

RESEARCH ARTICLE

Isotope hydrology and water sources in a heavily urbanized stream

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Abstract

Complex networks of both natural and engineered flow paths control the hydrology of streams in major cities through spatio-temporal variations in connection and disconnection of diverse water sources. We used spatially extensive and temporally intensive sampling of water stable isotopes to disentangle the hydrological sources of the heavily urbanized Panke catchment (~220 km²) in the north of Berlin, Germany. The isotopic data enabled us to partition stream water sources across the catchment using a Bayesian mixing analysis. The upper part of the catchment streamflow is dominated by groundwater (~75%) from gravel aquifers. In dry summer periods, streamflow becomes intermittent in the upper catchment, possibly as a result of local groundwater abstractions. Storm drainage dominates the responses to precipitation events. Although such events can dramatically change the isotopic composition of the upper stream network, storm drainage only accounts for 10%–15% of annual streamflow. Moving downstream, subtle changes in sources and isotope signatures occur as catchment characteristics vary and the stream is affected by different tributaries. However, effluents from a wastewater treatment plant (WWTP), serving 700,000 people, dominate stream flow in the lower catchment (~90% of annual runoff) where urbanization effects are more dramatic. The associated increase in sealed surfaces downstream also reduces the relative contribution of groundwater to streamflow. The volume and isotopic composition of storm runoff is again dominated by urban drainage, though in the lower catchment, still only about 10% of annual runoff comes from storm drains. The study shows the potential of stable water isotopes as inexpensive tracers in urban catchments that can provide a more integrated understanding of the complex hydrology of major cities. This offers an important evidence base for guiding the plans to develop and re-develop urban catchments to protect, restore, and enhance their ecological and amenity value.

KEYWORDS

ecohydrology, end member mixing analysis, isotopes, urban hydrology, wastewater

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1 | INTRODUCTION

With over 50% of the world's and 70% of Europe's population now living in cities, many key global challenges revolve about the sustainable management of urban water (United Nations, 2019). This is likely to lead to different priorities for urban water management, with various stakeholders, such as water supply and sewage disposal agencies, industrial users and local citizens having competing demands that local governance agencies have to mediate to maintain the quantity and quality of urban water bodies (Brears, 2016). However, quantitative understanding of the complex water sources and flow paths that sustain urban water bodies is often lacking compared to other environments. Urban streams and other water bodies are variously used as sources of water supply and a means of drainage and disposal of effluents (Gücker et al., 2006; House et al., 1993; Paul & Meyer, 2001); as well as being perceived as a potential hazard in terms of flood risk and pollution from effluents (Kundzewicz et al., 2014). Consequently, urban water systems are usually heavily managed with a range of complex infrastructure to control abstractions, stormwater drainage and effluent disposal. Further, in older cities, urban water has often been subject to an evolutionary history over centuries of ever-changing management decisions as societal needs and priorities have varied (Hassan, 2011; Winiwarter et al., 2016).

The inevitable decrease in catchment permeability – as built-up areas expand – leads to higher surface runoff in urban streams, mostly routed via stormwater drains and combined sewers, therefore reducing net-infiltration, and, thus, groundwater recharge (Arnold & Gibbons, 1996), mobilizing pollutants on roads and other urban surfaces (Brinkmann, 1985). This often increases connectivity with untreated wastewater in combined sewers that leads to episodic pollution from organic waste and pharmaceuticals (Klein et al., 2015; Komínková et al., 2016; Launay et al., 2016). However, the exact sources of pollutants, from either combined sewers or wastewater treatment plants (WWTPs) can be difficult to identify (Lee et al., 2010). In addition, urban infrastructure also includes other less obvious zones of subsurface connectivity via trenches carrying utility cables and pipelines, giving analogies to natural dual-flow hydrological systems and use of the term “urban karst” (Bonneau et al., 2017). Urban catchments can thus be conceptualized as a complex “spider's web” of highly connected water sources, combined with more disconnected areas in often extensive areas of urban green space (e.g., parks, gardens, urban forests, urban wetlands, etc.). Understanding the integrated interaction between different components of the engineered system and natural flow paths in urban green spaces is thus fundamental to understanding urban hydrology in an holistic way (Gessner et al., 2014).

Improving hydrological process understanding in urban areas requires integrating tools that provide insight into both large- and small-scale spatio-temporal variability in catchment function. In this regard, stable isotopes offer outstanding potential as natural tracers in urban hydrology (Ehleringer et al., 2016). The use of stable isotopes ratios of $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ within the water molecule has been applied in many investigations to trace precipitation through different

types of hydrological systems and at different scales to understand flow paths and the mixing dynamics of precipitation with water already stored in the catchment (Birkel et al., 2011; Soulsby et al., 2011; Soulsby et al., 2015a). Although urban studies are notably underrepresented in the isotope hydrology literature, this is rapidly changing. Recent studies have used isotopes to assess how urbanization affects the age distribution and travel times of runoff (Dimitrova-Petrova et al., 2019; Grande et al., 2020; Morales & Oswald, 2020; Soulsby et al., 2014; Soulsby et al., 2015b) and the dynamic influence of different water sources on the urban hydrograph (Jefferson et al., 2015; Pellerin et al., 2008). Additionally, Jefferson et al. (2015) used stable isotopes to investigate stormwater control measures and to assess their effects on event contributions.

The composition of tracers in streams and potential source waters can be used to separate the hydrograph into relative contributions from different sources with contrasting tracer characteristics (e.g., recent rainfall, groundwater and others). This was formalized in end member mixing analysis (EMMA) (Christophersen & Hooper, 1992) which, alongside other means of hydrograph separation, have proved valuable tools in isotope hydrology that have been widely used (He et al., 2020; Klaus & McDonnell, 2013). Preliminary studies have shown potential for source apportionment in urban areas: with tracers variously being used to disentangle tap water sources on a national scale (Bowen et al., 2007; West et al., 2014), or locally within a state or city (Jameel et al., 2016; Sánchez-Murillo et al., 2020; Tipple et al., 2017), providing a viable method for waterworks to understand their distribution system (Jameel et al., 2016). Furthermore, Houhou et al. (2010) and Kracht (2007) used distinct stable isotope signatures to identify sources within wastewater sewers, while Grimmeisen et al. (2017) used isotopes to understand groundwater contamination due to leaking sewers. Still, how the wider urban hydrological cycle is affected by integration of natural runoff sources, urban drainage and treated effluents is rarely investigated quantitatively through tracers (Follstad Shah et al., 2019; Kuhlemann et al., 2021b; Torres-Martínez et al., 2020).

Similarly, estimating metrics of water ages, such as mean transit times (MTTs), has proven insightful in isotope hydrology as a tool for assessing flow paths and mixing interactions in catchments. This is based on using the damping and lagging of the precipitation isotope time series in the rainfall-runoff transformation with lumped convolution integral models (McGuire & McDonnell, 2006; Tetzlaff et al., 2018), ensemble hydrograph separation (Kirchner, 2019) or more sophisticated tracer-aided hydrological models that track water and solute fluxes and their associated ages (Birkel & Soulsby, 2015; Douinot et al., 2019; Kuppel et al., 2018). Urban streams can integrate very young waters (<1 day old) as rainfall is routed via storm drains in rainfall events (Soulsby et al., 2015b), together with much older water (>decades) that recharges groundwater through urban green spaces (Gillefalk et al., 2021; Kuhlemann et al., ; Nouri et al., 2019). However, in urban areas where significant volumes of effluents are introduced into streams, there are conceptual difficulties in defining water ages, especially if wastewaters are derived from local sources and have similar isotopic signatures (Kuhlemann et al., 2021b). In such cases,

assessing the influence of recent rainfall in streamflow is possible by estimating the contribution of the young water fraction (YWF) to runoff (Kirchner, 2016a, 2016b). This is a simple method for quantifying the quick flow response of catchments based on the YWF, which is the contribution of water less than ~ 2 months old to the stream hydrograph. The method provides only a relatively coarse metric of complex age distributions, though it gives insight into the dynamics of catchment runoff responses and provides an index for inter-comparison studies (von Freyberg et al., 2018).

The motivation for this study is to apply isotopic methods in a complex, heavily urbanized catchment to understand the spatio-temporal dynamics of water sources contributing to streamflow. For this, we focus on the Panke catchment in Berlin, the capital city of Germany. The catchment has a long and ongoing history of urban development and a highly engineered water management system. However, the way in which this interacts with undeveloped areas in the catchment is poorly understood. Also, although the catchment is well-monitored hydrometrically and most effluent discharges are known, complex groundwater-surface water interactions affect the catchment water balance in a spatially variable way. Thus, tracers offer a means to disentangle effects of natural discharge, storm sewers and effluents. To do this, we collected daily precipitation and stream samples over 15 months, in conjunction with seasonal, spatially distributed synoptic sample surveys. This provided the data to achieve the following specific aims:

1. To characterize the short-term hydrological dynamics of outflow from the Panke catchment and its isotopic composition in relation to time-variant sources of streamflow.
2. To characterize the spatial and temporal variation in the isotopic composition of the stream network in relation to changes in the dominant sources of streamflow.

Our results also highlight more general insights into the opportunities and challenges for using isotopes in urban hydrological studies.

2 | STUDY SITE

The Panke catchment (220 km²; Figure 1) is located in the State of Brandenburg and Berlin in northeast Germany and forms the dominant surface water drainage of the northern part of the city of Berlin (Figure 1a,b). Much of the catchment is urban (Table 1). The Panke drains a fairly flat area that naturally ranges from 35 to 90 m a.s.l. with an average slope of 1.8%. Climatic conditions reflect both maritime and continental influences: the average annual precipitation is ~ 590 mm and the mean annual temperature is 9.5°C (1981–2010) (DWD & (Deutscher Wetterdienst), 2020). Rainfall is fairly evenly distributed between winter and summer, though the winter is dominated by longer low-intensity frontal rain, whilst summer experiences more high intensity, convective storms. The region is drought-sensitive and in 2018, Berlin only received ~ 420 mm of rainfall. During 2019

and 2020, annual precipitation was 589 mm and 513 mm, respectively (DWD, 2021).

