



Constraining Stream and Groundwater Transit Time Distributions with Chlorofluorocarbon Tracers

A Study in the Västrabäcken Subcatchment of
the Krycklan Study Basin

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Degree project/Independent project · 30 Credits
Swedish University of Agricultural Sciences, SLU
Department of Aquatic Sciences and Assessment
EnvEuro - European Master in Environmental Science

2026



Constraining Stream and Groundwater Transit Time Distributions with Chlorofluorocarbon Tracers. A Study in the Västrabäcken Subcatchment of the Krycklan Study Basin.

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Credits: 30 Credits

Course level: Master's level A2E

Course title: Master thesis in Environmental Science

Programme: EnvEuro - European Master in Environmental Science

Course coordinating dept Faculty of Natural Resources and Agricultural Sciences

Place of publication:

Year of publication: 2026

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Title of the series:

Part number in the series:

ISSN:

Keywords: hydrology, cfc, tracer, groundwater, transit time, steady state

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Abstract

In this study, we evaluated the conservative behaviour and the utility of Chlorofluorocarbons (CFCs) as tracers in a well-characterised hillslope transect. CFCs are widely used as environmental tracers to estimate groundwater ages and recharge histories. However, their application in snowmelt-dominated catchments is complicated by strong seasonal variations in soil temperature, which affect CFC solubility, and by the dominance of spring snowmelt in driving groundwater recharge, both of which may introduce systematic biases in modelled recharge temperatures and CFC concentrations. A steady-state physically based flow model was applied to simulate tracer signals in the groundwater and stream. Once recharged, CFC-11 and CFC-12 showed little evidence of non-conservative behaviour, supporting their use as effective tracers for water that entered the subsurface between approximately 1960 and 1990. Furthermore, the findings integrate the measured groundwater CFC concentrations into the established process understanding of the site. While the model successfully reproduced observed flowpaths and transit times in the shallower subsurface (< 3 m depth), it significantly overestimated water ages below this depth, a finding consistent with earlier suspicions but only now corroborated with CFC data. These results suggest that the current parameterization of saturated hydraulic conductivity decline with depth requires revision. Future work should recalibrate and advance the model to reduce the rate of hydraulic conductivity decline below 1.5 m depth, potentially reconciling modelled and observed CFC concentrations across the full vertical profile.

Keywords: hydrology, cfc, tracer, groundwater, transit time, steady state

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List of Abbreviations

Abbreviation	Description
SLU	Swedish University of Agricultural Sciences
CFC	Chlorofluorocarbon
CFCs	Chlorofluorocarbons
CFC-11	Trichlorofluoromethane
CFC-12	Dichlorodifluoromethane
CFC-113	Trichlorotrifluoroethane
DEM	Digital Elevation Model
pptv	parts per trillion volume
K_s	Saturated Hydraulic Conductivity
θ_s	Saturated Water Content, Porosity
R	Hydrologically effective rainfall
Q	Stream discharge
NSE	Nash-Sutcliffe Efficiency
AIC	Akaike's Information Criterion

1 Introduction

This section will describe the knowledge background of the master's thesis, outlining the important findings which have led to the current understanding. Firstly, environmental tracers and their importance for hydrology will be described. Then, the origin of transit time (i.e. age) distributions in hydrology and why they are important for process understanding will be outlined. Lastly, important findings from the study site will be introduced, concluding with the research aims of this study.

1.1 Environmental Tracers in Hydrology

The landscape-wide distribution of water through precipitation supplies the discharge in receiving streams. This hydraulic response to rainfall and snowmelt is the cumulative effect of surface and subsurface controls on the water storage within a catchment (Grip and Rodhe, 2000). Yet, research has not been able to accurately describe this behaviour in all of its complexity, to allow a good characterization of water movement through the subsurface of catchments (Beven, 1997).

To advance the understanding of water movement through catchments, distinguishing different sources in time and space is a powerful approach (Kirchner, 2006). Leverage is provided by techniques to “fingerprint” water from different sources by analysing for trace concentrations of compounds unique to sources in time and space (Kendall and McDonnell, 2006). Tracer hydrology, the field building upon this concept, has provided key insights to the process understanding of catchments (Kirchner, 2003; McGuire and McDonnell, 2006; Jung *et al.*, 2025).

The most prominent tracers in hydrology are stable isotopes of water (Kendall and McDonnell, 2006). In many regions, a recurring annual variation in isotopic signatures is observed (e.g., Figure 6), while individual precipitation events are unique (Kendall and McDonnell, 2006). This allows the separation of water sources, e.g., estimating the contribution from different precipitation events in stream discharge.

Research with stable water isotopes revealed the old water paradox, a crucial insight into stream discharge generation (Kirchner, 2003). It describes that the rapid hydrologic response in river discharge to a rain event is not composed of water from that same rain event, but of water which has been previously stored in that catchment.

However, the annual periodicity restricts the identifying ability of stable water isotopes to only a few months, unless prior knowledge of flow paths is available (Kirchner, 2016). For such “older” water, the question remains about where, and how fast that water moves through the subsurface zone before it is released as discharge into the stream.

Different environmental tracers have the potential to aid in researching longer time horizons. For this, they must be capable of determining water ages without a corresponding sample from precipitation (Kazemi, 2004; IAEA, 2006). A promising group are the Chlorofluorocarbons (CFCs), environmental trace gases in the atmosphere that dissolve into water (Kazemi, 2004; IAEA, 2006). The species CFC-11, CFC-12 and CFC-113 have a documented history of application in hydrological research (Kazemi, 2004; IAEA, 2006).

Unlike stable water isotopes, CFCs are anthropogenic chemical species which provide inter-annual variations in their tracer “signal” over the course of several decades (comp. Figure 6, Figure 8). They were introduced to the atmosphere starting between 1940 and 1960, depending on the species. After their introduction, the CFCs began “ramping up” over a period of decades until their peak atmospheric concentrations were reached between 1990 and 2000. Since then, the concentrations have slowly declined (see Figure 8). The reason for the decline is the Montreal Protocol (UNEP, 1987). It is an international agreement restricting the use of CFCs due to their negative effect on the ozone layer which protects the Earth from harmful UV radiation (UNEP, 1985).

The changing atmospheric concentrations allow CFCs to theoretically cover time horizons until 70 years ago, when they were first released (Kazemi, 2004; IAEA, 2006). CFCs in solution, however, can chemically and physically interact with the environment, influencing their transport behaviour (Kazemi, 2004; IAEA, 2006; Chambers, Gooddy and Binley, 2019; Kolbe and Bishop, 2024). Therefore, processes such as sorption, dispersion and degradation must be taken into consideration when applying CFCs as tracers (Kazemi, 2004; IAEA, 2006; Chambers, Gooddy and Binley, 2019; Kolbe and Bishop, 2024). Nevertheless, CFCs can enable insights into transit time distributions when correctly quantified and especially when used as complementary tracers with water stable isotopes.

1.2 Transit Time Distributions

The insights of tracer hydrology gave rise to the probabilistic interpretation of catchment processes as distributions of time (Botter, Bertuzzo and Rinaldo, 2010; Botter, Bertuzzo and Rinaldo, 2011; 2011). A stream or groundwater sample is always understood as a collection of water particles from different sources in space and time. They have travelled with different velocities and pathways through a catchment. Such a composite sample can then be described by a distribution of the time the water particles have spent underground, i.e. their age.

This probabilistic interpretation represents a spatially lumped description of the complex and possibly unknown processes governing the hydraulic response in a stream while uniting them in a single analytic framework (Botter, Bertuzzo and Rinaldo, 2010). The interpretation as distributions of age can capture key observations such as: (Botter, Bertuzzo and Rinaldo, 2011; Rinaldo *et al.*, 2015)

- The old water paradox, by describing the distribution of water ages in stream-flow;
- Tracer breakthrough curves, by describing the travel time distribution of received rainfall until its discharge in the stream;
- Groundwater ages, by describing the total distribution of water ages stored in a catchment.

Important to research is the assumption of a catchment-wide steady-state condition, for which the probabilistic travel time framework is crucially simplified (Botter, Bertuzzo and Rinaldo, 2010; 2011). There, the otherwise transient travel time distributions of received rainfall (i.e. forward) and water released at the outlet (i.e. backward) are equal. Here the term transit time distribution is used to describe travel times of particles in steady-state, i.e. their transit times.

Determining transit time distributions is of great interest to help characterize and define catchment behaviour (Berghuijs and Kirchner, 2017; Benettin *et al.*, 2022). Modelling efforts combined with tracer measurements have focused on determining shape and influences from catchment characteristics, in both steady-state and dynamic conditions (McGuire and McDonnell, 2006; Ameli *et al.*, 2016; Heidebüchel *et al.*, 2020; Benettin *et al.*, 2022).

However, in the very nature of a spatially lumped model, the purely probabilistic description does not include the explicit spatial distribution of water source areas and flow paths within a catchment. Nevertheless, this is critical for understanding chemical transformations (e.g., chemical weathering) and changes in water chem-

istry, since these depend on the sequence of subsurface environments that water is subjected to as it moves through a catchment (Erlandsson Lampa *et al.*, 2020). The lack of spatial resolution alone stands in the way of making full use of water tracers when sampled from within different parts of a catchment (Ameli *et al.*, 2021).

1.3 Västrabäcken, Krycklan

The intensely instrumented C2 Västrabäcken subcatchment in the larger Krycklan Catchment Study in northern Sweden is a thoroughly researched site with well-established process understanding (Stähli *et al.*, 2001; Laudon *et al.*, 2013; Laudon and Sponseller, 2018). There, the glacial till soil features an exponentially declining saturated hydraulic conductivity with depth (Amvrosiadi *et al.*, 2017). The importance of such a continuous and rapid change with depth has been shown (Jiang *et al.*, 2009), and is most pronouncedly associated with glacial till soils in upland headwaters (Ameli *et al.*, 2016; Ferris, Potter and Ferguson, 2020).

Many studies have focused on tracer measurements and modelling, exploring the concrete characteristics of flow paths and transit time distributions on this catchment and others in the vicinity of the Krycklan Catchment Study (Peralta-Tapia *et al.*, 2015; Ameli *et al.*, 2021; Bishop *et al.*, 2024; Jutebring Sterte, 2026). Key results in some of these studies are the distinct flow paths characterized by the transmissivity feedback mechanism of runoff generation in hillslope transects (Bishop, 1991; Seibert *et al.*, 2011).

The well-described nature of the flow system along a hillslope in the C2 catchment presents potentially a great opportunity to apply CFCs, providing insights into water “older” than a few months, which is already well characterized by water stable isotopes (Amvrosiadi *et al.*, 2017; Ameli *et al.*, 2021). Thus, applying CFCs may be able to provide insights into water from one to a few decades old, assuming CFCs function well as hydrological tracers at the site (Kolbe *et al.*, 2020; Kolbe and Bishop, 2024).

It must be noted that assumptions about how CFCs move in this catchment may be flawed. The success of CFCs as an indicator of age relies on both the correctness of current assumptions about how CFCs work as hydrological tracers in shallow subsurface flow systems, and the adequacy of the transmissivity-feedback model, as implemented on the hillslope, as a good approximation of the flow system. While efforts have been made to test this model using water stable isotope tracers (Ameli *et al.*, 2021), some parameters will most likely need to be changed to

improve the fidelity of the model across a broader range of water ages than stable isotopes alone could constrain. Two other possibilities that need to be considered are that the behaviour of specific CFC species does not match current assumptions and that there are shortcomings in the modelling of the flow system.

Recent research to describe the CFC observations in the study site included a Boussinesq model in a two-layer setup, which explained an effect termed lagged rejuvenation of groundwater, attributed to the low saturated hydraulic conductivity in the deeper layer (Marçais, De Dreuzy and Erhel, 2017; Kolbe *et al.*, 2020). Kolbe and Bishop (2024) showed that lagged rejuvenation is also indicated by the commonly used piston flow model (IAEA, 2006), when applied to measurements of CFCs in groundwater wells and the stream from the C2 catchment. However, model applications of MIKE SHE were not able to replicate the pattern of lagged rejuvenation (Jutebring Sterte, 2026).

The applied piston flow, Boussinesq and MIKE SHE models do not represent the transmissivity feedback mechanism, believed to be the dominant process of discharge generation at the site. Note however, that the ages of water that CFCs provide insight into (several decades old) are likely not the dominant fraction of the discharge leaving the catchment each year, which water stable isotopes and hydrometric considerations indicate to be a few months to years (Peralta-Tapia *et al.*, 2015; Amvrosiadi *et al.*, 2017; Ameli *et al.*, 2021).

1.4 Research aim

The research conducted by Ameli, McDonnell and Bishop (2016); Ameli *et al.* (2016); Ameli *et al.* (2021); Bishop *et al.* (2024) gave important insights into the effects of exponentially declining saturated hydraulic conductivity on transit time distributions along modelled flowpaths, while representing transmissivity feedback in their results.

This study aims to apply atmospheric concentrations of CFCs as tracers in a steady-state application of the model developed by Ameli, McDonnell and Bishop (2016); Ameli *et al.* (2016) to simulate CFC concentrations in groundwater and validate the results against CFC measurements from wells and the stream. The aims are to:

1. Analyse how the steady-state implementation of the model predicts CFC concentrations in groundwater wells and ^{18}O concentrations in stream discharge;

2. Apply the novel results on CFCs together with ^{18}O data of this and prior studies to constrain the transit time distributions of the site with multiple tracers.

Specifically, this study examines indications of CFCs not behaving in accordance with the assumptions generally made about the use of CFCs as tracers in hydrology ([Kazemi, 2004](#); [IAEA, 2006](#)). The limitations to the implementation of the hydrologic model are also considered, including the use of a single steady-state, boundary conditions and parameter calibrations, by analysing domain-wide results, groundwater well results and results for the stream.

2 Data

This section focuses on the description of the study site, by providing a general description of the catchment in [Section 2.1.1](#), the characterization of the soil properties of the hillslope transect in [Section 2.1.2](#) and the local climatic conditions in [Section 2.1.3](#). Furthermore the employed data series are specified by source and usage in [Section 2.2](#). Lastly, the groundwater CFC samples from [Kolbe and Bishop \(2024\)](#) are presented in [Section 2.3](#).

2.1 Study Site

2.1.1 General Description

The study site is located in the 12 ha Västrabäcken subcatchment, which drains to a V-notch weir commonly termed C2. This is part of the Krycklan Catchment Study, one of the most intensively monitored, sampled, and researched catchments ([Laudon *et al.*, 2013](#); [Laudon and Sponseller, 2018](#)). An overview map of the Västrabäcken subcatchment is displayed in [Figure 1](#) below.

