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Using <sup>18</sup>O and <sup>2</sup>H isotopes for investigating transport and PFAScontamination in Uppsala esker.

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## Abstract

An isotope analysis using stable water isotope ratios,  $\delta^{18}$ O and  $\delta^{2}$ H, paired together with PFAS monitoring has been conducted to achieve a comprehensive understanding of the groundwater origin, transport processes and PFAS contamination dynamics for a portion of the Uppsala Esker affected by artificial infiltration. This information is valuable in developing strategies to meet the water demand that is expected to increase with the growing population, manage and reduce the PFAS contamination and protect the drinking water supply in Uppsala. The foundation of this project is a large set of  $\delta^{18}$ O and  $\delta^{2}$ H isotope data stretching back to 2014 until today, provided by Uppsala Vatten, as well as water samples taken between September and November 2023 at six groundwater observation wells, Galgbacken's wellfield and Tunåsen's infiltration chamber where water from Fyrisån passes through before being infiltrated in the aquifer.

By determining the travel time of the water through the esker from the infiltration point to the wellfield using the stable isotopes  $\delta^{18}$ O and  $\delta^{2}$ H the travel time was found to be on average 225 days and the average speed of water at this site was found to be  $1 \cdot 10^{-4}$  m s<sup>-1</sup>. By calculating the percentage of infiltrated surface water from the Tunåsen infiltration chamber in Galgbacken wellfield, a blending ratio could be assessed. This blending ratio was found to be on average 89 % surface water from river Fyris and 11 % virgin groundwater originating from north of the study area. When investigating the PFAS concentration at the six sampling points between Tunåsen and Galgbacken sampling point D showed high concentrations of PFAS indicating that there might be a point source near that sampling point. The PFAS composition did not change drastically along the travel path and not all PFAS comes from infiltration.

The isotope analysis can be used as a tool to estimate when a high total PFAS concentration found at Tunåsen is likely to reach Galgbacken, however it cannot be used to draw conclusions about the transport of individual PFAS substances or composition profiles.

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## Sammanfattning

En isotopanalys med hjälp av stabila vattenisotoper,  $\delta^{18}$ O och  $\delta^{2}$ H, tillsammans med PFASövervakning har genomförts för att uppnå en heltäckande förståelse av grundvattnets ursprung, transportprocesser och PFAS kontamination i en del av Uppsalas rullstensås som påverkas av konstgjord infiltration. Denna information är värdefull för att utveckla strategier som hjälper till att möta vattenbehovet som förväntas stiga med ökad befolkning, hantera och minska PFAS förorening och skydda dricksvattenförsörjningen i Uppsala. Till grund för detta projekt ligger en stor uppsättning data som sträcker sig tillbaka till 2014, tillhandahållen från Uppsala Vatten, samt vattenprover tagna under en tremånadersperiod mellan september och november 2023 i sex provpunkter i området runt Tunåsen, Uppsala. Dessa sex provpunkter bestod av fyra grundvattenobservationsbrunnar, ett brunnsfält och en infiltrationskammare där vatten från Fyrisån passerar innan det infiltreras i akviferen.

Vattnets transporttid genom åsen från infiltrationspunkten till brunnsfältet hittades genom att titta på toppar av isotoperna  $\delta^{18}$ O och  $\delta^{2}$ H. Transporttiden var i genomsnitt 225 dagar och vattnets medeltransporthastighet var  $1 \cdot 10^{-4}$  m s<sup>-1</sup>. För provpunkten i Galgbackens brunnsfält beräknades det uppmätta blandningsförhållandet mellan ytvatten som infiltrerats ned i åsen via Tunåsens infiltrationskammare och det naturliga, opåverkade grundvattnet som flödat från norr om undersökningsområdet. Vattnets blandningsförhållande bestod i genomsnitt av 89 % ytvatten från Fyrisån och 11 % naturligt grundvatten. Vid undersökning av PFAS-koncentrationen i de sex provtagningspunkterna mellan Tunåsen och Galgbacken visade provtagningspunkt D höga koncentrationer av PFAS, vilket tyder på att det kan finnas en punktkälla i närheten av den provtagningspunkten. PFAS-sammansättningen förändrades inte drastiskt längs flödesvägen och PFAS kompositionen i varje enskild provpunkt tyder inte på att den uppmätta PFAS:en har sitt ursprung i Fyriån.

Isotopanalysen kan användas som ett verktyg för att uppskatta när en hög total PFAS-koncentration som upptäckts vid infiltrationskammaren sannolikt når Galgbacken, men den kan inte användas för att dra slutsatser om transport av enskilda PFAS-ämnen eller sammansättningsprofiler.

# Populärvetenskaplig sammanfattning

Idag bor det 190 000 människor i Uppsala, en siffra som förväntas öka till 300 000 år 2050 (McCleaf et al. n.d). Med en ökad befolkning följer en ökning av stadens dagliga vattenbehov. I Uppsala utvinns dricksvatten av grundvatten. För att säkerställa att vattnet räcker till hela befolkningen, likaväl nu som år 2050, fylls det naturliga grundvattnet på med vatten från Fyrisån (Uppsala vatten n.d). Denna påfyllning sker genom att vattnet från Fyrisån pumpas upp och infiltreras ned i grundvattenakviferen genom den rullstensås som Uppsalas dricksvattenförsörjning är uppbyggd kring. Denna process kallas artificiell infiltrering. Det blandade vattnet färdas genom marken innan det pumpas upp, renas och distribueras över staden. Detta är ett komplext system och ytterligare kunskap om grundvattnets ursprung och åsens hydrogeologi är viktig för den framtida dricksvattenproduktionen.

Allt vatten på jorden färdas genom ett kretslopp. Isotoper är atomer med samma antal protoner i kärnan, men olika antal neutroner. Isotoper delar samma kemiska egenskaper men beroende av antalet neutroner skiljer de i massa och därför i fysikaliska egenskaper (International Atomic Energy Agency 2022). Vattenmolekylen, H<sub>2</sub>O, består av en syreatom, som i grundform har 16 neutroner (<sup>16</sup>O), och två väteatomer som i grundform har 1 neutron (<sup>1</sup>H). <sup>18</sup>O är en stabil isotop av syre som förekommer naturligt i vattnets kretslopp. Den består av två extra neutroner och är därför tyngre än <sup>16</sup>O. Samma princip gäller för den neutrala, stabila isotopen av väte, <sup>2</sup>H, som kallas deuterium. Vattenmolekyler som består av dessa tyngre isotoper är de första som faller när det regnar, och de sista som evaporerar från sjöar och hav. Detta innebär att vatten med olika ursprung kan ha olika isotopsammansättnigar. Genom att studera ett dokument med omfattande vattendata som stäcker sig tillbaka till 2014 kombinerat med att ta vattenprover i fyra grundvattenobservationsbrunnar, en infiltrationskammare och ett vattenverk, alla lokaliserade runt Tunåsen som är en del av Uppsalas rullstensås, har ett blandningsförhållande samt vattnets resetid från infiltration till vattenverk hittats. Blandningsförhållandet visade att 89 % av vattnet som pumpas upp i vattenverket består av infiltrerat ytvatten och 11 % av naturligt grundvatten, som har sitt ursprung norr om det studerade området. Vattnets medeltransporthastighet var 1.10<sup>-4</sup> ms<sup>-1</sup>, vilket på sträckan från infiltrationen till vattenverket motsvarar 225 dagar.

Per- och polyfluorerade alkylsubstanser (PFAS) är en hälsoskadlig kemikalie som skapats av människor men som idag finns i naturen på grund av användandet av produkter innehållande

PFAS. Dessa inkluderar bland annat regnkläder, skidvalla och skumkoncentrat (AFFF) som används vid brandbekämpning. Från och med den 1 januari 2026 träder ett nytt gränsvärde för halten PFAS i dricksvatten i kraft. Det nya gränsvärdet blir 4 ng L<sup>-1</sup> för PFAS<sub>4</sub>, vilket innebär att summan av de fyra högst prioriterade PFAS-ämnena inte får överstiga 4 ng L<sup>-1</sup> (Livsmedelsverket 2022). Ett syfte med detta projekt var därför att får en djupare förståelse för PFAS-kontamineringen i projektområdet genom att para ihop vattenanalysen med en PFAS-övervakning. Denna information kan i framtiden vara värdefull i syfte att utveckla strategier för att hantera och minska PFAS-kontamination och för att skydda dricksvattenförsörjningen i Uppsala. Resultaten visade att kompositionen av PFAS-ämnen inte ändras anmärkningsvärt längs flödesvägen men att den totala koncentrationen mellan provpunkterna skiljer sig, vilket kan bero på en potentiell punktkälla.