The Panke is an effluent-impacted tributary of the River Spree, which flows into the River Havel downstream of Berlin (Kuhlemann et al., 2020). The river morphology class according to the German Water Framework Directive is between 5 and 7 (where 1 is least impacted and 7 is most heavily impacted) (Senate Department for Urban Development and the Environment, 2012). The Panke originates in the North and flows ~ 30 km in a south-westerly direction to the Spree. The catchment's headwaters are located on the northern edge of the Warsaw-Berlin glacial spillway which drained from Poland to the River Elbe (Figure 1c). The geology consists of >100 m of Quaternary deposits (Limberg & Thierbach, 2002). These form a series of aquifers in Berlin and the surrounding area; the aquifer terminology used is the same as Limberg and Thierbach (2002). For the Panke catchment, two main geological units form the shallow aquifer (AQ1) (Figure 1c). AQ1.1 is the sub-aquifer in the Barnim plateau (in the East) which is partially confined by an overlying ground moraine. The shallow "Panke aquifer" (AQ1.2), dominates the main river valley and is unconfined and characterized by sands and gravels above an aquitard of glacial till. The main aquifer beneath Berlin is AQ2, which is confined below the aquitard in the Panke (Limberg et al., 2007). The general direction of groundwater flow is south-west along the slope of the Barnim plateau, the main recharge area. Once the main glacial valley is reached, the groundwater flow is oriented to the South (Senate Department for Urban Development and Housing, 2019a). Berlin and Brandenburg's aquifers have been investigated using long-residence time tracers such as tritium and helium, showing decadal to centuries old water dominating the upper storage of unconfined aquifers, whilst deeper waters could be millennial (Bednorz & Brose, 2017; Massmann et al., 2009).

The North of the catchment has around 30% urban cover (Table 1) but is unaffected by large effluent discharges (Figure 1d). Typical for such lowland areas in northern Germany, streamflow generation is primarily groundwater dominated (Smith et al., 2021) with seasonally varying inflows from headwater tributaries with non-urban (forested and agricultural) land use. During our investigation, the stream was observed to emerge from a managed urban-wetland and lake. Despite this, flows can be intermittent in the upper reaches of the stream network during the summer which might reflect seasonal variation in storage and effects of local groundwater abstractions for garden irrigation (Jasechko et al., 2021; Kleine et al., 2021). In this area, there is one waterworks with three main well galleries taking groundwater from the deeper confined AQ2 aquifer. It assumed by local government that this does not affect flows in the headwaters due to the confining layer (Figure 1d).

Within the lower catchment, the more densely urbanized area is characterized by increasing densities of roads and stormwater drains that discharge during rainfall events (Figure 1d, Table 1). Around 26.5 km² of the Panke catchment is connected to Berlin's rainwater drainage system; this includes 13.6 km² of sealed surface (Senate Department for Urban Development and Housing, 2018). The

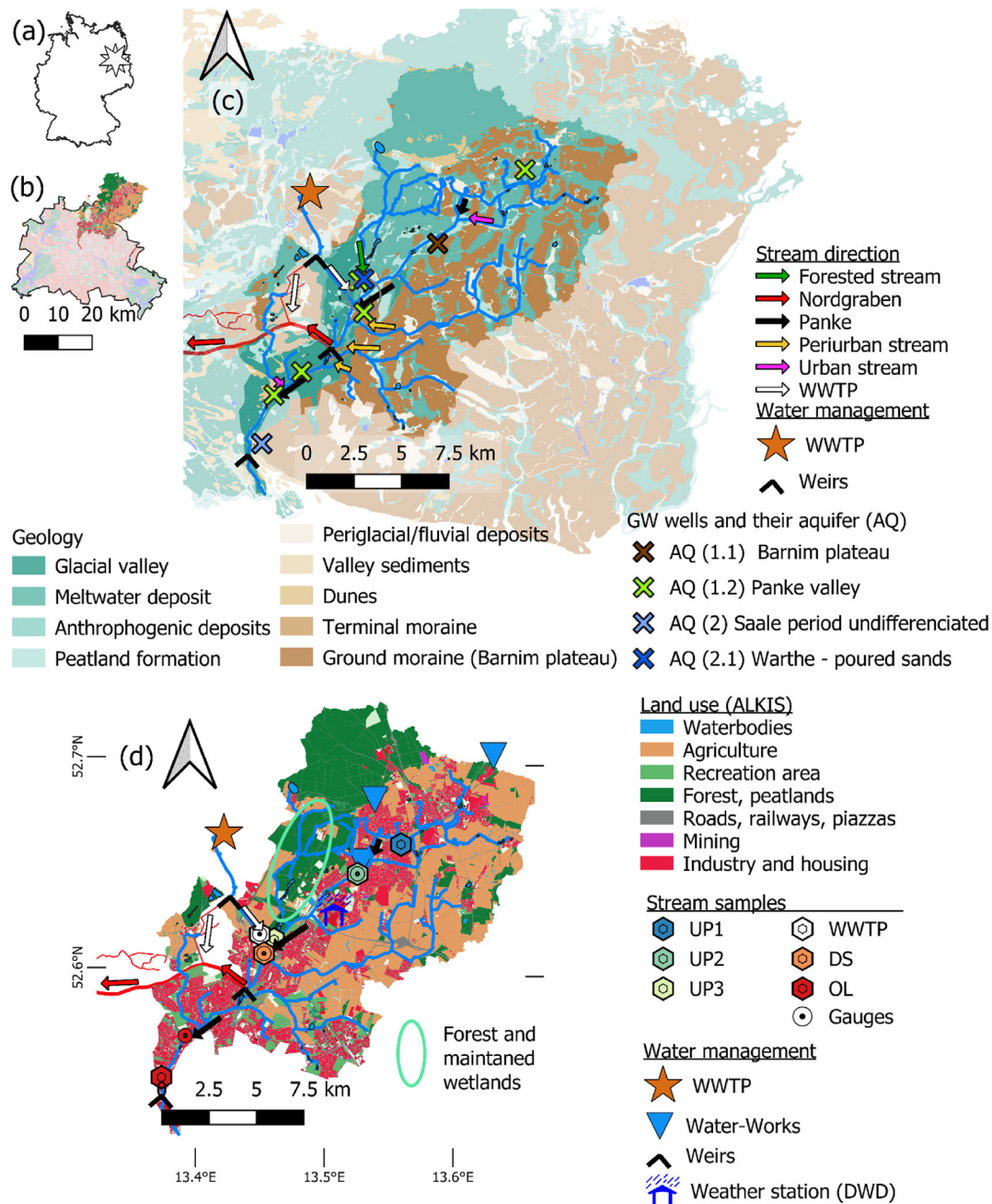


FIGURE 1 Overview of site locations. (a) and (b) show the location in Germany and related to Berlin, respectively (c) Geology map (LBGR, 2020) showing groundwater (GW) monitoring wells related to aquifers (AQ); (d) Land use map of the Panke catchment (modified Basemaps: (Landesvermessung und Geobasisinformation Brandenburg (LGB), 2020; Umweltatlas Berlin/ALKIS, 2020); stream sampling locations of the regular stream isotopic surveys upstream the wastewater treatment plant (WWTP) (UP1, UP2, UP3), downstream the WWTP (DS), and discharge gauges. WWTP is wastewater treatment plant

stormwater overflows (SWOs) result in estimated ~ 3.1 Million m^3/y rainwater discharge as direct runoff into the Panke (Senate Department for Urban Development and Housing, 2019b). Some of the built-up areas (17.8%) are drained by combined sewer systems, with the remainder mostly having standard separations between wastewater and stormwater (Senate Department for Urban Development and Housing, 2018). In the South of the Panke, combined stormwater overflows dominates the drainage infrastructure (Möller &

Burgschweiger, 2008). Sewer runoff is partially influenced by reverse gradients which are controlled by a discharge threshold and only activate in larger storms. Mixed, untreated wastewater with storm runoff can also be discharged into the Panke from a pumping station close to the WWTP (Figure 1d).

In the downstream half of the Panke, the stream is increasingly regulated, and flow control structures can divert water into and out of the catchment (Figure 1). WWTP effluents can be either discharged

TABLE 1 Aggregated land use for the Panke sub-catchments (as shown in Figure 1) for the individual sampling sites (upstream of the wastewater treatment plant WWTP: UP1, UP2, UP3, downstream of the WWTP: DS and at the catchment outlet OL) (modified. Landesvermessung und Geobasisinformation Brandenburg (LGB), 2020; Umweltatlas Berlin/ALKIS, 2020)

Site	Sub-catchment area		Urbanized ^a		Road coverage ^b		Forested and peatland		Green-spaces ^c		Agri-culture		Diverse ^d	
	km ²		km ²	%	km ²	%	km ²	%	km ²	%	km ²	%	km ²	%
UP1	26.5		6.0	22.7	2.0	7.6	2.4	9.0	0.5	2.0	14.8	55.9	0.7	2.7
UP2	46.9		14.8	31.6	4.6	9.9	3.5	7.5	1.0	2.1	22.1	47.1	0.9	1.9
UP3 and DS	114.0		23.8	20.9	8.5	7.5	42.5	37.3	2.7	2.4	34.6	30.3	1.9	1.7
OL	216.3		53.5	24.7	20.3	9.4	49.2	22.8	15.0	6.9	74.8	34.6	3.5	1.6

Note: % is related to the upstream-subcatchment.

^aHousing (incl. private gardens), industry.

^bIncl. railroads, streets, roads, squares.

^cIncl. recreation areas, allotments and cemeteries.