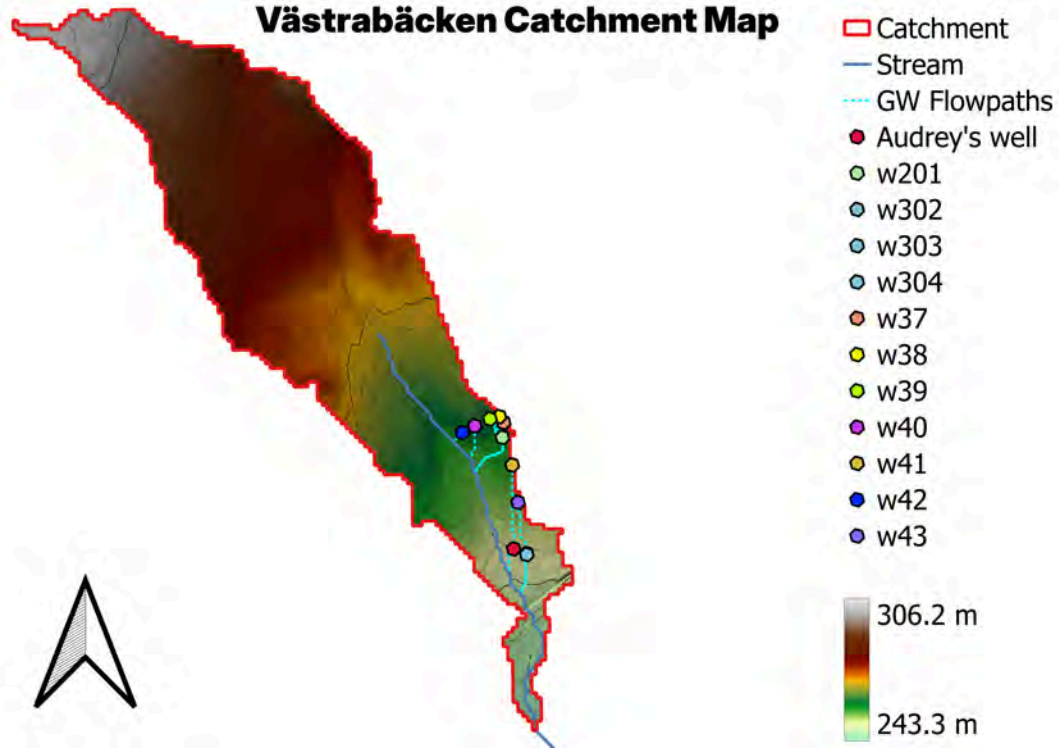


Figure 1: Catchment Map Västrabäcken. The stream (solid blue line) is sampled at the catchment outlet, a V-notch weir termed C2. Groundwater wells (coloured spheres) are scattered to the east of the stream. Groundwater flowpaths (dashed light blue lines) visualize the estimated subsurface travel path from a well to the stream. The wells w37, w38, w41, w43 in close proximity of the water divide were mirrored over at the eastern catchment boundary, thereby copying them from C7 into the displayed C2 at equal distance to the water divide.

The spatial information of the catchment boundary polygon, the stream line and the digital elevation model (DEM) of resolution $0.5 \text{ m} \times 0.5 \text{ m}$ in [Figure 1](#) were retrieved from the webpage of the Department of Forest Ecology and Management at SLU ([Krycklan Data](#), no date). Spatial information on groundwater well positions are given in ([Kolbe et al., 2020](#); [Kolbe and Bishop, 2024](#)). The detailed coordinates of the sampling wells therein were obtained from personal correspondence with Jean Marçais. Groundwater flowpaths were estimated from topographic analysis utilizing Whitebox Workflows for QGIS ([Whitebox Workflows for QGIS, 2026](#)) and GRASS ([GRASS Development Team, 2025](#)) inside QGIS ([Dawson et al., 2025](#)). The D8-pointer algorithm was used for flowpath routing, for which a feature preserving smoothed version of the DEM was employed.

The vast majority of the area is covered by pine and spruce forest ([Kolbe et al., 2020](#)). The catchment is fully covered by a glacial till soil ([Kolbe et al., 2020](#)), which

consists of a shallow ablation till until 3 m deep and a dense basal till until the bedrock (Nyberg *et al.*, 2001; Kolbe *et al.*, 2020). The bedrock itself is a poorly weathered meta-greywacke gneiss (Grabs *et al.*, 2009; Kolbe *et al.*, 2020). The stream channel was deepened during the 1910s to improve forest drainage (Kolbe *et al.*, 2020). The C2 stream is a tributary of the 50 ha C7 Svartberget stream.

2.1.2 Hillslope transect

The catchment is collapsed into a 2-D hillslope transect for the model application (a 2-D analytical solution, see Section 3.2), which models groundwater flowpaths through the soil to the wells and the stream. The shape and dimensions of the transect were obtained from Ali Ameli after personal correspondence (Ameli *et al.*, 2021; Bishop *et al.*, 2024).

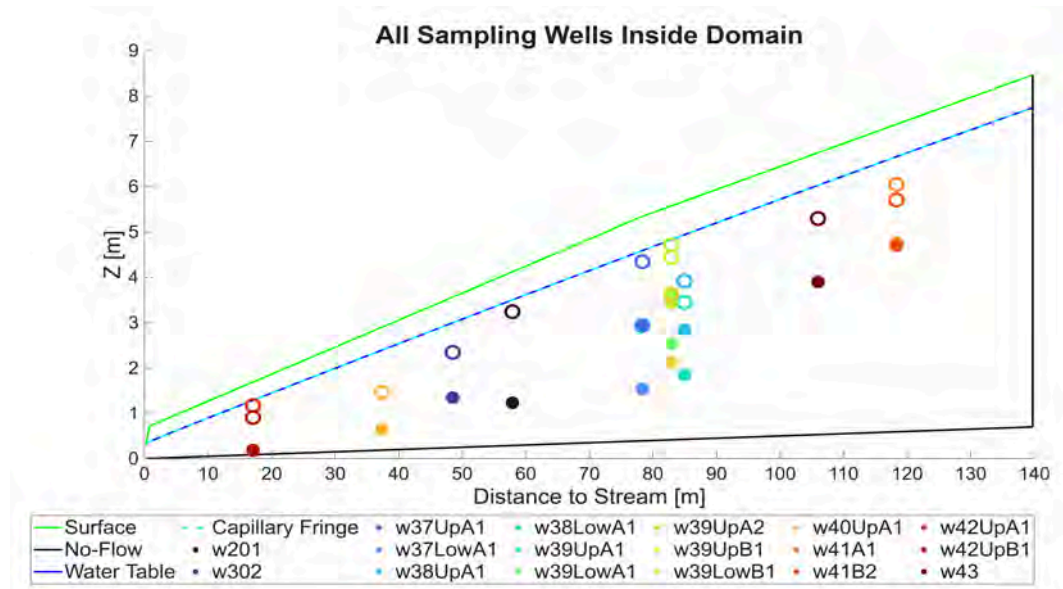


Figure 2: Sampling wells inside the groundwater domain of the model projected on the representative hillslope transect. Wells are mapped into the transect by their groundwater flowpaths. Screening top as hollow circles and screening bottom as filled circles, both coloured the same for a given well.

The hillslope transect represents the hillslope profile from the stream to the water divide. In Figure 2, the surface is visualized as a green solid line and the no-flow boundaries along the bottom and the right are black solid lines. In this representation, the stream begins directly to the left of the surface line, outside the figure. The water table and capillary fringe are shown as a solid blue line and a dashed light blue line, respectively. The scattered groundwater well samples (see Section 2.3)

from [Kolbe and Bishop \(2024\)](#) are mapped into the transect by their distance to the stream, which is calculated as the flowpath length of the groundwater from the well to the stream (see explanation below [Figure 1](#)). This differs from the approach in [Kolbe et al. \(2020\)](#) and resulted in increasing differences with increasing distance to the stream (see [App. Tab. 5](#)). Only wells inside the modelled groundwater zone are included in the analysis (see [Table 1](#)). Detailed well information is given in [App. Tab. 8](#).

It is important to point out the shallowness of the aquifer next to the stream and the distorted shape (i.e., a decreasing aquifer size from the water divide to the stream). This shape is the result of prior research and model optimization by [Ameli et al. \(2016\)](#) and applied in [Ameli et al. \(2021\)](#).

The soil of the transect is a glacial till soil, which is characterized by exponentially decreasing porosity θ_s and saturated hydraulic conductivity K_s with depth ([Bishop, Grip and O'Neill, 1990](#); [Laudon et al., 2004](#); [Amvrosiadi et al., 2017](#); [Ameli et al., 2021](#)). This anisotropic heterogeneity is described in [Ameli et al. \(2021\)](#) with the following two relationships:

$$K_s(d) = 100 \cdot \exp(-2.5 \cdot d) \quad (1)$$

$$\theta_s(d) = 0.49 \cdot \exp(-0.26 \cdot d) \quad (2)$$

Where d refers to the depth in $[m]$, which is orthogonally downwards positive from the surface. K_s is given in $\left[\frac{m}{day}\right]$ and the porosity is referred to as the saturated volumetric water content in $\left[\frac{m^3}{m^3}\right]$. It is important to highlight, that for the scope of this study the above given relationship for the saturated hydraulic conductivity is not the best fit to the soil measurements ([Bishop, 1991](#); [Ameli et al., 2016](#); [Ameli et al., 2021](#)). Instead, the relationship used is from the model applications by [Ameli et al. \(2021\)](#). The unsaturated soil properties are described in [Section 3.2](#).

It is likely that the exponential decline in K_s does not continue until the bottom no-flow boundary, as implemented here. Characterizing the decline with an approaching asymptote at ca. 2 m depth is possibly more accurate and similarly for the porosity depth relationship ([Bishop, 2026](#)).

2.1.3 Temperature & Precipitation

The general climatic description of the site according to the ICOS webpage information is:

The cold humid climate type of the site is attributed by relatively short summer (the growing season is 150 days/year) and permanent snow cover during winter (170 days/year). The mean annual air temperature is 1.8°C and annual precipitation sums up to 614 mm (data period 1981-2010).

Data for the 1961-1990 climatological normal from the close by SMHI station Vindeln characterizes the climate as a Dfc-climate (after Köppen), i.e. humid subarctic with cold summers and cold winters. (*ICOS Sweden, no date*)

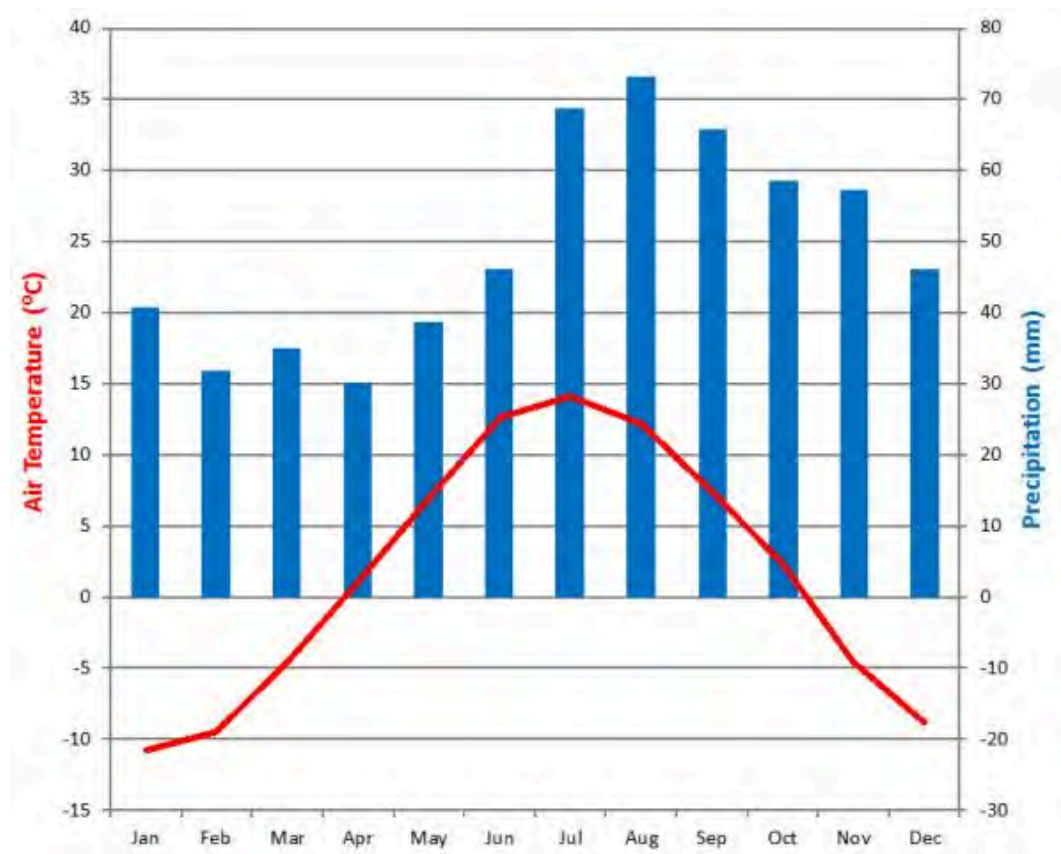


Figure 3: Climate diagram for the Svartberget site, which includes the Västrabäcken catchment. (*ICOS Sweden, no date*)

In contrast to air temperature at the site, the soil temperature rarely falls below 0.0 °C. To compute recharge concentrations of CFCs (see [Section 3.1](#)) daily soil

temperatures at 20 cm depth are used (*Meteorological Data from Svarthøget, Hygget AWS, 1991–2015, 2025a; Meteorological Data from Svarthøget, Hygget AWS, 2016–2018, 2025b; Meteorological Data from Svarthøget, Hygget AWS, 2019–2024, 2025c*). The observational record of daily air and soil temperatures at Svarthøget ranges from 1991 to 2024 (see [Appendix 1b](#)).

2.2 Data Series

2.2.1 Hydrologically effective rainfall

The model employed in this study does not represent transient conditions, which is especially important for the vadose zone. Transient evapotranspiration of soil water, which interacts with changing infiltration and percolation, is not modelled. Therefore, hydrologically effective rainfall (R) is used, which is here defined as “[...] the amount of net water entering the soil each day and accounts for snowmelt processes, overland flow, and the proportion of precipitation returned to the atmosphere as evapotranspiration” (*Ameli et al., 2021, p. 6*). From personal correspondence with Ali Ameli, the previously used time series of weekly averages of R used in *Ameli et al. (2021)*. Summary statistics of the R record are given in [App. Tab. 3](#).

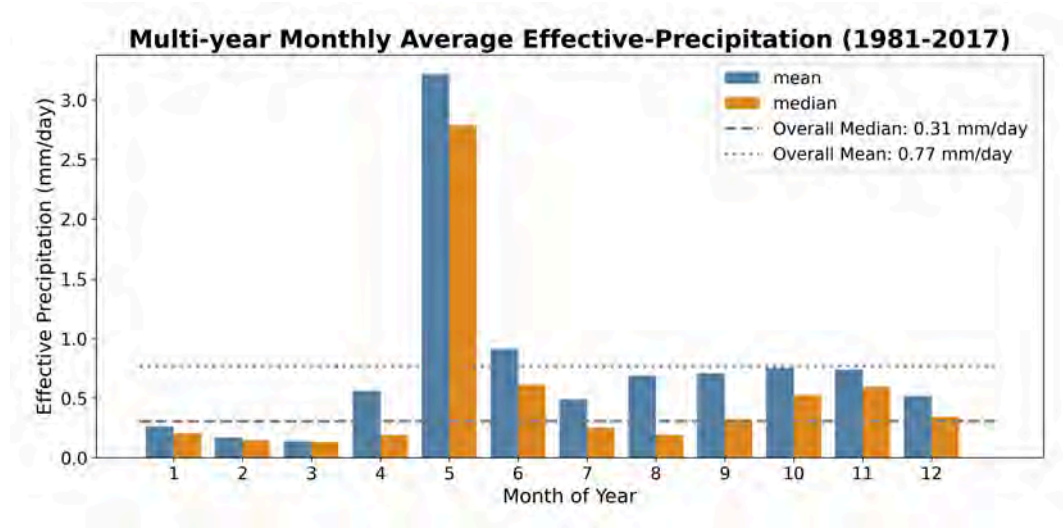


Figure 4: Multi-year monthly average hydrologically effective rainfall (1981-2017). Monthly mean values in blue, monthly median values in orange. The overall mean as a gray dotted line, the overall median as a gray dashed line.

