H₂Open Journal

Water geochemical markers allow estimation of the impact of climate change on the hydrological regime of an Alpine river (River Arve, France, Switzerland)

Pascale Nirel[a,*], Ion Iorgulescu[a] and Montserrat Filella[b]

[a] Office cantonal de l'eau (OCEau), Service de l'écologie de l'eau, Rue des Gazomètres 7, Case postale 206, CH-1211 Geneva 8, Switzerland

[b] Department F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland

*Corresponding author. E-mail: lilimme@yahoo.fr

Abstract

The impact of climate change upon the hydrological regimes of streams has become an issue of major concern that requires adapted tools to detect and follow the scale of possible changes. In this study, we use a geochemical approach that exclusively relies on measurements of chemical concentrations in order to investigate the effect of climate change on the hydrological regime of the River Arve, a Franco-Swiss river running from the Alps to the River Rhône. Our method relies on the use of a dimensionless parameter, the ratio of uranium and barium concentrations in river waters. This marker has the advantage of not needing the measurement of river discharges. Its application to 25 years of data collected in the River Arve by Canton Geneva, Switzerland, leads to the conclusion that the glacio-nival signature is appearing earlier in the year and lasts for longer periods.

Key words: Alpine river, climate change, geochemical markers, glacier melting, hydrological cycle

Highlights

- Given the increasing concern for the possible impact of rising temperature on water supplies, we believe that the findings presented in our paper will be of value to readers.
- After initially researching geochemical tracers allowing determination of water geological print, we examined the use of a geochemical approach to establish the impact of climate change on the freshwater hydrological regime.
- Our approach relies on a long-term survey and can valorise databanks.

INTRODUCTION

The impact of climate change upon hydrological regimes and water quality has become a major issue, raising the need of adequate tools to detect both the existence and magnitude of changes (Delpla *et al.* 2009; Blöschl *et al.* 2017, 2019). Climate change does not only affect the magnitude and frequency of floods but also water quality, biodiversity, and landscape and human activities (Schmutz & Sendzimir 2018).

Chemical signatures might provide a useful tool to follow the potential impact of climate change upon hydrological regimes because the processes controlling the chemical composition of a given water body are dependent upon bioclimatic variables (e.g., temperature, frequency and amplitude of rainfall, type and abundance of microflora). In practice, however, understanding chemical signatures is far from straightforward because, on the one hand, they are also dependent on properties of the physical environment (e.g., porosity and hydraulic conductivity) (Garrels & Mackenzie 1967; Meybeck 1987) and, on the other hand, many factors aggregate giving a complex signature which is difficult to disentangle. In spite of these difficulties, a large number of chemical parameters have been used in order to characterise the water composition according to its origin such as isotopes, the presence of (organic and inorganic) pollutants, radioactive and radiogenic elements. Although these approaches have proven their efficacy, they often rely on the use of concentrations which, in rivers, require to be associated with corresponding water discharges in order to be meaningful. Streamflow measuring and monitoring is a challenging and time-consuming task due to technical difficulties and metrological issues.

The use of chemical signatures to identify possible climate-associated changes requires access to long-term, coherent data. Such data sets are scarce because few institutions ensure long-term monitoring. The Canton of Geneva, Switzerland, has controlled water quality data for several decades with major elements having been analysed on a regular basis since the 1960s, dissolved trace elements since 1994 and discharge from the beginning of the 20th century (https://www.hydrodaten.admin.ch/fr/2170.html). This data set has been used for detecting temporal trends in Lake Geneva's trace element concentrations (Rodríguez-Murillo et al. 2018) and for the establishment of a methodology for water typisation according to a geochemical signature based on the concentration ratio of two chemical elements, barium and uranium (Filella et al. 2014). The use of elemental ratios – a dimensionless parameter – has the unique advantage of suppressing the need for knowing water discharge. In Filella et al. (2014), the possibility of using the U/Ba ratio to identify hydrological regimes in an Alpine river, the River Arve, was sketched. This work is extended here. The River Arve is not only a major tributary of the River Rhône but is also a source of drinking water; consequently, it receives special attention with at least 12 sampling campaigns per year in Canton Geneva. This river presents a mixed hydrological regime: pluvial in the winter and glacio-nival in summer following the melting of snow and upstream glaciers.

METHODS

Study area

The River Arve (France, Switzerland) is an Alpine river having a drainage basin of 2,080 km^2 and a mean annual flow of 77 m^3 s^{-1}. About 140 km^2, or 6% of the basin, are covered by glaciers. Its sources are on the northern side of the Mont Blanc massif (Figure 1). Catchment elevations span a very wide range from 4,810 m a.s.l. at the top of the Mont Blanc to 370 m a.s.l. at the confluence with the Rhône River in Geneva. Mean catchment elevation is 1,370 m a.s.l. and 60% of the drainage basin has an elevation above 1,000 m a.s.l. Precipitation, distributed quite evenly throughout the year is enhanced over complex terrain, with mean annual precipitation ranging from 950 mm/y in the low-lying areas to over 2,000 mm/y in high-elevation part of the basin.

The main tributaries are Arveyron d'Argentière, Arveyron de la Mer de Glace, Bon Nant, Sallanches, Foron du Reposoir, Giffre, Borne, Menoge, Foron, Seymaz, and Aire. The only tributary entirely in Switzerland is the Seymaz.