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# Glossary

AFFF Aqueous film forming foam

**DO** Dissolved oxygen

GMWL Global meteoric water line

**Groundwater** Water that is found beneath the Earth's surface, in the saturated zone, in the pores and spaces between rocks and soil.

LMWL Local Meteoric Water Line

**ORP** Oxidation-reduction potential

**PFAS** Per- and polyfluoroalkyl substances

PFHxS Perfluorohexane sulfonic acid

PFNA Perfluorononanoic acid

PFOA Perfluorooctanoic acid

PFOS Perfluorooctane sulfonic acid

SPC Specific conductance

Surface water Water that is found on the Earth's surface in lakes, rivers, streams and oceans.

VSMOW Vienna Standard Mean Ocean Water

<sup>18</sup>O Oxygen-18

<sup>2</sup>H Deuterium

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# **1** Introduction

Groundwater in the Uppsala Esker is utilized to meet the water requirement in Uppsala, Sweden (Winquist 1977). However, per- and polyfluoroalkyl substances (PFAS) contamination has been discovered in Uppsala's groundwater which require treating the drinking water for removal of PFAS (Sörengård et al 2022). In Europe, a new drinking water guideline has been implemented and for Sweden the new drinking water limit will be 100 ng  $L^{-1}$  for sum of 21 PFAS (PFAS<sub>21</sub>) and 500 ng  $L^{-1}$  for total organic fluorine (Livsmedelsverket 2022). In addition, in 2026 a newly proposed Swedish drinking water guideline of 4 ng  $L^{-1}$  for the sum of the four PFAS perfluorohexane sulfonic acid (PFHxS), perfluorononanoic acid (PFNA), perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS) will be implemented (LIVSFS 2022:12). The purpose of this study is therefore partly to get an overall picture of today's PFAS contamination in the Uppsala Esker. Besides new drinking water guideline values, the population in Uppsala is expected to increase from today's 190,000 to 300,000 by 2050. To meet approximately 50% of the city's water demand of (2023) 45 000 m<sup>3</sup> d<sup>-1</sup> and to prevent overexploitation of the esker's naturally occurring groundwater, it is supplemented by artificial infiltration of surface water from the nearby Fyris river through a complex water system. This infiltration can lead to elevated levels of contamination and affect the quality of the natural groundwater. Given the anticipated growth and newly implemented drinking water guideline values, it is important that we learn more about our drinking water, its origin, and the hydrogeology of the esker (McCleaf et al. n.d). Therefore, the purpose of this study is also partly to investigate general water conditions in the esker, more specifically the ratio between surface and groundwater as well as the average travel time of water. One method that can be applied for this is tracer elements, such as naturally occurring stable isotopes. The use of the isotope ratio between naturally occurring stable isotopes of oxygen and hydrogen is denoted as  $\delta^{18}$ O and  $\delta^{2}$ H and have proven to be effective in study hydrological processes, determining the age and origin of water and acknowledging the water source (Mazor 2003; Stadnyk et al., 2005).

# 1.1 Aim

By analysis of  $\delta^{18}$ O and  $\delta^{2}$ H water isotopes paired with PFAS monitoring, the overall aim of this thesis is to achieve a comprehensive understanding of the groundwater origin, transport processes and PFAS contamination dynamics in the Uppsala esker between Tunåsen infiltration and Galgbacken wellfield. This can be valuable in developing strategies to meet the water demand, manage and reduce the PFAS contamination and protect the drinking water supply in Uppsala. The specific objectives are:

- Determine the water's average travel time from the infiltration basins at Tunåsen to Galgbacken drinking water wellfield.
- Assess the blending ratio of artificial groundwater with virgin groundwater at Galgbacken.
- Paired analysis: Evaluate if there is a change in PFAS concentration at the six sampling points that can be explained by the results above.

# 2 Background

## 2.1 Per- and polyfluoroalkyl substances (PFAS)

PFAS are a large group of anthropogenic chemicals that have gained increasing concern worldwide due to their environmental and health impacts (Gagliano et al. 2020). They are characterized by a strong carbon-fluorine bond and do not degrade easily in the environment (National Institute of Environmental Health Science 2023). Because of their useful properties to be both water and oil repellant as well as being able to endure high temperatures, PFAS chemicals have been used in industrial processes and consumer products since the 1940's (EPA 2021). Some everyday things that contain PFAS include cosmetics, water repellant outer garment, food-packaging, ink, and aqueous film forming foam (AFFFs) (Swedish Chemical Agency 2015). PFAS enter the groundwater mainly through *direct* sources such as AFFFs from firefighting training sites, leachate from wastewater treatment plants, landfills, and process water from industrial processes as well as *indirect* sources such as precipitation (Dasu et al. 2022).

#### 2.1.1 PFAS toxicity

The two most regulated subgroups of PFAS are perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), which differ in their functional group (Ahrens et al. 2013). Meaning that the PFCAs contain a carboxylic acid as its functional group and PFSAs contain a sulfonic acid as its functional group. Furthermore, PFAS can also be divided into groups of long- and short chained compounds, depending on the number of fluorinated carbons that the chain consists of (Li et al. 2023). The toxicity can be determined by the chain length, where long chained PFASs are generally more toxic than the short chained, and for the functional groups, where PFSAs are generally more toxic than the PFCAs (Ahrens et al. 2013; Shittu et al. 2023).

#### 2.1.2 PFAS exposure

In Sweden, the main PFAS exposure of the population is via food and drinking water (Swedish Chemical Agency 2023). In 2012, elevated levels of PFAS were discovered in the water in Uppsala and with the use of a digital water model that track the movement of the

waterflow in the ground, Uppsala Vatten was able to trace the PFAS discharge and pinpoint the source to Ärna airfield which belongs to the Swedish military (Uppsala Vatten 2023a). The area has been used as a training site for firefighting by the Swedish Armed Forces where they have used AFFFs containing PFAS (Sveriges Riksdag 2021). Since this discovery, the PFAS contaminated water in Uppsala with PFAS levels above the Swedish Food Agency's (SLVs) guideline values has been treated using active carbon filtration (Uppsala Vatten 2023a).

Given the extensive and complex nature of PFAS, there are still many unknowns concerning health effects from these substances. However, if PFAS are stored for a long time in the body or if we are exposed for a long period of time, our health can be affected (Naturvårdverket n.d.). For example, increased risk of some cancers, reproductive effects such as decreased fertility and interference with the body's natural hormones (EPA 2021).

#### 2.1.3 PFAS regulation in drinking water

Starting on January 1st, 2026, a new limit on PFAS in drinking water will take effect. The new limit will be 4 ng  $L^{-1}$  for PFAS<sub>4</sub>, which means that the sum of the four highest priority PFAS substances must not exceed 4 ng  $L^{-1}$  (LIVSFS 2022:12). These four PFASs are PFOA, PFOS, PFHxS and PFNA, which are considered to account for approximately half of the most bioavailable and toxic PFASs in the environment (Stockholm Länsstyrelse 2022).

In addition, the new drinking water limit will be 100 ng  $L^{-1}$  for sum of 21 PFAS (PFAS<sub>21</sub>) and 500 ng  $L^{-1}$  for total organic fluorine (LIVSFS 2022:12).

## 2.2 Uppsala Esker

#### 2.2.1 What is an esker?

An esker is a distinctive landform that is composed of sediments left behind by a retreating ice sheet (SGU 2020a). It is a long ridge of stratified loose material deposited of glacial meltwater, mainly coarse-grained material such as sand and gravel (Persson 2010). When the ice sheet melted, large amounts of water formed glacial rivers carrying sediments, stones, gravel, and sand under the ice sheet. As the water approached the edge of the ice sheet, the speed and the water's transport capacity decreased, which lead to that the material sank to the

bottom and was deposited as glacial sediment, which created today's eskers (SGU 2020a). As a result of the last ice age many eskers have been formed around Sweden (Bar-Am et al. 2019). The Uppsala esker being one of them.