Above in [Figure 4](#) the multi-year monthly averages of R are displayed. There are clear differences visible between the mean and median values. Noteworthy, the spike of R in the month May is representing the annual snowmelt event at the site. Notably, the overall median approximates monthly conditions better than the overall mean. The sum of monthly absolute differences between the overall median and the monthly mean is 6.19 mm day^{-1} , and between the overall median and the monthly median is 4.08 mm day^{-1} . The sum of monthly absolute differences between the overall mean and the monthly mean is 5.25 mm day^{-1} , and between the overall mean and the monthly median is 6.97 mm day^{-1} . In this study, since R is applied to consider the steady-state condition of the modelling efforts, we use the overall median to represent R . This is further discussed in [Section 3.3](#).

2.2.2 Streamflow

Daily observations of stream discharge (Q) and stream level for Västrabäcken were obtained from the SITES data portal ([Water Balance - Stream Water Level and Discharge from Västrabäcken, Catchment 2, 2005-04-06–2024-09-03, 2024](#)). Observations of discharge are given in $[\text{m}^3 \text{ s}^{-1}]$ and were converted to $[\text{mm d}^{-1}]$ by division by the catchment area, which is given as 0.119 km^2 in the obtained datafile. Summary statistics of the observational record are given in [App. Tab. 4](#).

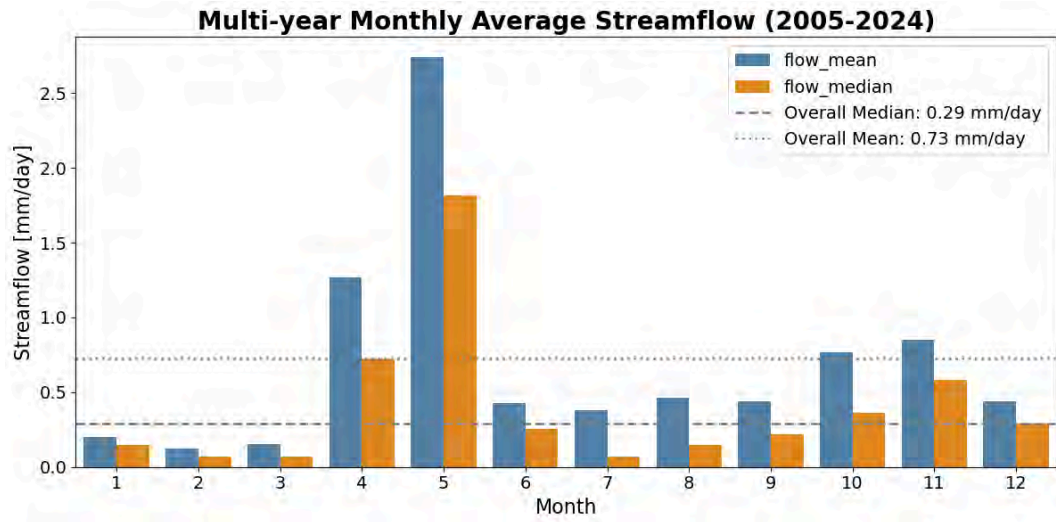


Figure 5: Multi-year monthly average stream flow (2005-2024). Monthly mean values in blue, monthly median values in orange. The overall mean as a gray dotted line, the overall median is as a gray dashed line.

Above in [Figure 5](#), the multi-year monthly averages of Q are displayed. Similar to R in [Figure 4](#), there are clear differences visible between the mean and median values. Noteworthy are the increased values of Q in the months of April and May, reflecting the annual snowmelt event in the stream. Streamflow observations are important for the considered steady-state condition in the modelling efforts of this study. This is further discussed in [Section 3.3](#).

2.2.3 Stable water isotopes

From personal correspondence with Ali Ameli, the undated time series of average ^{18}O per calendar week used in [Ameli et al. \(2021\)](#) was obtained. The date index was reconstructed from the following information: “The simulation period included a warm-up period (1981-2007) and then the study period (2008-2017)” ([Ameli et al., 2021, p. 8](#)). Consequently, the date 2017-12-31 was assumed as the end date. Reconstructing the date index in steps of one calendar week centred on Wednesday resulted in the start date on 1981-02-11 and the end date on 2017-12-27. The full time series is displayed in [App. Fig. 40](#), and the study period of [Ameli et al. \(2021\)](#) is shown below in [Figure 6](#).

The isotopic signatures underlying the weekly averages were measured “[...] using a Picarro cavity ring-down laser spectrometer and a vaporizer module (V1102-i and later the A0211)” ([Ameli et al., 2021, p. 4](#)). The original observational data record of ^{18}O signatures has been used in prior research ([Peralta-Tapia et al., 2016](#)), but was not available for this study .

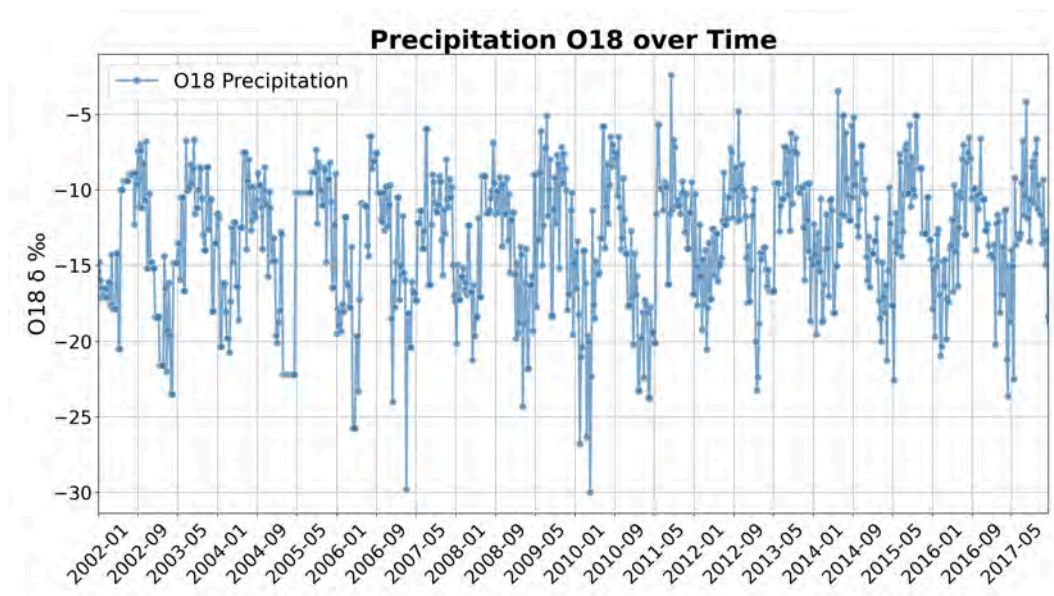


Figure 6: Weekly average ^{18}O precipitation values shown in blue, data points connect with lines. Averages calculated from observations.

The ^{18}O signatures in Figure 6 above show the typical yearly variations. Where, isotopic signatures are lower in winter months and higher in summer months, reflecting the seasonal change in evaporative forcing (Ingraham, 1998). Noteworthy is that the intra-annual variations show a strong similarity from year to year, except for a few outliers.

The time series of water stable isotopes in precipitation will be used in the modelling efforts of this study. The isotopic data are required for model analysis and verification. This is further explained in Section 3.6

2.2.4 Atmospheric Chlorofluorocarbons

Atmospheric concentrations of CFCs are assumed to be homogeneous for the northern hemisphere (Kazemi, 2004; IAEA, 2006). Measurements of atmospheric CFCs are available from NOAA (no date) and were here retrieved from USGS (no date) with observations every half year. The observational record of atmospheric CFC concentrations is shown below in Figure 7.

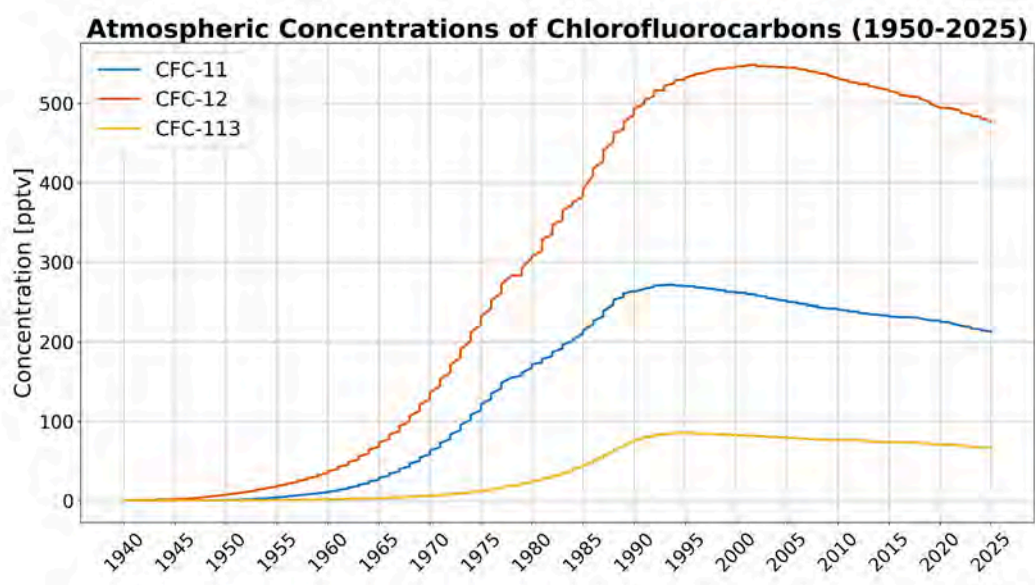


Figure 7: Atmospheric concentration of CFCs in pptv. Data record obtained from [USGS \(no date\)](#).

The evolution of atmospheric CFC concentrations is clearly visible in [Figure 8](#) above. Striking is the rapid increase in atmospheric concentrations of CFC-11 and CFC-12 over three decades, starting in 1960 and lasting until 1990. CFC-113 was introduced later into the atmosphere, but it also reaches its peak shortly after the year 1990. After the year 2000, the concentrations of all three species begin to decline slowly. Noteworthy, the rate of decline is much smaller than the rate of increase for all three species.

The time series of atmospheric CFC concentrations will be used to estimate the concentration of CFCs in recharging groundwater. This is further explained in [Section 3.1](#).

2.3 CFC Samples

[Kolbe and Bishop \(2024\)](#) sampled groundwater wells in the year 2021 inside the study area for CFC concentrations. In total, 24 samples are inside the catchment area, of which 17 are located inside the model domain (see [Table 1](#) and [App. Fig. 41](#)). To improve sample identification, the identifiers “Up”, “Low” and an alphanumeric labelling (e.g. “A1”) are derived here from physical well information. The identifiers “Up” and “Low” refer to the sample packers applied to the groundwater wells, which split the screening depth into an upper and a lower part, resulting in two samples. The alphanumeric labelling describes repeated sampling at the same

date (e.g. “A1”, “A2”, etc.) and repeated sampling at different dates (e.g. “A1”, “B1”, etc.). Furthermore, for the results section wells are categorized in three groups (“shallow”, “intermediate” and “deep”) by the depth to their midpoint (see [App. Tab. 8](#)). Below in [Table 1](#), the sampled CFC concentrations from [Kolbe and Bishop \(2024\)](#) are presented. Importantly, the original measurements in [pmol L⁻¹] were not available. Instead, they were converted back from the reported observations in pptv in [Kolbe and Bishop \(2024\)](#) according to the therein described calculations.

Table 1: The total available 24 CFC samples from groundwater measurements located in the Västrabäcken catchment for this study. Inside the domain and groundwater zone is indicated with binary values: 0 = inside, 1 = outside.

Well sample	Sampling Date	CFC-11 [pmol L ⁻¹]	CFC-12 [pmol L ⁻¹]	CFC-113 [pmol L ⁻¹]	Inside
Audrey's well	18/08/2021	2.348	1.889	0.27	0
w303	31/05/2021	0.612	2.787	0.189	0
w304	06/08/2021	6.065	0.606	0.121	0
w40B1	02/09/2021	1.645	2.733	0.455	0
w40LowA1	24/06/2021	5.766	3.761	0.648	0
w42LowA1	21/06/2021	5.906	3.391	0.594	0
w42LowB1	31/08/2021	5.275	2.609	0.412	0
w201	31/05/2021	5.927	3.265	0.55	1
w302	31/05/2021	2.358	1.292	0.252	1
w37LowA1	18/06/2021	6.692	4.015	0.768	1
w37UpA1	18/06/2021	6.443	3.578	0.658	1
w38LowA1	20/08/2021	5.603	3.406	0.066	1
w38UpA1	20/08/2021	5.753	1.212	0.07	1
w39LowA1	17/06/2021	5.906	3.663	0.657	1
w39LowB1	31/08/2021	5.439	2.905	0.066	1
w39UpA1	17/06/2021	6.033	3.652	0.643	1
w39UpA2	17/06/2021	6.306	3.511	0.636	1
w39UpB1	31/08/2021	5.31	2.955	0.062	1

w40UpA1	24/06/2021	5.496	3.31	0.591	1
w41A1	08/06/2021	5.711	3.481	0.626	1
w41B2	02/09/2021	1.547	2.783	0.121	1
w42UpA1	21/06/2021	5.762	3.267	0.607	1
w42UpB1	31/08/2021	5.646	3.133	0.07	1
w43	13/09/2021	5.972	3.248	0.36	1

Additionally, [Kolbe and Bishop \(2024\)](#) presented water samples from the streams in the Krycklan Catchment Study. For the Västrabäcken stream C2 a single sample was provided from the 2023-03-15 with 5.907 pmol L⁻¹, 4.1049 pmol L⁻¹, 0.409 pmol L⁻¹, for CFC-11, CFC-12 and CFC-113, respectively.

For the discussion of analytical methods on CFC analysis of groundwater samples, this study refers to [Kazemi \(2004\)](#); [IAEA \(2006\)](#); [Chambers, Gooddy and Binley \(2019\)](#); [Kolbe *et al.* \(2020\)](#); [Kolbe and Bishop \(2024\)](#) and [Labasque *et al.* \(2014\)](#). Important to this study are the measurement errors of the “[...] purge and trap gas chromatography, with a precision of ±4% for high concentrations and ±20% for samples near the quantification limit (0.1 pmol L⁻¹)” ([Labasque *et al.*, 2014](#); [Kolbe and Bishop, 2024](#)). Furthermore, [Kolbe *et al.* \(2020\)](#) conclude that CFC-12 is the least reactive compound and therefore the most reliable tracer, due to its low sorption and degradation ([IAEA, 2006](#); [Chambers, Gooddy and Binley, 2019](#)). While [Labasque *et al.* \(2014\)](#) found the lowest uncertainties in age determination for CFC-11 due to its high solubility.

CFC concentrations in the groundwater wells and the stream will be compared to the model results for analysis and verification (see [Section 3.6](#)).

3 Methods

3.1 CFC Recharge Concentrations

It is assumed that CFCs dissolve into water under solubility equilibrium with the surrounding air according to Henry's law ([Kazemi, 2004](#); [IAEA, 2006](#)). In the event of recharging water, the water from the unsaturated zone and the top of the groundwater table gets displaced below the groundwater table. This recharging water is assumed to have been in equilibrium with the soil air, and consequently carries the respective equilibrium concentrations deeper. For shallow aquifers, the concentrations of CFCs in the soil air are assumed to be equal to the concentrations in the atmosphere. Consequently, the respective recharge concentration at a point in time can be calculated from the atmospheric concentration of CFCs and the temperature at the time of recharge, which governs the solubility equilibrium ([Kazemi, 2004](#); [IAEA, 2006](#)). If observations of recharge temperature are not available, the long-term annual mean air temperature is suggested for yearly estimates of recharge concentrations ([Kazemi, 2004](#); [IAEA, 2006](#)).