^dIncl. mining, landfills and water bodies.

directly into the Panke, or transported out of the catchment via the Nordgraben. The WWTP serves a population of ~700,000 with a dry weather discharge capacity of 105,000 m³/d (Möller & Burgschweiger, 2008). About 86,400 m³/d (mean 1 m³/s, from 0.83 m³/s up to a maximum of 2.7 m³/s (Kade, 2020)) of the treated wastewater are directly discharged into the Panke. The rest is drained into the Nordgraben and is usually transferred to the neighbouring Tegeler catchment (Figure 1), where other waterworks for drinking water treatment are supplied by river bank filtration. A proportion of peak flows can also be diverted out of the catchment via the Nordgraben to reduce flood risk. The adjustable weirs that regulate flows are not automated but are manually controlled, most notably in advance of heavy rainfall events, depending on the forecast of a flood risk model (Kade, 2020). Other weir operations were observed during the study period to alter the input of treated effluents to enhance base flows in the Panke. A small proportion of treated effluents are also discharged for maintaining a former sewage-irrigation farm which is now a wetland and forested area on the north-west side of the catchment, which is drained by forested stream just upstream of the WWTP (Figure 1a) (INKA BB, 2014; Kade, 2020; Lischeid et al., 2015).

The Panke stream is morphologically altered along its length, though in some places limited restoration has been proposed and undertaken (Lange et al., 2015; Wasser- und Bodenverband "Finowfließ", 2011). The last three kilometres of stream length are heavily canalized, with steel piling and almost no visible bed sediment due to walling of the channel boundary (Senate Department for the Environment, Transport and Climate Protection (SenUVK), 2019). The latter might limit groundwater-surface water exchange processes as described in (Lewandowski et al., 2019).

3 | DATA AND METHODS

The locations and frequency of sampling as well as the sources of external data are summarized in Table S1. The German Weather Service (DWD) climate station (at Buch) in the catchment was used for precipitation and temperature data (Figure 1). Daily precipitation

samples for isotope analyses were collected at the Urban Eco-hydrological Observatory at Steglitz ~10 km south of the catchment where continuous precipitation isotope samples have been collected since the beginning of 2019 (Kuhlemann et al.,). Samples collected from Buch in summer 2020 were very similar to those from Steglitz which we use here for the longer time series. Samples were protected against evaporation with a ~3 mm Paraffin layer (IAEA/GNIP, 2014).

Stream discharge and water level data for sites on the Panke (Figure 1d) were provided by the Senate Department for the Environment, Transport and Climate Protection (Senate Department for the Environment, Transport and Climate Protection (SenUVK), 2021b) in 15 min intervals (Senate Department for the Environment, Transport and Climate Protection (SenUVK), 2021a). Daily WWTP volumes draining into either the Nordgraben or Panke were provided by the Berlin Water Works (Berliner Wasserbetriebe, BWB) and their subcontractor (Umweltvorhaben-Berlin Brandenburg, U-BB) (BWB, 2021; Kade, 2020). Daily stable isotope samples were collected from the catchment outlet (OL) near the most downstream gauging station (Figure 1d). Gaps occurred at the end of December 2019 and due to a reduced sampling frequency (2–3 times weekly) during COVID19 lockdown (Mid of March – End of April 2020).

At six locations along the Panke (Figure 1d), grab samples of stream water for stable isotope analysis were taken from October 2019 to December 2020. Initially samples were collected monthly (January–April 2020) and thereafter every two weeks. Three sites (UP1, UP2, UP3) were upstream of the WWTP inflow, one was sampled from the WWTP outflow, just upstream of its confluence with the Panke (WWTP), one site was downstream (DS) of the WWTP inflow and one at the catchment outlet (OL) (Figure 1d). At all locations, the fortnightly sampling captured a diverse range of hydro-climatic conditions and discharge levels. In addition, four seasonal synoptic surveys (October and December 2019, April and July 2020) were undertaken along the Panke, including its major tributaries, encompassing 30 grab sampling locations, to investigate the isotopic transformation and seasonality within the stream and their tributaries.

Groundwater was sampled for isotope analysis on a monthly basis from January to October 2020 (except for COVID19 gaps in April)

from seven wells across the Panke catchment capturing different shallow aquifer systems within AQ1 and AQ2 (Figure 1c). We purged the wells through pumping for 30–90 min, to ensure that at least twice the exchange volume was removed and water quality determinants such as pH, electric conductivity, and oxygen concentration were measured until they stabilized using a WTW Multi probe 3630.

All isotope samples were decanted and filtered (0.2 μm cellulose acetate) into 1.5 mL vials in the field and refrigerated until laboratory analysis. They were analysed for water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) by Cavity Ring-Down Spectroscopy with a L2130-I Isotopic Water Analyser (precision: ± 0.025 $\delta^{18}\text{O}$ and $\pm 0.1\%$ $\delta^2\text{H}$, Picarro, Inc., Santa Clara, USA, 2020). Isotope values are described in delta-notation using four standards and reference to Vienna Standard Mean Ocean Water (VSMOW) from the International Atomic Energy Agency (IAEA) for calibration. Data correction was performed by the “Chem Correct” software from Picarro to identify potential organic contaminants (Picarro, Inc., Santa Clara, USA, 2018).

For data processing and analyses, R (Version R version 4.0.3 “Bunny-Wunnies Freak Out” (2020-10-10)) was used. All isotope samples were referenced to the deviation of the Local Meteorological Water Line (LMWL) for Berlin (Kuhlemann et al.,) as line-conditioned excess (lc-excess) as described by Landwehr and Coplen (2006):

$$\text{LMWL: } \delta^2\text{H} = 7.76 \delta^{18}\text{O} + 5.66$$

$$\text{lc-excess} = \delta^2\text{H} - 7.76 \delta^{18}\text{O} - 5.66$$

To identify different streamflow sources, we applied the Bayesian EMMA using MixSIAR (version 3.1.12) for the different stream sites along the Panke. MixSIAR is an open-source Bayesian model for R, using a Gibbs sampler, allowing the use of prior distributions. For calculation, a Markov Chain Monte Carlo (MCMC) method was used for estimation of probability density functions (Stock et al., 2018; Stock & Semmens, 2016). For each site, one EMMA was applied with three tracers ($\delta^2\text{H}$, $\delta^{18}\text{O}$ as well as lc-excess) to characterize different potential streamflow components. Although the lc-excess is dependent on both stable water isotopes, a particularly marked and useful negative lc-excess signal was introduced by the WWTP as a source, while groundwater generally only had positive or close to zero values, and hence, could lc-excess acted as an additional tracer. Despite this, the integration of the LMWL of precipitation in the lc-excess calculation provides a separate signal of variation that can differentiate end members.

We separated the data set for each site into seasonal data (Winter: December–February; Spring: March–May; Summer: June–August; Autumn: September–November, Northern Hemisphere) categories for the analysis. We assumed that open water fractionation within the stream was negligible and that the tracers behaved conservatively in the channel. For the outlet, the complete dataset (biweekly and daily data) was used. The end member mixing analysis provides two internal statistics to evaluate model performance. The Gelman-Rubin-test should be < 1.05 for calculating the chain, though a value of < 1.1 is still acceptable and close to 1 is needed for a convergent

model, but must be > 1 to allow calculation (Gelman et al., 2014; Stock & Semmens, 2016). The Geweke test is a two-sided z-test, high z-scores give a basis for model rejection. Less than 5% of rejected values for the model is considered as favourable (Stock et al., 2018; Stock & Semmens, 2016) (details in Table S2).

In the mixing analysis, the stream was considered a potential mix of groundwater, recent precipitation (routed by storm drains), wastewater effluent (where present) and any streamwater inflow from upstream. This means that the regularly sampled stream sites (UP1 to 3), and DS (except WWTP) were also used as end members in MixSIAR for sites further downstream. For groundwater, AQ1.1 (Barnim aquifer) and AQ1.2 (Panke aquifer) were kept separate due to the potential higher intra-annual variability of the unconfined AQ1.1. The WWTP was only applied as a potential source for DS and OL. Standard deviations for the different sources were calculated to assess the variability of each source contribution for the given endmember. EMMA provides a distribution of the source contribution, which we used as quantification of variability and uncertainty. The higher the standard deviation is, the higher the variability of the source contribution over time and the more uncertain is the result.

