Uranium isotopes ($^{234}U/^{238}U$) in rivers of the Yukon Basin (Alaska and Canada) as an aid in identifying water sources, with implications for monitoring hydrologic change in arctic regions

Thomas F. Kraemer · Timothy P. Brabets

Abstract The ability to detect hydrologic variation in large arctic river systems is of major importance in understanding and predicting effects of climate change in high-latitude environments. Monitoring uranium isotopes (^{234}U and ^{238}U) in river water of the Yukon River Basin of Alaska and northwestern Canada (2001–2005) has enhanced the ability to identify water sources to rivers, as well as detect flow changes that have occurred over the 5-year study. Uranium isotopic data for the Yukon River and major tributaries (the Porcupine and Tanana rivers) identify several sources that contribute to river flow, including: deep groundwater, seasonally frozen river-valley alluvium groundwater, and high-elevation glacial melt water. The main-stem Yukon River exhibits patterns of uranium isotopic variation at several locations that reflect input from ice melt and shallow groundwater in the spring, as well as a multi-year pattern of increased variability in timing and relative amount of water supplied from higher elevations within the basin. Results of this study demonstrate both the utility of uranium isotopes in revealing sources of water in large river systems and of incorporating uranium isotope analysis in long-term monitoring of arctic river systems that attempt to assess the effects of climate change.

Keywords Radioactive isotopes · Climate change · Groundwater/surface-water relations · USA · Canada

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T. F. Kraemer (✉)
US Geological Survey,
12201 Sunrise Valley Dr., MS 430, Reston, VA 20192, USA
e-mail: tkraemer@usgs.gov
Tel.: +1-703-6485868

T. P. Brabets
US Geological Survey,
4210 University Dr., Anchorage, AK 99508, USA

Introduction

The Yukon River Basin (YRB) in Alaska and northwestern Canada (Fig. 1) is the fourth-largest drainage basin in North America with an area of 854,700 km^2, about the size of the state of California, and has an average annual discharge of 6,457 m^3/s (Brabets et al. 2000). The body of evidence for recent climate warming in the YRB is building. River-ice breakup dates on the Yukon River at Dawson, Yukon Territory (YT) and the Tanana River at Nenana, Alaska (AK) are trending to earlier in the year (Brabets and Walvoord 2009). There is a general upward trend in groundwater contribution to streamflow in the Yukon River with no change in annual flow, suggesting increased permafrost thawing and infiltration of water to deeper flow paths (Walvoord and Striegl 2007). Glaciers are retreating throughout the region (BESIS 1997). Flow and chemical composition of the Yukon River and its tributaries are expected to adjust in response to these changing climatic influences.

From 2001–2005, the US Geological Survey conducted a 5-year reconnaissance study of rivers in the YRB in an effort to characterize high-latitude North American river-drainage response to the effects of global climate change. Water chemistry, sediment chemistry, isotopic characteristics of the flow system, and physical measurements of flow and suspended sediment were made at five fixed-site stations: the mainstem Yukon River at or near Eagle, Stevens Village, and Pilot Station and on two tributaries of the Yukon River—the Tanana River at Nenana and the Porcupine River near Ft. Yukon (Fig. 2; Schuster 2003, 2005a, b, 2006, 2007). Smaller rivers and other locations along the Yukon River were also sampled in 2002 and 2003 (Halm and Dornblaser 2007; Dornblaser and Halm 2006). Information gained from this effort provides a baseline against which future change can be detected, and has revealed changes in river chemistry and hydrology that may reflect changes in climate that are already occurring (Dornblaser and Striegl 2007; Striegl et al. 2005, 2007). Uranium isotopes were measured as part of this effort, and in this paper the use of this unique dataset to illuminate the evolving hydrology of the YRB and its relationship to climate science is considered.

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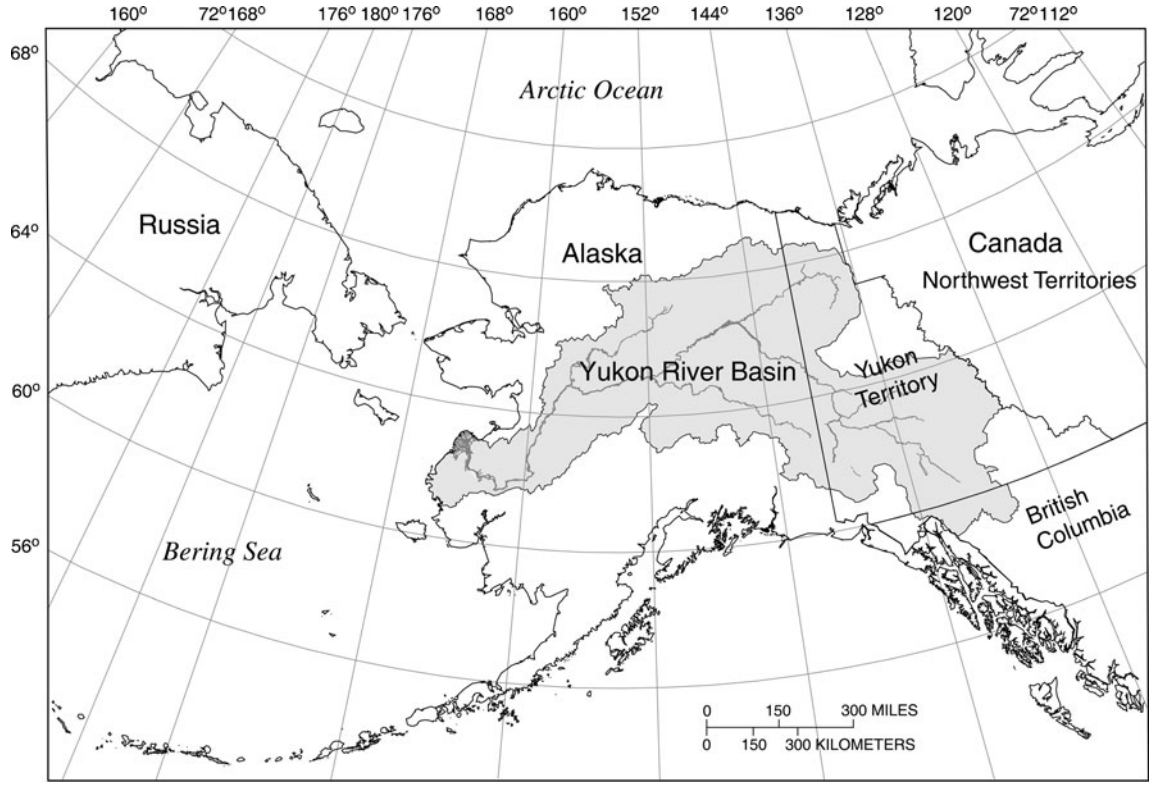

Fig. 1 Location map for the *Yukon River Basin* in Alaska and northwestern Canada (Brabets et al. 2000)

Uranium isotopes in hydrology

Uranium isotopes occur in natural waters and can be used as natural tracers to identify water sources. The uranium isotope ^{234}U ($t_{1/2}=2.45\times10^5$y) fractionates with respect to its parent, ^{238}U ($t_{1/2}=4.468\times10^9$y), in response to physical and chemical environments existing during weathering (Kigoshi 1971; Chabaux et al. 2003). During the decay

