Using stable isotopes to resolve transit times and travel routes of river water: a case study from southern Finland†

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ABSTRACT
The stable isotopic composition of two rivers, the Vantaanjoki River and the Kokemäenjoki River, in southern and southwestern Finland was studied to resolve the transit times and travel routes of the river water in the two different catchments. The Kokemäenjoki River is dominated by great lake basins whereas the Vantaanjoki River has been reported having a significant groundwater component. The mean residence time of the young surface flow component could be resolved by sine function fitting onto the annual fluctuations of the isotopic signal, and the amount of base flow was estimated by using the isotopic composition of the river and groundwater. In this study, we found that the methods work for simple two component catchments. In more complex cases with three different components mixing, the solution becomes increasingly difficult and requires more study.

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1. Introduction
Determining the source and the residence time of water in catchments can assist in predicting the behaviour and lifetime of possible contaminants in the catchment [1]. The residence time of river water is affected by the route precipitation travels, as surface or base flow, for example, before entering the river. The cross-sectional area of the river channel is inversely related with the mean flow velocity and therefore also affects the residence time of river water. Lake storage extends the mean residence time (MRT) of river water from days to more than a year, even centuries [2,3]. Rivers with a significant base flow component originating from groundwater can be expected to have longer residence times as the age of groundwater can vary from years to several hundred years.

The stable isotope ratios of oxygen and hydrogen are a tool that can assist in examining the groundwater and surface water interaction and transit times in the catchment [1,4–6]. The $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios of precipitation in a certain locality are mainly dependent on the average annual temperature of the locality. Lower temperatures lead to precipitation more depleted in $^{18}\text{O}$ and $^2\text{H}$ isotopes [7–9]. In addition, in high latitude temperate climate, air temperature shows wide seasonal variation which produces higher $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$
ratios in the summer and lower ones in the winter, with sinusoidal curves apparent in graphs of the isotope ratios with respect to time [8,10–12].

The seasonal variation of isotope ratios in precipitation is often inherited by river water. This feature can be utilized in determining the MRT of the fast components of river or groundwater by two simple sine fitting methods: the amplitude damping, and the phase shifting method [4,13]. The amplitude damping is due to waters from different seasons mixing, and the phase shift is due to retention of the signal. The annual variation in the isotopic signal is damped beyond detection limits in a few years [14]. These methods give accurate results in one component systems where the water originates from one known source, whether groundwater, surface flow or a lake [4]. In more complex systems with multiple components with different residence times mixing, calculations by the sine fitting methods tend to underestimate the MRT [15–17].

Evaporation changes the isotopic composition of water. The fractionation of isotopes in evaporation leads to a preferential increase of $^{18}$O and $^2$H so that the remaining water is then enriched in $^{18}$O and $^2$H [7,10]. Evaporation has a considerable effect on the isotopic composition of water in lakes where the lake water is exposed to evaporation for a considerable period of time [10]. In contrast, groundwater in high latitude temperate climate undergoes negligible evaporation, and its isotopic composition therefore usually remains close to the mean annual composition of precipitation [11]. Therefore highly evaporated waters in rivers are a sign of lake storage, less evaporated ones suggest that any damping of the observed isotopic signature is more likely due to storage as groundwater than in lakes. The degree of evaporation can be evaluated by using the deuterium excess ($d$-excess) value [7].

The two rivers, the Vantaanjoki and the Kokemäenjoki River, were chosen for this study because of the differences in water storage predominantly either in lakes or in groundwater. In this study, the amplitude damping, and the phase transfer effects of the isotopic signal in the river water were evaluated, and the results compared to what is known from the catchments, in an attempt to understand the transit time of river water in groundwater and in lake water dominated catchments.

2. Study sites

In this study, two rivers were examined, the Kokemäenjoki and Vantaanjoki rivers (Figure 1). The Vantaanjoki River is located in a densely populated area in southern Finland, approximately 100 km in length, and discharges into the Gulf of Finland [18]. The catchment covers 1700 km$^2$, encompasses few lakes, and one fifth of the land use is agricultural [19]. It is the most densely populated area in Finland, with over one million people living in the catchment [19]. The mean annual discharge of the Vantaanjoki River is 16 m$^3$ s$^{-1}$. This mean discharge includes the discharge of the spring flooding, up to 200 m$^3$ s$^{-1}$, lasting about two weeks. During this time the discharge increases 100 fold in comparison to other parts of the year [20].