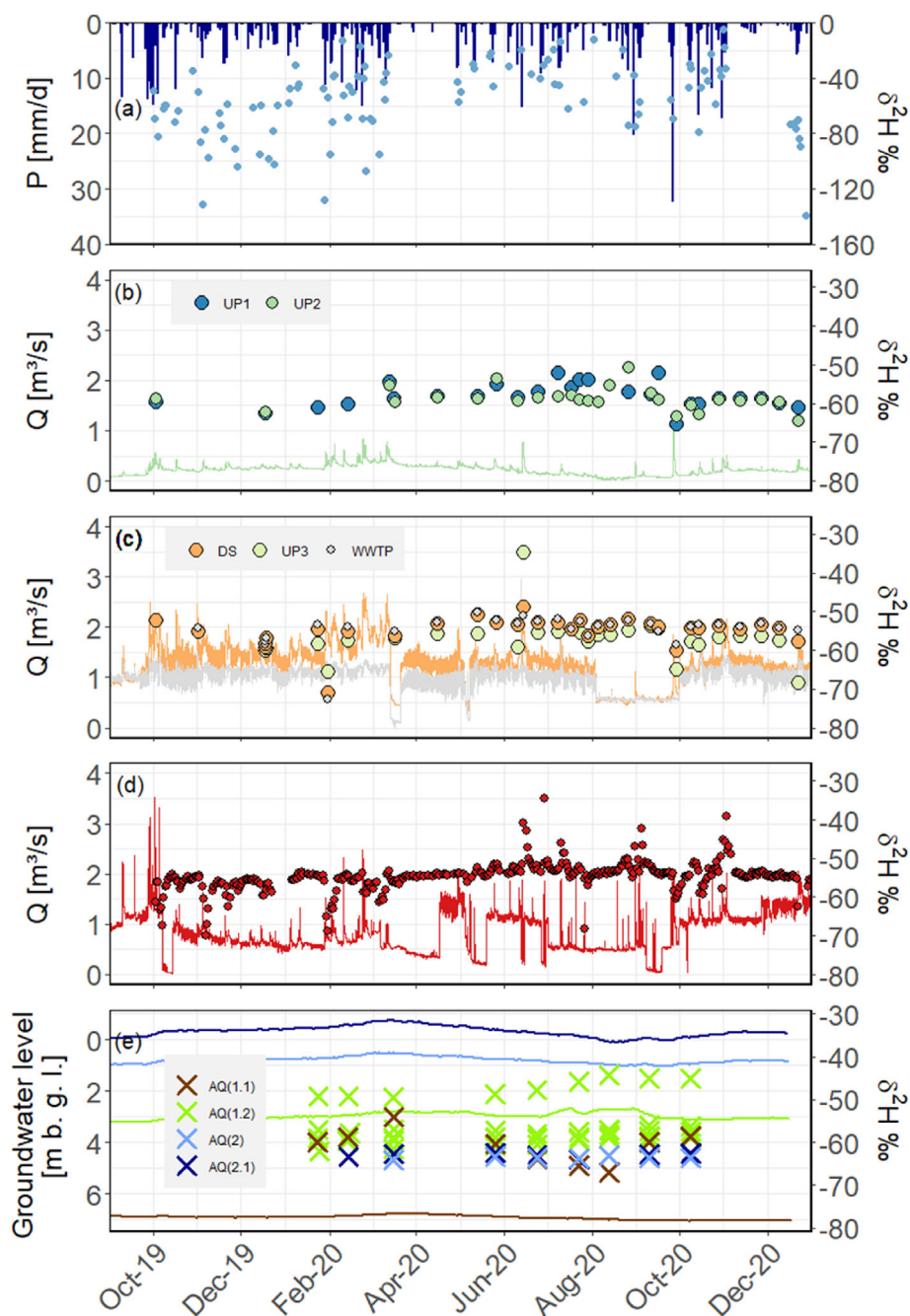
We also estimated the young water fraction (YWF) contribution to stream flow at all sites to assess the influence of urban storm runoff. YWF is a simple but useful measure to estimate the contribution of water younger than around two months to streamflow (Kirchner, 2016b). As the seasonal cycle of precipitation is damped due to storage and mixing processes, it gives insights into overall catchment function in terms of young water contributions to streamflow (Kirchner, 2016b; von Freyberg et al., 2018). A robust estimation was derived from the ratio between the sinusoidal regressions of seasonal variations in precipitation and stream isotopes. The ratio between the amplitude of the sinusoidal regressions of stream and precipitation is the YWF. The calculation was performed via an iterative re-weighted least squares (IRLS) R script which was used to minimize the outliers. The script was that provided by von Freyberg et al. (2018). We used a discharge weighting for the YWF from the OL site. As goodness-of-fit measures between the regression and observed stable isotopes we used the coefficient of determination (R^2), residual standard error (RSE) and the hypothesis significance testing (p -value, (Fischer, 1925)).

4 | RESULTS

4.1 | Rainfall-runoff characteristics of the Panke catchment

Overall, the sampling period was characterized by relatively dry conditions. After initial rainfall in October, the winter of 2019/20 exhibited frequent, but low amounts (< 5 mm) and intensities of daily rainfall inputs, with February being the wettest month (Figure 2a). March and April were then relatively dry, but early summer was characterized by wetter conditions, particularly with some regular heavy convective rainstorms. Late summer was again dry, though late September saw

FIGURE 2 Time series of (a) Precipitation amount and isotopes; (b) Discharge in UP2 and $\delta^2\text{H}$ in streamwater in UP1 and UP2; (c) Discharge in DS and WWTP as well as $\delta^2\text{H}$ in streamwater in UP3, WWTP and DS; (d) Discharge and $\delta^2\text{H}$ in streamwater at OL; (e) Daily groundwater levels with colours respective and representative of the aquifers in meter below ground level (m b. g. l.) and $\delta^2\text{H}$ in groundwater at the 4 AQs 1.1, 1.2, 2, 2.1. Precipitation and stream isotopes are plotted at different scales



the highest daily rainfall of the year with a relatively dry early winter 2020/21 following.

Flows in the upper catchment were measured at UP2 and were unaffected by WWTP discharge, but showed the characteristic seasonality of a groundwater-dominated stream with higher winter baseflows (Figure 2b). However, the stream was responsive to storm events even after prolonged dry antecedent baseflows conditions in summer 2020. Between UP2 and UP3, a water level gauge (not shown) followed the general dynamics of UP2, though comparison of long-term flow data between the two sites suggest losing conditions during summer (Zeifelder, 2021, pers. communication). Flows from the WWTP enter between the UP3 and DS sampling points

(Figure 2c) and flows at DS were strongly influenced by weir operations. The WWTP effluents also showed diurnal variations and other changes which were still evident at the Panke outlet OL (Figure 2d). While runoff peaks generated by urban storm drains in the lower catchment were also evident in DS and OL (Figure 2c,d), a proportion of runoff peaks were transferred out of the catchment between these two points via weirs at the Nordgraben.

Flows at OL showed a flashy discharge response, typical of an urban catchment, to all substantial precipitation events (Figure 2d). Such abrupt, transient increases in flow were followed by rapid recessions once rainfall stopped. Similarly abrupt, but more persistent changes in discharge were related to the weir operations, causing

increases and decreases in baseflows which could range from 0.3 to 1.4 m³/s. From higher flows in early October 2019 until the beginning of February 2020, discharge generally decreased from baseflows of ~1 m³/s to ~0.5 m³/s. After a wet February 2020, flows recovered to 0.8–1 m³/s and declined again during a very dry April. The dry weather sub-daily flow variation during these conditions showed the effect of diurnal changes in WWTP effluents. This was followed by a step change in flows where the volume of wastewater effluent flowing into the river was increased during the drier summer via weir operations to enhance baseflows. Conversely, during wetter periods in October 2019 and 2020 flows were diverted out of the catchment into the Nordgraben to reduce flood risk.

In Figure 2e, daily groundwater levels are shown for selected wells in the Panke catchment that were also sampled for isotopes. In the partly confined AQ(1.1) aquifer, the water table is ~4–5 m below the ground surface, and around 2–3 m in the unconfined AQ(1.2). Artesian conditions prevail in AQ(2) below the confining later. After the dry periods of 2018 and 2019, groundwater levels increased by around 0.1 m until March 2020 for AQ(1.1), and by ~0.25–1 m in AQ(1.2). Only small differences in the synchronicity of seasonal water level variations were observed, though the AQ(2) aquifer responded later to recharge. During the summer period after the dry April, water levels fell until September, where they stabilized, except in AQ1.1, which had lower levels by about 0.1 m compared to the year before (Senate Department for Urban Development and Housing, 2010).

4.2 | Isotope dynamics in the Panke catchment

Stable isotopes in precipitation showed a high variability (SD = 3.6 and 26.9‰ for δ¹⁸O and δ²H, respectively, Table 2); as expected, there was pronounced seasonality with samples enriched in heavy

isotopes during summer and depleted during winter months. However, day-to-day variability can be high in both seasons (Figure 2a).

Isotope sampling at UP1 was not always possible when the stream had dried out completely; for example, the 26/08/2020 sample was the first possible sampling following a rain event after a prolonged dry period (Figure 2b). During this late August period, UP1 and UP2 showed the most enriched isotope values of –57.0‰ and –50.65‰ for δ²H respectively, whilst winter values reached around –64.0‰ for δ²H at both sites. The sample sites UP3, WWTP and DS all showed broadly similar isotopic dynamics but UP3 was generally more depleted, WWTP was more enriched. DS was usually between both site signatures at high flows, but was more strongly influenced by the WWTP (Figure 2c). Standard deviations for all sites are given in Table 2. The WWTP introduced a variable isotope signal during events probably from the mixed stormwater received in the WWTP and discharged within hours or days.

The daily stream samples at the catchment outlet showed that the seasonal variation of the inputs was greatly damped (SD = 0.45 and 3.6‰ for δ¹⁸O and δ²H, respectively, Table 2), but the rainfall signal was translated to the stream during storm events, with the effect more pronounced in the larger events (Figure 2d). Consequently, seasonal variations in rainfall were also evident in the stream, with more enriched and depleted values in summer and winter, respectively. Usually, the rainfall signal only remained apparent in the stream for a day, but in the case of larger events, the effect could persist over several following days.

Isotopic signatures in groundwater (Figure 2e) showed some seasonal variability in AQ1.1 and AQ1.2, though this was very damped (SDs of 0.46 and 3.93‰ for AQ1.1 and 1.00 and 4.95‰ for δ¹⁸O and δ²H AQ1.2, respectively) compared to precipitation or stream signatures. The isotopic composition of water in the deeper and confined AQ2 showed even less change and was the most depleted. Thus, AQ1

TABLE 2 Summary of isotopic compositions of precipitation, the different stream sampling locations and groundwater aquifers

		δ ¹⁸ O				δ ² H				lc-excess	
		<i>n</i>	Max	Median	Min	SD	Max	Median	Min	SD	Median
		[–]	‰	‰	‰	‰	‰	‰	‰	‰	‰
Precipitation		138	–0.29	–7.67	–17.31	3.60	–12.19	–52.59	–131.33	26.90	0.17
Sampling sites	UP1	28	–6.98	–8.21	–9.28	0.61	–51.93	–58.40	–65.14	3.13	0.03
	UP2	26	–5.85	–8.41	–9.17	0.58	–44.48	–59.01	–64.40	2.90	0.68
	UP3	30	–4.83	–7.91	–9.53	0.78	–34.54	–56.41	–68.42	5.47	–0.96
	DS	32	–6.68	–7.28	–9.40	0.49	–48.72	–54.04	–71.01	3.76	–2.87
	OL	370	–5.16	–7.35	–9.53	0.45	–34.54	–54.46	–69.96	3.60	–2.96
WWTP		31	–6.85	–7.18	–9.49	0.50	–50.28	–53.55	–72.67	2.90	–3.25
Ground-water	AQ(1.1)	9	–7.90	–8.67	–9.46	0.47	–54.06	–59.91	–66.92	3.93	1.31
	AQ(1.2)	43	–5.31	–8.19	–8.62	1.00	–44.18	–58.24	–62.09	4.95	–0.16
	AQ(2)	15	–8.84	–9.02	–0.22	0.10	–62.4	–63.3	–64.1	0.54	0.66

Note: Arrow represents stream direction.