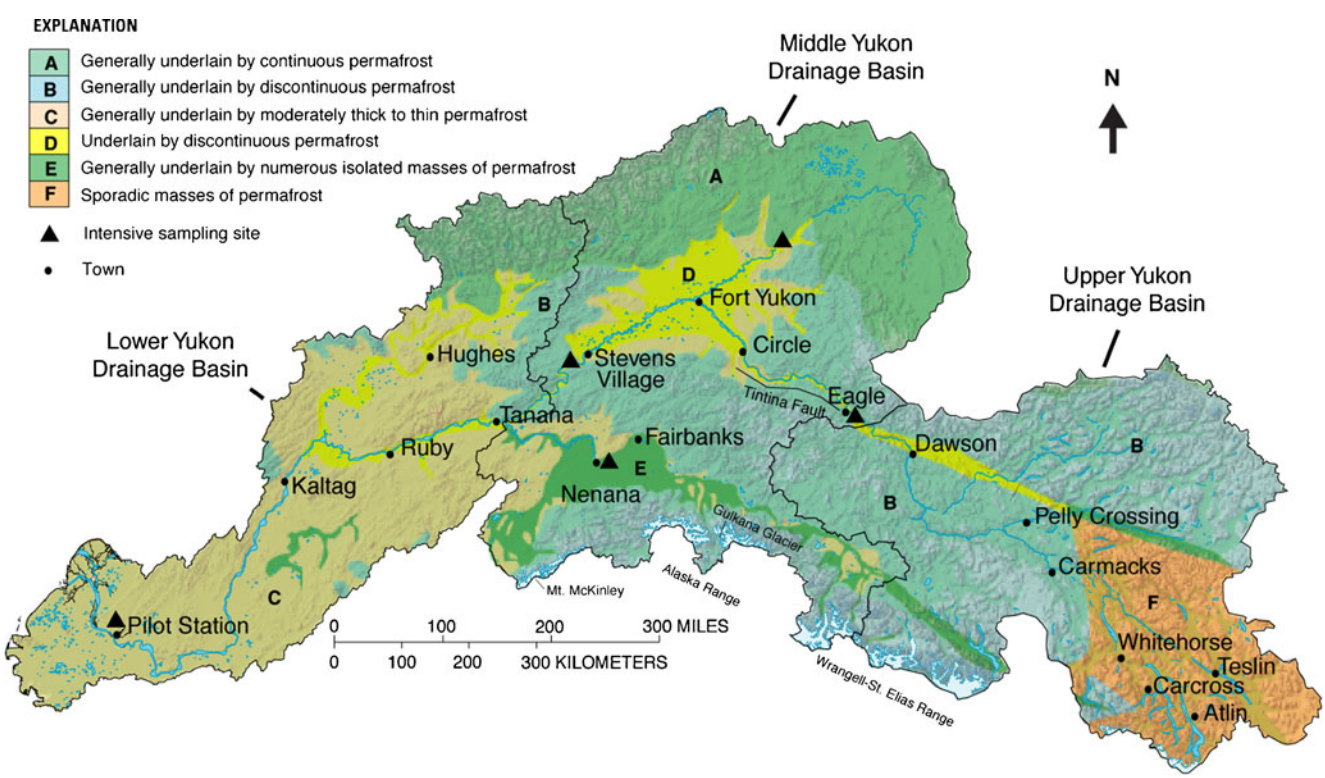

Fig. 2 Location of intensive sampling sites, major drainage basins, and permafrost regions of the Yukon River Basin (Brabets et al. 2000)

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process from ^{238}U to ^{234}U, the original atom undergoes alpha-particle-induced recoil dislocation within the grain where it is located, causing lattice damage in the host mineral's structure. This damage makes the material in the grain immediately surrounding the ^{234}U atom more susceptible to dissolution or, if the atom is near enough to a grain boundary, the decay process can eject the atom across the grain boundary into solution directly.

Owing to the enhanced susceptibility of ^{234}U to transport into the aqueous phase, water that saturates geologic material for an extended period of time often develops an excess of ^{234}U activity over ^{238}U activity, generally over timescales in excess of thousands of years. The ratio of ^{234}U activity to ^{238}U activity (the UAR, or uranium activity ratio) that develops in water is a function of mineral-surface area, water/rock ratio, U-content of the mineral and water phases, dissolution/precipitation rates, and time (Chabaux et al. 2003; DePaolo et al. 2006; Porcelli and Swarzenski 2003). Especially high UAR values are generated in water by high-U content, intensely fractured igneous and metamorphic rocks, as well as very fine-grained rocks (Wood et al. 2004; Bagard et al. 2008) where large surface area allows maximum alpha-recoil effect.

As a result of these factors, groundwater can develop UAR values much in excess of 1.000, the value in a closed system under secular equilibrium. UAR values for groundwater have been reported in excess of 25 (Osmond and Cowart 1976); these highest values are typically associated with long residence-time, low uranium concentration waters that accumulate a large excess of recoiled ^{234}U as compared to ^{238}U in solution. Once the groundwater is discharged to a surface environment, the UAR becomes characteristic of that water and can be used to help distinguish it from other waters.

The UAR of natural waters has been used by investigators to estimate river flow and mixing characteristics, groundwater contributions to surface-water flow, and mixing ratios of confluent tributaries merging into main-branch streams (Tuzova 1986; Tuzova and Filkin 1991; Tuzova and Novikov 1991; Riotte and Chabaux 1999; Chabaux et al. 2003; Snow and Spaulding 1994; Kraemer et al. 2002). Other recent work on rivers has focused on erosion rates, weathering, and sediment transport using uranium-series disequilibrium between sediment and water (Dosetto et al. 2006; Vigier et al. 2006). To date, no published studies of uranium isotopes describe in detail large river systems over multi-yearly hydrologic cycles. Furthermore, the behavior of uranium isotopes in rivers of cold regions, with their unique hydrologic characteristics, has not been studied in detail.

Methods

Dissolved uranium isotopes were determined for most of the sites sampled during this study. Uranium concentrations and UAR values were determined by quadrupole inductively coupled plasma/mass spectrometry (ICP/MS; Kraemer et al. 2002). This technique allows the rapid analysis of many samples for uranium isotopic composition without the intensive sample preparation and analysis time required by other methods. The technique is ideal for routine determinations of UAR in waters for an intensive, long-term sampling project such as the Yukon River Basin project.

Analytically, uranium concentration and UAR were measured in two separate steps. First a 10-ml aliquot of sample was spiked with a known quantity of ^{236}U to act as an internal standard and run on the ICP/MS in the elemental mode using EPA method 200.6 (US EPA 1994). Then a 1-L sample (or larger) volume was processed for UAR determination by evaporation to low volume (or dryness) and adjusting the final solution strength to 8 N HCl. The sample was then placed on a 1×8 anion exchange resin column to separate uranium from most of the common anions and cations. The adsorbed uranium was then eluted with distilled water into a vial for introduction into the ICP/MS. If a sample was thought to contain high levels of iron, as indicated by a yellow color of the 8 N HCl solution and a dark layer at the top of the resin column after passage of the solution through the column, the sample was rinsed with 7 N HNO_3 before uranium elution, which allows iron to elute while retaining most of the uranium on the resin. This extra step, however, was rarely necessary.

The instrument was tuned for maximum ^{234}U response using NIST 4321B (natural uranium standard) at a concentration of 80 μg/L and calibrated for $^{234}U/^{238}U$ activity ratio based on the reported value of the standard (0.963 ± 0.003). The instrument was then checked for stability and reproduction of a known ratio by introducing a Congo uranium-ore solution with a previously determined UAR of 1.000 ± 0.0005. Once the instrument was calibrated, samples were introduced. Three samples were analyzed in series, for a total of at least 15 measurements of ^{234}U and ^{235}U for each sample, followed by a Congo ore or NIST 4321B standard run to check for instrument drift. Blanks were run for each set of samples processed at the same time. Final UAR values were calculated and associated errors were propagated based on isotopic signal intensity, blank contribution, and instrument drift correction as necessary.

Hydrologic and geologic setting

The Yukon River Basin can be conveniently divided into three distinct areas (upper, middle, and lower) based on drainage area, physiographic characteristics, and permafrost occurrence (Fig. 2).