In the catchment of the Vantaanjoki River, Precambrian bedrock is overlain by relatively flat lying Quaternary deposits [21]. The lowermost part of the sediment is till, and aquifers are located in glaciofluvial sand and gravel deposits [21–23]. Interaction between the Vantaanjoki River water and groundwater has been investigated by using thermal imaging, which showed several points of groundwater discharge into the river channel along the
It was inferred that a significant component of the river water is sourced from groundwater.

The Kokemäenjoki River is situated in southwestern Finland (Figure 1). The catchment is 27,000 km\(^2\) in area, of which 60 % is forest [24]. The mean annual discharge of the Kokemäenjoki River is 180 m\(^3\) s\(^{-1}\), and its flow increases three-fold during the spring melt water flood event with two months of high discharge. During the spring flooding, discharge rates average over 300 m\(^3\) s\(^{-1}\) [24]. The bedrock in the catchment of the Kokemäenjoki River contains Precambrian granitoids and gneisses, and the topography of the area is relatively flat, varying from 45 to 122.4 m above sea level [24,25]. Approximately a quarter of the soil in the area is clay that is used for agricultural purposes, approximately 6 % is peat land, and 11 % of the catchment area consists of natural lakes [24].

### 3. Material and methods

The isotopic composition of oxygen and hydrogen in precipitation was analysed for monthly samples in the Espoo Global Network of Isotopes in Precipitation (GNIP) station, southern Finland (Figure 1) from November 2000 to February 2012. In total, 135 monthly samples were collected according to the guidelines given by the International Atomic Energy Agency (IAEA). The isotopic composition of precipitation was submitted to the GNIP database of the IAEA [26].

The sampling of the Vantaanjoki River took place in 2010–2011. The samples were collected monthly from the mouth of the river, and once during the winter of 2010 from the pond in the beginning of the river channel (Figure 1). During the spring flood of the year 2011, the sampling was executed daily; in total 23 samples from the Vantaanjoki River were collected. Samples, 137 in total, from the Kokemäenjoki River were collected monthly during the years 2000–2011, at Karhiniemi, 60 km above the mouth of the
river (Figure 1). The two lakes discharging into the river channel right before the sampling point were also sampled once in autumn 1999. Lake Roine, situated further from the sampling site in the catchment of the Kokemäenjoki River, was monitored during 2002–2005; 36 samples were collected. Oxygen and hydrogen isotope ratios were analysed from all surface water samples. The mean volume of discharge of the rivers was taken from the HERTTA database, maintained by the Finnish Environment Institute [27].

Samples from snow cover were collected in March 2013 at four sites in and close to the catchment of the Vantaanjoki River (Figure 1). In order to obtain samples representative of the whole snow cover at the sample localities, a cross-section covering the whole snow profile was collected. The samples were packed in plastic bags and melted in the laboratory. After melting, the isotopic compositions of oxygen and hydrogen were analysed using the same procedure as was used for the river water samples.

The isotopic composition of water is expressed as δ values according to:

\[
\delta_{\text{sample}} = \left( \frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \times 1000 \%
\]

where \(R_{\text{sample}}\) is the isotope ratio in the sample and \(R_{\text{std}}\) the one in a standard. For waters, the standard is Vienna Standard Mean Ocean Water (VSMOW).

Evaporation can be monitored with the \(d\)-excess value [7], which is calculated from the \(\delta^{18}\text{O}\) and \(\delta^2\text{H}\) values by the formula:

\[
d\text{-excess} = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}.
\]

The samples for oxygen and hydrogen isotope analysis were collected in 50 mL HDPE plastic bottles which were entirely filled up, leaving no air space. \(^2\text{H}/\text{H}\) and \(^{18}\text{O}/^{16}\text{O}\) were analysed by a Picarro cavity ring-down spectrometer (CRDS) at the Department of Geosciences and Geography at the University of Helsinki, and at the Geological Survey of Finland. In both facilities, laboratory standards were calibrated against two international reference standards (VSMOW and SLAP). The samples from the Kokemäenjoki River and some samples from the Vantaanjoki River were also analysed for \(^{18}\text{O}/^{16}\text{O}\) by isotope-ratio mass spectrometry (IRMS) with CO2 equilibration. The Vantaanjoki samples were analysed by a Thermo Finnigan Delta Advantage mass spectrometer with Gas Bench II, the Kokemäenjoki samples by a Thermo Finnigan MAT 251 gas source mass spectrometer with a dual inlet source. Furthermore, the Kokemäenjoki samples were analysed for \(^2\text{H}/\text{H}\) after reduction of water to H\(_2\) using zinc metal. The zinc reagent was prepared by adding Na as an impurity [28]. The accuracy of the analysis was 0.1 \(\%\) for oxygen and 1 \(\%\) for hydrogen isotopes for the IRMS, and 0.1 \(\%\) and 0.5 \(\%\) for the CRDS, respectively. The results used in this paper are from the Picarro analysis for the Vantaanjoki River and averages of the two for the Kokemäenjoki River and precipitation.

