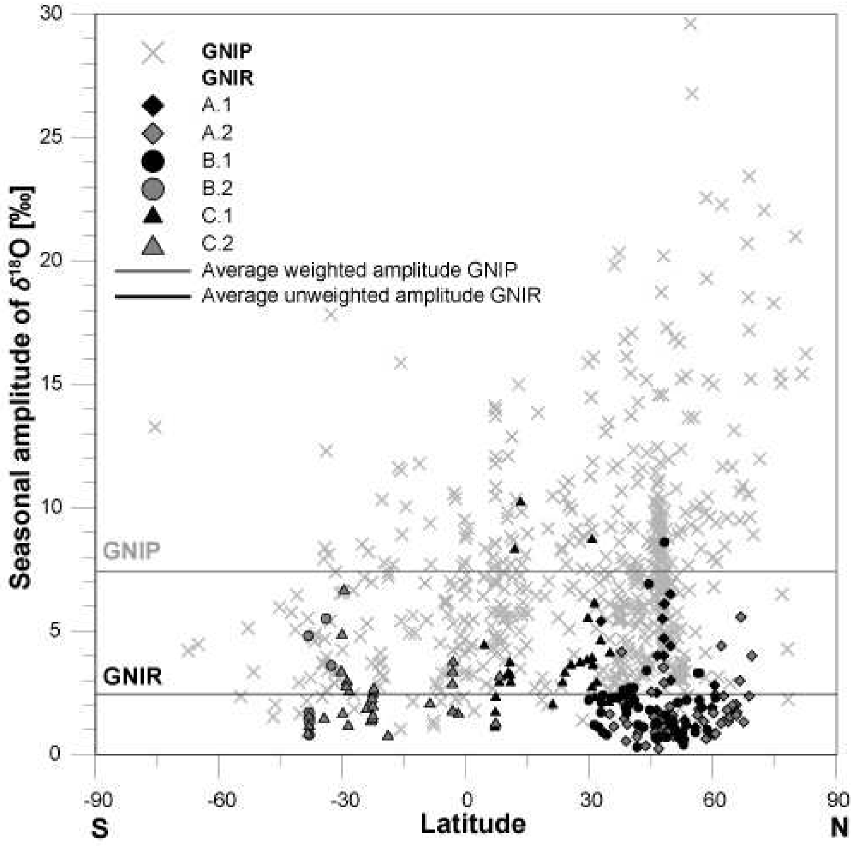

Fig. 4 Seasonal amplitude of δ^{18}O in rivers

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).