The upper part of the river flows through a plutonic basement before reaching alluvial terrains (limestone, marl, sandstone, and glacial till).
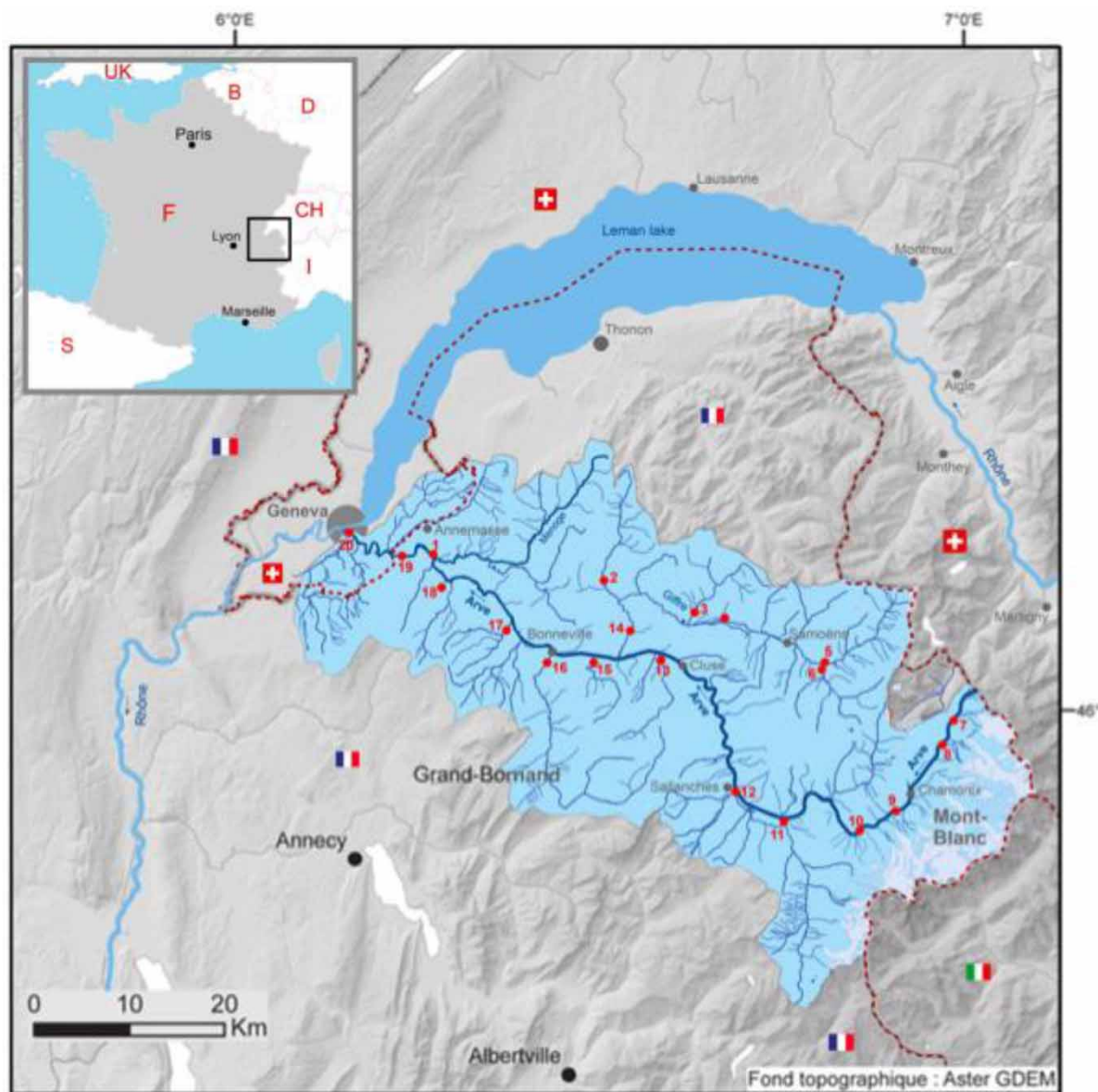
Figure 1 | The River Arve and tributaries with location of sampling sites (numbered 1 to 20): 1, Menoge at Bonne; 2, Risse at St Jeoire; 3, Foron at Taninges; 4, Giffre upstream Taninges; 5, Giffre upstream Sixt; 6, Giffre south; 7, Arve at Mont-Roc; 8, Lognon; 9, Arveyron; 10, Arve at Les Houches; 11, Bon Nant at St Gervais; 12, Arve at Sallanches; 13, Foron du Reposoir; 14, Giffre at Marignier; 15, Bronze; 16, Bonne; 17, Foron de la Roche; 18, Berny at la Fornasse; 19, Arve at Arthaz; 20, Arve at Geneva.

Sampling

Concentration data used in this study were collected as part of a water-quality monitoring programme (1994–2018) set-up by the Service de l'Ecologie de l'Eau (SECOE; Service for Water Ecology) of the Canton of Geneva, Switzerland. The survey network comprises six sampling sites on the River Arve, but we will only use data from one sampling site (site 'Arve', #20 in Figure 1) with 289 samples.

A complementary campaign on the River Arve watershed was planned in order to check the tributaries' influence on the water composition of River Arve. These sampling campaigns took place in May and August 2016 and January 2017 in order to cover a wide range of hydrological regimes. Twenty stations were sampled (Menoge at Bonne, Risse at St Jeoire, Foron at Taninges, Giffre upstream Taninges, Giffre upstream Sixt, Giffre south, Arve at Mont-Roc, Lognon, Arveyron, Arve at Les Houches, Bon Nant at St Gervais, Arve at Sallanches, Foron du Reposoir, Giffre at Marignier, Bronze, Bonne, Foron

de la Roche, Berny at la Fornasse, Arve at Arthaz, and Arve at Geneva); the locations are shown in Figure 1. The total number of samples was 59 (one sample was lost during the January campaign).

Sample collection and treatment

Individual water samples were hand-collected in polyethylene vials that had previously been soaked in 10% v/v nitric acid (Suprapur®, Merck) and thoroughly rinsed with MilliRo-Milli Q water® (Millipore). Samples were filtered within a few hours after sampling through 0.45 μm filters (Millex Durapore, Millipore), acidified with 2% v/v nitric acid (Suprapur®, Merck) and preserved at $2 \pm 2\,°C$ until analysis. Thus, this study is based on so-called dissolved concentrations.