Here, recharge concentrations are estimated according to the descriptions of [Kazemi \(2004\)](#) (see [Appendix 2a](#)). The approach of [Kazemi \(2004\)](#) differs from the descriptions in [IAEA \(2006\)](#). The latter includes the partial pressure dependence of water vapor separately, while [Kazemi \(2004\)](#) references solubility equations that include this aspect directly. This results in minor differences in the computed recharge concentrations (see [Appendix 3a](#)), but is neglected from further analysis.

Daily soil temperatures at 20 cm depth (*Meteorological Data from Svarthøget, Hygget AWS, 1991–2015, 2025a*; *Meteorological Data from Svarthøget, Hygget AWS, 2016–2018, 2025b*; *Meteorological Data from Svarthøget, Hygget AWS, 2019–2024, 2025c*) are applied to the method of [Kazemi \(2004\)](#) to compute CFC recharge concentrations. This is necessary, to account for the insulation of the soil from the snow cover at the site during the winter months. The records of daily air and soil temperature observations (1991–2024) are compared in [Appendix 3a](#). The potential effect of frozen soil on CFC dissolution is not considered.

For each day of the year, the mean and standard deviation of soil temperature were computed across all years in the observational record. Each daily value was then clipped to two standard deviations around the corresponding day-of-year mean. This removes the extreme tails of the distribution before backward extension, preventing individual extreme events from being systematically repeated

in the reconstruction. This affected 632 of 12,349 daily values (5.1%), distributed uniformly across the year. The harmonized record was then copied backward in blocks of its length by day of year. The resulting daily series is shown in [Figure 8](#), together with its annual means, the long-term annual mean air temperature (see [Section 2.1.3](#)), and the atmospheric CFC concentrations.

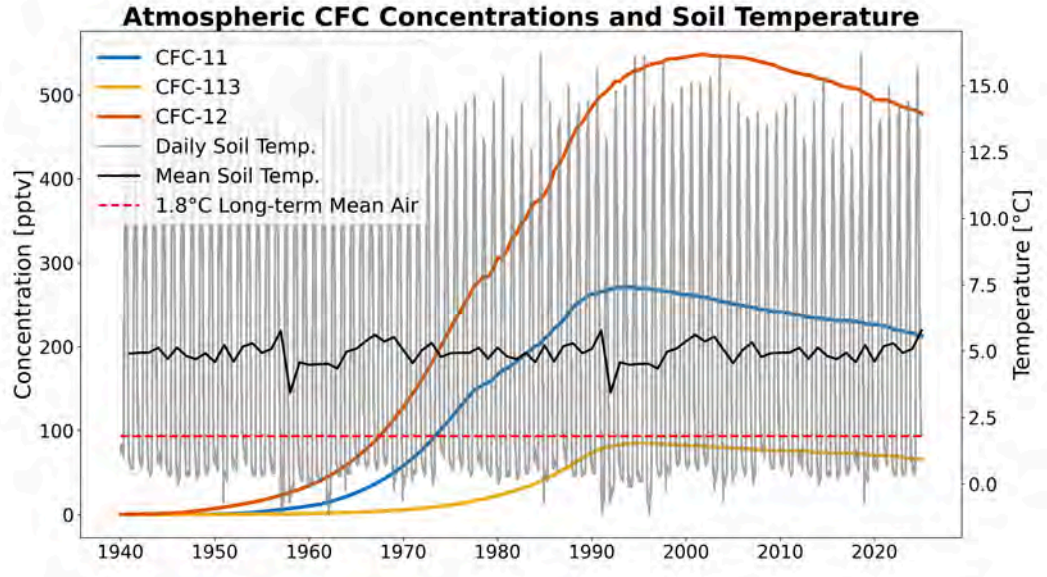


Figure 8: Daily average soil temperature in °C at 20 cm depth and atmospheric concentrations of CFCs in pptv. Soil temperature in gray, CFC-11 in blue, CFC-113 in yellow, CFC-12 in orange, annual mean soil temperature in black and long-term mean air temperature in dashed red.

[Figure 8](#) pronounces the strong intra-annual variations in soil temperature compared to atmospheric CFC concentrations. The annual mean (black solid line) visualizes the backward extension by repetition of the daily soil temperature observations. The long-term annual mean air temperature of 1.8 °C in dashed red is distinctly lower than the annual mean soil temperature, highlighting the importance of the insulation from the snow cover. In [Section 4.1](#), the computed recharge concentrations are presented.

3.2 Model Formulation

This study applies the model demonstrated by [Ameli, McDonnell and Bishop \(2016\)](#); [Ameli et al. \(2016\)](#) and [Ameli et al. \(2021\)](#). The relevant parts of the model formulation therein are repeated here in brief.

The linearization of the steady-state form of Richard's Equation in 2-D domain for an exponential decline in K_s with depth, is achieved with the Discharge potential ϕ_s for the saturated zone (see [App. Eq. 20](#)) and the Kirchhoff potential ϕ_u for the unsaturated zone (see [App. Eq. 21](#)), see [Appendix 2b](#) for details ([Bakker and Nieber, 2004](#); [Ameli, Craig and Wong, 2013](#); [Ameli, McDonnell and Bishop, 2016](#)). The linearized steady-state forms are then solved in a Fourier-Series type solution for ϕ_s and ϕ_u ([Ameli, McDonnell and Bishop, 2016](#)).

$$\phi_s(x, z) = A_0 + \sum_{n=1}^{N_s} \left[A_n \cos\left(\frac{n\pi}{L}x\right) \exp(\gamma_n z) + B_n \cos\left(\frac{n\pi}{L}x\right) \exp(\bar{\gamma}_n z) \right] \quad (3)$$

Where:

- x, z = Spatial coordinates [L]
- A_n, B_n = Series coefficients
- N_s = Number of series terms (saturated)
- L = Aquifer length [L]
- $\gamma_n, \bar{\gamma}_n$ = Eigenvalues, see [App. Eq. 23](#)

$$\phi_u(x, z) = C_0 [\exp(-\beta z)] - \sum_{m=1}^{N_u} \left[C_m \cos\left(\frac{m\pi}{L}x\right) \exp(\xi_m z) \frac{\xi_m}{\frac{m\pi}{L}} + D_m \cos\left(\frac{m\pi}{L}x\right) \exp(\bar{\xi}_m z) \frac{\bar{\xi}_m}{\frac{m\pi}{L}} \right] \quad (4)$$

Where:

- β = Gardner's sorptive number [L^{-1}], see [App. Eq. 18](#)
- C_n, D_n = Series coefficients
- N_u = Number of series terms (unsaturated)
- $\xi_n, \bar{\xi}_n$ = Eigenvalues, see [App. Eq. 25](#)

Derivatives of ϕ_s and ϕ_u with respect to x and z give Darcy flux vectors in x, z directions for every point in the hillslope ([Ameli, McDonnell and Bishop, 2016](#); [2016](#); [Ameli et al., 2021](#)) (see [App. Eq. 26](#), [App. Eq. 27](#)). Darcy fluxes are also presented as Fourier-Series type solutions ([Ameli, McDonnell and Bishop, 2016](#)).

$$q_{sx}(x, z) = -e^{\alpha(z-Z_t(x))} .$$

$$\sum_{n=1}^N \frac{n\pi}{L} \left[A_n \sin\left(\frac{n\pi}{L}x\right) \exp(\gamma_n z) + B_n \sin\left(\frac{n\pi}{L}x\right) \exp(\bar{\gamma}_n z) \right];$$

$$q_{sz}(x, z) = e^{\alpha(z-Z_t(x))} .$$

$$\sum_{n=1}^N \left[\gamma_n A_n \cos\left(\frac{n\pi}{L}x\right) \exp(\gamma_n z) + \bar{\gamma}_n B_n \cos\left(\frac{n\pi}{L}x\right) \exp(\bar{\gamma}_n z) \right]$$
(5)

$$q_{ux}(x, z) = e^{\alpha(z-Z_t(x))} .$$

$$\sum_{m=1}^M \left[C_m \sin\left(\frac{m\pi}{L}x\right) \exp(\xi_m z) \xi_m + D_m \sin\left(\frac{m\pi}{L}x\right) \exp(\bar{\xi}_m z) \bar{\xi}_m \right];$$

$$q_{uz}(x, z) = e^{\alpha(z-Z_t(x))} .$$

$$\sum_{m=1}^M \frac{m\pi}{L} \left[C_m \cos\left(\frac{m\pi}{L}x\right) \exp(\xi_m z) + D_m \cos\left(\frac{m\pi}{L}x\right) \exp(\bar{\xi}_m z) \right]$$
(6)

Where:

- α = Exponential relationship parameter [-], see [App. Eq. 17](#)
- $Z_t(x)$ = Topographic surface elevation [L], see [App. Eq. 17](#)

The remaining unknown series coefficients (A_n, B_n, C_n, D_n) in the series solutions of ϕ_s , ϕ_u and the Darcy fluxes are solved in a least square scheme for 280 control points located every 0.5 m along each interface (i.e., soil surface, water table, bottom no-flow) ([Ameli, McDonnell and Bishop, 2016](#); [Ameli et al., 2021](#)). To solve the least square scheme, here the boundary conditions of [Ameli et al. \(2021\)](#) are assumed:

- The infiltration rate at the surface equals the hydrologically effective rainfall
- The right side of the domain, i.e. the water divide, is a no-flow boundary;
- The bottom of the domain, i.e. the bedrock, is a no-flow boundary;
- The surface of the water course is represented by uniform hydraulic head;
- Continuity of flux and pressure head at the interface of unsaturated and saturated zone.

The solved series terms represent a full analytical solution of continuous fields for ϕ_s , ϕ_u and the Darcy fluxes inside the domain. These are the basis for modelling water movement in [Section 3.4](#). It is important to point out, that in the course of this study, only one steady-state condition is assumed. Consequently, all modelling

efforts build upon one solved domain and series solution. [Ameli et al. \(2021\)](#) demonstrated a “quasi-steady-state” model application, where weekly steady-state solutions are computed, and intermediate timesteps are interpolated. This model was not available for this study.

3.3 Steady-state assumption

Here, only a single steady-state is considered, which requires a representative condition of R to be chosen as the top boundary condition in the model domain (i.e. infiltration rate at the soil surface). The overall median of R (see [Figure 4](#)) is chosen, which is corroborated by the overall median of Q being close to R (comp. [Figure 5](#)). The overall median is chosen as it represents the most typical flow condition and is less influenced by extreme events, which are likely not representative of the long-term steady-state assumed for the model. This is supported by the overall median approximating recharge conditions better than the overall mean for most months (see [Figure 4](#)). However, the median is significantly lower than the overall mean of R and Q (see [Figure 4](#), [Figure 5](#)) and it does not resolve to the total annual recharge amount.

3.4 Pathline Computation

[Ameli et al. \(2016\)](#) have shown how pathlines of water particles can be computed from the continuous Darcy flux fields by employing a particle random walk scheme. [Ameli et al. \(2021\)](#) demonstrated this application to trace stable water isotope signals. The descriptions of [Ameli et al. \(2016\)](#) and [Ameli et al. \(2021\)](#) on the particle random walk are repeated here in brief first. Then the application of the particle random walk to generate pathlines for groundwater wells and the stream is described.

3.4.1 Particle Random Walk

The computation of water transport as particle movement through the soil is described by the porewater velocity V , which relates the Darcy flux q to the water content θ . In the 2-D domain studied here, the porewater velocity V at a point (x, z) is computed as follows ([Ameli et al., 2016](#)).

$$\begin{aligned}
V_{sx}(x, z) &= \frac{q_{sx}(x, z)}{\theta_s(x, z)}; & V_{sz}(x, z) &= \frac{q_{sz}(x, z)}{\theta_s(x, z)}; \\
V_{ux}(\varphi, x, z) &= \frac{q_{ux}(x, z)}{\theta_u(\varphi, x, z)}; & V_{uz}(\varphi, x, z) &= \frac{q_{uz}(x, z)}{\theta_u(\varphi, x, z)}
\end{aligned} \tag{7}$$

The unsaturated water content θ_u additionally depends on the suction pressure head φ and is estimated with $\theta_u(\varphi, x, z) = \theta_s(x, z) \exp(\beta(\varphi - \varphi^e))$, reflecting Gardner's constitutive function for K_u (see [App. Eq. 18](#)) ([Ameli et al., 2016](#)). The saturated water content θ_s is given by the porosity-depth relationship (see [Section 2.1.2](#)).

From the obtained V vector field, [Ameli et al. \(2016\)](#) described a particle random walk scheme based on [Salamon, Fernández-García and Gómez-Hernández \(2006\)](#). The uniform random walk step of a water particle p is given by the following equations ([Ameli et al., 2016](#); [Ameli et al., 2021](#)).

$$\begin{aligned}
x_p^k &= x_p^{k-1} + V_x^{k-1} \Delta t + \sqrt{2D_L^k \Delta t} \cdot X_L \cdot \frac{V_x^{k-1}}{|V^{k-1}|} - \sqrt{2D_T^k \Delta t} \cdot X_T \cdot \frac{V_z^{k-1}}{|V^{k-1}|} \\
z_p^k &= z_p^{k-1} + V_z^{k-1} \Delta t + \sqrt{2D_L^k \Delta t} \cdot X_L \cdot \frac{V_z^{k-1}}{|V^{k-1}|} - \sqrt{2D_T^k \Delta t} \cdot X_T \cdot \frac{V_x^{k-1}}{|V^{k-1}|}
\end{aligned} \tag{8}$$

Where:

- x_p^k, z_p^k = position of particle p at time step k
- V_x^k, V_z^k = Porewater velocities in x, z direction [$L T^{-1}$]
- Δt = time step [T]
- $|V^k| = \sqrt{(V_x^k)^2 + (V_z^k)^2}$
- $D_L^k = \alpha_L |V^k|$; longitudinal mechanical dispersion coefficient [$L^2 T^{-1}$]
- $D_T^k = \alpha_T |V^k|$; transverse mechanical dispersion coefficient [$L^2 T^{-1}$]
- α_L = longitudinal dispersivity coefficient [L]
- α_T = transverse dispersivity coefficient [L]
- X_L^k, X_T^k = random numbers drawn from a standard normal distribution $\mathcal{N}(0, 1)$ for each particle and each time step k

The longitudinal and transverse dispersivity coefficients are set to 1.0 and 0.01 cm, respectively ([Ameli et al., 2021](#)). The particle random walk is solved iteratively with a numeric integrator. Heun's method, a two stage Runge–Kutta scheme is employed to integrate the particle walk numerically. This corresponds to the

applications in Ameli, McDonnell and Bishop (2016); Ameli *et al.* (2016) (see Section 3.7). The particle p requires k_{end} steps of the particle random walk from start to endpoint. Consequently, the transit time t_p^T from start to endpoint is $t_p^T = \Delta t \cdot k_{\text{end}}$ (see Equation 9).

The V field and random walk scheme allow for particle tracking anywhere inside the model domain, with forward tracking (following the physical direction of velocity vectors) and backward tracking (the opposite direction to the velocity vectors).

3.4.2 Pathlines to Groundwater Wells

Pathlines to groundwater wells are computed to estimate transit time distributions (i.e., the distribution of water ages) of the water in a well, and to simulate tracer concentrations in a well for model analysis and verification against measurements.

Groundwater wells are scattered throughout the groundwater zone of the model domain (see Figure 2). To simplify the computation for wells, pathlines are computed backward, i.e. from the well to the surface. Particles are seeded uniformly along the screening depth of a well, resulting in a particle set where all particles initially share the same x -coordinate but vary in their z -coordinate. From the starting coordinates, the random walk scheme is applied until the particles exit the domain. Particles are only counted as valid if they exit the domain through the soil surface.

Here, pathlines are computed for every well once with a set of $N = 2,000$ particles, resulting in N particle-wise transit times t_p^T from startpoint to endpoint. This set is subsequently used to estimate the transit time distribution to the well and to simulate the CFC concentrations in the well.