4. Results

The results from the two different measurement methods (IRMS and CRDS) gave the same results within the margins of error. The results from years 2010 and 2011 for the O and H isotope analysis and the calculated \(d\)-excess values are given in Table 1 for the Vantaanjoki and the Kokemäenjoki River. The results for the Kokemäenjoki River from 2000–2009 and
for the Lake Roine from 2002 to 2005 can be found in the supplementary online material and the precipitation data in the GNIP database [26].

The δ18O values of precipitation had an annual variation with maximum values between May and August, with the exact timing of the peak varying from year to year, and minimum values between November and March (Figure 2). The variation of the δ18O values was from −21.6 ‰ in February 2003 to −5.9 ‰ in May 2007. The δ2H values in precipitation followed the annual variation of the δ18O values, with a minimum value of −163 ‰ in February 2003 and the maximum −37 ‰ in May 2007 (Figure 2).

The δ18O values in the Kokemäenjoki River varied between −10.7 ‰ in May 2001 and −8.5 ‰ in September 2006. The annual maximum values were between August and October and minimum values in April or May, during the spring flooding. The δ2H values varied between −76 and −70 ‰ following the variations in the δ18O values
The lakes in the catchment had \( \delta^{18}O \) values of \(-8.8\) and \(-7.4\ \%\), and the \( \delta^{2}H \) values of \(-70\) and \(-62\ \%\), respectively.

In the Vantaanjoki River, the lowest \( \delta^{18}O \) value was \(-15.1\ \%\) in April 2010 and the highest \(-9.4\ \%\) in August 2010 (Figure 2). The \( \delta^{2}H \) values varied from \(-110\) to \(-73\ \%\). The pond at the headwaters of the river had \( \delta^{18}O \) value of \(-8.4\ \%\) and the \( \delta^{2}H \) value of \(-69\ \%\).

The \( \delta^{18}O \) values of snow cover varied from \(-15.8\) to \(-13.6\ \%\) with the mean of \(-15.1 \pm 1\ \%\). The values for \( \delta^{2}H \) varied from \(-116\) to \(-98\ \%\) with the mean of \(110 \pm 8\ \%\). The sample from Kumpula, outside the catchment of the Vantaanjoki River differed most from the others. This one removed, all other snow samples showed \( \delta^{18}O \) values between \(-15.8\) and \(-15.3\ \%\) (Table 2).

**Table 2.** The isotopic composition of snow samples collected in 2013 from the catchment of the Vantaanjoki River.

| Sampling site | Date      | \( \delta^{2}H \) | \( \delta^{18}O \) |
|--------------|-----------|-------------------|-------------------|
| Nurmijärvi   | 2.4.2013  | \(-116\)          | \(-15.8\)         |
| Hyvinkää     | 29.3.2013 | \(-114\)          | \(-15.7\)         |
| Kumpula      | 1.4.2013  | \(-98\)           | \(-13.6\)         |
| Rajamäki     | 8.4.2013  | \(-113\)          | \(-15.3\)         |
| Mean         |           | \(-110\)          | \(-15.1\)         |
| Std. dev.    |           | \(8\)             | \(1.0\)           |
5. Discussion

5.1. Characterization of annual variability

The annual variability of the isotope signal can be characterized by fitting a sinusoidal curve to the data (Figure 3). The following equations were obtained by finding the closest fit to the data by using least squares curve fitting:

Precipitation: $\delta^{18}O = -3.24 \sin(0.02t - 2.10) - 11.60$

Vantaanjoki River: $\delta^{18}O = -1.50 \sin(0.017t - 3.45) - 10.93$

Kokemäenjoki River: $\delta^{18}O = -0.36 \sin(0.017t - 3.47) - 9.41$

where $t$ is time in days from the beginning of the sampling.

In the phase shift method, the MRT in years is calculated from the equation:

$$\text{MRT} = \tan\left(\frac{\alpha}{2\pi}\right).$$

where $\alpha$ is the phase displacement, when the full phase is $2\pi$ [29].

A phase shift of one year leads to the original position of the curve. Accordingly, a phase shift exceeding one year cannot be unequivocally determined. The phase shift method (Equation (3)) applied for the isotopic records from the Vantaanjoki River and the Kokemäenjoki River indicate an apparent MRT of approximately two and a half months, with an indeterminate number of years added to this.