Analytical method

Concentrations were measured by ICP-MS on a Fisons PQ2+ before 2006 and on a Thermo-Fisher X7 II from 2006 to 2018, both in their standard configurations at the Service de l'Ecologie de l'Eau (SECOE) of the Canton of Geneva, Switzerland. The analytical accuracy was followed by analysing certified reference materials CRM SLRS-4 and SLRS-5 (National Research Council Canada). SLRS-4 was used until 2010, results on 134 measurements are Ba: 13.23 ± 0.54 before 2006, 12.99 ± 0.52 after 2006 and U: 0.051 ± 0.007 before 2006, 0.046 ± 0.002 after 2006 (certified values: Ba: 12.2 ± 0.6 and U: 0.05 ± 0.003). From 2011, SLRS-5 was used ($n = 56$) and measured Ba: 14.46 ± 0.46 and U: 0.085 ± 0.004 (certified value: Ba: 14.0 ± 0.5 and U: 0.093 ± 0.006). All values in $\mu g\,L^{-1}$ units. The increase of accuracy linked to the change of ICP-MS does not affect our study. Detection limits ($\mu g\,L^{-1}$) are Ba: 0.3 and U: 0.01. The analytical laboratory is accredited for the analysis of the trace elements in freshwaters (accreditation number: STS245; ISO norm 17025).

Data treatment

Non-parametric methods are required to analyse temporal trends in water because data are usually non-normally distributed. Thus, temporal trends have been studied by applying the Mann–Kendall (MK) method (Helsel & Hirsch 2002). This method calculates a parameter S, the sign of which indicates whether the concentration trend vs time is generally decreasing (negative S value) or increasing (positive S value). The statistical significance of the trend is obtained in MK methods using the Z-statistic test of the sum of signs of the differences between every pair of values; Z shows a normal distribution, and therefore, the statistical significance of the temporal trend can be evaluated by the p-value. The average change over time was calculated using Sen's slopes (Sen 1968). A Sen slope is the median of the slopes between all possible pairs of temporal data ($N(N - 1)/2$), where N is the number of pieces of data in the series.

We used two classification methods in order to ascertain the transition point between two different hydrochemical signatures (U/Ba ratios) of the Arve River at Geneva, one characteristic of winter low-flows (January, February, and March) and the other one of summer high-flows (June, July, and August). For this analysis, we retained only the water samples collected in the 6 months cited above. Samples collected in the winter season were labelled as 'W', while those collected in the summer months were labelled as 'S'. We use Classification Trees (Breiman et al. 1984) for finding the U/Ba value that splits the set in two, such that each of the two resulting sub-sets is as homogeneous as possible. The criterion used for selecting the optimal split value is the Gini impurity (see Breiman et al. 1984). The second classification method uses a binary logistic model (see, e.g., Perlich et al. 2003), with the label ('W' and 'S') as the dependent variable and the U/Ba ratio as the independent variable. The two parameters of the logistic model were estimated by minimising the sum of squares of the residuals using the Solver functionality of Excel®. The estimated parameters

allow calculating the value of U/Ba for which the probability of 'S' in the logistic model is higher than 0.5, which is a sensible choice for the transition point.

RESULTS AND DISCUSSION

Hydrological regimes

The hydrological regime at the Arve River outlet integrates a wide range of within-basin hydrological regimes. There is a very close relationship between elevation and the hydrological regime, which is explained by the influence that elevation has on climate, and as a consequence on snow and ice accumulation and melt processes. Therefore, mountainous areas are characterised by minimum flows in winter when incoming precipitation accumulates at the catchment surface as snow and maximum flows in late spring or summer when snow and ice melt. The high-elevation Mont Blanc and Aiguilles Rouges Massifs are characterised by glacial or glacio-nival hydrological regimes, with high flows in late summer, while the mid-elevation mountainous areas have nival or nivo-pluvial hydrological regimes with maximum flows in late spring or early summer. Low-lying areas have a pluvial regime, with minimum flows in late summer and early fall and maximum flows in winter.

As argued elsewhere in this paper, there is also a close association between elevation and the hydrochemical signature of outflow explained by the geological setting of the catchment. Therefore, a good relationship, mediated by elevation, between sub-catchment hydrological regime and its hydrochemical signature should be expected.

At the catchment outlet, the areas with glacio-nival regimes dominate the discharge and imprint to the Arve River an overall nival regime. During the late spring-early summer high-flows, the discharge is dominated by snow and ice melt from the higher elevation areas of the catchments, with low-lying areas making a small contribution. However, during the cold season, the absolute and relative contribution of sub-basins having a pluvial hydrological regime is much more important and shifts the hydrochemical signature closer to the fingerprint of low-lying areas. This succession is illustrated in Figure 2 by the variation of the monthly Pardé coefficients of the Arve River at Geneva as well as for three sub-basins having distinct hydrological regimes: Arve at Chamonix, Borne at St Jean-de-Sixt, and Aire at Thairy. Monthly Pardé coefficients are the ratio between mean monthly flows and the mean annual flow.

Use of U/Ba ratio as a water regime indicator

A methodology for stream water classification according to its geochemical signature, based on the calculation of the U/Ba concentration ratio, was developed in a previous study (Filella *et al.* 2014). Uranium is enriched in plutonic rocks/crystalline minerals (Mason & Moore 1982; Garnier–Laplace *et al.* 2010), whereas barium is mostly associated with sedimentary rocks (Mason & Moore 1982). Both uranium and barium are geogenic elements subject to relatively little influence from human activities (Seyler & Boaventura 2003; Féraud *et al.* 2009; Roeske *et al.* 2012).