#### 2.2.2 Groundwater in an esker

Where the earth's pores are fully saturated with water, groundwater is found (SGU 2020b). The groundwater can be a few weeks or even thousands of years old (Norrvatten n.d). The geological transformations of material in an esker in combination with Sweden's climate has meant that the country has favorable conditions for extraction of high-quality groundwater (SGU 2020b).

When water flows through the different layers of loose materials in an esker it is purified in a natural way (Hägg et al. 2021). This due to the esker's good permeability and beneficial properties of separating organic matter and other unwanted substances through decomposition, absorption, and separation (Hansson 2000). It is therefore optimal to place infiltration basins on the top of eskers (Forsling 2014).

Today, nearly half of all the drinking water in Sweden is derived from virgin groundwater or what is known as *artificial groundwater* (SGU 2020b) which is described in more detail below.

#### 2.2.3 Groundwater in the Uppsala Esker

In Uppsala, groundwater extracted from the esker is utilized to meet the city's drinking water requirement (Uppsala Vatten 2023b). In the middle of the 1950s the water demand increased, since Uppsala as well as many other cities, expanded rapidly post-war. It was therefore made clear that it was necessary to increase the natural water resources of the esker by implementing artificial infiltration using water from the river Fyris (Winquist 1977). Today approximately 50% of Uppsala's daily water demand of 45 000 m<sup>3</sup> d<sup>-1</sup> is provided by this artificial recharge (McCleaf et al. n.d.).

## 2.3 Artificial infiltration

Artificial infiltration is the human-controlled processes used to increase the amount of water entering an aquifer. This artificial recharge of groundwater can be made by diverting water through canals, infiltration basins or sprinkler systems, alternatively by simply injecting water directly into the subsurface through injection wells (Chellamuthu et al. 2022). Artificial infiltration results in a significantly larger amount of groundwater being infiltrated than when natural groundwater is being formed (Forsling 2014).

#### 2.3.1 Artificial infiltration through infiltration basin

The principle behind artificial infiltration is to replicate the water infiltration that occurs in nature (Hanson, 2000). In Uppsala, this is made through infiltration basins. Water from river Fyris is pumped uphill to infiltration basin facilities located on the Uppsala Esker and is then infiltrated in the esker where it percolates into the subsurface through the esker material before mixing with the natural groundwater (Yu et al. 2022), see Figure 1.



Figure 1: Schematic overview of Uppsala's artificial infiltration (not to scale).

In 2023, there are four facilities in Uppsala where the Fyris water is infiltrated in the esker, these are Husby, Vallskog, Lövstalöt and Tunåsen. From the Tunåsen infiltration facility, there are several observation wells from which water samples can be taken before the water reaches Galgbacken in central Uppsala where Galgbacken's wellfield is located (Stenberg

2018). The water from Galgbacken's wellfield is then distributed in the city as drinking water after treatment at Gränby water treatment plant (Yu et al. 2022).

## 2.4 Stable Oxygen and Hydrogen

The water molecule, H<sub>2</sub>O, consists of two hydrogen (H) atoms and one oxygen (O) atom (Ortega et al. 2019). The molecule can contain various isotopes of these atoms, each with different prevalence. Isotopes are atoms that have the same number of protons in the nucleus but differ in the number of neutrons. Isotopes share the same *chemical* properties but depending on the number of neutrons they differ in mass and therefore in *physical* properties (International Atomic Energy Agency 2022).

There are two naturally occurring stable isotopes of hydrogen (<sup>1</sup>H and <sup>2</sup>H) and three naturally occurring stable isotopes of oxygen (<sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O) which means that the water molecule has nine possible combinations of these isotopes. The lightest isotope is the most abundant of each (Galewsky et al. 2016).

## 2.4.1 Using <sup>18</sup>O and <sup>2</sup>H to trace the origin of water

As water goes through different phase changes in the hydrological cycle, the number of heavy isotopes (<sup>18</sup>O and <sup>2</sup>H) relative light isotopes (<sup>16</sup>O and <sup>1</sup>H) can change (Bruckner 2024).

This isotopic fractionation is expressed as a ratio of the concentration between the heavy and the light isotopes. The ratio is denoted as delta values,  $\delta^2 H$  (<sup>1</sup>H:<sup>2</sup>H) and  $\delta^{18}O$  (<sup>16</sup>O:<sup>18</sup>O), and is often used to study hydrological processes, determining the age and origin of water and to trace the water source (Stadnyk et al., 2005; Ortega et al. 2019). For example, surface water can have different isotopic ratios during different seasons. These variations can be reflected in the groundwater if the surface water infiltrates the aquifer, except the curve is delayed in time and has a reduced amplitude (Kendall et.al 2012). The delay can provide insights into the duration it takes for surface water to infiltrate the aquifer (Sköld 2017).

#### 2.4.2 Vienna Standard Mean Ocean Water (VSMOW)

The isotope ratio is calculated by dividing the heavier isotope by the lighter isotope  $(^{2}H/^{1}H)$  and  $^{18}O/^{16}O$  and is further expressed as delta values in per mil [‰] deviation from the Vienna Standard Mean Ocean Water (VSMOW) ratio, according to equation:

$$\delta^{18}O, \delta^{2}H (\%_{0}) = \left(\frac{R_{Sample}}{R_{VSMOW}} - 1\right) \cdot 1000 (1)$$

where  $R_{Sample}$  is the oxygen or hydrogen isotope ratio of the concentrations of (<sup>18</sup>O/<sup>16</sup>O) or (<sup>2</sup>H/<sup>1</sup>H) in the sample and  $R_{VSMOW}$  is the standard value of the oxygen or hydrogen ratio (Yang 2018). The resulting  $\delta$ -value, with units per mil [‰] is often negative (Dee et al. 2023). A negative value for  $\delta$ <sup>18</sup>O indicates that the water sample has less <sup>18</sup>O than <sup>16</sup>O compared to the VSMOW standard (Sköld 2017). The same goes for  $\delta$ <sup>2</sup>H.

The VSMOW is the standardized composition of isotopes in ocean water. It was originally developed by Craig (1961) and was initially referred to as SMOW but was later updated by the International Atomic Energy Agency (IAEA) to VSMOW which is still used today (IAEA 1995).

#### 2.4.3 Global Meteoric Water Line (GMWL)

The correlation that describes the global average variation between  $\delta^{18}$ O and  $\delta^{2}$ H of water from various locations on earth that comes from meteoric water, such as precipitation, is called the Global Meteoric Water Line (GMWL) (Wolfe et al 2006). This is a linear correlation that is defined by Craig (1961) and can be fit to the equation:

$$\delta^2 H = 8 * \delta^{18} O + 10$$
 (Craig 1961).

It has a slope of 8 and an intercept of 10 on a  $\delta^2$ H vs.  $\delta^{18}$ O plot. This means that for every 1 ‰ increase in  $\delta^{18}$ O, there is an 8 ‰ increase in  $\delta^2$ H. This equation is based on extensive global measurements of precipitation. The r<sup>2</sup> is over 0.95 and this correlation between the coefficients shows that there is a relation between the stable isotopes of oxygen and hydrogen in water molecules, which is why the isotopic ratios and fractions between these are typically discussed together (Kendall 2012).

Deviations from the GMWL provide information about precipitation in a specific area. Local Meteoric Water Lines (LMWL) illustrate the site-specific variation of stable hydrogen and oxygen over time. The LMWL may differ from the GMWL and the main factors that control the isotopic composition of precipitation at a certain location is primarily due to two key factors: the temperature at which the precipitation condenses and the degree of rainout in the air mass (Kendall 2004).

#### 2.5 Transport of water in the hydrological cycle

The hydrological cycle is the eternal movement of water recycling on earth (Pagano et al. 2002). It represents the continuous flow of water on Earth through evaporation and condensation (Yang et al. 2021). These are mass- and temperature dependent processes and affect how water molecules with different isotopes move though the cycle (Galewsky et al. 2016). Water molecules with lighter isotopes are the first to evaporate from the sea, forming clouds with specific isotopic signatures. These clouds have a mixture of different molecules that fall in the form of precipitation, which fills our lakes, rivers, and aquifers. Water molecules with heavier isotopes are the first to fall and as the clouds shed these heavier isotopes, they move further inland and there at the higher altitudes lighter isotopes precipitate in a greater extent (Ortega et al. 2019).