The geology of the upper Yukon basin consists of two main geologic regimes that are separated by the Tintina fault, a strike-slip fault that parallels the Yukon River. The northeast region is composed of a thick sequence of sedimentary rocks and the southwestern region is composed of a complex mosaic of mainly igneous and metamorphic rock types. The main tributaries to the

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Yukon in this area are the Teslin River (average annual flow of 334 m^3/s, or 5.2% of the average total flow of the Yukon River), Pelly River (385 m^3/s, 6% of total flow), White River (566 m^3/s, 8.8% of total flow) and Stewart River (453 m^3/s, 7% of total flow; Fig. 3; Table 1). The White River (drainage area 46,879 km^2, 5.5% of the total area of the Yukon River Basin) is one of only two large rivers in the entire Yukon River Basin that are predominantly glacier-fed. The Pelly (48,174 km^2, 5.6% of the area), Stewart (51,280 km^2, 6% of total area) and the Teslin (33,928 km^2, 4% of the total area) rivers are large, low-suspended-sediment rivers that drain the Yukon-Tanana uplands, a large area of generally flat, alluvium-floored valleys and ridges, with mountains up to 1,525 m in elevation. Mountains of the Wrangell-St. Elias Range mark the southern boundary of this area, characterized by peaks up to 5,790 m and ice fields from 914 to 2,133 m in altitude in interconnected valleys.

The middle basin of the Yukon River Basin includes the Porcupine and Tanana rivers and the physiographic region of the Yukon Flats, a large wetland area surrounding Fort Yukon. The Tintina Fault is in this sub-basin, and to the northeast of the fault there is a sequence of unmetamorphosed sediments (Precambrian–Mississippian). The area southwest of the Tintina Fault is a sequence of complex igneous rocks, metamorphosed sedimentary rocks, and volcanic rocks.

The Porcupine River Basin is underlain by continuous permafrost and is the largest sub-basin in the Yukon River drainage area, with an area of 116,550 km^2 (14% of the entire Yukon River Basin area). Average discharge of the Porcupine River is approximately 484 m^3/s (8% of the average annual Yukon River flow). The Porcupine River drains the Porcupine Plateau physiographic region, an area of low ridges and rounded to flat summits of 392–654 m. Valley floors are broad. The plateau has no glaciers and is composed of Paleozoic and Mesozoic sedimentary rocks as well as less abundant Paleozoic intrusive rocks.

The glacier–fed Tanana River is the second largest tributary to the Yukon River by area, with a drainage area of 114,737 km^2, draining 13% of the total Yukon River Basin. Average discharge is about 1,172 m^3/s (18% of the average annual flow of the Yukon River). The Tanana River Basin is bounded on the south by the Alaska Range/Northern Foothills Range, a rugged, glaciated region of snow-capped mountains. Mt. McKinley (6,195 m) is located in this basin. Most of the rivers flowing from this region enter the Tanana River from the south. They are swiftly flowing and braided, with headwaters at glaciers. Valley glaciers up to 40 km long and 5 km wide occur here. The Yukon/Tanana uplands area on the north side of the Tanana River is characterized by rounded ridges less than 914 m in elevation, as well as more rugged mountains, some greater than 914 m in altitude.

The lower Yukon River Basin is generally a narrow, low-relief area with the exception of a mountainous region in the upper part of the Koyukuk River Basin. The Koyukuk River drains another large basin (81,326 km^2, about 10% of the basin area) that, like the Porcupine basin, is underlain by continuous permafrost in its upland portion. It has an average annual discharge of about 821 m^3/s (about 13% of the average annual flow of the Yukon). The Koyukuk River Basin consists primarily of volcanogenic and andesitic-volcanic rocks of Early and Early–Late Cretaceous age. The other main drainage in the lower Yukon Basin is the Innoko River, which drains a large wetland area.

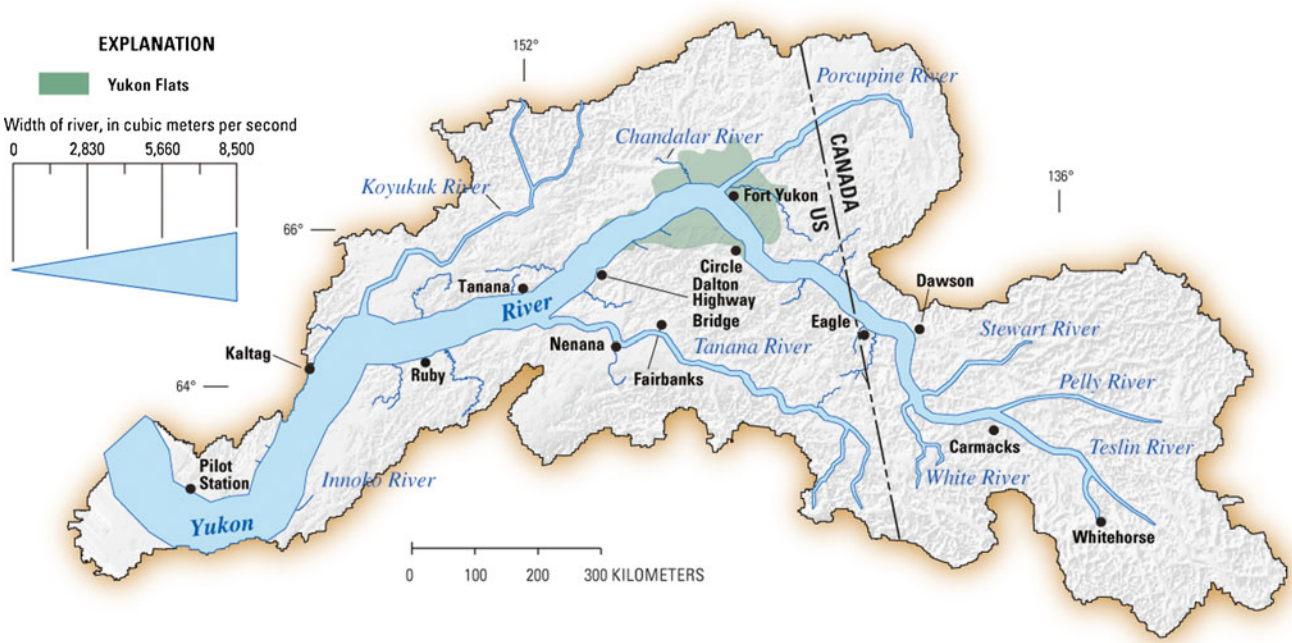

Fig. 3 Location and average annual flow of major rivers sampled in this report (from Brabets and Schuster 2008)

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Table 1 Characteristics of major rivers in the Yukon River Basin

River	Area (km^2)	% of Yukon River Basin	Average discharge (m^3/s)	% of total Yukon River flow	Permafrost coverage	Predominant rock type	Other notable features
Upper Yukon							
Stewart	51,282	6.0	464	7.0	Discontinuous	Mesozoic/Paleozoic	
Pelly	48,174	5.6	396	6.0	Discontinuous	Mesozoic/Paleozoic	
Teslin	33,929	4.0	334	5.2	Sporadic	Mesozoic Sedimentary	
White	46,879	5.7	566	8.8	Discontinuous	Cenozoic	Glacier fed
Middle Yukon							
Porcupine	116,550	14.0	623	8.0	Continuous	Cenozoic	
Chandalar	35,483	4.3	210	2.7	Continuous	Paleozoic	
Tanana	114,737	13.0	1,246	18.0	Discontinuous	Cenozoic/Paleozoic	Glacier fed
Lower Yukon							
Koyukuk	90,650	10.0	770	13.0	Continuous	Mesozoic/Paleozoic	Advanced stage permafrost melting

A typical hydrograph of a stream or river in the Yukon River Basin can be characterized by four seasons (Fig. 4; also see Brabets et al. 2000). Winter flow occurs from January 1 to March 31 and represents the period when streams are ice covered, terrestrial surface layers are frozen, and a deep-source groundwater is assumed to be the only input into the Yukon River and its tributaries. During April and May, ice breakup occurs, snowmelt begins, and flow increases rapidly. From June to September, snowmelt continues but flow gradually decreases as snowmelt ends. Flow is sustained or increased as a result of rainfall throughout the basin and high-altitude glacial melting. From October 1 to December 31 flow diminishes as surface runoff decreases and river-ice formation begins. Table 1 summarizes some of the geologic and hydrologic/permafrost conditions in the basin.