![Figure 3](image_url) 

Figure 3. The $\delta^{18}O$ values of precipitation and river water, and the sinusoidal curves fitted into the data. The sinusoid fitting was done using all the available $\delta^{18}O$ data: precipitation and Kokemäenjoki River water between 2000 and 2011, Vantaanjoki River water between 2010 and 2011.
Damping of the amplitude of the isotopic curve is an alternative method for calculating MRTs, most commonly used for groundwater. For this method the equation is:

$$MRT = \frac{1}{2}\pi(1 - C)^{1/2}/C,$$

where $C$ is the amplitude damping given as $C = B/A$, where $A$ is the amplitude of $\delta^{18}O$ values in precipitation and $B$ that of $\delta^{18}O$ values in river water [4]. The amplitude damping method (Equation (4)) suggests an apparent residence time of 14 months for the Kokemäenjoki River and of 2 months for the Vantaanjoki River. As the amplitude damping method can resolve multi-year residence times, this result appears to be in agreement with the outcome from the phase displacement method (Equation (3)), with the indeterminate number of years mentioned in connection with the phase displacement method being one for the Kokemäenjoki River and zero for the Vantaanjoki River.

The residence time calculations presented above assume a simple system, in which river water is derived directly from precipitation. If river water is an admixture of waters from other sources with different residence times, the simple MRT estimates do not necessarily describe the actual residence times of water. Most natural river systems do not behave as one component systems, which makes estimating the true MRT of river water by these methods impossible. However, the MRT calculated by the phase displacement method gives a good estimate of the residence time of the fastest component in the system which is the spring flooding component in case of both, the Vantaanjoki and the Kokemäenjoki Rivers. The rest, presumably base flow and lake water, has a longer residence time which cannot be evaluated by using this method.

5.2. Surface flow and base flow

River water in natural catchments is seldom derived only from direct surface flow caused by precipitation. Other potential sources of water are groundwater and water stored in lakes. These water components may show only weak seasonal isotope shifts, or they may completely lack seasonal trends. However, due to the seasonal isotope signal in precipitation, the isotopic composition of river water may still show a distinct seasonal pattern. Nonetheless, the calculated phase shift and the attenuation of the signal are necessarily not directly connected to the MRT.

A groundwater dominated river may be described as a two component system, where part of the water is derived as base flow from groundwater and part from surface flow. In temperate regions, the isotopic composition of oxygen in groundwater has been shown to follow relatively closely that in local average precipitation [11]. Kortelainen and Karhu [11] noticed that the difference between $\delta^{18}O$ in the local precipitation and that in groundwater is less than 0.5‰. Therefore, the river water in this case may be modelled as a mixing process, where a groundwater component with a constant isotopic composition is mixed with a precipitation derived component with a seasonal isotope signature. Amplitude damping of the seasonal signal will be dependent on the residence time of the surface flow component and the mixing ratio between the two components. The relative effects of these two components cannot be resolved. In contrast, the phase shift retains useful information, as it tells the residence time of the surface water component [15]. This, however, should not be confused with the MRT of the river water.
The water in the Vantaanjoki River can be modelled as a two component system: direct surface flow, and groundwater base flow. The catchment contains only a few lakes (Figure 1), and lake storage is insignificant for the water balance.

The phase displacement calculation for the Vantaanjoki River yielded a shift of two and a half months. MRT of the snow cover, and therefore in essence the whole surface flow component, is given by the phase displacement method. The phase shift for the Vantaanjoki River is largely contributed by the spring flooding event, which was responsible for 71 % of the annual discharge in 2010 and 33 % in 2011 [27].

The proportion of groundwater in the Vantaanjoki River varies drastically over the year. In the winter time, the river is frozen, and nearly all water is derived from base flow. This is also supported by the isotope data. During the winter months, from January to March, the $\delta^{18}O$ value of the river water varies from $-10.5$ to $-11.0$ ‰ (Table 1). This is relatively close to the average values of $-12.1$ ‰, measured for groundwater in the catchment of the Vantaanjoki River [11]. Mass balance calculations give the groundwater base flow component as being approximately 60 % (Table 3) assuming that the headwater pond is not groundwater originated but representing a second, isotopically heavy, component mixing with groundwater in the river. Hence, this calculation gives a minimum estimate of groundwater influence after the headwaters of the river, but it can be assumed that the actual groundwater influence in the river is in fact higher than this. In contrast to the winter flow, the spring flood is dominated by snowmelt. The minimum $\delta^{18}O$ values for the river water during the spring flooding were $-15.1$ ‰ in 2010 and $-13.4$ ‰ in 2011 (Table 1). These values can be compared to $\delta^{18}O$ values of $-15.1 \pm 1.0$ ‰, measured from the snow pack in the Vantaanjoki River catchment in 2013 (Table 2). This confirms that during the spring flooding water in the Vantaanjoki River is derived almost entirely as surface flow from the melting snow pack (Table 3).