It should be noted that, for wells, repeated computations of pathlines for a smaller sample size were tested, e.g. 200 repetitions per well with a set of $N = 200$ particles each. This allows for a more diverse representation of the random displacement due to dispersion in the random walk scheme.

However, due to the considerable computation times (> 8 hours for all wells), the repeated pathlines computation was abolished in favour of the simpler approach with a single set of particles, but of much greater size. This facilitates a much finer spatial resolution of seeded particles, a particularly critical consideration under the exponentially declining K_s , where depth is a highly sensitive parameter.

3.4.3 Pathlines to the Stream

As for groundwater wells, pathlines to the stream are computed to estimate the transit time distribution (i.e., the distribution of water ages) of water in the stream, and to simulate tracer concentrations for model analysis and verification against measurements.

Pathlines to the stream are computed forward, i.e., from the soil surface until the stream. Particles are seeded uniformly along the top boundary of the domain, resulting in the particle set where all particles initially feature unique x, z -coordinates. From the starting coordinates, the random walk scheme is applied until the particles exit the domain. Particles are only counted as valid if they exit the domain at the left boundary (i.e., the stream).

Here, pathlines to the stream are computed once with a set of $N = 10,000$ particles, resulting in N particle-wise transit times t_p^T from startpoint to endpoint. This set is subsequently used to estimate the transit time distribution to the stream, to simulate CFC concentrations and the ^{18}O signal in the stream.

It should be noted that no tests were conducted for the stream on particle set sizes of $N > 10,000$. It was found that estimates converged for set sizes of $N > 5,000$. The repeated computation of pathlines to the stream was investigated, but ultimately rejected on the basis of its considerable computational demand.

3.5 Transit Time Distributions

Particle-wise transit times t_p^T result from the numerical random walk algorithm in the pathline computation (see [Section 3.4.1](#)). The transit time of a particle is the sum of all integration steps required from startpoint to endpoint,

$$t_p^T = \Delta t \cdot k_{\text{end}} \quad (9)$$

The computation of a sufficiently large set of particles enables consistent estimates of transit time statistics and distributions. This is of particular interest for the water samples taken either at a groundwater well or at the stream. Each water sample is represented by its particle set S_i , where i is the sample index. Each particle set is computed as described in [Section 3.4.2](#) and [Section 3.4.3](#).

Due to computational restrictions, a full Lagrangian model approach was not feasible in the scope of this study (see [Section 3.4.2](#), [Section 3.4.3](#)). This restriction

requires averaging that respects the actual contribution of individual particles. Here, the flux-averaged transit time is defined as the weighted mean of the particle-wise transit times, using the particles' flux weights w_p .

$$\widehat{T}_{S_i} = \frac{\sum_{p \in S_i} (w_p \cdot t_p^T)}{\sum_{p \in S_i} w_p} \quad (10)$$

The w_p are computed as the point value of the Darcy flux q in x -direction at the particles' sampling points, where q in x -direction is always dominant. For ground-water wells, the flux vectors at the startpoint (i.e., in the well) are used as weights, while for the stream the flux vectors at the endpoint (i.e., in the stream) are used. Note that, for domain-wide results, each particle directly represents a discrete spatial unit within the model domain, for which averaging is not performed (see [Section 4.2](#)).

It is of interest to extend the information provided by the flux-averaged transit time by identifying distribution functions capable of reflecting all transit times within a computed particle set (see [Section 4.3.2](#), [Section 4.4](#)). Four candidate distributions (Gamma, Inverse Gaussian, Log-normal, and Weibull) are compared to determine which provides the best fit. The procedure is as follows:

1. The set of transit times is resampled by weighted random sampling with replacement from the particle-wise transit times, with sampling probabilities proportional to the flux weights w_p .

The resampled set is of the same size as the original set.

1. The four candidate distributions are fitted (by maximum likelihood estimation) to the resampled data using the `fitdist()` function from the "Statistics and Machine Learning Toolbox" in MATLAB.
2. The distributions are compared using the Akaike's Information Criterion, and the distribution with the lowest AIC is selected as the best fit.

3.6 Tracer Simulation

The value of simulating tracer signals lies both in capturing their temporal evolution and in reproducing observations at specific points in time. Tracer signals are always inferred from the particle transit times to a point inside the domain. Due

to the steady-state of the model, the transit times are time-invariant, while tracer inputs are time-variant.

At a given time t , the water at a point (x, z) inside the domain is represented by a particle p , with the transit time t_p^T from the surface to the point, which results from the computed pathlines (see [Section 3.5](#)). It is assumed that the tracer signal of the particle does not change. Therefore, the tracer signal of the particle $c_p(t)$, at time t , can be inferred from the tracer input it received when it was recharged at the recharge time t_p^R , given by $t_p^R = t - t_p^T$. The tracer input $J(t)$ is a time series (e.g. [Figure 11](#), [Figure 6](#)), and the particle carries the signal $J(t_p^R) = c_p(t)$.

A water sample i is represented by its particle set S_i (see [Section 3.4.2](#), [Section 3.4.3](#)). To represent the tracer signal in a water sample at time t , the flux-averaged signal $\widehat{C_{S_i}}(t)$ is calculated as the weighted mean of these particle-wise signals, using the particles' flux weights w_p (see [Section 3.5](#)).

$$\widehat{C_{S_i}}(t) = \frac{\sum_{p \in S_i} (w_p \cdot c_p(t))}{\sum_{p \in S_i} w_p} \quad (11)$$

To simulate tracer concentrations over time (e.g. in a well or the stream), this procedure is applied iteratively for each time step t under consideration, yielding a time series of flux-averaged tracer signals.

For a given sample i , with the particle set S_i , a measured concentration c_i^M corresponds to the water sample taken at the fixed sampling time t_i^M . The simulated concentration at t_i^M is obtained by linearly interpolating $\widehat{C_{S_i}}(t)$ to t_i^M . For model analysis and verification, relative errors between simulation and observation are computed as follows.

$$\delta_{\text{rel},i} = \frac{\widehat{C_{S_i}}(t_i^M) - c_i^M}{|c_i^M|} \quad (12)$$

The sign of $\delta_{\text{rel},i}$ is retained (rather than taking its absolute value) so that negative and positive relative errors indicate an under- or overestimation of tracer signals by the model, respectively.

Here, the simulation period spans from 1940 (the onset of atmospheric CFC release) to 2025, encompassing the 2021 groundwater sampling campaign and the 2023 stream sample. The tracer signal of the CFCs is here interpreted as the concentration in pmol L^{-1} , whereas for ^{18}O the signal is interpreted as $\delta^{18}\text{O}$. The tracer input time series $J(t)$ corresponds to the estimated recharge concentrations for the CFCs (see [Figure 11](#)) and to the ^{18}O input from precipitation (see [Figure 6](#)). When the discrete time series $J(t)$ has no entry for a recharge time t_p^R , linear inter- and extrapolation is applied for CFCs, resulting in CFC concentrations of 0.0 pmol L^{-1} for particles recharged before 1940. For ^{18}O , spline interpolation is applied, and extrapolation is held constant at -13.235 ‰ , the long-term mean of the precipitation ^{18}O .

3.7 Code description

Ali Ameli made his personal MATLAB code repository available for the scope of this study ([Ameli, McDonnell and Bishop, 2016](#); [Ameli et al., 2016](#); [Ameli et al., 2021](#)). This included the algorithm for solving the series solution for the saturated and unsaturated domain, as well as the particle random walk algorithm used for the pathline computation. The software repository contains a variety of code, some of which was written approximately 15 years ago and lacks comprehensive documentation. Furthermore, several runtime errors occurred, most likely due to the age of the code. It was not possible to resolve errors consistently, as their source and implications were ambiguous. This approach was ultimately deemed impractical for the integration of the requisite analysis of CFC tracer signals at groundwater wells.

Consequently, the decision was made to replicate the existing repository and adopt contemporary MATLAB formulations. This approach was adopted to achieve a substantial enhancement in computation speed, reusability and the documentation of the code. It is imperative to emphasise that this is a replica which accurately reflects the algorithm provided by Ali Ameli. The results obtained are consistent with those previously reported. Discrepancies emerge from the vectorisation of the code and are attributable to numerical precision issues (i.e. $< 10^{-6}$).

4 Results

The results for the computed recharge concentrations will be shown first. Then, the results for the whole model domain are presented, i.e. the solved darcy flux vector field, groundwater age and groundwater cfc concentrations. Thirdly, the results obtained for the groundwater wells are shown and the results for the stream are given last.

4.1 CFC Recharge Concentrations

Recharge concentrations are computed from available observations of half-yearly atmospheric concentrations of CFC and daily soil temperature at 20 cm depth (see [Section 2.2.4](#)). This results in daily recharge concentrations which are aggregated to coarser temporal resolution. The accordance of different temporal resolutions is examined for CFC-11 in [Figure 9](#) below. The different temporal resolutions overlap visually well, except yearly aggregates (YS). Accordingly, the Nash-Sutcliff Efficiency remains above 0.95 for the aggregates of weeks (WS), months (MS) and hydrological quarters (QS-NOV).

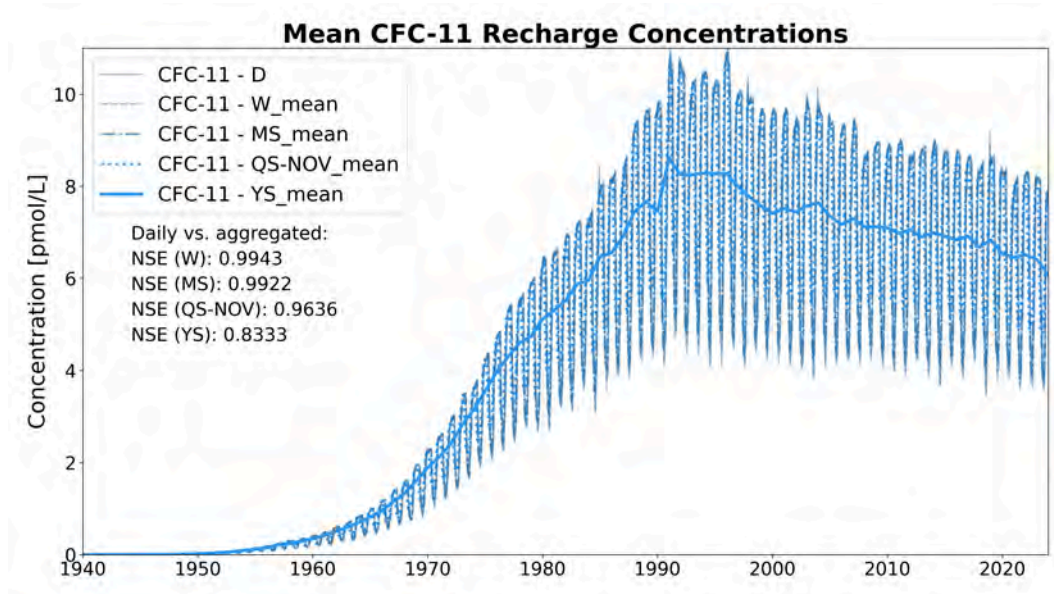


Figure 9: Recharge concentrations of CFC-11 in daily (D, faint solid), weekly (WS dashed), monthly (MS dash-dot), hydrologic quarters (QS-NOV dotted) and yearly (YS solid) temporal resolution. Aggregates as arithmetic means from daily data over the respective period. NSE computed between aggregates and daily data.

With regard to the single long-term steady-state of the model, especially yearly recharge concentrations are of interest. Different methods of aggregation to yearly averages exist. Here, the arithmetic mean, the median and the volume weighted average are chosen. Volume weighted averages aim to reflect the strong intra-annual variations in recharge and discharge amount (see. [Figure 4](#), [Figure 5](#)). Additionally, annual recharge concentrations are computed with the long-term annual mean air temperature (1.8°C, see [Section 2.1.3](#)), following reference guidelines (see [Section 2.2.4](#)). Below, the comparison of the aggregation methods is presented. The focus is again exclusively on CFC-11, as it is the compound with the highest solubility and therefore with the largest variations.

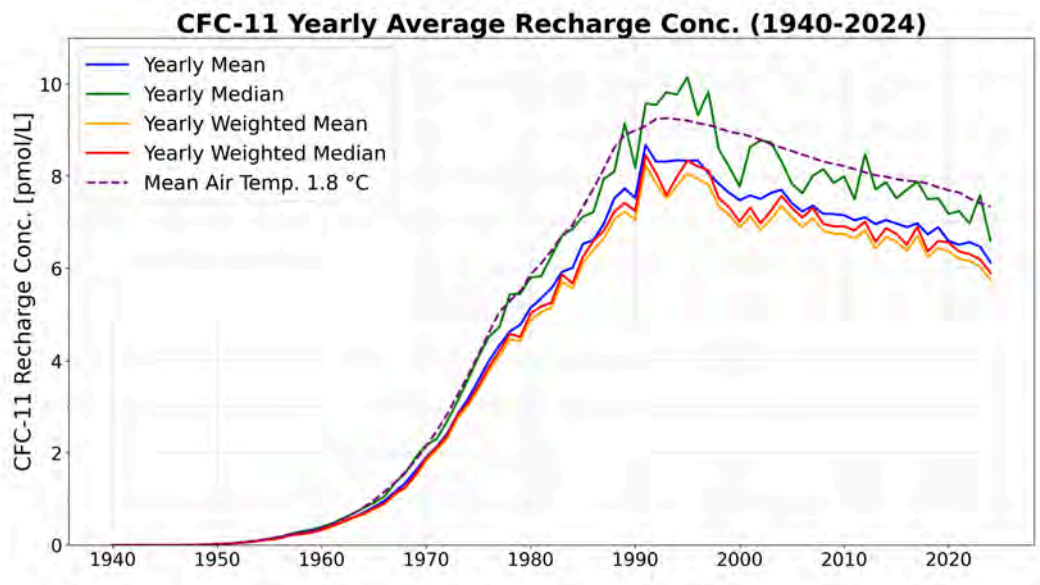


Figure 10: Yearly CFC-11 recharge concentrations as different aggregates from atmospheric concentrations and daily soil temperature at 20 cm depth following Henry's law equilibrium solubility: unweighted yearly arithmetic mean (blue, Yearly Mean); unweighted yearly median (green, Yearly Median); weighted average with monthly mean R (orange, Yearly Weighted Mean); weighted average with monthly median R (red, Yearly Weighted Median). Additionally, yearly recharge concentration with long-term annual mean air temperature in purple dashed (Mean Air Temp. 1.8 °C).

In [Figure 10](#) above, computed recharge concentrations with the long-term annual mean air temperature of 1.8 °C at the site show good accordance with daily data aggregated to yearly values by their median. Both differ visibly from the other methods of yearly aggregation. Daily data aggregated to yearly values by their arithmetic mean show good accordance with daily data aggregated to weighted yearly averages. The weighted averages use monthly median and mean values of

hydrologically effective rainfall (see Figure 4) as weights. Notably, both weighted averages remain slightly lower than the arithmetic mean. These patterns are confirmed by pairwise comparison of the yearly aggregates (see App. Fig. 49, App. Fig. 50).

Given the good accordance between the arithmetic mean and the weighted mean, the arithmetic mean is selected as the aggregation method, as it is simpler and requires less input data than the volume-weighted alternative. In Figure 11 below, the resulting yearly recharge concentration for all three CFC species are presented. To highlight intra-annual variability, monthly mean aggregates are also presented for each CFC species.