Results and discussion

Overview

The general isotopic nature of uranium in Yukon River Basin rivers is shown in Fig. 5, which illustrates characteristics of the rivers with respect to flow and uranium concentration. The figures are generated from the data that has previously been published in USGS reports (US Geological Survey 2001–2005) and are not reproduced here in tabular form.

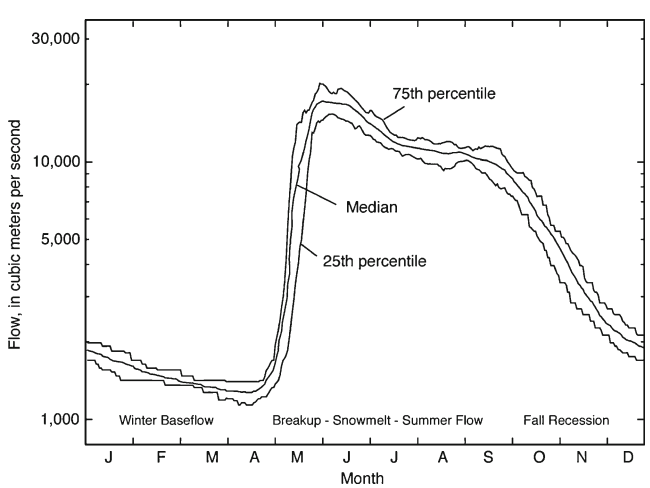

Fig. 4 Hydrographs of the Yukon River at Pilot Station, Alaska, based on records from 1977–2005. Location of Pilot Station is shown on Fig. 3

In general, the Porcupine River has the highest UAR values of any of the rivers, ranging from approximately 1.6 to 2.6, under all flow conditions or uranium concentrations. The Tanana River has the lowest UAR values, reaching minimum UAR values of just above 1.10. The Yukon samples (at Eagle, Stevens Village and Pilot Station) reflect UAR values that are intermediate between the Porcupine and Tanana rivers under most conditions, and, for the Pilot Station samples, reflect ratios of uranium contributed by all sources within the basin. As a result, UAR values do not vary greatly overall (between 1.3 and 1.6), but differences do exist when examined in detail.

Porcupine River

The Porcupine River exhibits a complex variation in uranium isotopic composition that represents the interplay of several water sources. The UAR values range from 1.60 to 2.56 and correlate with river discharge and uranium concentration. The high UAR (>2) values occur at low discharge when the uranium concentration is highest, mostly during the winter, but also during periods of drought and low flow in the summer. This pattern reflects a deep-groundwater-dominated source that supplies water to the river even when shallower sources are frozen or depleted. Lower UAR (to 1.6) values correlate with higher discharge and lower uranium concentrations, reflecting the influence of a combination of snowpack melt, atmospheric precipitation and runoff, and thawing and movement of shallow groundwater.

Water that enters the river as a result of direct atmospheric precipitation and melting of accumulated snowpack has little interaction with mineral matter, and as a result does not accumulate appreciable uranium. This water serves only to dilute the deep and shallow groundwater sources. The seasonally frozen, shallow groundwater environments (river-valley floodplain deposits characterized by seasonally frozen water) have lower UAR values and uranium concentrations compared to the deeper, longer residence-time and possibly higher rock/water ratio groundwater source.

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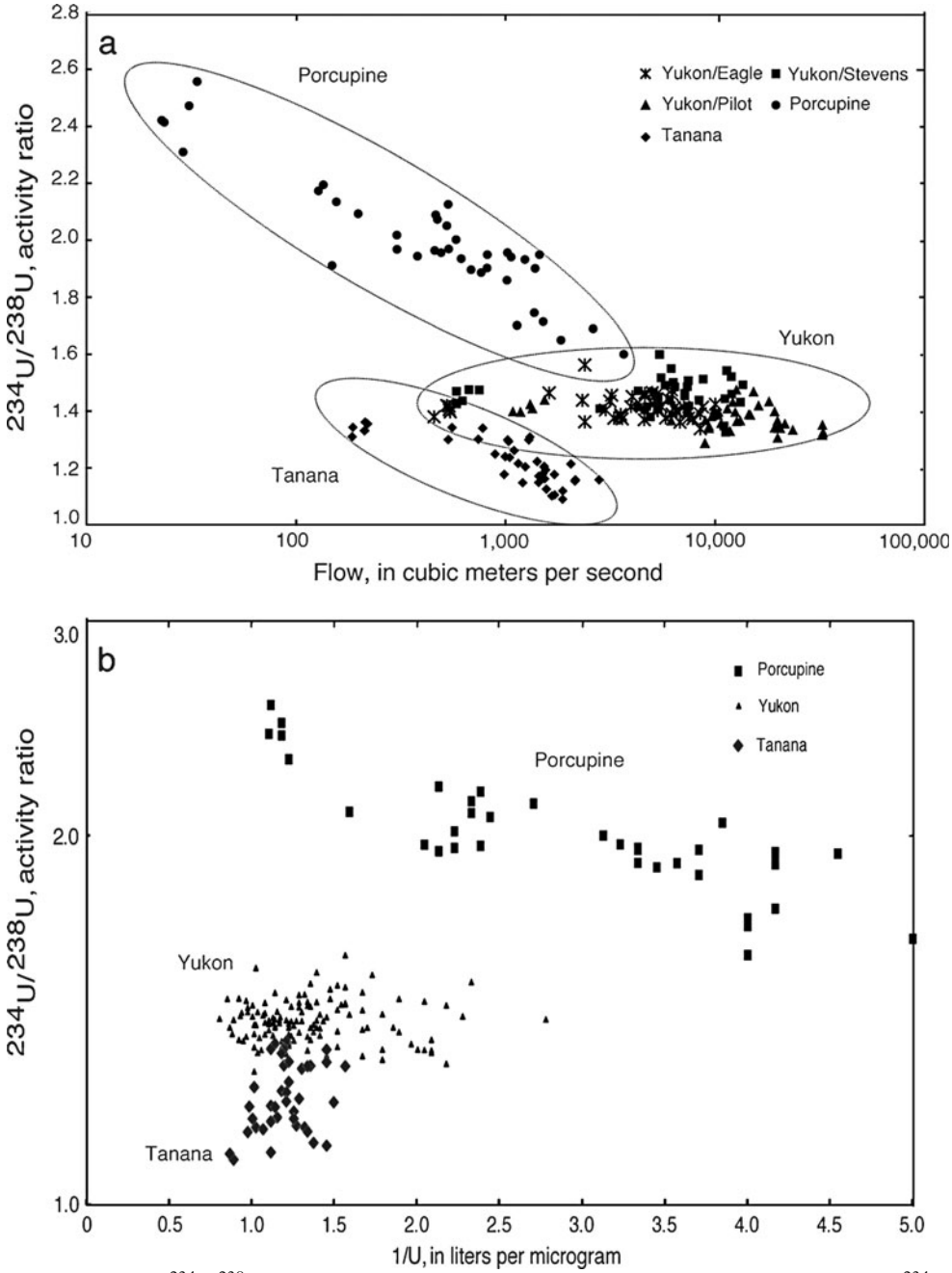

Fig. 5 Plot of **a** river flow versus $^{234}U/^{238}U$ activity ratio (UAR) and **b** reciprocal uranium concentration versus $^{234}U/^{238}U$ activity ratio for all mainstem Yukon River Basin fixed sites from 2001 to 2005

From the data presented in Fig. 5 and knowledge of the physical hydrography of the area, it can be reasonably concluded that three significant types of water contribute to the uranium isotopic characteristics of the Porcupine River: a deep, year-round source of groundwater; a shallow groundwater subject to seasonal freeze/thaw cycles; and snowmelt and atmospheric precipitation that contains little to no uranium and serves only to dilute the uranium from the other two sources.