The application of a concentration ratio to follow the hydrological regime requires that the elements behave in a conservative way along the river. Uranium behaves conservatively in rivers (Windom *et al.* 2000). Ba is present mostly in the particulate fraction in rivers (Coffey *et al.* 1997). Thus, changes in water chemistry might be expected if Ba is released from the particulate phase, but this has been observed only in estuaries (Edmond *et al.* 1985; Santos *et al.* 2011). On the other hand, the well-known non-conservative behaviour of Ba in oceans is due to the formation of barite which is linked to productivity (Carter *et al.* 2020), but these processes have not been described in freshwaters.
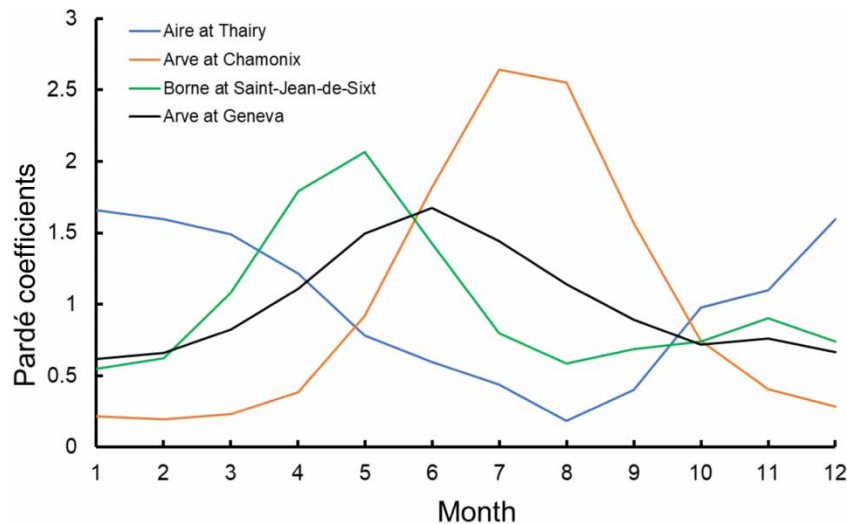
Figure 2 | Hydrological regime of the Arve River at Geneva and of three sub-watersheds that illustrate distinct hydrological regimes glacio-nival (Arve at Chamonix), pluvial (Aire at Thairy), and nivo-pluvial (Borne at Saint-Jean-de-Sixt). From upstream to downstream: Arve at Chamonix, Borne at St Jean-de-Sixt, Aire at Thairy, and Arve at Geneva. Hydrological regime is expressed through the evolution of the Pardé coefficients throughout the year.

Here, the application of the same U/Ba ratio to River Arve water concentration values along the year in Geneva (Figure 3) shows that this ratio is related to the hydrological regime of the Arve River and its sub-basins, River Arve at Chamonix in particular (Figure 2).