Abbreviations: *n*, number of samples; SD, standard deviation.

showed a higher variability compared to AQ2, suggesting the greater influence of near-surface flow pathways, and mixing. Groundwater from the main unconfined Panke valley (AQ1.2) was quite homogeneous, except for a wetland-influenced groundwater well (the most enriched GW-well in Figure 2e and located upstream of UP3 adjacent to the outflow of a wetland/forested tributary, Figure 1) which showed some inter-annual variability. The highest variability in isotopic signatures was measured for the Barnim aquifer (AQ 1.1), with the most enriched groundwater isotopes in March, and most depleted in July. Comparison with UP2, which is close to this particular AQ1.1 well often showed an overlapping isotope signature possibly implying surface water connectivity.

4.3 | Spatial variability in isotopes

The isotopic signatures of the different sampling sites and potential source waters showed some clear differences in ranges and deviations from the LMWL when plotted in dual-isotope space (Figure 3). Precipitation had the highest variability, and less than half of this variability was observed in the stream during events, while during baseflow conditions almost no variation occurred (cf. Figures 2d and 3a). At OL, enriched stormflow samples during summer events plotted almost directly along the LMWL, while during winter a slight offset was apparent. The relative stability of most groundwater samples was evident, plotting mostly along the LMWL. An exception was the previously mentioned well in AQ1.2 which received wetland drainage and plotted distinctly below with a more enriched and fractionated signal. Importantly, the groundwater signal was very similar to the stream

signature at UP1 and UP2 throughout the year. The stream became progressively more enriched between UP2 and UP3, probably caused by enriched inflows from the north bank tributary draining forested and wetland areas (Figures 1d and 3b) where surface evaporation is likely (Kuhlemann et al., 2020; Sprenger et al., 2017). However, below the WWTP, similar isotopic signatures in the lower stream system showed a strong influence of effluent waters. The samples from downstream of the WWTP plotted parallel to the LMWL and were very similar to samples in OL, indicating minimal influence from tributaries or other sources downstream of the WWTP.

Urban inflows were those streams flowing through urbanized areas, while peri-urban pass more agriculture-dominated sub-catchments. The main forested stream has its confluence with the Panke about 2 km upstream of UP3, while urban headwater tributaries can be found along the whole catchment. The peatland inflow is between UP2 and UP3, south of the forested stream, close to the wetland-lakes. Samples from the urban and peri-urban tributaries showed higher isotopic variation than the forested stream or the peatland inflows (Figure 3b). The peatland inflow showed the most enriched and fractionated signatures of any tributary (mean δC -excess: -4.79% (Table 3)).

The results of the seasonal synoptic surveys are shown in Figure 4, where the regular sample sites are also shown for orientation. Throughout all seasons, the north of the catchment (i.e., UP1–UP3) was characterized by more depleted isotopic signals being mostly similar to those of groundwater (Figure 4a). However, the most upstream synoptic sampling site flowed from a lake which became enriched during summer. The October samples still showed evidence of such enriched water sources, but during December 2019 and April

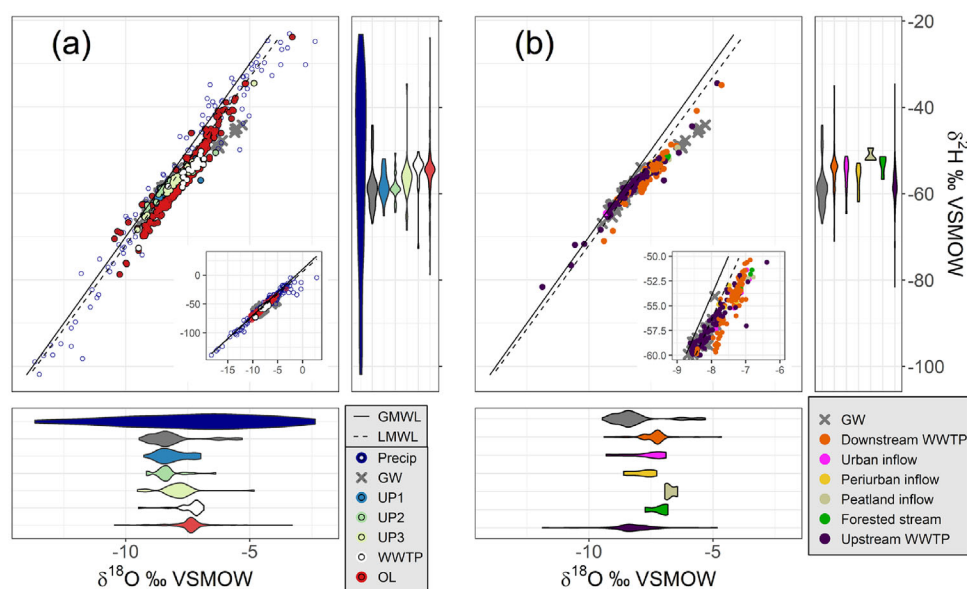


FIGURE 3 Dual isotope plots with respective violin plots for (a) precipitation, lumped groundwater samples from AQs 1.1, 1.2, 2, 2.1, regularly sampled streamsites (UP1-3, DS), treated wastewater (WWTP), daily and sub-daily samples (from OL), inset shows the complete range to cover precipitation variation. The enriched and fractionated GW samples are from AQ1.2 and a wetland influenced well. (b) Samples from the synoptic surveys for inflowing tributaries along the Panke catchment related to the WWTP inflow. Inset “zooms in” to better distinguish the sites. Local Meteorological Water Line (LMWL) is for Steglitz, Berlin; Global Meteorological Water Line (GMWL)

TABLE 3 Summary of isotopic composition of the synoptic surveys regarding their tributaries

	<i>n</i>	$\delta^{18}\text{O}$				$\delta^2\text{H}$				<i>lc-excess</i>
		Max	Median	Min	SD	Max	Median	Min	SD	Median
		[–]	‰	‰	‰	‰	‰	‰	‰	‰
Upstream WWTP	117	–4.83	–8.22	–11.88	0.84	–34.54	–58.48	–81.63	5.18	–0.37
Downstream WWTP	124	–4.65	–7.44	–9.40	0.56	–34.97	–54.85	–71.01	3.97	–2.79
Forested stream	4	–6.82	–7.14	–7.74	0.43	–51.40	–53.30	–56.68	2.40	–3.56
Peatland inflow	3	–6.43	–6.72	–6.94	0.26	–49.44	–51.27	–52.24	1.58	–4.79
Periurban inflow	6	–7.27	–7.85	–8.60	0.53	–52.96	–56.47	–61.85	3.39	–1.18
Urban inflow	11	–6.90	–7.64	–9.31	0.81	–51.39	–55.71	–64.58	4.17	–2.09

Abbreviations: *n*, number of samples; SD, standard deviation.

2020, the entire northern part of the catchment exhibited depleted isotopic signatures. The July 2020 sampling showed more enriched isotopic signatures again, especially at the most upstream lake site. Further downstream, below the WWTP seasonal variability became larger, with December 2019 most depleted and October 2019 most enriched.

The spatial influence of inputs from the WWTP on the DS and OL sites were clearer for *lc-excess*, though with some seasonal variation (Figure 4b). The seasonal patterns for *lc-excess* in the lower catchment were more complex than for $\delta^2\text{H}$, with slightly lower values being estimated in winter, showing greater fractionation effects in the effluent waters. The *lc-excess* varied between \sim –4‰ and –4.5‰ during November–March and \sim –2.5‰ to –3‰ from April to October.

The spatial surveys in December, April and July revealed some of the more subtle influences of tributary streams on the Panke, especially in the central part of the catchment where the WWTP discharge enters (Figure 4, insets). For example, throughout the year, and even in winter, the outflow of the wetland and forest stream upstream of the WWTP inflow was enriched and contributing to flows which resulted in enriched signatures and low *lc-excess* values compared to the mainstream. Spatially, the WWTP inflow provided an enriched signal. Overall, downstream of the WWTP signatures remained similar along the stream for all sampling occasions with more enriched and fractionated values than upstream the WWTP.

4.4 | Temporal variability in streamflow sources

The end member mixing analysis helped to constrain the sources of flow in the Panke and quantify their contributions to the mainstream (Figure 5; Table 4). Tables S2 and S3 provide model performance statistics, which were good for both metrics. The Gelman-Ruby test resulted in values below 1.05 showing all models converged and showed no multimodal posterior distribution, while the Geweke diagnostics only rejected a maximum of 13% of the variables for the MCMC chains, indicating good model performance.

UP1 was dominated by groundwater, with roughly similar (though the standard deviations in Table 4 uncertain) contributions from AQ1.2 and AQ1.1 accounting for around 70% of the flow for most of the year (Figure 5a). However, the overall contribution of precipitation from urban storm drains was also the highest of all sample sites, being greatest in autumn and winter, though still only accounting for around 30%–40% of runoff, in this time period. At UP2, the groundwater contribution again had similar inflows from AQ1.1 and AQ1.2, though overall contributions from upstream (UP1) accounted for around 44% of flows (Figure 5b). These were lower in summer when the streamflow became intermittent. This leakage from the upper catchment may also explain why the modelled contribution from rainfall was also lower, as summer inflows from storm drains leak into the aquifer before reaching UP2. At UP3 (Figure 5c), a broadly similar picture was evident, though the estimated contributions from upstream were only around 21% of flows, and AQ1.2 appeared to become the dominant source of streamwater, presumably reflecting inputs from the north bank forested tributary. The proportions from upstream (UP2) were relatively low, especially during summer suggesting losing conditions occurred. Precipitation generally contributed \sim 10%, though this increased in summer, in response to greater storm influence and inflows from drains.