Figure 2: Simplified schematic view of the hydrological cycle. The water vapor gradually becomes lighter as the relatively heavier water falls as precipitation, this in turn leads to lower  $\delta^{18}O$  values further from the water

source. The same pattern follows for  $\delta^2 H$  but that is not illustrated in this figure. The values taken from Bruckner 2024.

With respect to different factors, such as the amount of evaporation, the frequency of rainout events, continentality, elevation and temperature; water from different sources within this cycle may have different abundances of heavy isotopes relative to light isotopes, called isotopic ratios (Mazor 2003). These ratios can be compared to unique fingerprints or signatures, and these signatures can provide information about the waters origin and play a crucial role in tracing the movement of water as it navigates the hydraulic cycle (Smith et al. 1997).

# 3 Method and data

The following section includes an overview of the study area as well as a presentation of the material and method that was used to collect the groundwater samples. It also includes a presentation of the method used when analyzing the results.

## 3.1 Site description – Tunåsen and reference point

The area of Tunåsen is part of the Uppsala esker and is found in the northern part of Uppsala. The whole area covers approximately 18 hectares (Alvehus 2002) and is part of a nature reserve where people can walk, run and connect with nature (Uppsala kommun 2014). The ridge of Tunåsen rises approximately 30 meters above its surroundings which consists of mostly open landscape and fields (Alvehus 2002). The selection of the location for this project was partly chosen due to long history of water infiltration at Tunåsen, which began approximately 1956 along with extraction at the Galgbacken wellfield. Additionally, a dataset of water quality and isotope values along with groundwater level measurements are available for groundwater wells at this site dating back to 2014 (Uppsala Water and Waste, AB, isotope data set 2014-2024, unpublished).

#### 3.1.1 Groundwater reference point

Björklinge is found a few kilometers north of Tunåsen, upstream from the project's study area. Here, we find virgin groundwater that is not affected by artificial infiltration. In total 20 samples from two sampling wells in this area serve as the isotope reference point for this project. Furthermore, the isotopic composition of this unaffected groundwater represents the signature for the groundwater not influenced by artificial infiltration and is acting as the standard against which water from the other sampling points, affected by artificial infiltration, are compared. Therefore, the reference values are essential to this study to assess and understand how water in other sampling points, affected by artificial infiltration, differs isotopically from the natural state in this area as well as from each other.

#### 3.1.2 Sampling points along Tunåsen

The sampling points consisted of four groundwater observation wells situated around Tunåsen as well as the Tunåsen distribution chamber and Galgbacken wellfield. These sampling points were A (groundwater observation well), B (Tunåsen groundwater distribution chamber), C (groundwater observation well), D (groundwater observation well), E (groundwater observation well) and F (Galgbacken wellfield) (Figure 3).

Out of the six sampling points in this project, A is situated most north and is therefore the point that the virgin groundwater reaches first and mixes with the artificially infiltrated water. Sampling point A is also the only sampling point situated north of the distribution chamber, sampling point B, where the water from river Fyris is infiltrated. The water in sampling point B consists solely of infiltrated water. The rest is found south of sampling point B. All sampling points except Tunåsen infiltration chamber (B) consists of a blend between the infiltrated surface water from river Fyris and the natural groundwater coming from the north. The wellfield in Galgbacken, sampling point F, represents the southernmost and final sampling point in this study. The sampling points distance from infiltration (sampling point F) in the general direction of the groundwater flow can be seen in Figure 4 as well as Table 1 which also shows the depth of the sampling point in the well according to the Swedish national height system, RH2000.



Figure 3: Map from SGU showing the study area around Tunåsen. On the map there is red markers showing the approximate location of the observation wells. From sampling point A being the northernmost to sampling point F being the southernmost. The arrows indicate the approximate groundwater flow direction.



Figure 4: The sampling points plotted by their exact coordinates. The x-axis shows the distance from infiltration where Tunåsen, sampling point B, is set to zero as it represents the point of infiltration. A is negative since it is found upstream from the point of infiltration and the other sampling points are found downstream. The y-axis shows the RH2000 elevation for the assumed sampling depth measured in meters above sea level. The orange line represents the ground surface.

**Table 1:** The groundwater wells form which water samples for this study was taken. The horizontal distance of the wells from the infiltration site in Tunåsen and the depth of the sampling point in each groundwater well (see Figure 4).

Groundwater well	Sampling point	Distance from infiltration in the general direction of the groundwater flow [m]	Depth of the sampling point in the well (meters above sea level RH2000)
Α	Observation well	-30	6
В	Tunåsen infiltration	0	45
С	Observation well	0	1
D	Observation well	220	-1.5
Е	Observation well	875	-11
F	Galgbacken wellfield	2025	-8 to 0

#### 3.1.3 Historical investigations

In a functional analysis from 2017 provided by Uppsala Vatten, there is an estimate of a blending ratio and residence time for each of the sampling points on the distance between Tunåsen infiltration and Galgbacken (McCleaf 2017). These are based on samples taken between the years of 2014-2016 and can be seen in Table 2.

**Table 2:** Historical data from December 2014 to June 2023. From Uppsala Vatten. The sampling points from which historical water samples were taken. The mean residence time for water in that sampling point as well as the proportion of naturally formed groundwater in that sampling point and the average hydraulic conductivity according to the historical data set. Also, the period for which the historical data is available and the number of days that period comprises as well as the number of samples that is available for each sampling point in the historical data set.

Sampling point	Mean residence time [d]	Proportion of naturally formed groundwater [%]	Average speed of water [m d <sup>-1</sup> ]	Average speed of water [m s <sup>-1</sup> ]	Historical data span	Sampling period [d]	Number of samples
А	5	10-15	10	1.2.10-4	2014-07-07 - 2016-03-07	609	18
В	NA	0	NA	NA	2015-01-12 - 2023-05-05	3035	297
С	2	0-5	NA	NA	2015-02-09 - 2016-03-21	406	25
D	35	5-10	6.3	7.29.10-5	2014-12-15 - 2019-01-25	1502	20
E	80	0-5	11	1.3.10-4	2014-12-17 - 2020-07-16	2038	30
F	240	15–20	8.4	9.7.10-5	2014-12-16 - 2023-01-31	2968	81

NA = not available

## 3.2 Method

#### **3.2.1 Data collection**

#### 3.2.1.1 Equipment

The equipment used in the field study for groundwater sampling were a YSI Professional Plus meter, a portable lithium battery, a Proactive Environmental Products *Low Flow with Power Booster 2 Controller*, a groundwater depth measurement electric tape, as well as single-use plastic gloves, one 800 mL plastic container and two 30 mL HDPE plastic containers.

#### 3.2.1.2 Collection of water samples

Once every other week, during the period of three months (September to November 2023), water samples were collected from the six groundwater observation wells extending from the Tunåsen infiltration basin to Galgbacken water treatment plant. Previously installed 12-volt pumps within each groundwater well (installed by Uppsala Water and Waste) were powered by a portable lithium battery to extract water from the aquifer. For some of the pumps a Proactive *Low Flow with Power Booster 2 Controller* voltage transformer was used to be able to pump up water from the aquifer, due to the depth to groundwater. Before each individual sampling, comprehensive water quality measurements were ensured at each sampling point via a YSI Professional Plus meter equipped with sensors for measurement of water temperature, pH of the water, dissolved oxygen (DO), specific conductance (SPC) and oxidation-reduction potential (ORP).

During the collection of water samples, it was important to ensure that three well-volumes were purged from the observation wells to guarantee the collection of fresh groundwater for the following analysis. Therefore, sufficient turnover time was found before each sampling by measuring the flowrate and the volume of water within each well, which enabled the calculation that determined the time required to pump three well-volumes. The flowrate was determined by timing the seconds it took to fill a one-liter bottle with water from the well (X seconds) and calculate  $\frac{1}{x} = flowrate [l s^{-1}]$ . To measure the volume of water a Solinst water level meter Model 101 were lowered in the well until it detected water. At one observation point (E), the pump sat at a level far down the pipe and the flow was slow. Since it is not good for the pump to run for too long, a time interval of 30 minutes was chosen even if it would take about 1.5 hours to let three well-volumes pass.