Low U/Ba values correspond to the winter months, when the low-lying parts of the basin having a pluvial regime make a significant contribution to the discharge, while high U/Ba are characteristic to high flows in summer and early autumn, when the discharge is dominated by glacier melt. One can also note that the rise in discharge during spring precedes that of the U/Ba ratio, which might be an indication of early snowmelt in the mid-elevation parts of the basin as the increase of dispersion (beginning in May) may depict. In autumn and early winter, both discharge and U/Ba ratio decrease, with the shift in discharge again preceding that in the U/Ba ratio. Apparent outliers correspond to
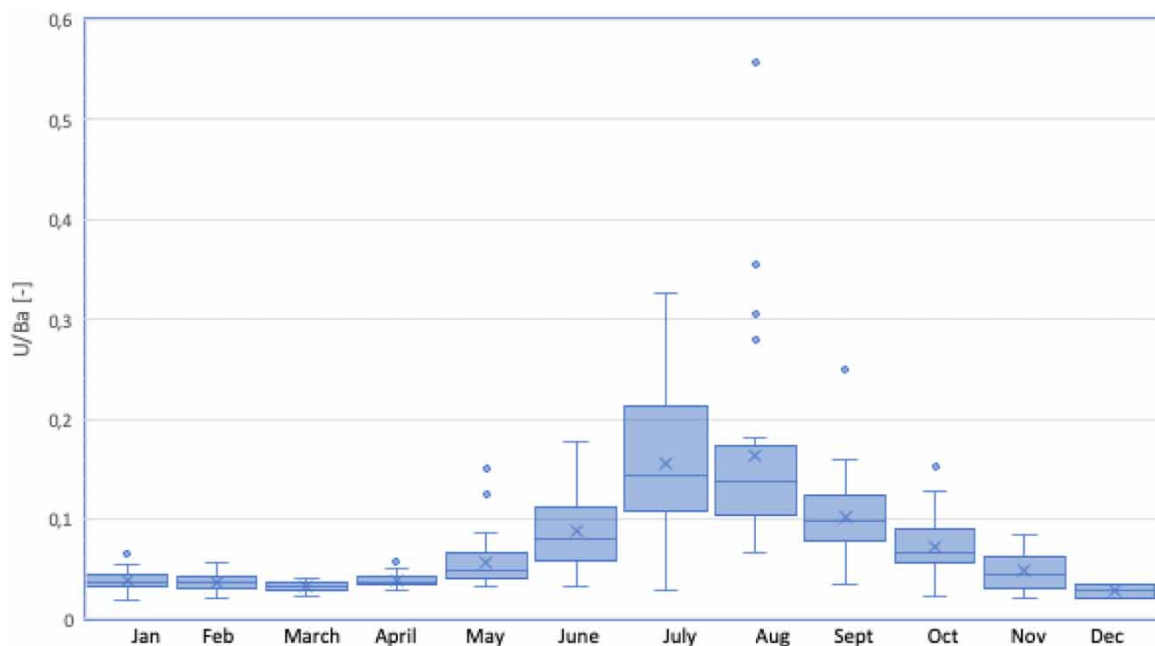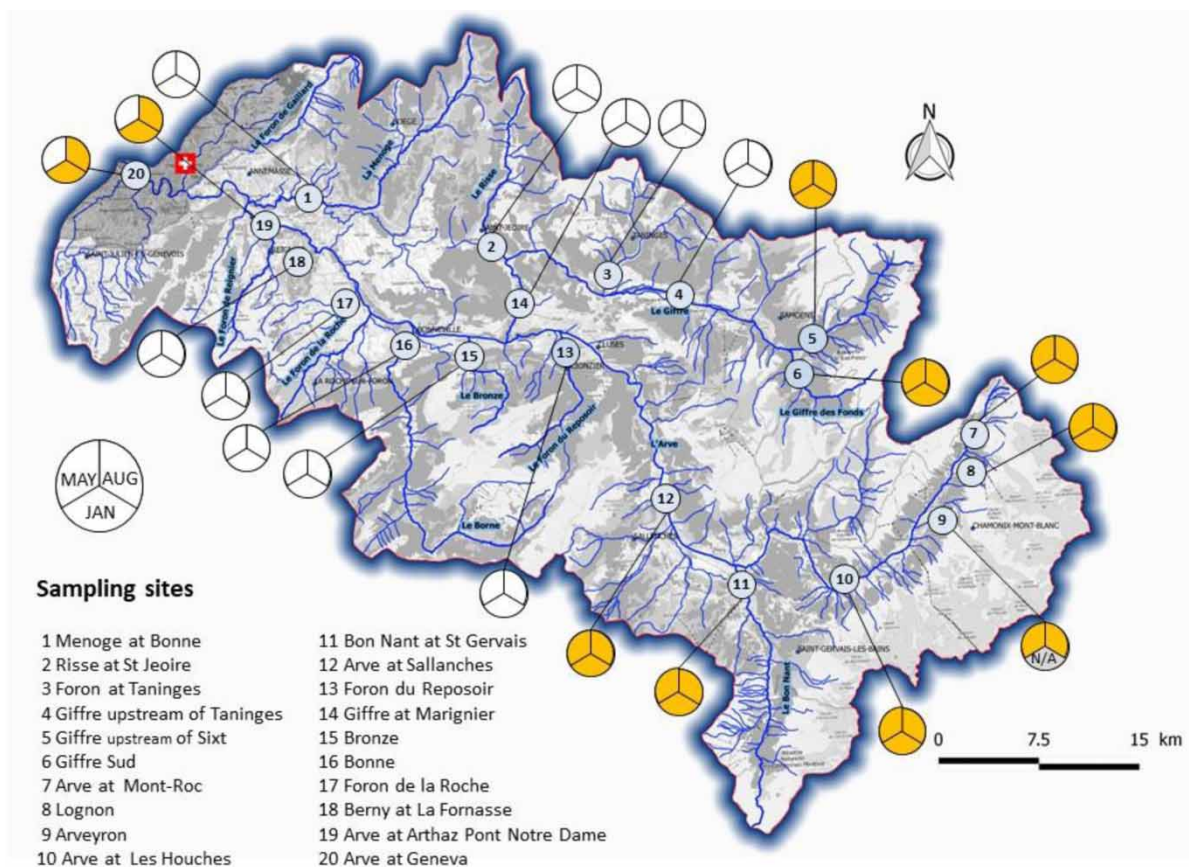

Figure 3 | Box plot of the monthly U/Ba ratio measured at the River Arve in Geneva from 1994 to 2018 ($n = 288$). Monthly values have been assigned to the middle week of the month.

extreme events such that, for instance, the heat wave in the summer of 2003 with U/Ba = 0.558 on 26 August. During this period, intense melt occurred in the glaciered part of the basin that produced a significant flood at Chamonix (Station 8, Figure 1), while the lower part of the catchment experienced a severe drought.

When applied to the Arve River data, the two classification methods described in the Methods section give similar results (see Supplementary Material) and suggest that a U/Ba ratio of 0.055 can be used as a meaningful transition point between the two hydrochemical characteristic behaviours described above.

Confirmation of the U/Ba ratio as a water regime indicator

Figure 4 shows the result of the application of the U/Ba threshold value of 0.055 to the data obtained in three sampling campaigns along the River Arve and major tributaries covering the whole range of hydrological conditions over the year (January, May, and August). The stations presenting glacio-nival characteristics are tagged in orange in the Figure. As expected, the U/Ba ratios obtained in the different locations reflect the geological composition of the underlying basement (i.e., mostly crystalline at the head and limestone, marl, sandstone, and glacial till in the alluvial plain): upstream stations, fed by snowmelt and glaciers (5, 6, 7, 8, 9, 10, and 12), systematically have glacio-nival U/Ba ratios (note that sample 9 was lost in January), while stations located in the plain (1, 2, 3, 4, 13, 14, 15, 16, 17, and 18) systematically show pluvial U/Ba values.

Sampling sites

1 Menoge at Bonne	11 Bon Nant at St Gervais
2 Risse at St Jeoire	12 Arve at Sallanches
3 Foron at Taninges	13 Foron du Reposoir
4 Giffre upstream of Taninges	14 Giffre at Marignier
5 Giffre upstream of Sixt	15 Bronze
6 Giffre Sud	16 Bonne
7 Arve at Mont-Roc	17 Foron de la Roche
8 Lognon	18 Berny at La Fornasse
9 Arveyron	19 Arve at Arthaz Pont Notre Dame
10 Arve at Les Houches	20 Arve at Geneva

Figure 4 | Sampling sites and hydrological regime type in the sampling campaigns of 17 May and 23 August 2016 and 23 January 2017. Glacio-nival signature is highlighted in orange.