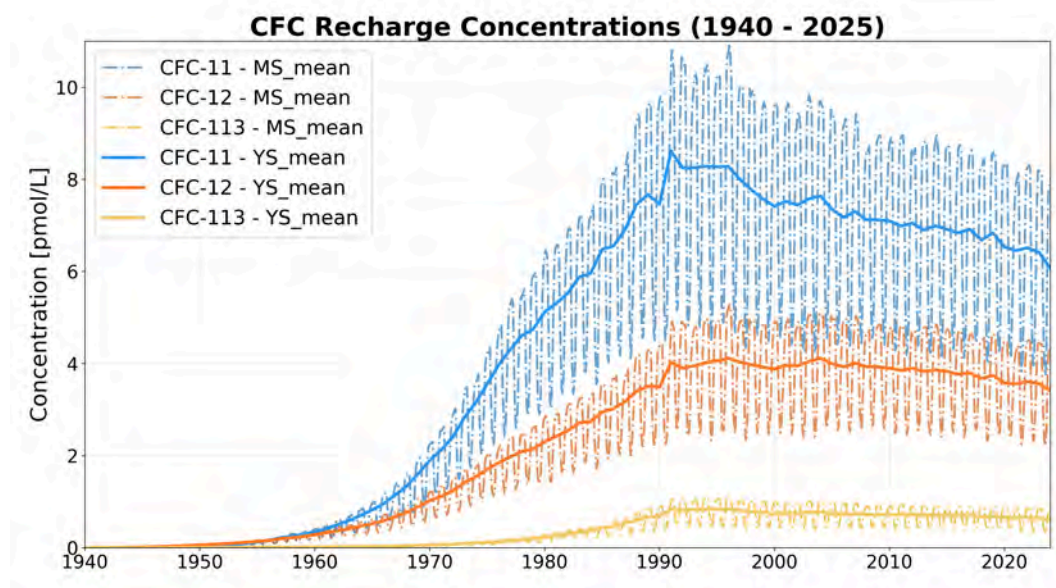


Figure 11: Yearly mean and monthly mean CFC recharge concentrations in $[pmol L^{-1}]$, CFC-11 in blue, CFC-113 in orange and CFC-12 in green. Recharge concentrations computed from atmospheric concentrations and daily soil temperature at 20 cm depth following Henry's law equilibrium solubility. Daily values aggregated as arithmetic means to monthly and yearly values.

The computed recharge concentrations in Figure 11 reflect the pattern of the atmospheric concentrations in Figure 8 with a peak before the year 2000. Clearly visible are the strong monthly variations due to the temperature changes. Low temperatures facilitate greater solubility and vice-versa for high temperatures. In contrast to Figure 8 the recharge concentrations of CFC-11 are the highest, due to its high solubility in water.

4.2 Domain Wide Results

Solving the model for the assumed steady-state condition (see [Section 3.2](#)) results in continuous vector fields of Darcy fluxes in (x, z) -direction. In [Figure 12](#) below, a discrete number of vectors from the continuous flux field are displayed. The orientation of the arrows is determined by their individual magnitudes in x - and z -direction. Noteworthy, the large combined magnitudes of the vectors in the unsaturated zone, i.e. above the capillary fringe, highlight fast particle movement into the saturated zone. Also the no-flow boundaries at the right hand side of the domain (subcatchment water divide) and at the bottom are emphasized by the arrows.

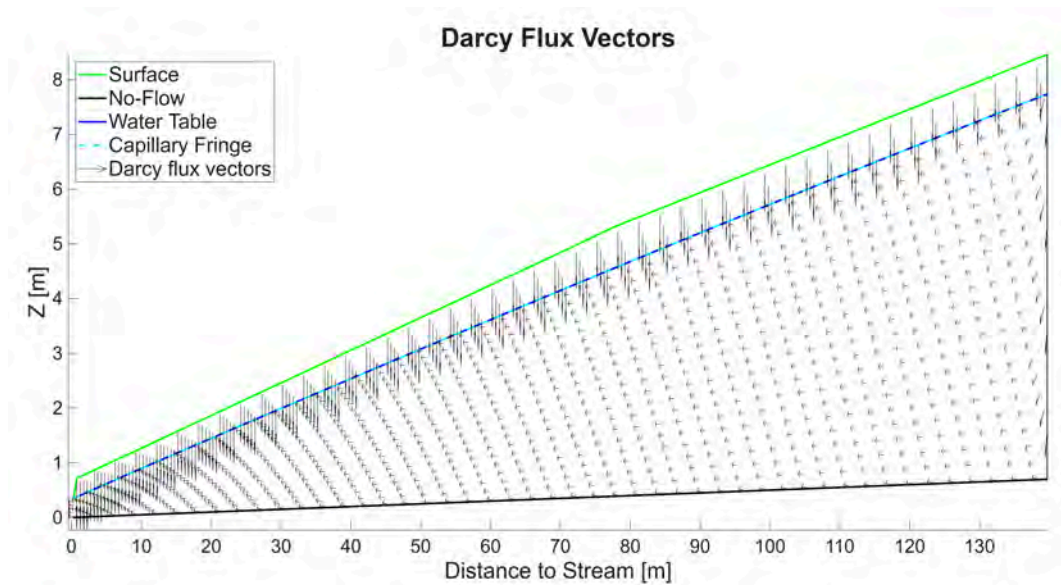


Figure 12: Darcy flux vector field of the solved steady-state condition, $R = 0.031 \text{ mm day}^{-1}$. Magnitude of vectors represented by their arrow size. Surface in green, the bottom and right no-flow boundary in black, water table in blue and capillary fringe in light blue.

From the Darcy flux field the groundwater age can be determined for any point in the hillslope. In [Figure 13](#) below, a hillslope wide representation of groundwater ages is computed for 14,000 points, 280×50 in x - and z -direction, respectively. The age is computed as the backward transit time from every point to the surface.

Striking in [Figure 13](#) is the unsaturated zone, which is homogeneously coloured in dark red, resembling ages younger than 0.2 years. Beneath the unsaturated zone, the groundwater age increases rapidly with depth. A large zone of the deep groundwater shows modelled groundwater ages older than 512 years. Noteworthy,

at the stream (left boundary of the domain, 0..10 m) only marginal amounts of old water exists, which are hardly visible in [Figure 13](#).

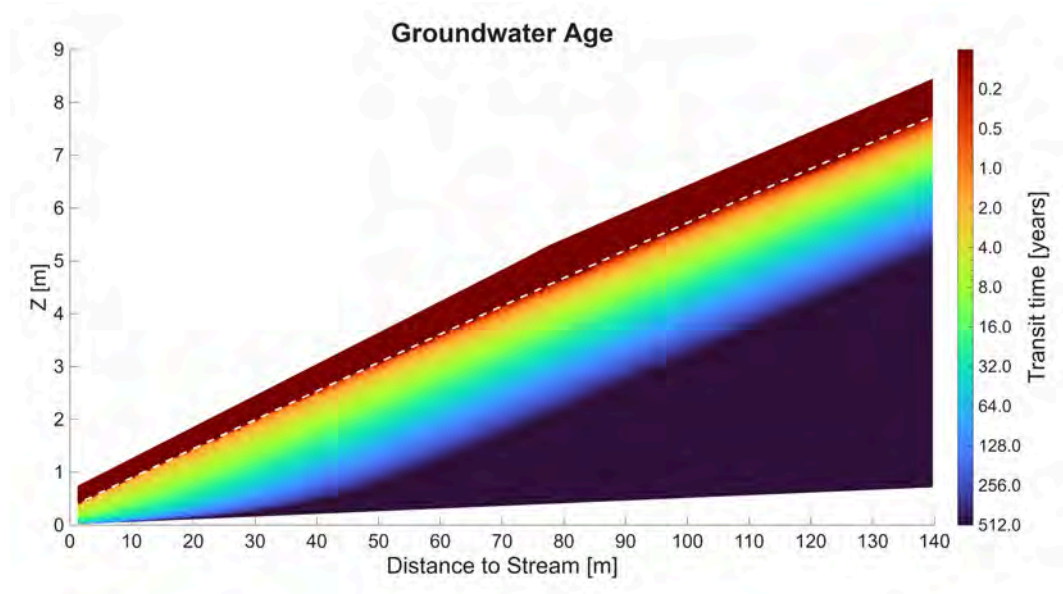


Figure 13: Steady-state groundwater age in years estimated for 14,000 points, 280×50 in x - and z -direction. Age is computed as the backward transit time from every point to the surface. Water table as a white dashed line.

From the domain wide results of groundwater age (i.e. transit time) the CFC concentrations throughout the hillslope are inferred (see [Section 3.1](#)). In [Figure 14](#) below, the hillslope wide estimation of CFC-11 concentration in the soil and groundwater is shown for the year 2021, when the groundwater samples were taken. The same set of points as in [Figure 13](#) is used for [Figure 14](#). Striking are the high concentrations in the shallow groundwater (unsaturated zone and < 1 m beneath the water table). This is followed by a steep decline of concentrations over less than half a meter. Beneath the end of the rapid decline, the model simulates no CFC-11 in the groundwater. This leaves a large zone of the groundwater, without any CFCs present. Noteworthy again, at the stream (left boundary of the domain, 0..10 m) only marginal amounts of CFC free water contribute to the water column.

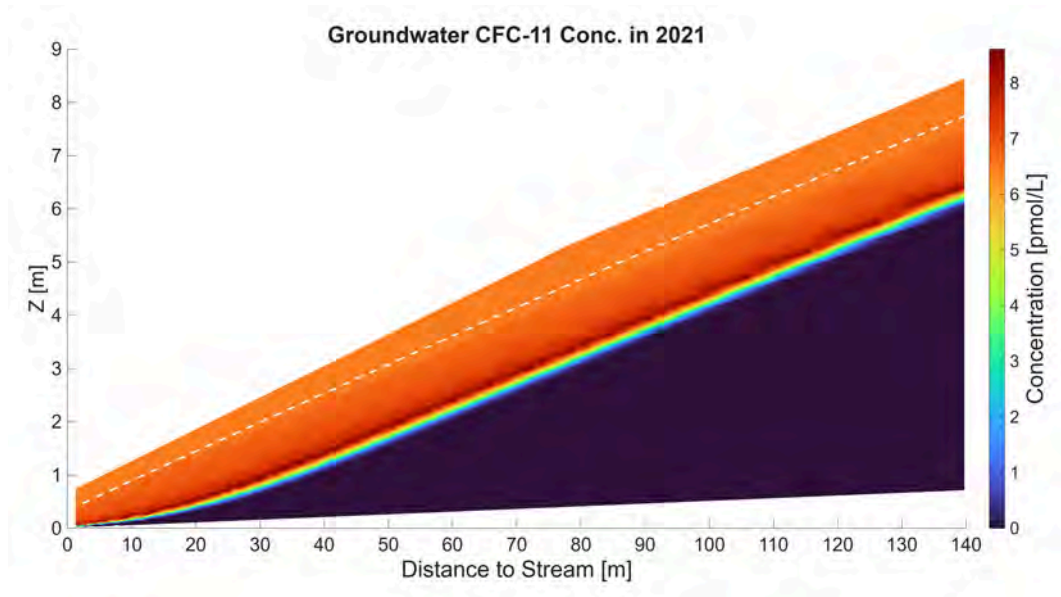


Figure 14: CFC-11 concentration in pmol/L estimated for 14,000 points. 280 in x-direction, 50 in z-direction. Concentration is inferred from the groundwater age and the yearly recharge concentration. Water table as a white dashed line.

4.3 Well Results

For the purposes of brevity, the results of only four well samples (w37UpA1, w37LowA1, w43, w40UpA1) are presented here. The wells selected are illustrative of the broader findings. Well positions inside the model domain, with respect to domain wide results are shown in [Figure 15](#) below and [Figure 24](#). The results obtained from all wells are presented in [Appendix 4](#).

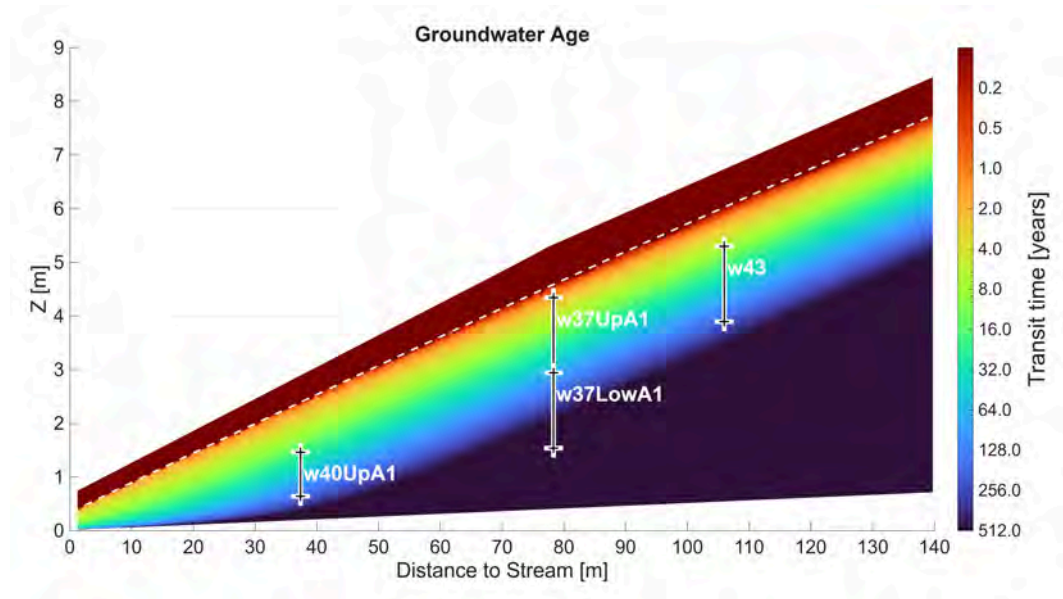


Figure 15: Placement of selected wells (w37UpA1, w37LowA1, w43, w40UpA1) in the computed water age of soil and groundwater.

4.3.1 Well Pathlines

Pathlines for groundwater wells are computed backward, with one set of 2,000 particles seeded uniformly across the screening depth (see [Section 3.4.2](#)). The results for well “w37” are presented first.

The well “w37” was segregated by a packer during the sampling process, enabling the extraction of an upper and lower sample. Consequently, the particles in [Figure 16](#) and [Figure 17](#) travel to the same x -coordinate but at different depths.

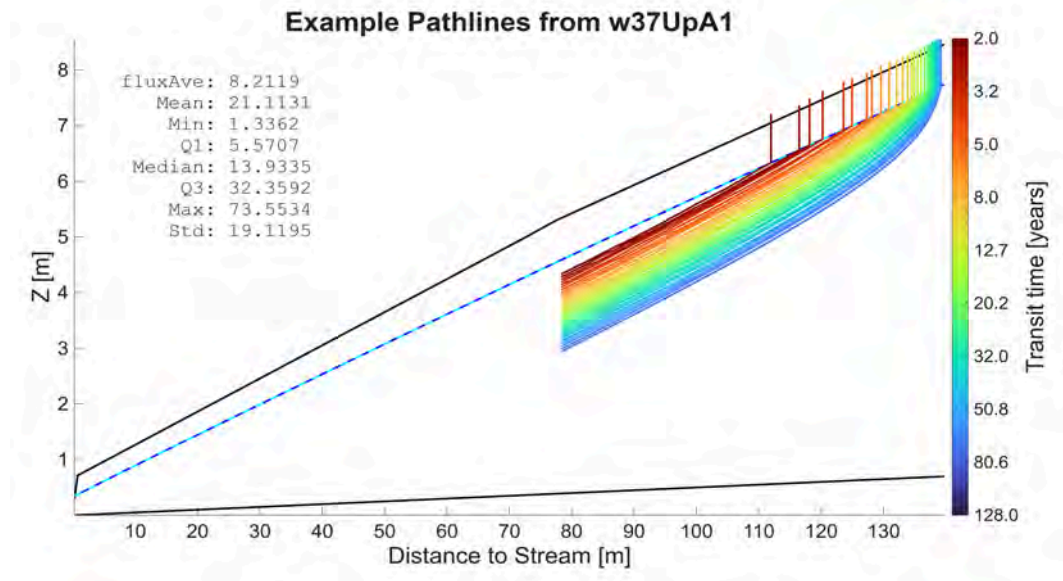


Figure 16: Pathlines computed backwards from w37UpA1 with 2,000 particles, seeded uniformly across the screening depth and coloured by their transit time. Summary statistics are given in the inset, in years. The “fluxAve” is the flux-averaged mean of the particle-wise transit times.