In the Porcupine Basin, the river water, deep groundwater and snowmelt uranium isotopes can be fairly well estimated, and the flow of the Porcupine at sampling times has, in most cases, been measured or accurately estimated. The isotopic composition of the shallow groundwater end-member, however, is at present less well constrained and very possibly could change seasonally and geographically. However, it is likely that an average UAR of the shallow groundwater source is similar to the summer flow of the Yukon River after the meltwater fraction has passed through, which generally has a UAR in the range of 1.3–1.6 and a uranium concentration of about 1 μg/L, if mineralogy, uranium content, water residence time, degree of weathering and grain size distribution of the composite sediment mantle in both basins is assumed to be similar.

 DOI 10.1007/s10040-012-0829-3

Another possible type of shallow groundwater composition could be that of water released by thawing permafrost, which underlies most of the Porcupine Basin (Brabets and Schuster 2008). In order to examine this possible source of water a sample of permafrost from the US Army's Cold Region Engineering and Environmental Laboratory experimental tunnel near Fairbanks, AK was collected and found to have a UAR of 1.33 and a uranium concentration of 0.7 μg/L. These uranium concentration and UAR values imply that permafrost water is not significantly different from the previously discussed shallow alluvial water source and could not be used to distinguish between these two types of water on a regional, basin-wide scale, but may be useful on a site specific, local basis.

If the source water uranium and UAR values are assumed to be as described, and represent the only or most significant sources of water to the river, the contributions of each source to flow in the Porcupine River can be estimated using the relationships:

$$f_{\mathrm{d}} + f_{\mathrm{s}} + f_{\mathrm{m}} = 1 \tag{1}$$

$$f_{\mathrm{d}}\left(^{234}\mathrm{U}\right)_{\mathrm{d}} + f_{\mathrm{s}}\left(^{234}\mathrm{U}\right)_{\mathrm{s}} + f_{\mathrm{m}}\left(^{234}\mathrm{U}\right)_{\mathrm{m}} = \left(^{234}\mathrm{U}\right)_{\mathrm{r}} \tag{2}$$

$$f_{\mathrm{d}}\left(^{238}\mathrm{U}\right)_{\mathrm{d}} + f_{\mathrm{s}}\left(^{238}\mathrm{U}\right)_{\mathrm{s}} + f_{\mathrm{m}}\left(^{238}\mathrm{U}\right)_{\mathrm{m}} = \left(^{238}\mathrm{U}\right)_{\mathrm{r}} \tag{3}$$

and

$$Q_{\mathrm{d}} + Q_{\mathrm{s}} + Q_{\mathrm{m}} = Q_{\mathrm{r}} \tag{4}$$

where f is the fraction of deep groundwater (d), shallow groundwater (s), melt-water (m), or river water (r), ^{234}U and ^{238}U are the activities of the respective dissolved uranium isotope, and Q is the flow of the respective end-member or river-water component.

The flow contributions of the hypothetical end-members to the total Porcupine flow are shown in Table 2 using flow data measured at or as close to the sampling date as possible, a shallow end-member with uranium isotopic characteristics of UAR=1.5 and U=1.0 μg/L, a deep component water of UAR value=2.6 and a U concentration of 1.0 μg/L, and uranium-free meltwater.

These results demonstrate that meltwater/rain can make up more than half of the total flow in the Porcupine River during the non-winter flow period, whereas the deep groundwater fraction is predominant only during the winter flow period. Additionally, the deep groundwater appears to contribute significantly to flow in the river during the non-winter months as well. Data in Table 2, although only approximate, would imply that in the Porcupine Basin, when the spring flow increases, not only do the melt/rain and shallow groundwater sources increase, but the deep groundwater flow increases as well, up to about five times its winter base-flow amounts. These increases make the deep groundwater supply relatively more significant during the non-winter months compared to the winter months. The reason for the enhanced deep groundwater flow during the summer compared to the winter months may simply be that when the shallow groundwater freezes during the winter its contribution to hydraulic head is eliminated when the water is frozen and becomes immobile. As a result, flow below the permafrost to the river channel is significantly less than during the summer, when the water is liquid and contributes to the head. If true, this implies that there are conduits through the permafrost that allow flow communication between deep and shallow groundwater zones.

Figure 6 illustrates the relative importance of the flow components to the Porcupine main-channel flow. During the lowest flow, deep groundwater is the sole provider of flow to the river, but during higher flow periods, the shallow groundwater and melt/rain contribution are by far the most significant contributors, with deep groundwater being relatively much less significant.

Figure 7 illustrates the temporal UAR trend of the Porcupine River and demonstrates differences that could be attributed to variations in seasonal mixing of the deep and shallow end-member waters. During the first year of observation (2001), the winter sample had a high UAR value (~2.4) and the later, warmer-weather samples clustered at lower values, ranging between 1.8 and 2.0 for the remainder of the year. During succeeding years, the yearly minimum UAR values of the river water decreased and the annual spread of UAR values increased. It is possible that this pattern is in part due to lack of sample coverage in the early parts of the year for the first few years, when samples were not collected due to logistical concerns caused by ice in the river, but it is highly unlikely that the entire observed annual increasing spread of values is attributable solely to this cause. Rather, there appears to be an overall correlation between the annual hydrograph flow history and the spread of UAR values with time of year.

During the first three years of monitoring, the hydrographs indicate years of light snow pack and relatively wet summers, resulting in relatively high flows during most of the summer. The last two years, however, reflect a greater accumulated snow pack, resulting in much higher peak flow during the thaw warming period, but much dryer summers in general. The Porcupine River also shows a progressively more dramatic and rapid trend toward re-establishing its high winter-time, deep groundwater UAR value, highlighted by the years 2004 and 2005, the periods of least rainfall in the basin.

Further monitoring of the river would be valuable in understanding the relationship between deep and shallow groundwater contributions to the river and its causes. Such a relationship may be useful in studying hydrologic response to changes in atmospheric patters. For example, it has been reported (Hartman and Wendler 2005) that when the Pacific Decadal Oscillation (PDO) shifted to the present warm phase in 1976, the amount of annual

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Table 2 Flow contribution of various end-members to total Porcupine River flow

Porcupine River						
	Shallow GW end-member UAR=1.50					
	Deep GW end-member UAR=2.60					
Date	U conc. μg/L	UAR ratio	Total flow m^3/s	Shallow GW m^3/s	Deep GW m^3/s	Meltwater m^3/s
3/29/2001	0.85	2.472	31	3	23	5
6/30/2001	0.32	2.002	581	102	84	395
7/16/2001	0.24	1.896	685	106	59	521
8/7/2001	0.41	2.073	473	93	100	279
8/13/2001	0.45	2.018	303	72	64	166
8/27/2001	0.37	2.126	532	85	112	335
9/17/2001	0.31	1.969	535	96	70	369
3/11/2002	0.91	2.422	23	3	17	2
6/6/2002	0.30	1.902	816	156	88	571
6/18/2002	0.24	1.932	1,238	181	116	941
6/26/2002	0.28	1.901	1,385	248	140	997
8/13/2002	0.26	2.051	524	68	68	388
8/26/2002	0.30	1.956	1,023	181	126	716
8/29/2002	0.30	1.949	820	146	99	574
9/27/2002	0.49	1.968	303	86	63	155
4/4/2003	0.90	2.557	34	1	29	3
6/9/2003	0.24	1.745	1,374	258	72	1,044
6/19/2003	0.45	1.956	493	131	91	271
7/1/2003	0.42	1.964	459	112	81	266
7/23/2003	0.29	1.886	765	145	77	543
8/19/2003	0.27	1.859	1,017	186	88	742
9/22/2003	0.47	1.944	379	107	71	201
4/9/2004	0.82	2.310	29	6	17	5
6/2/2004	0.20	1.649	1,841	320	48	1,473
6/8/2004	0.25	1.714	1,515	307	72	1,136
6/11/2004	0.24	1.941	1,065	154	102	809
7/29/2004	0.63	2.093	198	58	67	73
8/9/2004	0.22	1.935	615	82	53	479
9/9/2004	0.43	2.135	156	29	39	89
4/6/2005	0.85	2.415	24	3	17	4
5/7/2005	0.19	1.911	149	18	10	121
5/11/2005	0.25	1.600	3,661	837	78	2,746
5/19/2005	0.25	1.689	2,622	546	109	1,967
5/25/2005	0.27	1.949	1,453	234	159	1,061
6/7/2005	0.25	1.701	1,136	233	50	852
7/14/2005	0.43	2.089	464	93	106	265
8/3/2005	0.47	2.195	135	24	40	72
8/26/2005	0.42	2.174	128	21	33	74