Comparison of values of discharges and U/Ba ratios (for three locations along the river, one in the head area (Chamonix, #8) and two in the alluvial plain (Arthaz, #19 and Geneva, #20, close to the mouth of the river) confirms that U/Ba ratios in downstream locations follow the water mixing along the river, and its dependency on the succession of hydrological conditions along the year (Table 1). In effect, the percentage of the final discharge in Geneva waters from Chamonix (which follow a glacio-nival regime all the year) represent 11% in January, 9% in May, but 47% in August. It is in August when the U/Ba chemical signature of a glacial regime is usually found in Geneva. The glacial fingerprint observed in January is an unusual event related to a very severe drought in December 2016 and January 2017 that greatly reduced the contribution of the pluvial part of the basin. The corresponding sample appears as an outlier in Figure 3. This means that the U/Ba ratio is an efficient tool allowing investigators to follow the hydrological regime without the need for measuring discharge values along the river.

Table 1 | Discharges ($m^3 s^{-1}$), percentages of the discharges with respect to the mouth of the river (%) and U/Ba ratios in different locations of the River Arve during our sampling campaigns

Station	17.5.2016			23.8.2016			23.1.2017		
	Discharge / $m^3 s^{-1}$	%	U/Ba	Discharge / $m^3 s^{-1}$	%	U/Ba	Discharge / $m^3 s^{-1}$	%	U/Ba
Geneva (#20)	97.0[a]	100	0.048	49.5[a]	100	0.126	13.2[a]	100	0.061
Arthaz (#19)	85.2[b]	88	0.052	49.0[b]	99	0.132	11.7[b]	89	0.065
Chamonix (#8)	8.34[b]	36	0.840	23.2[b]	47	0.552	1.49[b]	11	0.392

Glacio-nival type highlighted in green, corresponding discharges in orange.
[a]Swiss Confederation: https://www.hydrodaten.admin.ch/fr/2170.html13.
[b]Banque hydrologique française: http://hydro.eaufrance.fr/presentation/procedure.php.

Temporal trends of the U/Ba ratio

The glacio-nival dominated period is assumed to start when, for the first time in the year, two or more successive samples have a U/Ba ratio above the 0.055 threshold. When applied to the 1994–2018 concentration data value of the Geneva sampling station, a tendency for the period to start earlier in the year is observed (Figure 5). This trend is confirmed by a negative MK S value, with an estimated decrease of ~1.3 days per year (Sen's slope = −0.190 week y⁻¹) over the period considered. The decrease is statistically significantly ($Z = -2.32$, $p = 0.020$ (two-tailed)). The glacio-nival dominated period is assumed to end when, for the last time in the year, two or more successive samples have a U/Ba ratio above the 0.055 threshold. The last among these successive samples defines the end date. The length of the glacio-nival dominated period is simply defined as the difference between its end and its start. This length shows an increase from 1994 to 2018 (Figure 6), confirmed by a positive MK Z-value. This trend is also statistically significant ($Z = 3.37$, $p = 0.0008$ (two-tailed)). The system studied is subject to a linear increase of the duration of the melting season, with an average increase of ~9.3 days per year over the period considered (Sen's slope = 1.326 week y⁻¹). A plateau-type response can be expected once the current phase of depletion of the water stocked in glaciers is completed.