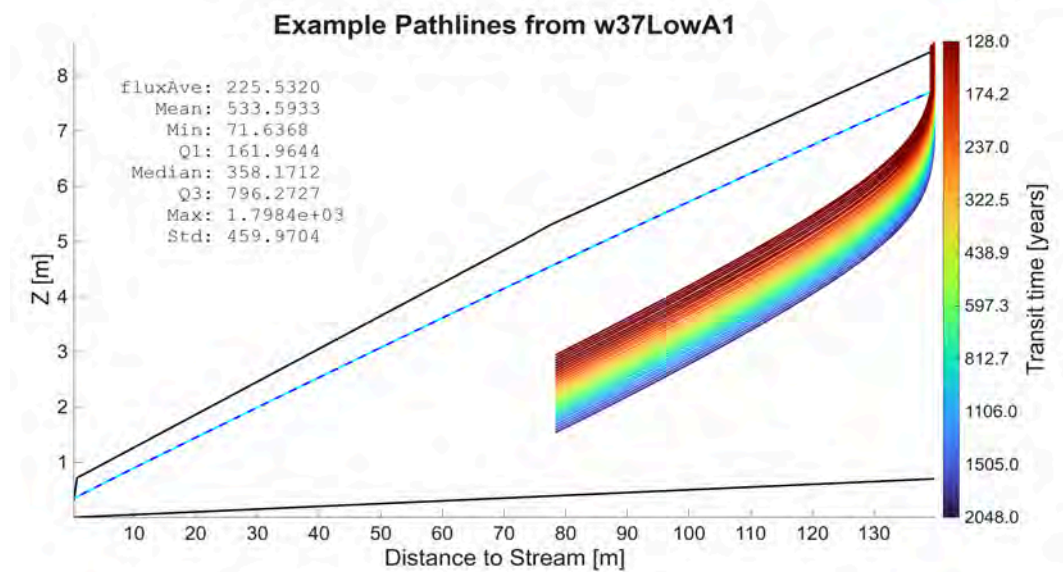


Figure 17: Pathlines computed backwards from w37LowA1 with 2,000 particles, seeded uniformly across the screening depth and coloured by their transit time. Summary statistics are given in the inset, in years. The “fluxAve” is the flux-averaged mean of the particle-wise transit times.

Noteworthy in Figure 16, the screening depth of the shallow well w37UpA1 is smaller than the surface length contributing particles. Conversely, in Figure 17, all contributing particles originate from a narrow strip at the right no-flow boundary of the model domain. A notable observation is the significantly longer transit times for the deep well w37LowA1 compared to w37UpA1. For both wells, the comparison of the “fluxAve” to the “mean” and “median” suggests a heavily skewed transit time distribution.

A comparison of Figure 18 and Figure 19 reveals contrasting flux-averaged transit times for the wells w43 and w40UpA1. While “Q1” and “median” transit times differ, the “mean” and “Q3” transit times are similar. Notably, w40UpA1 is positioned roughly 60 m closer to the stream than w43, but at similar depth (see App. Tab. 8). Analogous to the observations for well w37, the intermediate wells w43 and w40UpA1 and exhibit a small contributing surface length.

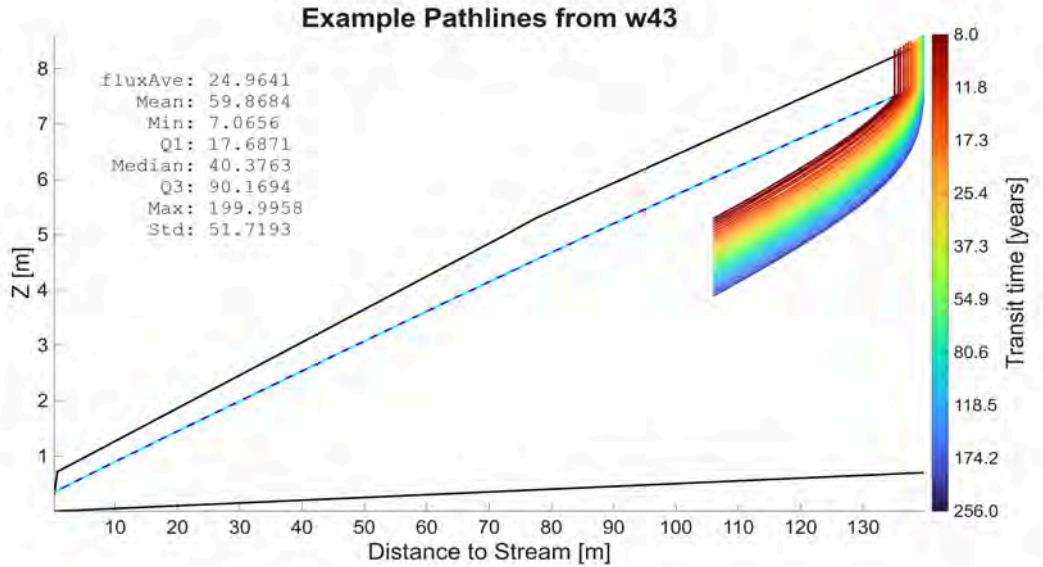


Figure 18: Pathlines computed backwards from w43 with 2,000 particles, seeded uniformly across the screening depth and coloured by their transit time. Summary statistics are given in the inset, in years. The “fluxAve” is the flux-averaged mean of the particle-wise transit times.

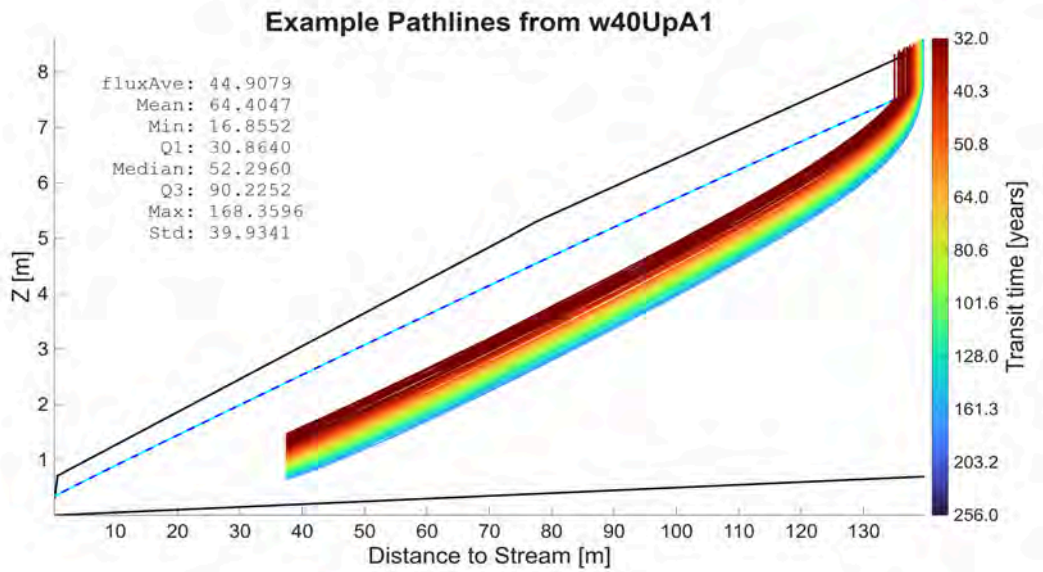


Figure 19: Pathlines computed backwards from w40UpA1 with 2,000 particles, seeded uniformly across the screening depth and coloured by their transit time. Summary statistics are given in the inset, in years. The “fluxAve” is the flux-averaged mean of the particle-wise transit times.

4.3.2 Well Transit Time Distributions

Transit time distributions for the wells are fitted to the computed set of 2,000 particles for each well (see [Section 3.5](#)). An overview of the results for each well is given in [App. Tab. 13](#).

Below, in [Figure 20](#) to [Figure 23](#), the computed particle-wise transit times are resampled by their flux weights and shown in a histogram with 100 bins. The Inverse Gaussian distribution is displayed together with the histograms, as it consistently provides the best fit under Akaike’s Information Criterion (see [App. Tab. 12](#)). Additionally, the flux-averaged transit time (i.e. the mean of the resampled data) is shown as a dashed gray line in the figure. Notably, the Inverse Gaussian distribution provides inherently the same mean as the underlying data (see [App. Tab. 13](#)).

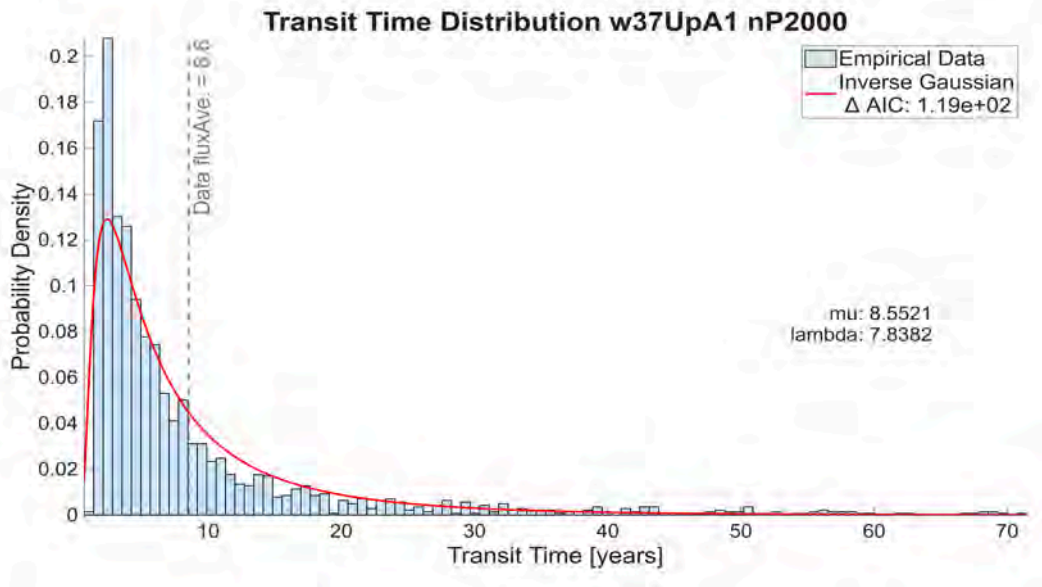


Figure 20: Estimated transit time distribution for well w37UpA1. Resampled transit time data as bars ($n=100$). Best fitting distribution under Akaike's Information Criterion in red, Δ AIC is the difference between the best and second best fit. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.

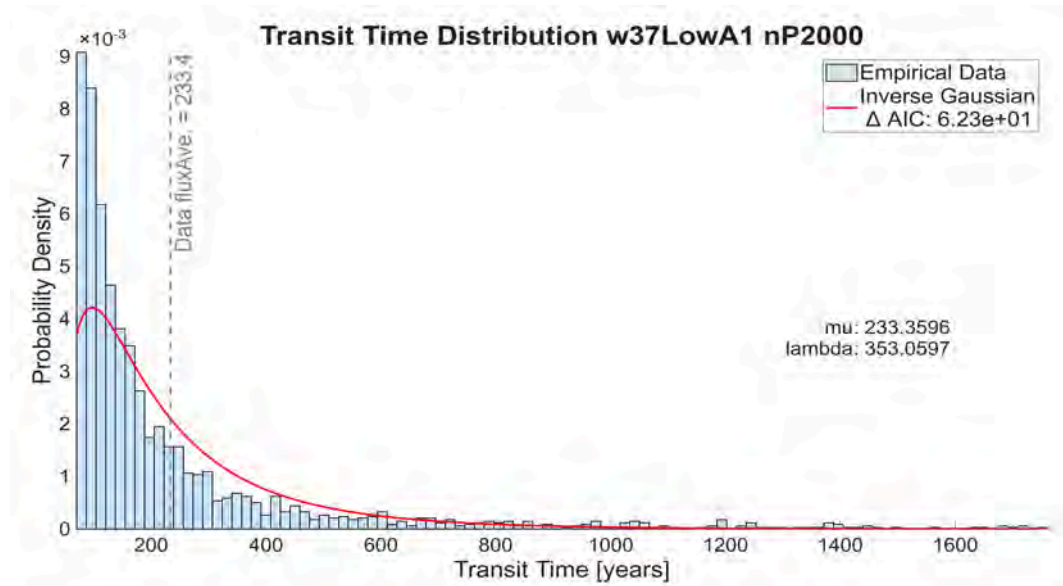


Figure 21: Estimated transit time distribution for well w37LowA1. Resampled transit time data as bars ($n=100$). Best fitting distribution under Akaike's Information Criterion in red, Δ AIC is the difference between the best and second best fit. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.

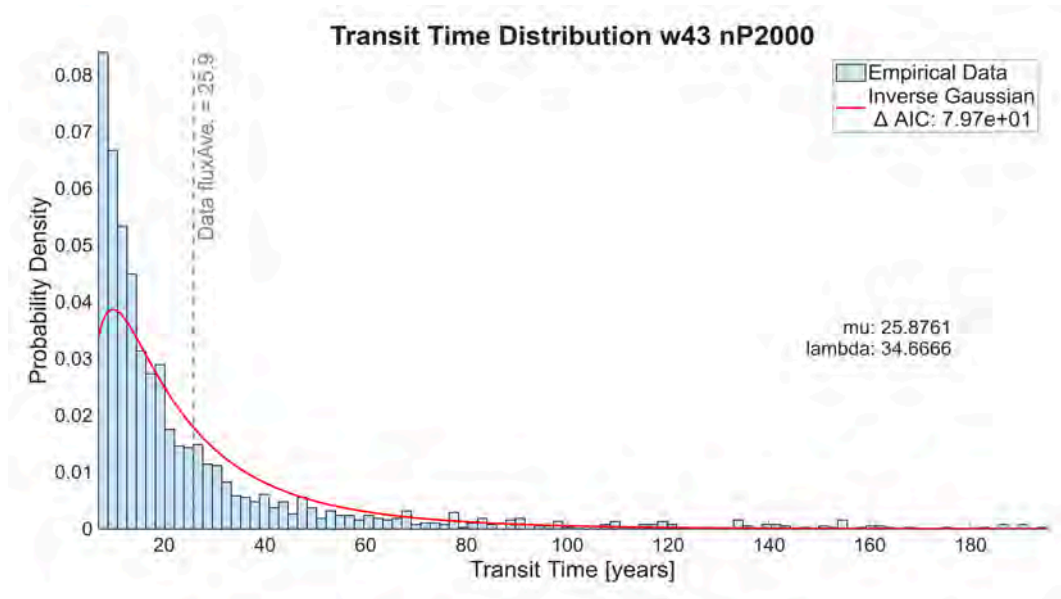


Figure 22: Estimated transit time distribution for well w43. Resampled transit time data as bars ($n=100$). Best fitting distribution under Akaike's Information Criterion in red, Δ AIC is the difference between the best and second best fit. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.