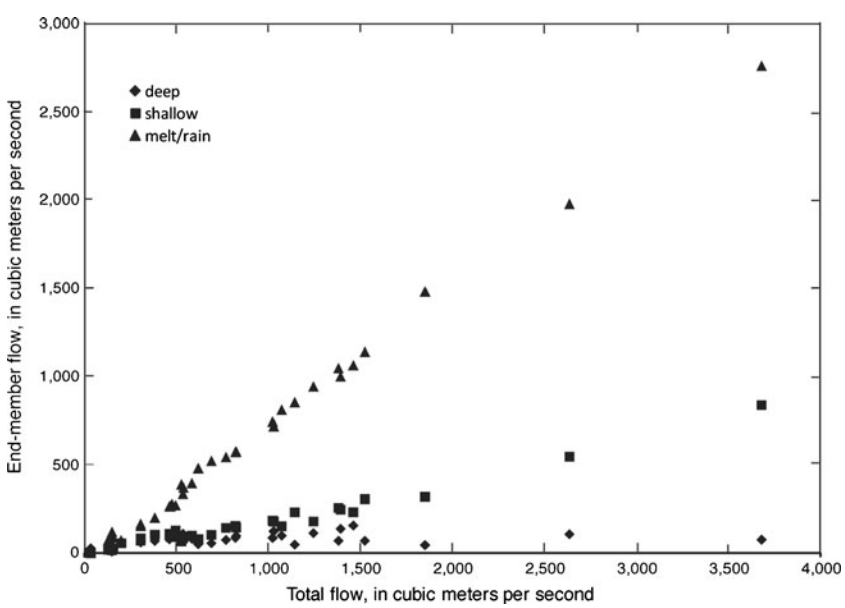

Fig. 6 Plot of calculated *melt/rain*, *shallow* groundwater, and *deep* groundwater flow versus total estimated flow of the Porcupine River

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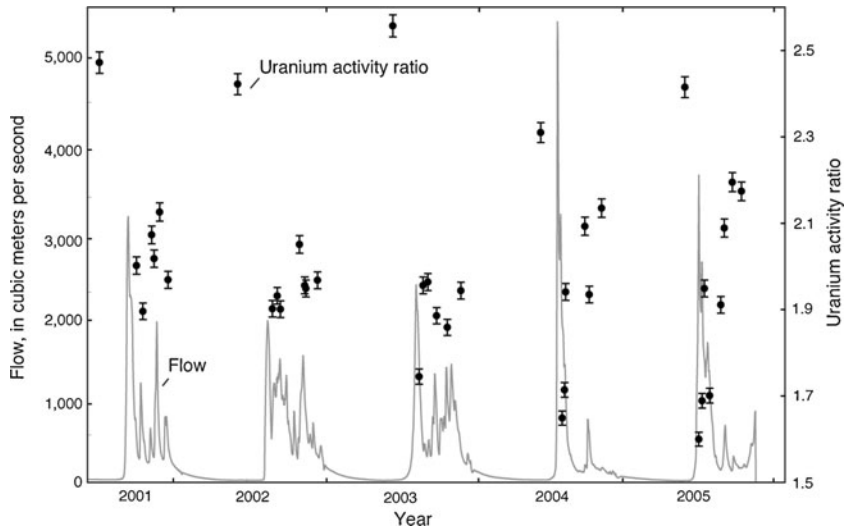

Fig. 7 Plot of flow and UAR values versus time for the Porcupine River near Ft. Yukon fixed sampling site from 2001 to 2005. *Bars* on UAR data points represent ±1% 1-sigma error

precipitation in the interior region of Alaska decreased significantly. A decrease in the annual average discharge of the Porcupine River has been attributed to this effect (Brabets and Walvoord 2009). At the same time, an increase in air temperature resulted in enough warming to start thawing areas of discontinuous permafrost (Osterkamp and Romanovsky 1999). UAR values in the river water may change in response to these larger effects, and would be useful in interpreting resulting changes of the hydrology of a region responding to these changes.

Tanana River

The Tanana River uranium data form a field completely separate from the Porcupine River data and nearly separate from the Yukon data in Fig. 5, with generally lower UAR values. When the ^{234}U versus ^{238}U activity data for the Tanana samples are plotted (Fig. 8), the results cluster in such a way that bounding lines of constant UAR values radiating out from the plot's origin encompass all the Tanana data points.

The actual activities of water sources A and B are not constrained in this diagram, but probably plot along their respective lines at or beyond the maximum values of the most U-enriched samples. The simplest assumption is, therefore, that the Tanana River samples are mixtures of meltwater and two major sources of water with UARs of approximately 1.10 and 1.43. Information on the nature and sources of these two uranium-containing water types is limited, as is information as to why their UAR values differ so significantly. Some understanding can be gained by examining the temporal variation of the uranium isotopes in the river over yearly cycles.

Winter base-flow water almost certainly originates from within the lower- elevation, wide, deep Tanana valley alluvium and from that of its major tributaries, mostly to the north of the river, where a large amount of groundwater is stored in a liquid state throughout the year.

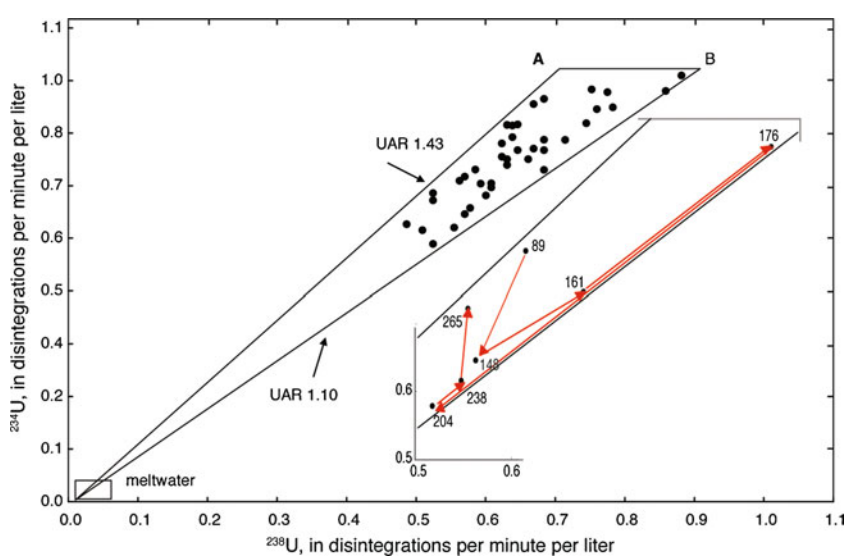

Fig. 8 Plot of ^{234}U activity versus ^{238}U activity of Tanana River fixed sampling site samples from 2001 to 2005. Constant *UAR lines* are drawn to bracket the data points and suggest reasonable end-member UAR values. The hypothesized end-members of the mixing system are indicated as *A*, *B*, and *meltwater*. Inset is of the data points for the Tanana River during the year 2004 showing changes in the UAR of the river water throughout that year

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These wide, deep alluvial valleys supply water to the Tanana during times when high-altitude glacial melting and the higher-elevation, smaller alluvial valley supplies are minimal to non-existent due to water being frozen. As a result, the UAR of the Tanana River at this time is characteristic of deep, lower-altitude alluvium water. Figure 9 shows the flow and UAR values of the Tanana with time, and reveals the strong influence of low UAR values in the channel water during the warm months of the year.