Both the early start and the longer duration of the glacio-nival regime can be safely attributed to climate change. Alpine ecosystems are particularly sensitive to climatic changes (Beniston 2003, 2005); with rising temperatures expected strongly to affect runoff regimes via the impact on snow cover and ice melting. These general predictions are mostly based on simulation approaches (e.g., Zierl & Bugmann 2005; Horton et al. 2006) and in line with our evaluation based on measured parameters.
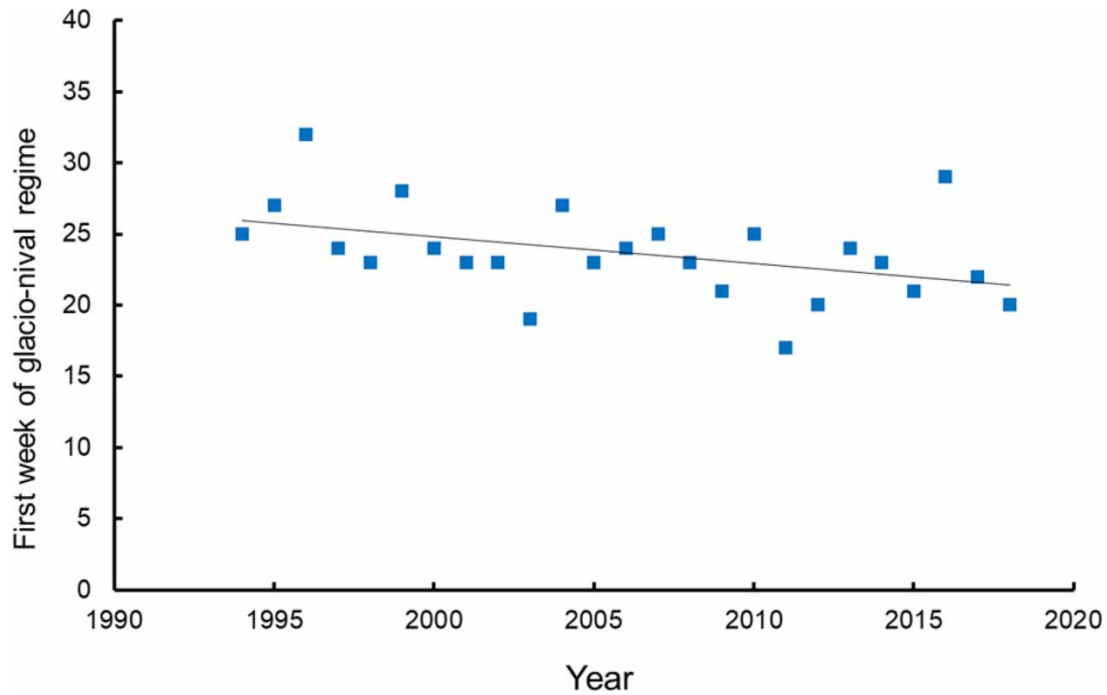
Figure 5 | Temporal evolution between 1994 and 2018 of the start of the glacio-nival dominated period, as defined in the text, in the River Arve.
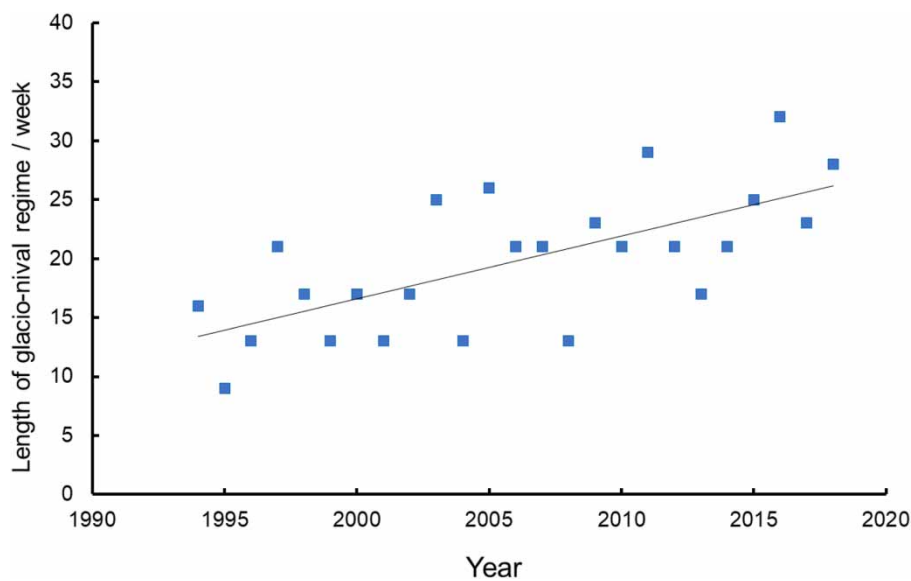
Figure 6 | Duration between first and last occurrence in the year having a glacio-nival signature (U/Ba ratio >0.055) in the River Arve between 1994 and 2018 in the River Arve at Geneva between 1994 and 2018.

CONCLUSION

Our goal was to extend available tools allowing the evaluation of the impact of climate change upon the hydrological cycle. Current approaches mostly rely on the measurement of water discharges on a long timescale which is neither straightforward nor flexible and more affected by measurement uncertainties than the measurement of chemical concentrations. Since our approach is based on concentration ratios, it gets rid of discharge measurements.

On the basis of previous studies (Filella *et al.* 2014), we figured out the best candidate elements – uranium and barium – to characterise the water composition fingerprint. Their application to an

Alpine river with a complex temporal and spatial hydrological configuration allowed us to test and confirm the capacity of the method to discriminate between the periods of the year that are dominated by distinct hydrological regimes (high vs low discharge periods; glacio-nival vs pluvial regimes). Even if the approach is better suited to contrasted systems, it is applicable to any existing long-term database. As a result, we expect it to be a useful complementary tool for identifying the impact of changing climate on both hydrological regime and, eventually, water quality.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Beniston, M. 2003 Climatic change in mountain regions: a review of possible impacts. *Climatic Change* **59**, 5–31. doi:10.1023/A:1024458411589.

Beniston, M. 2005 Mountain climates and climatic change: an overview of processes focusing on the European Alps. *Pure and Applied Geophysics* **162**, 1587–1606. doi:10.1007/s00024-005-2684-9.

Blöschl, G., Hall, J., Parajka, J., Perdigão, R. A. P., Merz, B., Arheimer, B., Aronica, G. T., Bilibashi, A., Bonacci, O., Borga, M., Čanjevac, I., Castellarin, A., Chirico, G. B., Claps, P., Fiala, K., Frolova, N., Gorbachova, L., Gül, A., Hannaford, J., Harrigan, S., Kireeva, M., Kiss, A., Kjeldsen, T. R., Kohnová, S., Koskela, J. J., Ledvinka, O., Macdonald, N., Mavrova-Guirguinova, M., Mediero, L., Merz, R., Molnar, P., Montanari, A., Murphy, C., Osuch, M., Ovcharuk, V., Radevski, I., Rogger, M., Salinas, J. L., Sauquet, E., Šraj, M., Szolgay, J., Viglione, A., Volpi, E., Wilson, D., Zaimi, K. & Živković, N. 2017 Changing climate shifts timing of European floods. *Science* **357**, 588–590. doi:10.1126/science.aan2506.

Blöschl, G., Hall, J., Viglione, A., Perdigão, R. A. P., Parajka, J., Merz, B., Lun, D., Arheimer, B., Aronica, G. T., Bilibashi, A., Boháč, M., Bonacci, O., Borga, M., Čanjevac, I., Castellarin, A., Chirico, G. B., Claps, P., Frolova, N., Ganora, D., Gorbachova, L., Gül, A., Hannaford, J., Harrigan, S., Kireeva, M., Kiss, A., Kjeldsen, T. R., Kohnová, S., Koskela, J. J., Ledvinka, O., Macdonald, N., Mavrova-Guirguinova, M., Mediero, L., Merz, R., Molnar, P., Montanari, A., Murphy, C., Osuch, M., Ovcharuk, V., Radevski, I., Salinas, J. L., Sauquet, E., Šraj, M., Szolgay, J., Volpi, E., Wilson, D., Zaimi, K. & Živković, N. 2019 Changing climate both increases and decreases European river floods. *Nature* **573**, 108–111. doi:10.1038/s41586-019-1495-6.