There was an abrupt change in contributions downstream of the WWTP. The sampling point DS had a relatively constant, very high contribution of WWTP effluents (with low uncertainty, see Table 4) accounting for around 83% (Winter) – 96% (Summer) (mean: 86%) of discharge (Figure 5d, Table S3). Here, the seasonal variability of contributions was also low compared to the other sites, indicating the overall dominance of WWTP throughout the year. The slightly higher WWTP contribution during summer compensated low flow conditions in UP3. Groundwater and precipitation each contributed around 5% and 3% to annual runoff, respectively with low uncertainty. A similar distribution of sources was evident at the OL sampling point, with over 90% of contribution originating from DS, and with low variability (Figure 5e). The highest DS contribution of about 96% and 89% was during summer and autumn, respectively.

In summer, most urban tributaries dried out and the peri-urban tributaries had low water levels, while in autumn with the

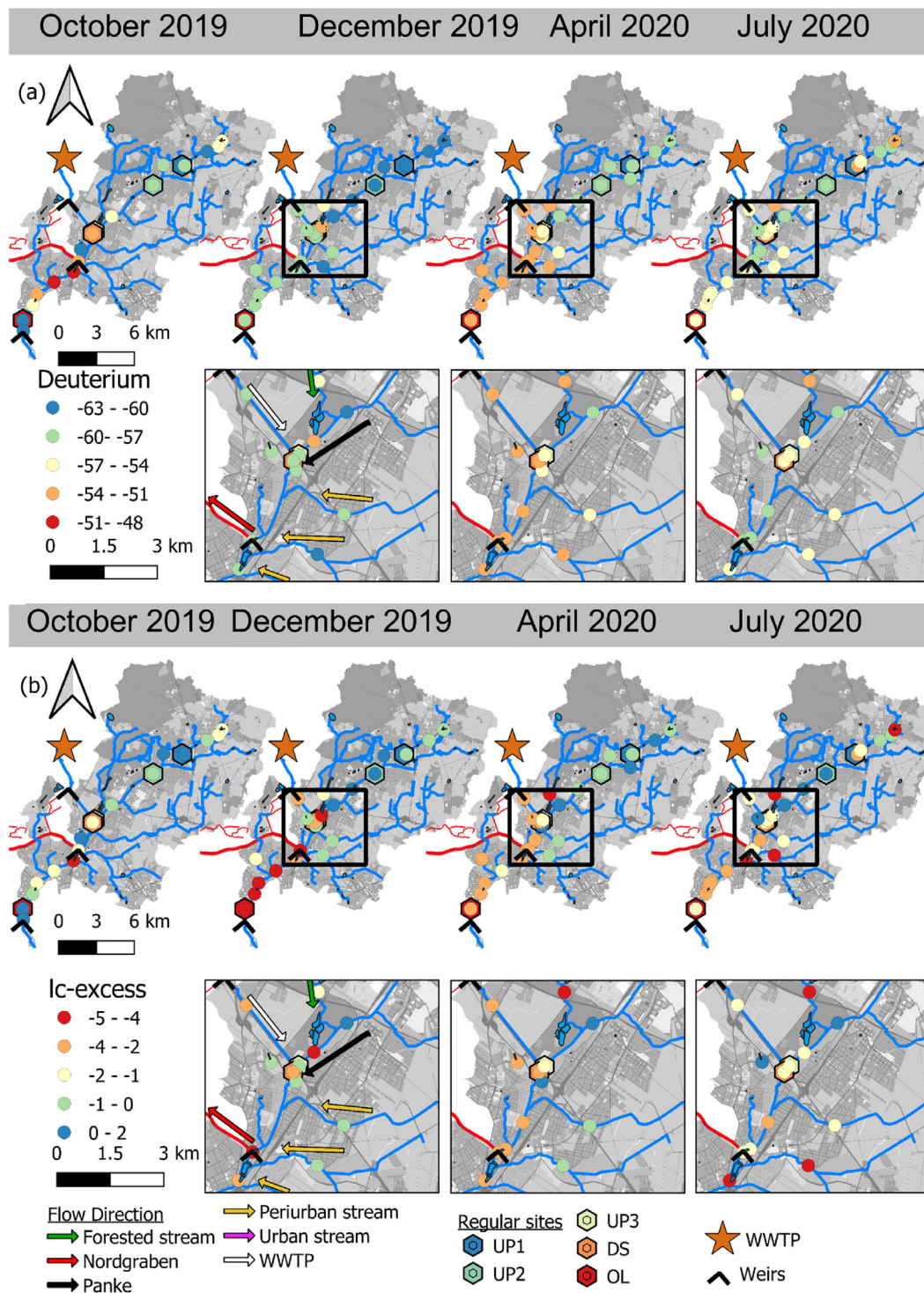


FIGURE 4 Results of the four seasonal surveys for (a) $\delta^2\text{H}$, and (b) $I_c\text{-excess}$. Tributaries have been sampled close to their confluence with the main stem. Regular sample sites are shown for reference. Background map: ALKIS (land use in black and white). WWTP: wastewater treatment plant with further distance. Background map: ALKIS (land use in black and white) see for legend: Figure 1

longest rainfall events during the sampling period, precipitation had the highest contribution of ~5%, which is related to prolonged rain over several days driving variability in the hydrograph. However, in general, precipitation and groundwater both made small contributions to the stream. Although low, the groundwater

contribution was also at its minimum during the summer months at OL, consistent with the seasonally minimum groundwater storage.

Figure 6 summarizes the average flux contributions from each source to each sampling site as a Sankey plot. The overall means from

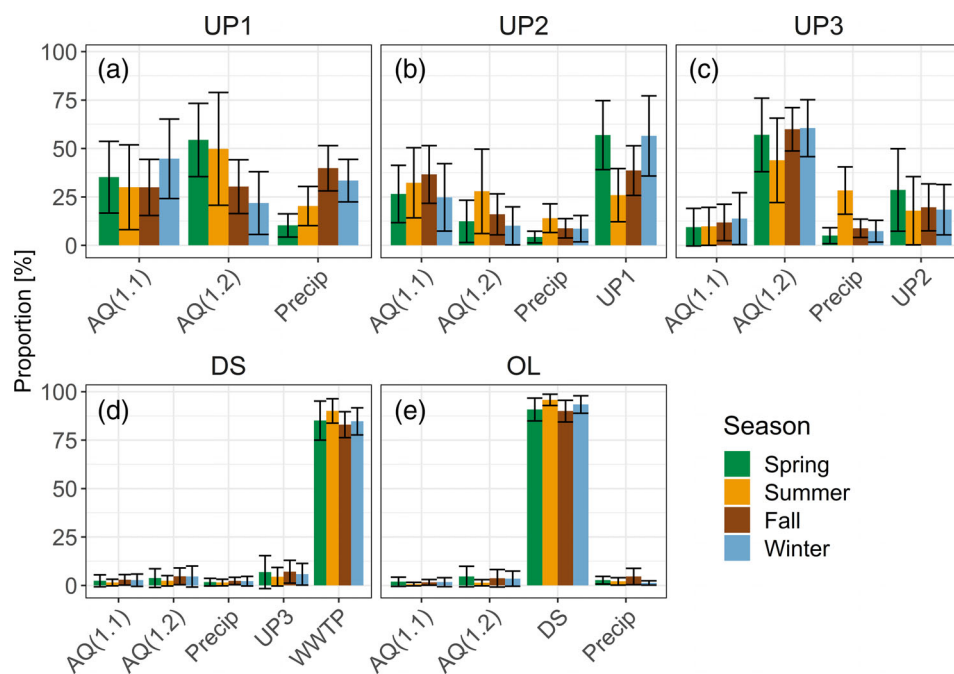


FIGURE 5 EMMA results for regular sampling locations across the four seasons. Lc-excess was applied as tracer information. Plots are shown following downstream from top left (a) UP1 (Upstream 1), to right (c) UP3 (Upstream 3) to (d) DS (Downstream) where WWTP (waste water treatment plant) is discharging into. (e) OL (outlet). GW sources are: Barnim Aquifer AQ(1.1) and Panke Aquifer AQ(1.2). Error bars indicate SD's as a measure of variability source contribution within one season

TABLE 4 EMMA results showing the % contribution of the different stream sources for the respective sites (lc-excess, $\delta^{2}\text{H}$ and $\delta^{18}\text{O}$ as tracer). SD's from source distribution

Endmember	Source	Spring		Summer		Autumn		Winter		Annual Mean
		Mean	SD \pm	Mean	SD \pm	Mean	SD \pm	Mean	SD \pm	
UP1	AQ(1.1)	35%	19%	30%	22%	30%	15%	45%	21%	35%
	AQ(1.2)	54%	19%	50%	29%	30%	14%	22%	16%	39%
	Precip	10%	6%	20%	10%	40%	12%	33%	11%	26%
UP2	AQ(1.1)	27%	15%	32%	18%	37%	15%	25%	17%	7%
	AQ(1.2)	12%	11%	28%	22%	16%	11%	10%	10%	17%
	Precip	4%	3%	14%	7%	9%	5%	9%	7%	9%
	UP1	57%	18%	26%	14%	39%	13%	57%	21%	44%
UP3	AQ(1.1)	9%	10%	10%	10%	12%	9%	14%	13%	11%
	AQ(1.2)	57%	19%	44%	22%	60%	11%	61%	15%	55%
	Precip	5%	4%	28%	12%	9%	5%	7%	6%	12%
	UP2	29%	21%	18%	18%	20%	12%	18%	13%	21%
DS	AQ(1.1)	2%	3%	2%	2%	3%	3%	3%	3%	2%
	AQ(1.2)	4%	5%	2%	3%	5%	4%	5%	5%	4%
	Precip	2%	2%	2%	2%	2%	2%	2%	3%	2%
	UP3	7%	9%	5%	5%	7%	6%	6%	6%	6%
	WWTP	85%	10%	90%	6%	83%	7%	85%	7%	86%
OL	AQ(1.1)	2%	2%	1%	1%	2%	2%	2%	2%	1%
	AQ(1.2)	5%	5%	1%	2%	4%	5%	4%	4%	3%
	DS	91%	6%	96%	3%	90%	6%	93%	5%	93%
	Precip	3%	2%	2%	2%	5%	4%	1%	1%	3%

Note: Arrow represents stream direction.

the end member mixing are plotted for the whole study period. Groundwater, particularly AQ1.2, dominates UP1-3 showing the significance of stream flow generation processes in addition to

precipitation from urban storm drains. The low GW contributions at OL reflect the disconnection of the surrounding landscape in the lower catchment and effluent dominance.