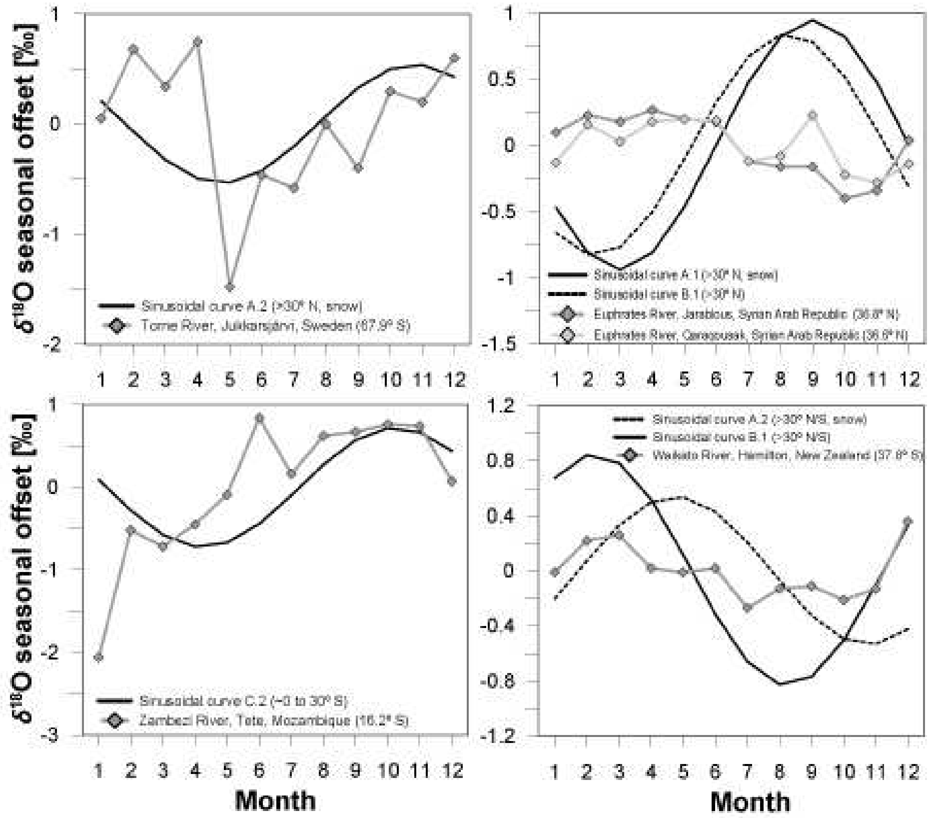

Fig. 5 Seasonality of δ^{18}O in reservoir influenced river systems

Hydrologic alterations and natural lakes affected the predicted seasonality of δ^{18}O in different river systems. The figure shows examples of GNIR stations for which seasonality of δ^{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).