5.3. Surface flow, base flow and lake storage

Lake storage brings additional factors to the estimation of the MRT of water in a river catchment. In addition to water supply from surface flow and base flow, the water is also stored in a lake system. It may be a single large lake or a complicated network of lakes connected in series and in parallel. An additional complication is that due to evaporation, the $\delta^{18}O$ and $\delta^2H$ values of water increase and are shifted off from the local meteoric water line (LMWL) [10]. In addition to lake storage, the amplitude damping of the seasonal isotope signal is also affected by water supplied from base flow. The amount of damping is largely defined by the mixing proportions of the components, and it does not provide information of the MRT. The phase shift of the isotope signal, in turn, reflects the residence time of the youngest water component [15].

Table 3. The groundwater percentages calculated in the winter and spring flooding times in the Vantaanjoki River.

|                  | Winter | Spring |
|------------------|--------|--------|
| $\delta^{18}O$ (‰ VSMOW) |        |        |
| Local groundwater| $-12.1$| $-12.1$|
| Vantaanjoki River | $-10.7$| $-15.1$|
| Beginning of path| $-8.4$ | $-15.1$|
| Groundwater (%)   | 63     | 0      |
| Groundwater (%)   |        |        |
The catchment of the Kokemäenjoki River is dominated by numerous small and large lakes (Figure 1). The ten-year isotope record shows a very shallow seasonal variation with an amplitude of about 1 ‰. The seasonal variations of the precipitation have been almost completely damped due to storage in groundwater and in lakes. Any inferences about the MRT of the river water cannot be made on the basis of amplitude damping.

The isotopic composition of the water in the Kokemäenjoki River falls clearly outside the LMWL, indicating evaporative enrichment of $^2\text{H}$ and $^{18}\text{O}$ (Figure 4). This is also seen in the $d$-excess value of 1.9 ‰ for the Kokemäenjoki River (Figure 5). Clearly evaporated river water points to a significant amount of lake storage as opposed to groundwater influence or direct surface flow.

The phase shift of the seasonal isotope trend for the Kokemäenjoki River is approximately the same as that in the Vantaanjoki River (Figure 3). This is interpreted to record the approximate MRT of snow cover in the catchment.

The two large lakes closest to the Kokemäenjoki River sampling location have $^{18}\text{O}$ values of −8.8 and −7.4 ‰ in the autumn (Figure 4). Lake Roine had a mean $^{18}\text{O}$

Figure 4. The local meteoric water line (LMWL) as defined by Kortelainen and Karhu [11] and the weighed mean annual $^2\text{H}$ and $^{18}\text{O}$ of the river waters, precipitation, lakes and the local groundwater in the river catchments.

Figure 5. Annual variations in $d$-excess in precipitation and both rivers, and the weighed annual means for precipitation (10.8 ‰), the Kokemäenjoki River (1.9 ‰) and the Vantaanjoki River (8.9 ‰).
value of $-8.5 \pm 0.2 \text{‰}$ during the monitoring period, which implies that the seasonal changes in lake water isotopic composition are relatively small. The mean $\delta^{18}O$ value of the water in the Kokemäenjoki River is $-9.1 \text{‰}$ (Table 1). The isotopic composition of water in the Kokemäenjoki River can be interpreted as a mixture of water from these two lakes and groundwater, or direct surface flow. The total MRT of water in the catchment of the Kokemäenjoki River cannot be estimated from the seasonal trend in the isotope data. The small seasonal signal likely represents surface flow and snowmelt upstream from the river water sampling site but not in the total catchment of the Kokemäenjoki River.

6. Conclusions

Seasonal variations in the stable isotope composition of precipitation can be used as a tracer to constrain the routes and the residence times of water in a catchment. Phase displacements of seasonal $\delta^{2}H$ and $\delta^{18}O$ curves in river water can be applied successfully to estimate the MRT of the younger component in the water. In temperate climate with a seasonal snow cover, the phase displacement reflects mostly the duration of snow cover in the region. If the catchment does not include lakes, the seasonal stable isotope pattern in river water may be dominated by the snowmelt and spring flooding events. The MRTs of older components derived from groundwater or storage in a complex lake system cannot be resolved from the shifts in the seasonal isotope signal.

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