Breiman, L., Friedman, J., Olshen, R. & Stone, C. 1984 *Classification and Regression Trees*. Chapman and Hall, New York, p. 368.

Carter, S. C., Paytan, A. & Griffith, E. M. 2020 Toward an improved understanding of the marine barium cycle and the application of marine barite as a paleoproductivity proxy. *Minerals* **10**, 421. doi:10.3390/min10050421.

Coffey, M., Dehairs, F., Collette, O., Luther, G., Church, T. & Jickells, T. 1997 The behaviour of dissolved barium in estuaries. *Estuarine, Coastal and Shelf Science* **45**, 113–121.

Delpla, I., Jung, A.-V., Baures, E., Clement, M. & Thomas, O. 2009 Impacts of climate change on surface water quality in relation to drinking water production. *Environment International* **35**, 1225–1233. doi:10.1016/j.envint.2009.07.001.

Edmond, J. M., Spivack, A., Grant, B. C., Ming-Hui, H., Zexiam, C., Sung, C. & Xiushau, Z. 1985 Chemical dynamics of the Changjiang estuary. *Continental Shelf Research* **4**, 17–36. doi:10.1016/0278-4343(85)90019-6.

Féraud, G., Potot, C., Fabretti, J.-F., Guglielmi, Y., Fiquet, M., Barci, V. & Maria, P.-C. 2009 Trace elements as geochemical markers for surface waters and groundwaters of the Var River catchment (Alpes Maritimes, France). *Comptes Rendus Chimie* **12**, 922–932. doi:10.1016/j.crci.2009.02.002.

Filella, M., Pomian-Srzednicki, I. & Nirel, P. M. 2014 Development of a powerful approach for classification of surface waters by geochemical signature. *Water Research* **50**, 221–228. doi:10.1016/j.watres.2013.11.046.

Garnier–Laplace, J., Colle, C. & Morello, M. 2010 *Natural Uranium and the Environment*. IRSN. Available at: https://www.irsn.fr/EN/Research/publications-documentation/radionuclides-sheets/environment/Documents/Uranium_UK.pdf (last accessed 28 April 2020)

Garrels, R. M. & Mackenzie, F. T. 1967 Origin of the chemical compositions of some springs and lakes. In: *Equilibrium Concepts in Natural Water Systems*, Vol. 67 (Stumm, W., ed.). American Chemical Society, Washington, DC, pp. 222–242. doi:10.1021/ba-1967-0067.ch010.

Helsel, D. R. & Hirsch, R. M. 2002 *Statistical Methods in Water Resources*. Techniques of Water-Resources Investigations of the United States Geological Survey. Book 4, Chapter A3, USGS, Reston, VA.

Horton, P., Schaefli, B., Mezghani, A., Hingray, B. & Musy, A. 2006 Assessment of climate-change impacts on alpine discharge regimes with climate model uncertainty. *Hydrological Processes* **20**, 2091–2109. doi:10.1002/hyp.6197.

Mason, B. & Moore, C. B. 1982 *Principles of Geochemistry*. Wiley, New York.

Meybeck, M. 1987 Global chemical weathering of surficial rocks estimated from river dissolved loads. *American Journal of Science* **287**, 401–428. doi:10.2475/ajs.287.5.401.

Perlich, C., Provost, F. & Simonoff, J. 2003 Tree inductions vs. logistic regression: a learning-curve analysis. *Journal of Machine Learning Research* **4**, 211–255.

Rodríguez-Murillo, J. C., Nirel, P. & Filella, M. 2018 Detecting trends in freshwater trace element concentrations: methodological issues and data treatment. *H2Open Journal* **1** (2), 87–98. doi:10.2166/h2oj.2018.006.

Roeske, T., Bauch, D., Rutgers, V. D., Loeff, M. & Rabe, B. 2012 Utility of dissolved barium in distinguishing North American from Eurasian runoff in the Arctic Ocean. *Marine Chemistry* **132–133**, 1–14. doi:10.1016/j.marchem.2012.01.007.

Santos, I. R., Burnett, W. C., Misra, S., Suryaputra, I. G. N. A., Chanton, J. P., Dittmar, T., Peterson, R. N. & Swarzenski, P. W. 2011 Uranium and barium cycling in a salt wedge subterranean estuary: the influence of tidal pumping. *Chemical Geology* **287**, 114–123. doi:10.1016/j.chemgeo.2011.06.005.

Schmutz, S. & Sendzimir, J. 2018 *Riverine Ecosystem Management: Science for Governing Towards a Sustainable Future*. Springer International Publishing, Cham. doi:10.1007/978-3-319-73250-3.

Sen, P. K. 1968 Estimates of regression coefficient based on Kendall's tau. *Journal of the American Statistical Association* **63**, 1379–1389. doi:10.1080/01621459.1968.10480934.

Seyler, P. T. & Boaventura, G. R. 2003 Distribution and partition of trace metals in the Amazon basin. *Hydrological Processes* **17**, 1345–1361. doi:10.1002/hyp.1288.

Windom, H., Smith, R., Niencheski, F. & Alexander, C. 2000 Uranium in rivers and estuaries of globally diverse, smaller watersheds. *Marine Chemistry* **68**, 307–321. doi:10.1016/S0304-4203(99)00086-9.

Zierl, B. & Bugmann, H. 2005 Global change impacts on hydrological processes in Alpine catchments. *Water Resources Research* **41**, W02028. doi:10.1029/2004WR003447.