To avoid unnecessary cross-contamination, single-use plastic gloves were worn during the sampling process and before the water was collected, each plastic bottle was filled halfway with water and shaken with the lid on three times, then emptied before the sample was taken. Additionally, two empty bottles with field blank samples were obtained at every other sampling for the Galgbacken and Tunåsen locations. The bottles consisted of one 60 mL high-density polyethene (HDPE) plastic bottle for PFAS samples. The bottles were shut airtight to prevent

evaporation. One bottle with isotope sample from each sampling occasion were sent to the JR AquaConSol lab in Graz, Austria and the other one to the Environmental Isotope Lab at the University of Waterloo, Canada. The PFAS sample was delivered to the Swedish Agricultural University (SLU) in Uppsala for PFAS analysis.

As an addition to the water samples that were gathered from the duration of this project (September 2023 to November 2023), water sample isotope and PFAS data collected from Tunåsen infiltration and Galgbacken wellfield from 2014 to 2023 were provided by Uppsala Vatten. The PFAS data originate from the project PFASMAR (2021-00510) funded by Formas.

#### **3.2.2 Laboratory procedures**

#### 3.2.2.1 <sup>18</sup>O and <sup>2</sup>H isotope measurements

After the isotope samples were collected in a 30 mL HDPE plastic bottle, they were kept chilled in a cooling bag to minimize the risk of evaporation until they were shipped off to the two separate laboratories. Measurements of field conductivity and pH from the different wells at the dates when the water was collected were also included in the shipping to University of Waterloo for <sup>18</sup>O and <sup>2</sup>H isotope measurements (University of Waterloo n.d).

To measure the isotopic signature the samples were studied with isotope ratio mass spectrometers and calibrated to the IAEAs VSMOW ratio. The <sup>18</sup>O and <sup>2</sup>H were presented as delta values ( $\delta^{18}$ O and  $\delta^{2}$ H) representing the per mil deviation from the VSMOW standard. The precisions for the samples were 0.2 % for  $\delta^{18}$ O and 0.8 % for  $\delta^{2}$ H (University of Waterloo n.d).

#### 3.2.2.1.1 Comparison of <sup>18</sup>O and <sup>2</sup>H isotope measurements

Two isotopic water samples from each groundwater well at each sampling occasion was send to different laboratories (i.e. JR AquaConSol and Environmental Isotope Lab), to investigate whether different laboratories detected different variations from the VSMOW standard. The results differed slightly and to assess if this was a significant difference a t-test was conducted. A t-test evaluates whether there is a significant difference between the mean values of two different groups or data. The t-test gave a value of 0.30 for oxygen measurements and 0.81 for hydrogen measurements, which is above the significance level of 0.05 and therefore the difference in the isotopic results from the two different laboratories cannot be seen as significant.

#### 3.2.2.2 PFAS

The 800 mL PFAS samples were analyzed at SLU, Uppsala. They were split into two samples of 400 mL each and analyzed in duplicates. The samples were sonicated, filtered, spiked with 5 ng absolute for each mass-labelled internal standard, and extracted via solid phase extraction. Two lab blanks were included in every extraction batch (9 samples) and the field blanks from the Galgbacken and Tunåsen sampling site were analyzed accordingly. The samples were then analyzed for 29 individual PFAS using an ultraperformance liquid chromatography-tandem mass spectrometer (UPLC-MS/MS, Sciex Triple Quad 3500) (Smith et al. 2022).

#### 3.2.3 Analyzing data

#### 3.2.3.1 Average travel time

 $\delta^{18}$ O and  $\delta^{2}$ H data spanning back to 2014 was examined in Excel to determine the time it takes for water to travel through the groundwater esker. The amount of historical data differed considerably between the different sampling points. Out of the six observation points included in this project, only Tunåsen infiltration chamber and Galgbacken wellfield had a substantial historical dataset. Therefore, the travel time was specifically calculated between these two sites rather than considering every individual point between Tunåsen and Galgbacken.

By scrutinizing the  $\delta^{18}$ O or  $\delta^{2}$ H peaks at Tunåsen and tracking in the plot to when the same oxygen or hydrogen peak reaches Galgbacken, the time interval shown on the x-axis can be estimated. This average time interval is given in days and corresponds to the time it takes for water to travel between these peaks. The average speed of water is then calculated on the distance and given in m s<sup>-1</sup>.

#### 3.2.3.2 Blending ratio

The blending ratio showed the proportion of infiltrated water in relation to the natural groundwater in a specific groundwater observation point. This ratio was calculated in excel. The principle behind the calculation is that the infiltrated water consists of heavy isotopes, <sup>18</sup>O and <sup>2</sup>H, and the groundwater of lighter isotopes, <sup>16</sup>O and <sup>1</sup>H. By analyzing the isotopic

composition in a specific groundwater sampling point with the groundwater reference point, potential isotopic differences, due to infiltration of surface water, can be identified.

So, by examination and comparison of the isotopic ratios in virgin groundwater originating from Björklinge and the isotopic ratios in the infiltrated water from river Fyris, a mixing ratio can be calculated. This ratio signifies the percentage of groundwater that originated from the infiltrated surface water.

Sköld 2017 describe the equation used in hydrological investigations to study water with two different origins:

$$F_{sw} = \frac{Y_{mixed} - Y_{gw}}{Y_{sw} - Y_{gw}} \quad (2)$$

where  $F_{sw}$  = the fraction of surface water in Galgbacken. Hence, the amount of water in Galgbacken sampling point that is originating from the infiltrated water from river Fyris.  $Y_{mixed} = \delta^{18}O$  or  $\delta^2H$  isotopic ratio for the water sample in the Galgbacken sampling point.  $Y_{gw} = \delta^{18}O$  or  $\delta^2H$  isotopic ratio for virgin groundwater. This value came from natural virgin groundwater originating from Björklinge and was -11.8 for  $\delta^{18}O$  and -83.68 for  $\delta^2H$ .  $Y_{sw} = a$  mean value of the  $\delta^{18}O$  or  $\delta^2H$  isotopic values for infiltrated surface water in the Tunåsen sampling point calculated between two peaks.

Since only Tunåsen infiltration chamber and Galgbacken wellfield had a substantial historical dataset, the blending ratio will not be calculated for each sampling point.

#### 3.2.3.3 PFAS

The results from the PFAS data were analyzed in Excel. A pie-chart showing the average percentage distribution of each PFAS substance in each of the sampling points was made. This was conducted to be able to see if the PFAS composition changed between the different sampling points. Also, a bar chart was made that showed the composition and the amount of each substance of PFAS as well as the total amount of PFAS for each individual sampling.

# **4 Results**

# 4.1 $\delta^{18}O$ and $\delta^2H$

The method consisted of gathering and analyzing stable oxygen and hydrogen water isotope ratios ( $\delta^{18}$ O and  $\delta^{2}$ H) which is a method that have been used successfully as a tool for tracking the movement of surface- and groundwater and for determining the origin of water extracted long distances from its point of infiltration (Mazor 2003). The water in Tunåsen infiltration chamber was measured to have higher values and a wider spread of  $\delta^{18}$ O and  $\delta^{2}$ H than sampling point Galgbacken which is because the water in sampling point Tunåsen consisted solely of surface water infiltrated from the river Fyris. The signature of surface water is affected by seasonal variations and reflect factors such as rainfall distribution, evaporation, and snowmelt to a greater extent than groundwater (Åkerman 2018). The difference in  $\delta$ -values shows that isotopic analysis is a suitable method for distinguishing surface and groundwater, which was done in this study.

#### 4.1.1 Tunåsen infiltration

In the Tunåsen infiltration chamber where water from river Fyris is infiltrated, the  $\delta^{18}$ O isotope follows a reoccurring annual trend (Figure 5). Between the years of 2015 to 2023 the highest  $\delta^{18}$ O was recorded in September 2017 (2017-09-18), reaching a value of -6.67 ‰. A consistent seasonal pattern can be found, which indicates that the highest values of  $\delta^{18}$ O occur during the months between August and late October each year. This is because during periods of warmer temperatures, the evaporation is at its highest and the lighter isotopes evaporate to a greater extent than the heavy ones (Kumar and Verma 2021). This leads to a higher proportion of heavy relative to light isotopes remaining in the water after warmer seasons which causes the high peaks. The lowest  $\delta^{18}$ O value was recorded in February 2015 (2015-02-26), at -13.20 ‰. The lowest measured  $\delta^{18}$ O of each year consistently falls between the months of January and April. This is due to inflow of snowmelt, since the proportion of heavy isotopes in natural water decreases at colder temperatures (Chizhova et al. 2022).