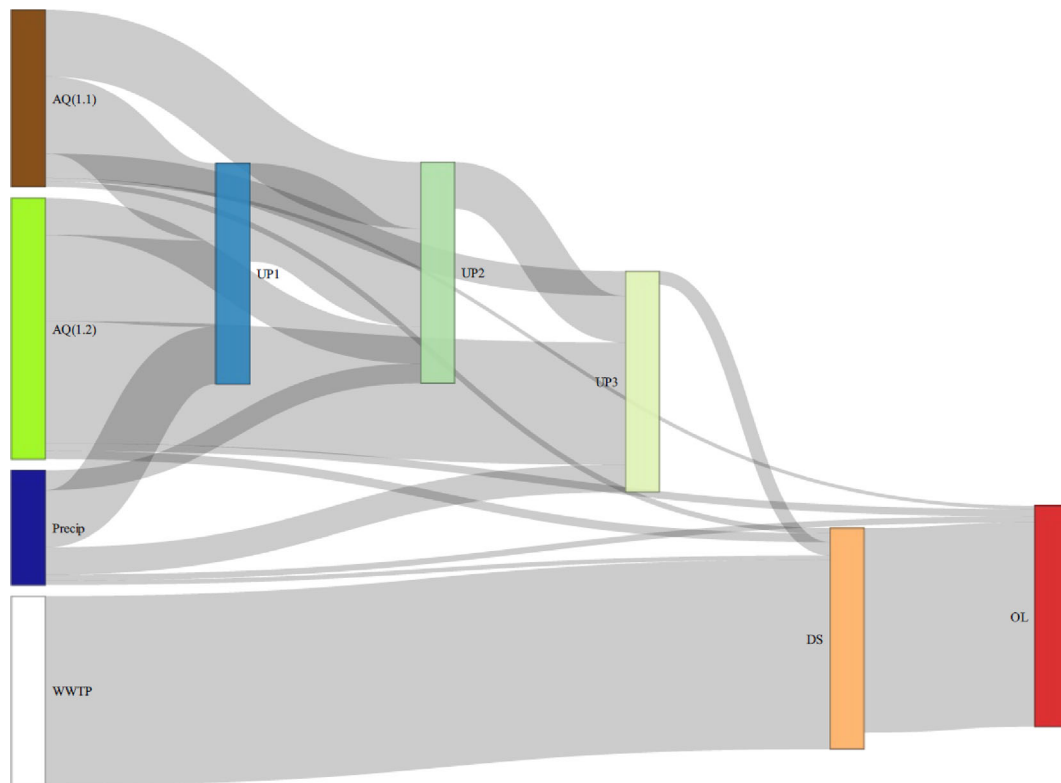


FIGURE 6 Estimated mean EMMA results over all seasons as a Sankey plot. Each stream sampling location represents 100%, link thickness represents the source ratio in %

TABLE 5 Site specific young water fractions (YWF) for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ related to their fitting diagnostics, with coefficients of determination (R^2) and residual standard errors (RSE) as fitting parameter

Site	$\delta^2\text{H}$				$\delta^{18}\text{O}$			
	YWF	R^2	p -value	RSE	YWF	R^2	p -value	RSE
Precip	[-]	0.33	5.80E-09	19.3	[-]	0.3	7.50E-09	2.52
UP1	0.14	0.52	2.00E-04	1.81	0.22	0.56	7.50E-05	0.33
UP2	0.06	0.2	8.00E-02	1.75	0.1	0.29	2.00E-02	0.27
UP3	0.1	0.33	4.00E-03	1.99	0.13	0.47	2.00E-04	0.25
WWTP	0.07	0.27	1.00E-02	1.61	0.05	0.11	1.90E-01	0.24
DS	0.09	0.35	2.00E-03	1.72	0.08	0.21	1.00E-02	0.22
OL	0.08	0.26	<2.2E-16	0.93	0.06	0.15	5.80E-14	0.12

The YWF at each site was used as an additional indicator of water sources, by estimating the “younger water” (<2 months) contribution to streamflow (Table 5), which primarily reflects the contributions of urban storm drainage. The dynamics between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were similar, however, they were slightly different regarding absolute values. At almost all sites, statistically significant fits ($p < 0.001$) were obtained. Despite the Panke being a heavily urbanized catchment, the YWFs were low at all sites (Table 5). Between both upstream sites UP1 and UP2, the YWF in $\delta^2\text{H}$ decreased from about 13% to 7%, respectively. At UP3, this increased to ~11%. The estimated YWF of the WWTP effluents was 7%, and ~10% for DS and OL, with a similar range of uncertainty of a residual standard error RSE of 0.12–0.24 (OL–DS/WWTP for $\delta^{18}\text{O}$). These results of YWF estimation are broadly consistent with the rainfall estimates from the EMMA of each

site, the groundwater dominance at UP1–3 and effluent dominance at DS and OL.

5 | DISCUSSION

5.1 | Runoff sources in the Panke catchment

Our study demonstrated that we could successfully use isotopes to identify the spatio-temporal dynamics of runoff sources in a complex, highly managed urban catchment in a major city. The first aim was to understand how well the short-term dynamics of isotopes at the catchment outlet could track changing dominant runoff processes. The daily isotope sampling at the outlet (OL) revealed a rapid

translation of rainfall to runoff in most storm events, though this was generally less dramatic – in terms of flow response (Figure 2d) – than has been reported in other urban studies (Soulsby et al., 2015b). This is the result of: (a) the relatively small proportion of the sealed surfaces in Berlin’s urbanized areas being directly connected to the Panke channel network; (b) the high outflows from the WWTP being the dominant stream water source in the lower catchment and (c) storm runoff from the upper catchment being transferred into the neighbouring Tegeler catchment for flood mitigation.

The more distributed, catchment-scale synoptic sampling campaigns achieved our second aim and allowed the complex spatio-

temporal dynamics of dominant streamflow sources in the Panke to be identified. The lowland headwaters of the catchment, where urbanization affects around 34% of the area, still reflects groundwater dominance in streamflow generation, albeit strongly affected by urban storm runoff. This resulted in the highest relative contributions of rainfall (annual mean: 26%, Table 4) and young water (mean between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ 18%, Table 5) to streamflow in the catchment at UP1. The spatial changes in runoff sources and stream-groundwater interactions are shown conceptually in Figure 7. Whilst tributaries from forested and wetland areas supplement flows in the catchment headwater, limited recharge from sealed areas (Roy et al., 2015; Wenger

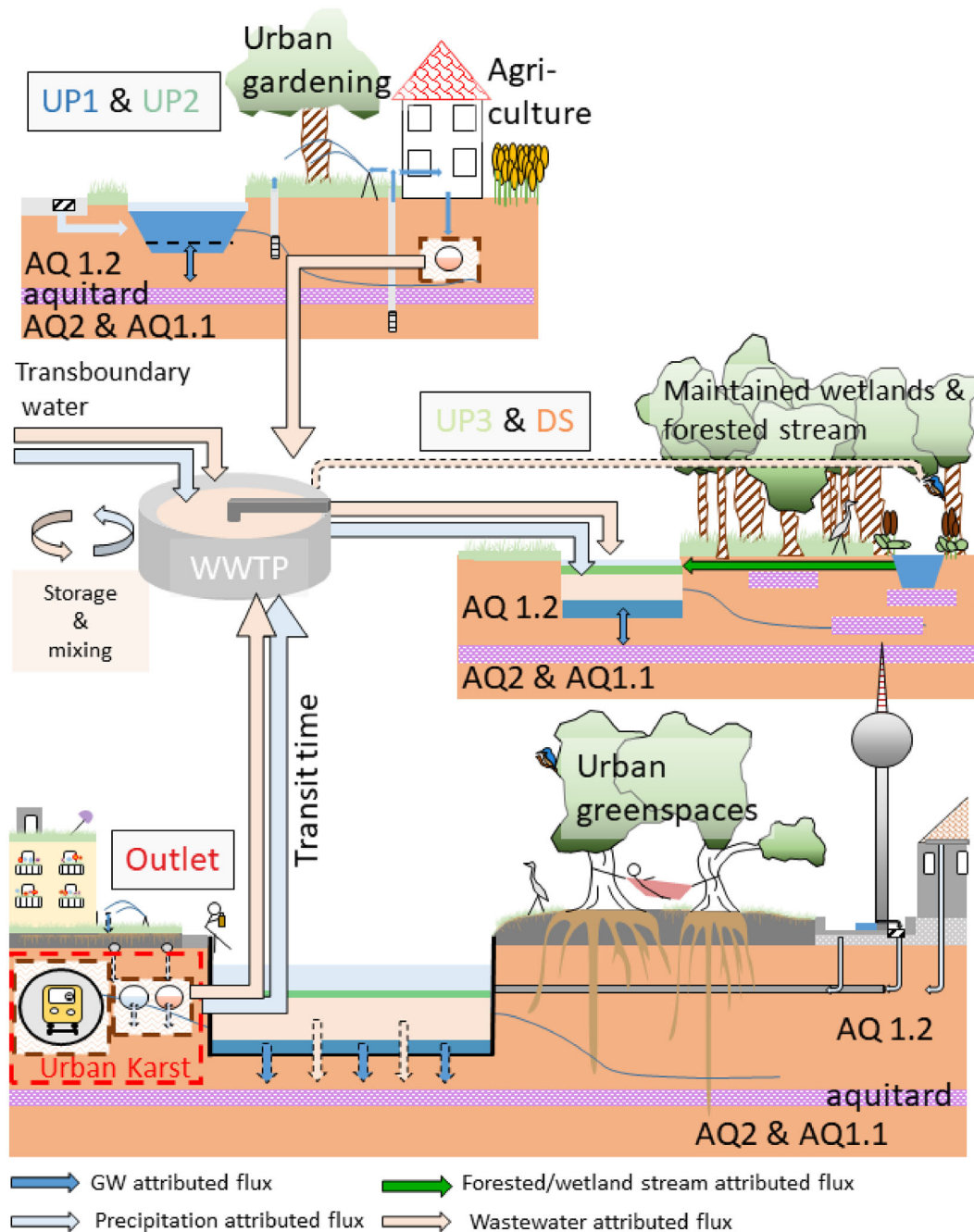


FIGURE 7 Conceptualized Panke river system showing main contributing sources and stream – groundwater interactions

et al., 2009) and unregulated local groundwater abstractions (Benejam et al., 2010; Jasechko et al., 2021; Vörösmarty & Sahagian, 2000) may result in the stream “losing” in the summer and leaking into the underlying aquifer. Such intermittent streams are particularly vulnerable to anthropogenic alterations (Brooks, 2009).