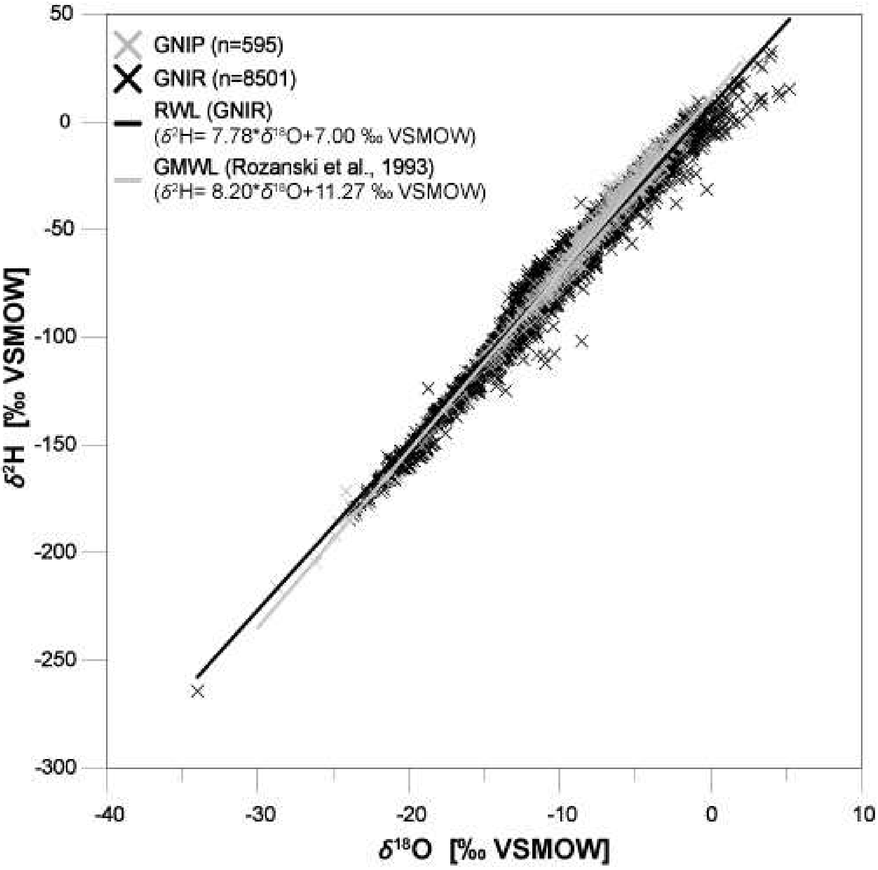

Fig. 6 GNIR vs GNIP

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

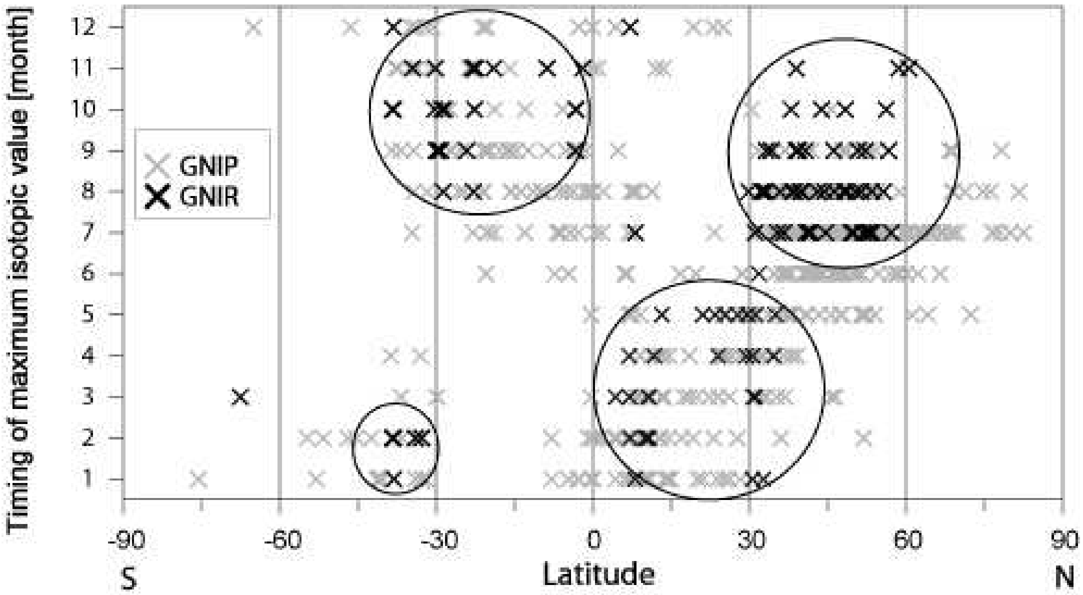

Fig. 7 Isotopic seasonality of GNIR compared to GNIP stations

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”.