The lower UAR values that are found in the warm months approach those of glacier runoff (Gulkana glacier, UAR=1.03, but low uranium concentration, Table 3) and higher-elevation headwaters of the Yukon River and its tributaries (1.10–1.20), supporting the concept that a non-meltwater component flowing in the Tanana River during the later summer is not from the deep alluvium typically found in river basins north of the river. Rather, a large component likely originates from the shallow alluvial valleys at higher altitudes on the more mountainous slopes located on the south side of the river basin.

Support for this conclusion comes from Anderson (1970), who noted that 85% of the annual runoff from the Tanana River Basin originates from areas with altitudes greater than 1,524 m, which occur predominantly to the south side of the river in the Alaska Range, mostly occurring between June and September. Thus, it seems likely that melting of high-elevation glaciers on the southern rim of the basin is responsible for both non-uranium-containing late-season meltwater and the less mature, lower-UAR alluvial water that is forming in the higher altitude, individually smaller alluvial deposits.

This interpretation is supported and further clarified by detailed examination of annual time-series sequences of samples for the Tanana River and provides additional information on meltwater sources of supply. Using the 2004 data as an example, a seasonally changing pattern of water sources is apparent, as indicated by the arrows on the Fig. 8 insert. During the winter (Julian day 89), base-flow is mostly the high UAR water type. As spring and summer progress, a shift occurs concurrently toward the lower-UAR water source and the meltwater source (plot origin; Julian day 148). With additional seasonal warming, the shift then becomes very pronounced toward the lower uranium activity ratio source only (Julian days 161 and 176) and away from both the meltwater and the higher UAR source. After this time, a second flush of meltwater occurs in the river, diluting the mostly lower-UAR end-member water (Julian day 204). Later in the year (after Julian day 204), as temperatures begin to drop in the drainage basin and the amount of water from high-elevation sources decreases, the river trends back toward higher uranium isotopic activity ratio (Julian day 265). Over the duration of the winter, the water in the river would trend back toward the higher-UAR base-flow water signature.

It therefore appears that two melt-water events, or pulses, passing through the Tanana River each year can be detected by use of uranium isotopes. One, early in the summer, occurs when local snowpack and ice melts. A second influx of meltwater occurs later in the summer, presumably when higher-elevation mountain glaciers start to contribute large amounts of meltwater as a result of warmer temperatures at higher elevation.

The uranium isotopic data for the Tanana River further suggests that the exposure of newly formed glacially produced fine material in contact with water will produce a dissolved UAR that is lower than that which forms from water in longer contact with older alluvial material. Robinson et al. (2004) suggest that high UAR values in surface waters can result from a combination of a high physical weathering rate releasing ^{234}U to water and a low flushing rate of the water which enables the accumulation of significant amounts of this recoiled isotope in the water. The present study suggests that if this model is correct, in the glaciated terrain of the Yukon Basin, the melt-water in the smaller, younger, high-elevation sub-basins does not have sufficient residence time to accumulate a significant

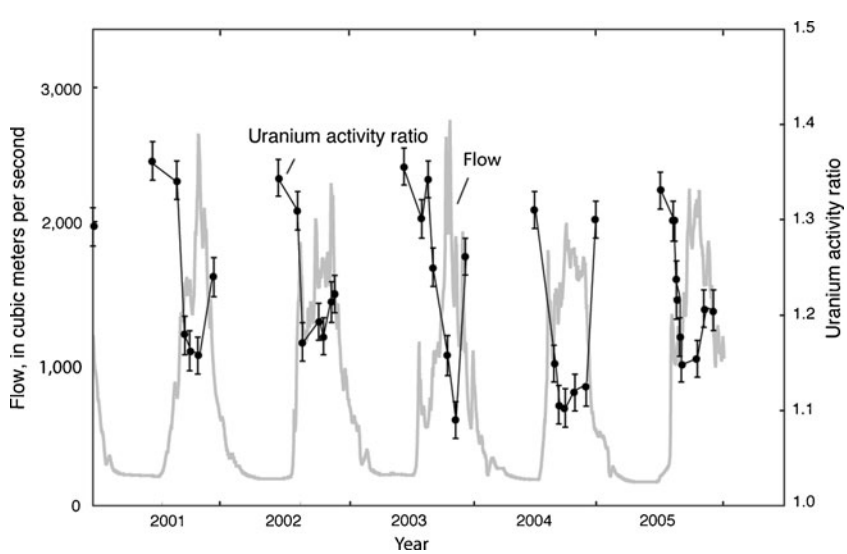

Fig. 9 Plot of flow and UAR values versus time for the Tanana River at Nenana fixed sampling site for 2001–2005. *Bars* on UAR data points represent ±1% 1-sigma error

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Table 3 Uranium data for rivers mentioned in text

River	Location	Date	U conc. μg/L	$^{234}U/^{238}U$ Activity ratio
Yukon	At Whitehorse	6/7/2004	0.74	1.177±0.007
	At Whitehorse	6/7/2004	0.70	1.154±0.009
	At Whitehorse	6/7/2004	0.71	1.118±0.006
	At Whitehorse	8/27/2004	0.65	1.150±0.005
	At Whitehorse	8/27/2004	0.65	1.134±0.007
Takhini	60°50′11"N 135°12′19"W	6/7/2004	0.46	1.141±0.007
	At Whitehorse	8/27/2004	0.26	1.146±0.005
Nares	60°09′54"N 134°42′29"W	6/5/2004	0.90	1.141±0.007
	At Carcross	8/25/2004	0.91	1.146±0.005
Atlin	59°35′57″N 133°48′48″W	6/6/2004	0.57	1.173±0.008
	Near Atlin	8/26/2004	0.61	1.170±0.010
Big Salmon	61°52′57″N 134°53′00″W	6/10/2004	0.83	1.122±0.007
	At Carmacks	8/30/2004	2.44	1.263±0.004
Teslin	61°34′16"N 134°54′07"W	6/9/2004	0.84	1.287±0.006
		8/29/2004	0.72	1.327±0.007
Koyukuk	64°57′25"N 157°33′48"W	6/9/2003	0.38	1.374±0.015
		8/29/2003	0.87	1.344±0.011
Gulkana glacier runoff	Basal flow	8/22/2003	0.15	1.030±0.009
Permafrost	64°50′N 147°35′W	2003	0.70	1.328±0.012

amount of recoil ^{234}U released as a result of the enhanced physical weathering caused by the glacial action on the substrate rock. The assumed longer residence time of the water in the more extensive, lower-elevation alluvial deposits, however, is sufficient to produce the elevated UAR values from the alpha-recoil process operating therein. Long-term monitoring of this isotopic behavior may allow evaluation of changes in the amount of water coming from higher-elevation sources, and help quantify the effects of glacial melting within the basin over longer periods of observation.

Mainstem Yukon River

The main-stem of the Yukon River integrates the flow of all sub-basins that comprise it. As a result, its waters contain a record of the processes that occur in the sub-basins and even record the changing intensity of those processes over time. Monitoring uranium isotopes of water at various locations along the main-stem of the river, therefore, can supply information that relates to such changes.