In the lower catchment, the dominant source of runoff is effluent from the WWTP, and the stream can be classified as “effluent-dominated” (i.e., where more than 50% of streamflow is comprised of effluent) (Hamdhani et al., 2020) (Figure 6). The isotopic composition of the wastewater carries a fractionation signal that allowed its annual contribution to streamflow (86%) to be estimated via end member mixing. Some preliminary data indicates that this fractionation signal is also evident in tap water (Marx unpublished), so most likely reflects fractionated signals in Berlin's surface waters (lakes) that are abstracted via bank filtration (cf Kuhlemann et al., 2020). The WWTP contributions to the Panke are managed and reduced for flood risk mitigation or increased for base flow enhancement, with weirs controlling the volume and timing of transfers. Overall, however, this dominant influence of WWTP effluents dictates that even in the lower catchment, where the urbanization accounts for ~40% of land cover, storm drains are limited to providing only <10% of annual runoff and low (<10%) young water fractions, at least part of which seems also to be water routed through the WWTP. However, this lower contribution of mixed storm runoff also partly reflects drainage of some peak-flows directly from the WWTP into the Nordgraben (median: ~30% of total WWTP outflows) rather than the Panke, as well as drainage from the Panke into the Nordgraben (median: 20% of the Panke [OL] flow). It should be stressed, however, that the Panke is unusual in such overwhelming dominance of treated wastewaters throughout the year; in major German catchments only around 25% of gauging stations have flows comprising >10% wastewater. However, at low flows, treated wastewater can comprise >60% of flows in heavily developed rivers such as the Main and Rhine (Drewes et al., 2018).

Although the isotopes helped resolve the “big picture” of spatio-temporal variations in runoff sources in the Panke many uncertainties remain that would need further work to resolve. For example, in the upper catchment (UP1 and UP2) the groundwater sources of stream flow are poorly constrained as a result of the similar isotopic composition of the AQ(1.1) and AQ(1.2) aquifer units. Linked to this, the changing nature of groundwater-surface interactions that lead to the stream drying remain unclear as is any role of the deeper confined aquifer. Further resolution of these issues would be dependent upon more intensive sampling and the use of other tracers. In the lower catchment, uncertainties are lower, given the dominance of water from the WWTP, which is broadly corroborated by hydrometric measurements of stream flow and WWTP outflows (Table S3), though these may be affected by groundwater leakage.

It is reassuring that the rainfall contributions estimated from the EMMA are generally similar to the YWF that was derived independently. Although the YWF are perhaps lower than expected given the degree of urbanization (for reasons already outlined), they are similar to other lowland catchments in Germany, such as the Demnitz Mill

Creek, south east of Berlin (Kleine et al., 2021) and the Bode catchment in central Germany (0.05–0.2) (Lutz et al., 2018). These catchments have lower YFW than the global median of 0.26 cited by (Jasechko et al., 2016).

A final caveat on the results of the study is the representativeness of the study year, given that rainfall levels were below average for most months in the study, and it followed the extreme drought year of 2018 (Kuhlemann et al., 2020). As such the contribution of rainfall and the YWF might be depressed due to the combined effect of smaller rainfall events and depleted catchment storage (Bansah & Ali, 2019; Clow et al., 2018; Wilusz et al., 2017). This might have increased the spatial extent and longevity of parts of the stream network drying out. This also underlines the need for longer-term studies to assess the role of hydroclimatic variability and extremes in controlling runoff sources and associated isotope dynamics (Kleine et al., 2021).

5.2 | Using isotopes in urban hydrology

The hydrology of any city uniquely reflects the interaction of the built urban fabric and the natural environmental characteristics. A particularly influential component of this is the management of water supplies, storm runoff and wastewater disposal. This in turn creates both opportunities and challenges for using isotopes to understand hydrological processes. For example, urban isotope hydrology in Berlin, or any city operating a largely “closed” water management system, is challenging due to the lack of isotopic differentiation between withdrawals and wastewater returns as well as inter-basin transfers in catchments like the Panke (Massmann et al., 2007). Fortunately, in Berlin, wastewater carries a strong fractionation signal (Kuhlemann et al., 2021b), so it can be differentiated from local groundwater and rainfall as an end member in hydrograph separation and for estimations of the young water fractions. The isotopes provided a basis for tracking water source contributions to complement hydrometric measurements of streamflow and effluent releases as reversals in local groundwater – surface water interactions. As noted above, the latter dictates that during summer, parts of the river become losing reaches and leak into the underlying groundwater as observed in neighbouring catchments (Kleine et al., 2021; Kuhlemann et al., 2021b). This, together with weather-related transfers of water into and out of the catchment, confound source attribution from hydrometric measurements alone. In other urban areas with water supply imports, especially involving inter-basin transfers from distal areas, isotopic differentiation of waste water from local surface and groundwater sources is usually easier. This has been demonstrated in studies tracking diverse drinking water supplies from tap water analysis (Bowen et al., 2007; Jameel et al., 2016; West et al., 2014), as well as investigations of local groundwater intrusion into sewers carrying waste waters (De Bondt et al., 2018; Kracht et al., 2007).

Because of the potential diversity of local and distal water sources influencing urban waste water, using water ages is conceptually challenging in complex urban systems compared to other

catchments where the hydro-demographics of different water sources (e.g., soils, groundwater, etc.) can be well-constrained (Sprenger et al., 2019). Whilst identifying young water fractions from recent rainfall or older groundwater from depleted isotope signatures or other dating tracers (CFCs, tritium and others) is possible, effluents are more problematic, both when they are derived from local and distant sources or from surface water and groundwater. Effluents combine a range of water ages, that is, in mixing “old” groundwater, surface water and “young” precipitation. For example, the calculated YWF of the WWTP was in the Panke was between 5% and 7%. Similar to precipitation, wastewater from outwith a catchment might be considered as “young” in terms of their release in the catchment, although its original age on abstraction can be much older, and therefore interfere with common methods to describe water ages. Further, infiltration and inflow to the sewer system from recent precipitation might play a role in affecting water ages but we do not have any data on this for this system.

Undoubtedly, in addition to stable isotopes, other geochemical or anthropogenically-introduced tracers will help further constrain urban end member assessment, identify particular runoff sources, and help better conceptualize and constrain water ages. The wide range of emerging pollutants from pharmaceutical metabolites is particularly promising in this regard (Bradley et al., 2020). It is easy to envisage that this will be a fruitful area in the coming years and will help develop a more integrated understanding of urban hydrology in a wide range of cities. This also has outstanding potential to help understand urban water quality issues, particularly when these involve the complex connectivity of the “urban karst” in the subsurface of large conurbations (Bonneau et al., 2018). However, such tracer studies may have most potential in understanding urban systems in poorer countries where hydrometric and effluent data are less readily available (Oiro et al., 2018). This would help understand water resource systems and their vulnerability to change (Ehleringer et al., 2016).

6 | CONCLUSION

We combined temporally intensive and spatially extensive sampling to monitor stable isotopes in rainfall, streamflow, groundwater, treated wastewater and urban storm runoff in the 220 km² highly urbanized Panke catchment in Berlin, Germany. The monitoring was aimed at assessing the temporal dynamics and spatial patterns of the sources of streamflow. This was achieved by using isotope data in Bayesian approaches to end member mixing to assess contributions by contrasting sources of stream flow. The Panke has a lowland catchment that is naturally groundwater dominated; however, urban surfaces cover ~35% of the catchment and urban storm drains have an important influence on runoff generation. In the upper catchment, groundwater and urban storm drainage accounted for around 75% and 25% of annual runoff, respectively. In the lower catchment, however, effluent from a WWTP accounted for 80% of streamflow, with groundwater and urban storm runoff each accounting for around 10%. Regulation of sources in the Panke by artificial weirs increased WWTP contributions to augment summer baseflows to >90%, and reduced

contributions from urban storm drains during high flows as a flood alleviation scheme diverted a portion of high flows into a neighbouring catchment. We also estimated the contribution of the young water fraction (i.e., water that is less than around 2 months old) of streamflow, which was low throughout the catchment, varying between around 10%–15%. However, age dating urban streams is challenging due to the undefined age of wastewaters. The study showed how isotopes can provide novel quantitative insights into how managed urban water systems integrated with the more natural hydrological processes in non-urban areas and urban green spaces. Such understanding is vital to a comprehensive understanding of urban hydrology needed to provide an evidence base for more sustainable management of urban waters.

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DATA AVAILABILITY STATEMENT

Stream data and groundwater level based in rating curves, presented in Figure 3b–e, are only available upon request from the Berlin Senate, the same applies for the wastewater effluent data which is available from the Berliner Wasserbetriebe (BWB). Precipitation data are available publicly from the Deutsche Wetterdienst (DWD), station Buch. Precipitation and stream isotopes are available upon reasonable request. Discharge and groundwater level data are available upon request from the Berlin Senate/BWB.

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