*Figure 5: Result from isotopic analysis of*  $\delta^{18}O$ *-data between 2015 to 2023 in Tunåsen infiltration basin.* 

The  $\delta^2$ H at the Tunåsen infiltration site follows the same reoccurring annual trend as the  $\delta^{18}$ O (Figure 6). The lowest measured value was recorded in February 2015 at -95.42 ‰, the same as the lowest value of  $\delta^{18}$ O at this site. The highest measured  $\delta^2$ H at Tunåsen infiltration site was recorded to be -56.12 ‰ in October 2016, which differs from the  $\delta^{18}$ O at this site, although their highest values were both repeatedly recorded around the same time of each year which can be seen in Figure 7 that is a combination of Figures 5 and 6.



Figure 6: Result from isotopic analysis of  $\delta^2$ H-data between 2015 to 2023 in Tunåsen infiltration basin.



Figure 7: Result from isotopic analysis from isotope data measured at Tunåsen infiltration chamber. The dark blue line represents the measured  $\delta^{18}O$  and the light blue line represents the measured  $\delta^{2}H$ .

#### 4.1.2 Galgbacken

In Galgbacken wellfield the lowest measured value of  $\delta^{18}$ O was -10.94 ‰ and occurred in October 2023 (2023-10-11). The trend is reoccurring, and the lowest values was measured in the months between October and December of each year. The highest value was -9.02 ‰ and was recorded in April 2018 (2018-04-03) (Figure 8). The highest values were repeatedly found between April and June.



*Figure 8: Result from isotopic analysis of*  $\delta^{18}$ *O-data at Galgbacken water intake facility.* 

The  $\delta^2$ H in Galgbacken follows the same trend as the  $\delta^{18}$ O in Galgbacken (Figure 10). The lowest measured value was recorded in October 2015 at -78,91 ‰ and the highest measured  $\delta^2$ H was -70,28 ‰ in April 2017 (Figure 9). The trend was reoccurring, and the lowest values were measured in the months between October and December of each year and the highest values were repeatedly found between April and June.



*Figure 9: Result from isotopic analysis of*  $\delta^2$ *H-data at Galgbacken wellfield.* 



Figure 10: Result from isotopic analysis from isotope data measured at Galgbacken wellfield.

## 4.1.3 A, C, D, E

The other sampling points, A, C, D, E, had too little historical data and no annual trend could be determined (Appendix 1). A prerequisite for comparing the curves is that sampling has taken place continuously and over a longer period. The assumption is that they consistently follow the same trend as the infiltration point (Tunåsen) and the ending point (Galgbacken), only that the peaks are time-shifted and have a slightly lower amplitude than at Tunåsen and a slightly higher amplitude than in Galgbacken.

#### 4.1.4 LMWL vs GMWL

The relation between the heavy isotopes,  $\delta^{18}$ O and  $\delta^{2}$ H, at the study site is presented in relation to the GMWL in Figure 11, where the surface water in Tunåsen represents the LMWL at the study area. The trend lines for Tunåsen, Galgbacken and other groundwater points (A, C, D and E) showed significant differences from the GMWL (Figure 11).

 $R^2$ -value for the water infiltrated in Tunåsen is 0.74 and for the mixed water in Galgbacken  $R^2$  is 0.72. The surface water is initially shown to the left of the GMWL and eventually cross it. It has a wider spread of heavy isotopes than the water in Galgbacken. The  $\delta$ -values measured at Galgbacken are below the GMWL or follows the GMWL.



Figure 11: The general relation between the heavy isotopes in precipitation water (GMWL) from Craig 1961, and the relation between the heavy isotopes measured at the study site (LMWL). Blue dots and blue line represent the measurements from Tunåsen infiltration site. Yellow represents the measurements at Galgbacken wellfield. The red represents the measurement at the observation points between Tunåsen and Galgbacken.

## 4.2 Average travel time

The travel time is the time that it takes the infiltrated water from river Fyris to reach Galgbacken, which is found by tracing the peaks where the  $\delta^{18}$ O and  $\delta^{2}$ H at Tunåsen and Galgbacken were illustrated over time (Figures 12 and 13). Since there was practically no blending with the natural groundwater at the Tunåsen location, the heavy isotopes are expected to exhibit a high concentration within the Tunåsen infiltration chamber, resulting in a higher amplitude on the graph for these samples than for the samples gathered at Galgbacken. When the water that has infiltrated in the Tunåsen infiltration chamber reaches

Galgbacken wellfield, it is mixed with natural groundwater and the concentration of the heavy isotopes is therefore lower, resulting in a lower amplitude on the graph.

The  $\delta^{18}$ O (Figure 12) and  $\delta^{2}$ H (Figure 13) in the infiltrated water in Tunåsen infiltration chamber, and the blended water in Galgbacken wellfield follows the same annual reoccurring cyclical trend but with a time delay. When the isotope ratio increased in Tunåsen, a corresponding increase was observed in Galgbacken, and the same trend followed for the reduction of the isotope ratio. This temporal lag time was interpreted as the transport time for surface water to infiltrate Galgbacken and corresponds to an average of 213±44 d (median 203) using  $\delta^{18}$ O isotopes and 236±47 d (median 225 d) using  $\delta^{2}$ H isotopes, which is on average 225 days using both isotope data sets (Table 3). Using 225 d and the distance between infiltration to wellfield (2025 m), the average pace of the water is 9 m d<sup>-1</sup>, which is equivalent to  $1 \cdot 10^{-4}$  m s<sup>-1</sup>.

Table 3: Overview of the transport time it takes for the water to travel from Tunåsen infiltration to Galgbacken. Interpreted from peaks in Figures 12, 13, 14 and 15.

Peak δ <sup>18</sup> O	Peak <b>δ</b> <sup>18</sup> O	Travel	Peaks δ <sup>2</sup> H	Peaks δ <sup>2</sup> H	Travel
Tunåsen	Galgbacken	time [d]	Tunåsen	Galgbacken	time [d]
infiltration [date]	wellfield		infiltration [date]	wellfield [date]	
	[date]				
2015-10-19	2016-05-24	218	2015-10-19	2016-05-24	218
2016-10-12	2017-04-03	173	2016-10-12	2017-04-03	173
2017-09-18	2018-04-03	197	2017-09-18	2018-05-03	227
2018-09-26	2019-07-23	300	2018-09-26	2019-07-23	300
2019-07-30	2020-03-31	245	2019-09-17	2020-04-27	223
2020-10-05	2021-04-27	204	2020-10-05	2021-05-25	232
2021-08-11	2022-03-01	202	2021-08-11	2022-03-01	202
2022-08-22	2023-01-31	162	2022-08-22	2023-06-29	311
Mean ± standard		213±44			236±47
deviation					
Median value		203			225



Figure 12: The blue line represents the measured  $\delta^{18}O$  in Tunåsen infiltration and the green line represents the measured  $\delta^{18}O$  in Galgbacken wellfield. The red dots mark the highest measured  $\% \delta^{18}O$  in Tunåsen and the black dots marks the highest measured  $\% \delta^{18}O$  in Galgbacken.



Figure 13: The blue line represents the measured  $\delta^2 H$  in Tunåsen infiltration and the green line represents the measured  $\delta^{18}O$  in Galgbacken wellfield. The red dots mark the highest measured  $\delta^2 H$  in Tunåsen and the black dots marks the highest measured  $\delta^2 H$  in Galgbacken.

## **4.3 Blending ratio**

The percentage of infiltrated surface water detected in Galgbacken wellfield between 2016 - 2023 was calculated using equation 2.

The fraction in the blending ratio differs over time with a blending ratio between 74 - 100 % surface water in Galgbacken (Table 4). The blending ratio also varies within the same year depending on whether it is measured using oxygen or hydrogen isotopes (Figure 16). The mean blending ratio was 89 % infiltrated surface water and 11 % virgin groundwater in sampling point Galgbacken. Some values exceed 100% and their actual calculated values are presented beneath Table 4.