The Yukon River at Whitehorse (Fig. 3; Table 3), high in the headwater area of the river and in an area subjected to recent mountain glaciation, has a much lower UAR value (1.11–1.18) than Yukon River sites further downstream. These headwater samples have UAR values similar to but slightly higher than that of the Gulkana glacier runoff, but contain greater uranium concentrations, indicating that the water in this section of the Yukon may have had time to interact with the recent, glacially produced material in the valley alluvium.

Similarly, the Takhini (UAR between 1.18–1.12), Nares (1.14), Atlin (1.17), Big Salmon (1.12–1.26) and Teslin (1.29–1.33) rivers, all high in the headwater area of the Upper Yukon Basin, exhibit UAR values lower than downstream samples and tributaries. At sampling sites progressively down stream on the Yukon below Whitehorse, the values tend to become higher as higher-UAR value tributaries empty into it. At Eagle, many tributaries of differing UAR values have contributed to the flow of the river.

Figure 10a shows the variation in UAR values of the river at Eagle over the period of study. The general characteristic of the UAR pattern is one of highest UAR values in the early spring flush period, with somewhat lower UAR values occurring through the summer and fall. The initial increase in flow in the channel near Eagle in the spring is, in addition to snowpack melt, the result of the thawing of local, broad valley-fill alluvial ice with a comparatively mature (high) UAR value compared to the higher-elevation river deposits which are still frozen and have not been contributing water to the system this early in the year. As temperatures rise above the melting point at the higher elevations of the catchment, the supply of groundwater from these lower-UAR sources increases, causing a lowering of the overall UAR value of the river at Eagle with time during a single year. Future monitoring may provide evidence of longer-term trends of freeze-thaw dynamics and flow variation. For example, a positive trend toward increasing flow, likely due to increased high altitude glacier melt, has been noted for the Tanana River (Brabets and Walvoord 2009) and may become clearly reflected in the Yukon River at Eagle uranium isotopic temporal patterns.

The Yukon River at Pilot Station (Fig. 10b) reflects the variation in relative contributions of the Porcupine River (2003, higher UAR values) and the influence of high-elevation alluvial water (especially the drought year 2005, lower UAR values). The Koyukuk River, which enters the Yukon River between Pilot Station and Stevens Village, is a large tributary to the Yukon River, but was not extensively monitored during this study, and its effect on the Yukon River at Pilot Station cannot be readily resolved. However, the two measured UAR values of the Koyukuk (1.34 and 1.37, Table 3), if characteristic of the

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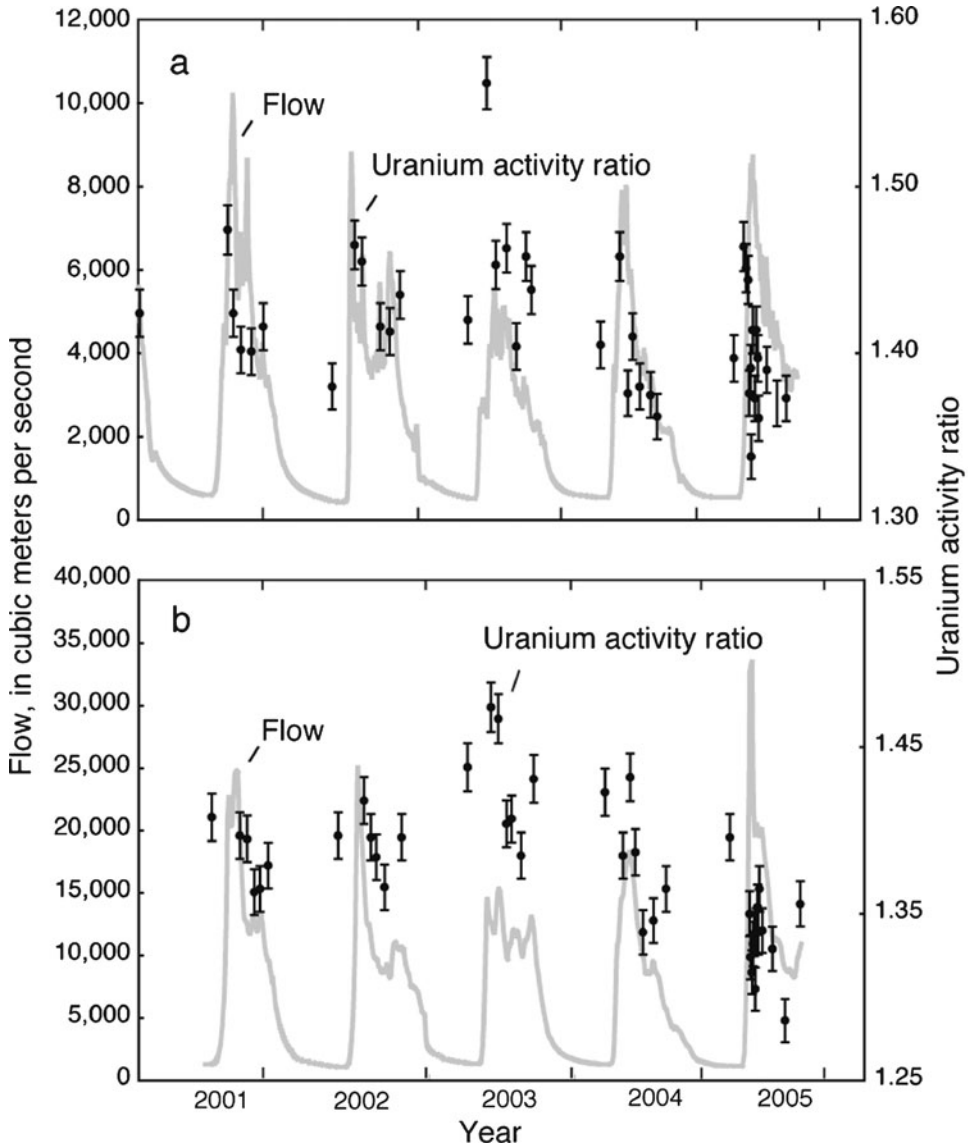

Fig. 10 Plot of flow and UAR values for the Yukon River at **a** Eagle and **b** Pilot Station fixed sampling sites from 2001–2005. *Bars* on UAR data points represent ±1% 1-sigma error

river throughout the year, make it unlikely to be the entire cause of the observed lowering of the UAR values at Pilot Station, at least for 2005, due to the even lower UAR values attained by the Yukon at Pilot Station. Thus, the continued low-UAR values of the Yukon River all the way to Pilot Station may continue to reflect the upland high-elevation alluvial contribution. The overall lowering of the UAR values in general over the period of this study for the Pilot Station samples may be attributable, at least in part, to changes in Koyukuk flow and merits further investigation.

In 2005, the annual discharge from the lower-UAR Tanana River was the highest for the 2001–2005 period, and likely accounts at least in part for the lower UAR values for the Yukon River at Pilot Station for that year. The same processes that account for the lowering of the UAR values at Eagle would also be reflected at the Pilot Station site. Increased glacial melting during this year, which is probably occurring on a basin-wide scale, is at least partially responsible for the decrease in UAR values at Pilot Station, thus making the UAR values at Pilot Station of possible value in monitoring processes occurring in headwater regions.

Conclusions and summary

Uranium isotopes have great potential to detect the effects of long-term changes in hydrologic processes in arctic environments if they can be monitored on a systematic basis. Evidence presented in this paper illustrates that uranium isotopes can be used to identify and separate, at least qualitatively, water origins in an arctic hydrologic environment. Signatures of water traveling overland (precipitation/meltwater); through bedrock, alluvial deposits and active zones; and glacial-melting environments can be used to demonstrate relative mixing patterns in a river throughout the year. Records of temporal changes in uranium isotopes taking place at various places within a

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monitoring network of a basin can provide inferences about the effects that changing climatic patterns are having on a high-latitude, glaciated basin's hydrology. Such information would be valuable in estimating changes in river-water quality and quantity in response to such induced stresses as climate change.

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