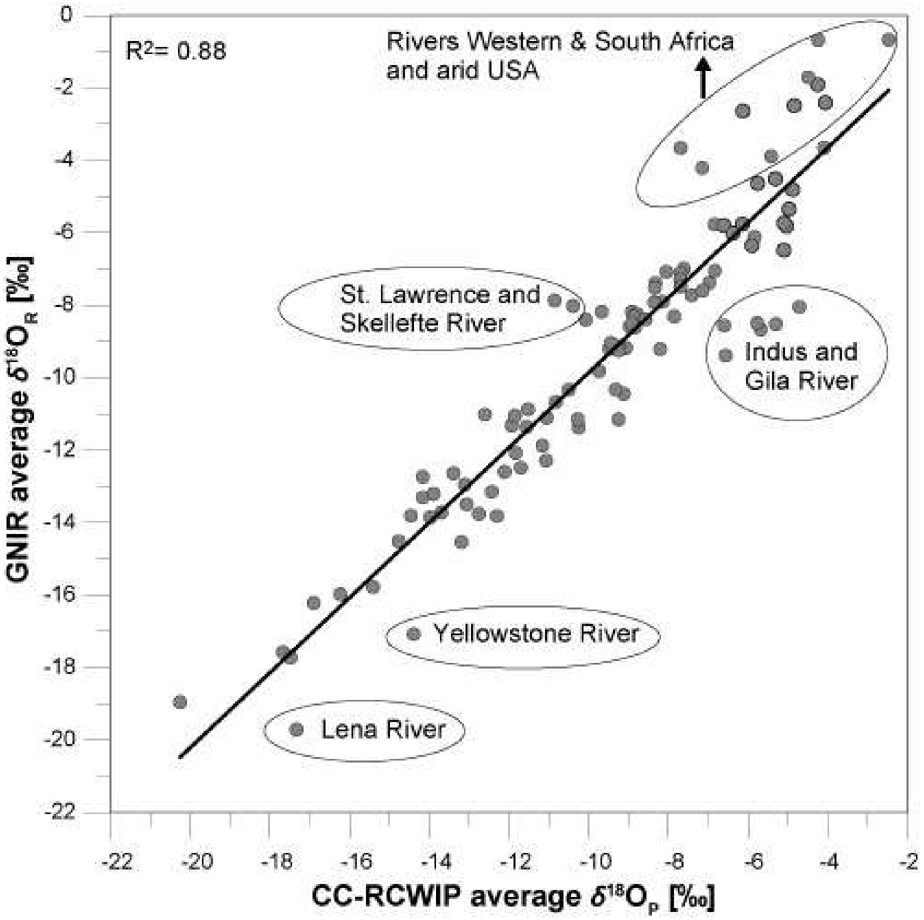

Fig.8 Comparison CC-RCWIP model and GNIR data

This figure depicted~~s~~ 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 ($\bar{\delta}^{18}O_R$).

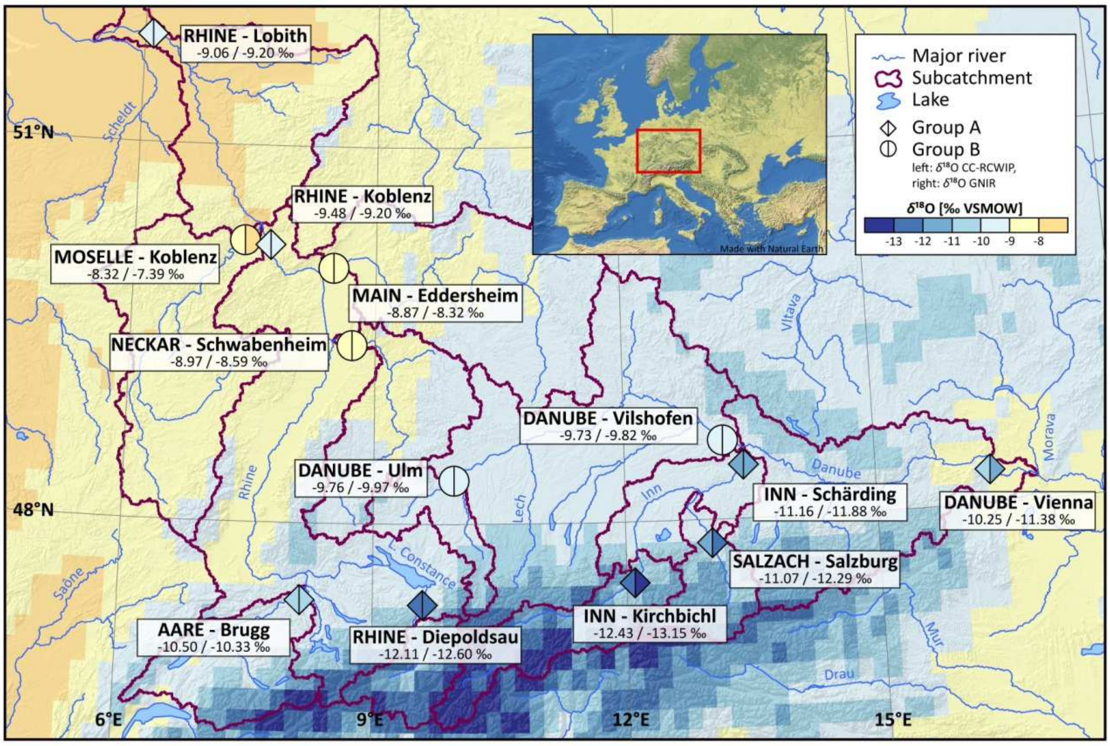

Fig. 9 Catchment Isoscapes for the Rhine and upper Danube River

This figure compareds 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, Netherlands.