Location	Date	% infiltrated surface	% infiltrated surface
		water ( $\delta^{18}$ O)	water (δ <sup>2</sup> H)
Galgbacken wellfield	2016-05-24	86	79
Galgbacken wellfield	2017-04-03	85	82
Galgbacken wellfield	2018-04-03	78	80
Galgbacken wellfield	2019-07-23	100 <sup>a</sup>	100 <sup>b</sup>
Galgbacken wellfield	2020-03-31	100 <sup>c</sup>	100 <sup>d</sup>
Galgbacken wellfield	2021-04-27	96	90
Galgbacken wellfield	2022-03-01	100 <sup>e</sup>	100 <sup>f</sup>
Galgbacken wellfield	2023-01-31	81	74
Mean $\pm$ standard		91±9.0	88 ± 10
deviation			
Median value		91	86

Table 4: The percentage of infiltrated surface water detected in Galgbacken wellfield between 2016 and 2023. Calculated using equation 1.

<sup>a</sup> 102%

<sup>b</sup> 113%

° 105%

<sup>d</sup> 116%

<sup>e</sup> 130%

 $^{\rm f}$  116%



Figure 16: The percentage of infiltrated surface water in Galgbacken is shown between 2016-2023. The green line shows the result based on mean values of measured oxygen and the blue line of mean values of measured hydrogen. The dotted line shows the overall mean blending ratio of 89 % infiltrated surface water.

## **4.4 PFAS**

From data based on Mumberg et al. (in preperation) 12 out of 29 targeted PFAS were detected at least once in the water samples. Figure 17 shows the total mean value concentration of  $\Sigma$ PFAS at each sampling location between September and November 2023 as well as the composition profiles.

There are significant variations in the PFAS concentration between the different sampling points. The highest concentration of PFAS is found in sampling point D with an average total concentration of 33 ng L<sup>-1</sup> for  $\Sigma$ PFAS. The lowest concentration of  $\Sigma$ PFAS is found in the surface water originating from river Fyris with an average concentration of 7.8 ng L<sup>-1</sup>.



Figure 17: Pie-charts that show the composition profiles and  $\Sigma$ mean PFAS concentration [ng L<sup>-1</sup>] in the groundwater at each sampling point. Data based on Mumberg et al. (in preperation).

A clear trend is that sampling point D always has the highest  $\Sigma$ PFAS concentration compared to the other sampling points (Figure 18). The highest  $\Sigma$ PFAS concentration is detected in September at 42.86 ng L<sup>-1</sup> in sampling point D and the lowest is found in September at sampling point Tunåsen at 4.85 ng L<sup>-1</sup>.



Figure 18: Stacked bar chart showing the composition profile and total PFAS concentration at each sampling. On the x-axis, each bar represents different sampling occasions at the different sampling points and the y-axis shows the concentration of PFAS [ng L<sup>-1</sup>]. Data based on Mumberg et al. (in preparation).

PFBA is the PFAS substance that is found in the largest amount and is found in all sampling points except Tunåsen. No PFAS substance that belongs to the functional group PFSA is found in sampling point Tunåsen, all the PFAS that is found in sampling point Tunåsen are PFCAs.

The result is based on 5 conducted samples between September and November in sampling point A, D and E, three samples from C and F and two samplings from sampling point B.

# **5** Discussion

#### **5.1** Average travel time

The distance between Tunåsen and Galgbacken is 2025 m which gave the water an average travel time of 225 days which is equivalent to an average speed of the water at  $1 \cdot 10^{-4}$  m s<sup>-1</sup>.

This average travel time was close to the ones in the historical dataset from 2017 provided by Uppsala Vatten that showed the average speed of water in sampling points A, D, E, F (Table 2) and is therefore assumed to be reasonable. The same functional analysis from 2017 in shows the average transport time of water from Tunåsen to Galgbacken of 240 days which is slightly higher than the average of 225 days but still within the same standard deviation range as the one found in this study.

Furthermore, this average travel time was compared to previous investigations in this area. In 1958 a tracer experiment was conducted by Bergström by adding the dye fluorescein in the Tunåsen infiltration basin which was later found in Galgbacken wellfield. The water was found to have a velocity of 7.5 m d<sup>-1</sup> which is equivalent to 270 days on the 2025 m between Tunåsen and Galgbacken (Bergström 1986 via Hummel 2014).

This result can also be compared with the horizontal hydraulic conductivity that was found for the distance between Tunåsen and Galgbacken by Hummel, 2014. The horizontal hydraulic conductivity is a measure of the soil's permeability to water and was found to be  $9.7 \cdot 10^{-3}$  m s<sup>-1</sup> (Hummel 2014) which is close to the average speed of water of  $1 \cdot 10^{-4}$  m s<sup>-1</sup> that was found in this study.

The time it takes water to travel between each of the observation wells in this project could not be found due to lack of relevant data. However, the assumption was that the water flowed at a continuous rate throughout the whole pathway, implying that the travel time between the sampling points A, C, D, E, followed the same pattern but with a different shift in time and another amplitude. Thus, it would have been a shorter time delay than the one in Galgbacken since the water passed through the other sampling points before reaching Galgbacken. Also, the amplitude would be lower than the one for the water at sampling point Tunåsen but higher than the one for sampling point Galgbacken.

## 5.2 The blending ratio of artificial groundwater with virgin groundwater

Once precipitation infiltrates the esker and becomes groundwater, the signature of that water can only change through mixing with water of a different isotopic content (Kendall 2012). The measured stable isotopes of the water in Galgbacken differed in composition from the virgin groundwater that was originating from the north of Tunåsen, i.e. the reference value that showed the natural isotopically signature in this area. It was therefore clear that surface water in river Fyris has infiltrated to the groundwater and that the water that is pumped up in Galgbacken is affected by the artificial infiltration.

If there had not been any artificial infiltration the calculation would show 0 %. The blending ratio is somewhat constant through the years studied in this project and was on average 89 %. This means that the blending ratio in Galgbacken consisted of 89 % artificial groundwater and 11 % natural groundwater. In the historical investigation from 2014-2016 provided by Uppsala Vatten the proportion of naturally formed groundwater in Galgbacken was found to be between 15-20 % which would mean that the percentage of artificial groundwater was slightly lower for these years than the average one found for the eight annual cycles of isotope data used in this study. One source of error that could cause this difference in results could be that the blending equation used in this study (equation 2) yielded values exceeding 100%, implying that more than 100% of the water that is pumped up in Galgbacken would consist of infiltrated water, which is not quite reasonable. The reason that some values are greater than 100% could be due to many factors. If the reference point is not correctly established, the result may exceed 100%. Also, incorrect measurements or collected data can lead to higher values. This may be due to errors in measuring instruments, sensors, or data recording.

The observed variability in the blending ratio during the eight annual cycles included in this study can be due to several factors, including variations in groundwater levels and flow rates. It would therefore be interesting to look into if the variation in the blending ratio between artificial and natural groundwater is affected by the level of infiltrated water during each year.

The relation between  $\delta^{18}$ O and  $\delta^{2}$ H in surface water and groundwater is presented in Figure 11 where the surface water represents the local meteoric waterline. As seen in Figure 11 most of the water in sampling point Galgbacken had a similar stable isotopic composition as the surface water from sampling point Tunåsen, since most of its composition fell on the LMWL.

The LMWL can be used to separate other sources of water from precipitation if the isotopic composition differs (Paulsson 2021). Although, the other sampling points also plotted mostly on the LMWL and therefore the water in these probably consisted of mostly infiltrated surface water. Although the lack of relevant data means that we cannot examine the exact blending ratio in each sample point, the assumption by looking at Figure 11 was that the ratio in these sampling points was similar to the ratio in Galgbacken.

## **5.3 PFAS**

# 5.3.1 PFAS concentration at the six sampling points between Tunåsen and Galgbacken

All sampling points had detectable levels of PFAS. The highest mean  $\Sigma$ PFAS levels was found in sampling point D at 33 ng L<sup>-1</sup> for  $\Sigma$ PFAS and the lowest mean  $\Sigma$ PFAS levels was found in sampling point B at 7.8 ng L<sup>-1</sup>. Out of the six sampling points included in this study, sampling point B was the only sampling point not affected by the natural groundwater. The five sampling points affected by the virgin groundwater had a large variability in mean  $\Sigma$ PFAS levels, where sampling point D had two times as much  $\Sigma$ PFAS as sampling point E that is located just downstream, and four times as much  $\Sigma$ PFAS as sampling point F which is located just downstream of sampling point E. The sampling points upstream of sampling point D had a more even mean concentration of  $\Sigma$ PFAS. Since the five groundwater sampling points in this project belong to the same catchment and geological location, the high levels of  $\Sigma$ PFAS in sampling points D and E indicate that there might be a point source around sample point D. Perhaps from an old landfill that is no longer in use. The proximity of such a point source could be the reason for the high levels of  $\Sigma$ PFAS in sampling point D. Although, this needs to be further investigated.

#### **5.3.2 PFAS composition along the travel path**

In total 12 out of the 29 targeted PFAS substances were detected at least once in these sampling points (based on Mumberg et al. (in preparation)). The other were under the detection limit and was therefore set to zero. The most frequently found substances were PFHpA, PFOA, L PFOS, B PFOS (6 out of 6 of sampling points) and PFBA, L PFHxS, B PFHxS (5 out of 6 of sampling points). The least frequently found substance was PFTriDA

that was found in one of six sampling points, sampling point B, and only at one sampling occasion, with a low concentration of 0.13 ng L<sup>-1</sup>. The highest mean value was found for PFBA at an average of 6.7 ngL<sup>-1</sup>. Overall, the average total PFAS composition in all samples were PFBA (42%), PFHpA (13%), PFOA (9%), PFBS (9%) L PFHxS (7%), PFHxA (6%), PFPeA (6%), L PFOS (4%), B PFOS (3%), B PFHxS (1%), PFNA (1%) (Appendix 2).

The composition profile in each sampling point consisted mostly of short chained PFCAs (PFBA, PFPeA, PFHxA, PFHpA) and one long chained PFCA (PFOS). Except for one measurement in Tunåsen for PFTriDA at 0.13 ng L<sup>-1</sup>, no PFAS substance with a chain length longer than 8 was found in either of the sampling points. The reason why no long chained PFAS substances were found could indicate that these sampling points are located far away from a pollution source. PFAS with long carbon-fluorine chains, binds to soil particles in a greater extent and short PFASs leach into the groundwater to a greater extent and spread faster in water than long-chained ones (Sörengård et al. 2022). Therefore, far away from a pollution source, the proportion of short chained PFAS can be expected to be higher than long chained PFAS (SGF 2023). Although, there are a lot of factors which are of importance when investigating the distribution of phase, such as the soil type, and the soil's content of organic matter as well as chemical properties such as pH, charges on minerals and presence of metals (Campos-Pereira et al. 2022). By looking at the limited area of this study it can be concluded that the composition of the total PFAS differ between the sampling points studied.

#### 5.3.3 PFAS source origin

From the sampling conducted in September 2023, it showed that none of the found PFAS substances that belong to the group PFSAs came from the infiltrated surface water. After examining the area, it can be concluded that not all PFAS contamination originated from the river Fyris via infiltration, nor from the natural groundwater from the north, but probably most of the PFAS came from a point source close to sampling point D or a pollution source upstream from this area.

#### **5.3.4 Paired PFAS and isotope analysis**

The isotope analysis proved useful in the analysis of PFAS in this area. By studying data provided by Mumberg et al (in preparation), which showed PFAS measurements at this site

over a year (September 2022 - September 2023), it was possible to see that the PFAS concentration had approximately the same travel time as the water.

This was found by looking at the highest PFAS concentration at both the infiltration and wellfield site. The time between these peaks was almost equivalent to the travel time of the water.

In that way, the transport time found in the isotopic analysis can be used as a tool to estimate when a high total PFAS concentration at Tunåsen is likely to reach Galgbacken.

However, the isotope analysis cannot be used to draw conclusions about the transport of individual PFAS substances or composition profiles.

#### 5.4 Evaluation of data quality and error sources

In this project, water samples have been collected over a three-month period from six different sampling points in the area stretching from the Tunåsen infiltration facility to the Galgbacken wellfield. Conducting analyses to understand water behavior and identify potential patterns requires data spanning a more extended timeframe, which has been provided by Uppsala Vatten. This historical data varies largely among the sampling points, with some observation wells having data spanning many years, while others have information from only a few or a single year. This deviation has posed challenges in terms of finding the travel time and the blending ratio in each sampling point. Therefore, the travel time and the blending ratio is analyzed including only historical data from Tunåsen (sampling point B) and Galgbacken (sampling point F). This means that the results do not show the time it takes for the infiltrated water to travel between all the observation wells between Tunåsen and Galgbacken, only the time it has taken for the water to travel from the point of infiltration (Tunåsen infiltration) to the southernmost and final sampling point for this project (Galgbacken wellfield). The same goes for the blending ratio. Because of the lack of historical data, the result does not show the isotopic differences in each of the sampling points, only in the point of infiltration (Tunåsen, which will aways be 100 % infiltrated surface water) and in Galgbacken.

During the sampling period, September to November 2023, it was Uppsala Vatten that collected samples from sample point B and sample point F, while I collected samples from the

remaining sample points. This has resulted in not all samples being taken on the exact same day, which is important for a more accurate comparison. This is also the reason why the number of samples from sample point F are fewer than the others. The reason why the samples are fewer in sample points B and C is because the infiltration was turned off and no samples could be taken in these points during these dates. This leads to a small uncertainty in the PFAS comparison because the average PFAS concentrations in the different sampling points are based on different numbers of samplings.

#### 5.5 Future investigations

Verification and more detailed studies over a longer period are recommended for the area around sampling point D since sampling point D showed elevated levels of PFAS concentration. Also, upstream monitoring could be valuable to reveal eventual pollution sources.

An interesting addition to this study would have been to connect the isotope analysis with data of the volume of infiltrated water over time. This is to investigate if the speed of the water is affected by the volume of infiltrated water and if the variation in the blending ratio between artificial and natural groundwater is affected by the level of infiltrated water during each year.

Also, as previously mentioned, there are four facilities in Uppsala where the Fyris water is infiltrated in the esker. It would have been interesting to do equivalent investigations in all these areas around Uppsala Esker to see if there might be more PFAS point sources and to further secure the drinking water quality in Uppsala.

# **6** Conclusions

• Determine the water's average travel time from the infiltration basins at Tunåsen to Galgbacken drinking water wellfield.

The stable isotope ratio showed a time delay in Galgbacken compared to Tunåsen. Based on this delay, the transport time for the water was estimated to be 225 days which gives the water an average speed of  $1 \cdot 10^{-4}$  m s<sup>-1</sup>.

• Assess the blending ratio of artificial groundwater with virgin groundwater at Galgbacken.

The blending ratio between the artificial groundwater and natural groundwater in Galgbacken was estimated to be 89 % surface water infiltrated from river Fyris through Tunåsen infiltration chamber and 11 % virgin groundwater originating from north of the study area.

• Paired analysis: Evaluate if there is a change in PFAS concentration at the six sampling points that can be explained by the results above.

There was a change in PFAS concentration at the six sampling points between Tunåsen and Galgbacken that indicates that there was a source along the flow path. This source was probably near sample point D where  $\Sigma$ PFAS levels were elevated. The PFAS composition stayed about the same and did not change along the travel path. Not all PFAS came from infiltration.

The transport time found in the isotopic analysis can be used as a tool to estimate when a high total PFAS concentration at Tunåsen is likely to reach Galgbacken. However, the isotope analysis cannot be used to draw conclusions about the transport of individual PFAS substances or composition profiles.

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# 8 Appendix

# Appendix 1



Isotope measurements,  $\delta^{18}O$  and  $\delta^{2}H$ , in sampling point A from historical measurements.



Isotope measurements,  $\delta^{18}O$  and  $\delta^2H$ , in sampling point C from historical measurements.



Isotope measurements,  $\delta^{18}O$  and  $\delta^{2}H$ , in sampling point D from historical measurements.



Isotope measurements,  $\delta^{18}O$  and  $\delta^{2}H$ , in sampling point *E* from historical measurements.

# Appendix 2 Pie-chart showing the average composition of the mean $\Sigma$ PFAS from all sampling points



Composition chart of mean **SPFAS** in all six sampling points