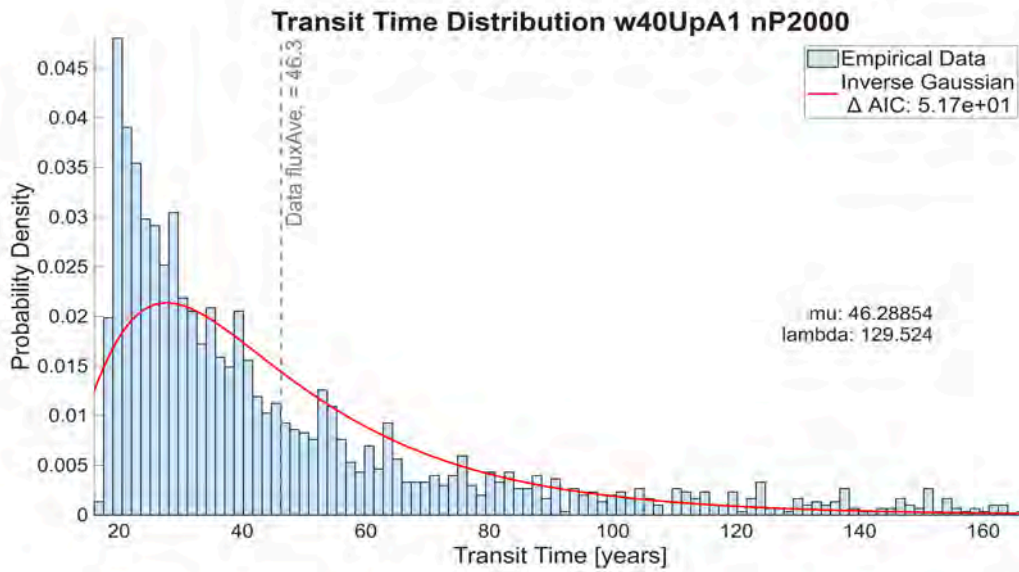


Figure 23: Estimated transit time distribution for well w40UpA1. Resampled transit time data as bars ($n=100$). Best fitting distribution under Akaike's Information Criterion in red, Δ AIC is the difference between the best and second best fit. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.

4.3.3 Well CFC concentrations

CFC concentrations at the groundwater wells are directly inferred from the computed transit times of the particles and the CFC recharge concentration in Figure 11 (see Section 3.2). Below in Figure 24, the four chosen wells are positioned in the simulated groundwater CFC-11 concentrations of Figure 14. Notably, the well samples w37UpA1 and w37LowA1 cover exclusively the CFC-enriched and depleted zones, respectively.

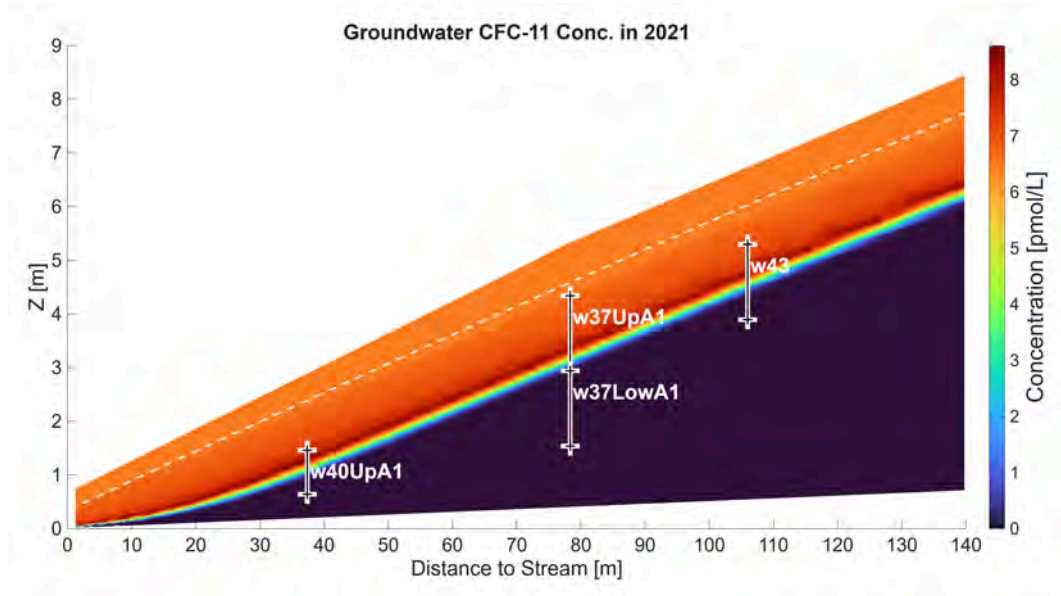


Figure 24: Placement of selected wells (w37UpA1, w37LowA1, w43, w40UpA1) in the computed CFC-11 concentration in soil and groundwater.

The time series from 1940 to 2021 of simulated CFC concentrations inside the wells are displayed below (Figure 25 to Figure 28). Measured CFC concentrations are indicated as cross marks. The vertical dashed line represents the sampling date, while the horizontal dashed lines highlight the simulated CFC concentrations at the sampling date. Green colours of the horizontal dashed lines emphasize absolute relative errors below 5 %. First, the results for well w37 will be presented.

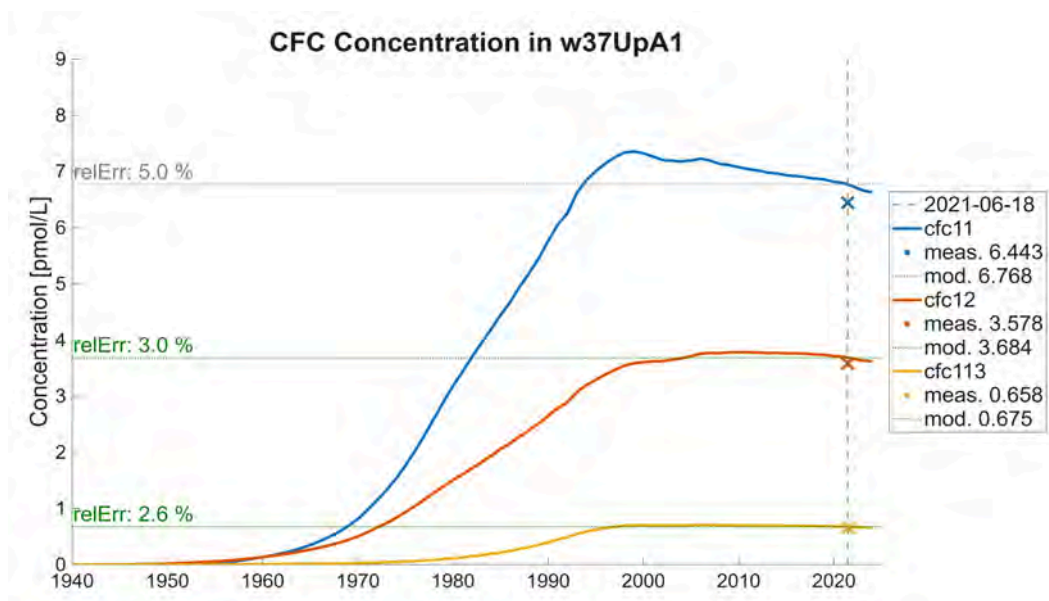


Figure 25: Time series of simulated CFC concentrations at well w37UpA1. Flux-averaged concentrations shown as solid lines and coloured by CFC species. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations and their relative errors.

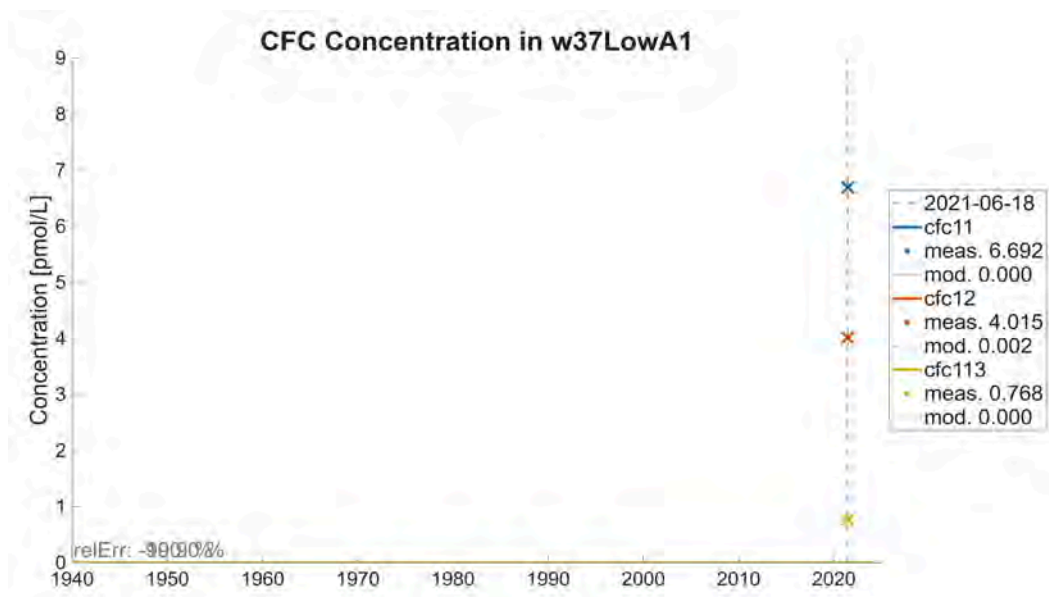


Figure 26: Time series of simulated CFC concentrations at well w37LowA1. Flux-averaged concentrations shown as solid lines and coloured by CFC species. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations and their relative errors.

Noteworthy are the low relative errors for “w37UpA1”, with simulated CFC concentrations closely matching the measurements (see Figure 25). The simulation replicates the peak in CFC-11 concentrations around the year 2000 followed by a slow decline, as observed for atmospheric CFC-11 (comp. Figure 7). For CFC-12 and CFC-113 the model predicts a hiatus from the year 2000 onward in w37UpA1. In contrast to the low relative errors exhibited by w37UpA1, the simulation for w37LowA1 results in a continuous concentration of almost zero for the displayed time period. This is due to the long transit times to the well, which almost entirely exceed the time period of CFC present in the atmosphere (see Figure 17). Note that, the measurements obtained for w37LowA1 are only marginally lower than those recorded for w37UpA1.

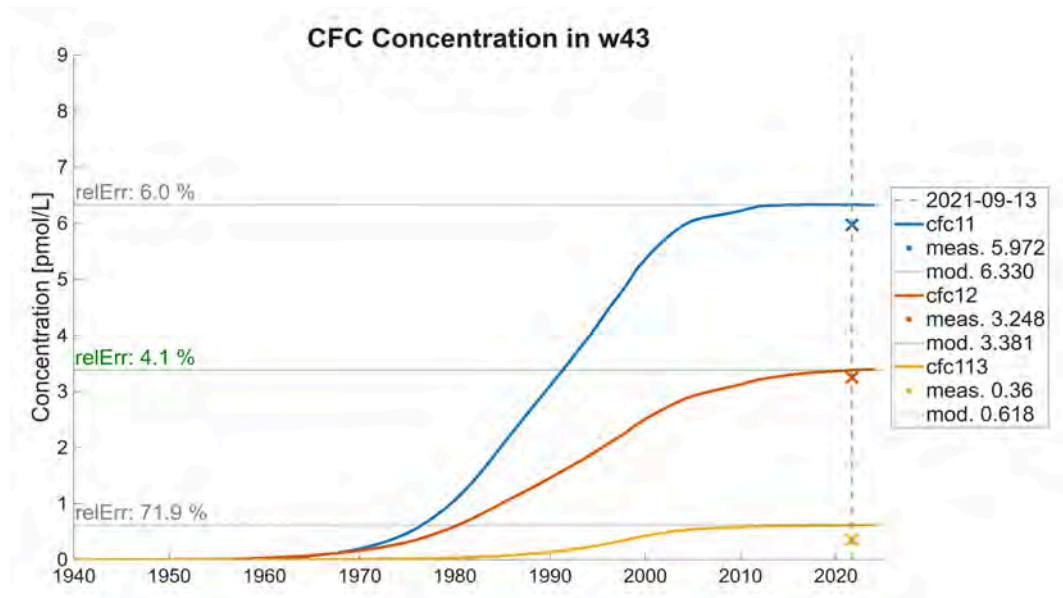


Figure 27: Time series of simulated CFC concentrations at well w43. Flux-averaged concentrations shown as solid lines and coloured by CFC species. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations and their relative errors.

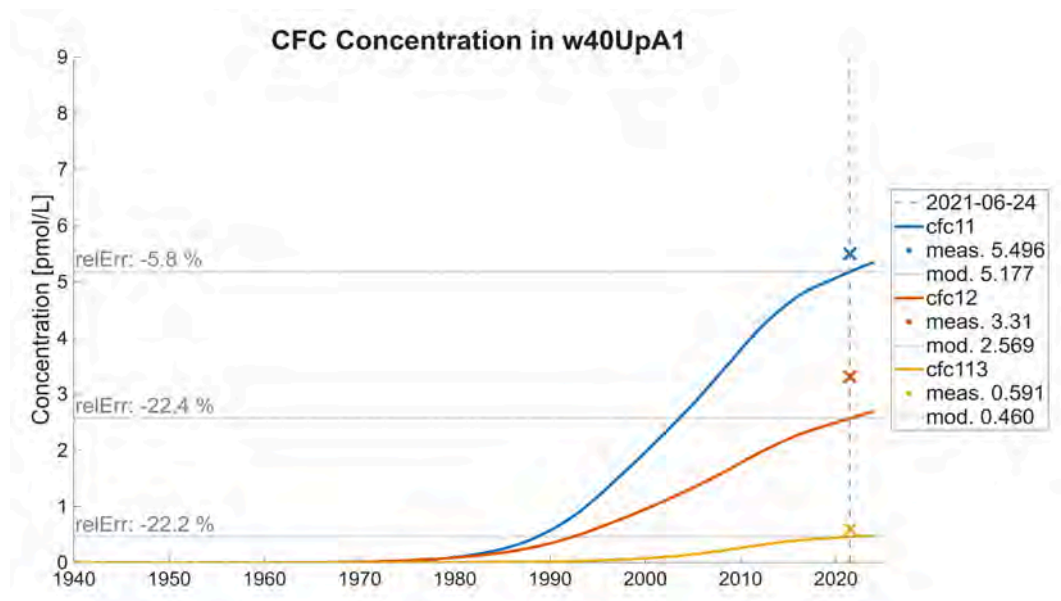


Figure 28: Time series of simulated CFC concentrations at well w40UpA1. Flux-averaged concentrations shown as solid lines and coloured by CFC species. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations and their relative errors.

A comparison of the well samples w43 and w40UpA1 in Figure 27 and Figure 28 reveals contrasting simulated CFC trajectories, despite similar relative errors to the measurements. For w43, the simulated CFC-11 reaches its peak close to the sampling date, while CFC-12 and CFC-113 continue to slightly increase after the sampling date. For w40UpA1, the simulated CFCs increase much later than for w43 and continue to strongly increase after the sampling date. However, both wells simulate CFC concentrations close to the measurements for CFC-11. Notably, the measured concentrations in w43 and w40UpA1 are similar.

4.3.4 Well Performance Summary

To analyse model limitations and strengths across the well samples, the simulated CFC concentrations in the groundwater wells are compared against the measurements. Here, performance is assessed as the ability to replicate a single measurement in a groundwater well and is evaluated as the relative error between modelled and measured CFC concentrations (see Equation 12).

In Table 2 below, the relative error for each well and each CFC species are displayed. The well samples are ranked by their combined absolute relative errors

of the three CFC species. The simulated and measured CFC concentrations are given in [App. Tab. 9](#).

Table 2: Relative errors of modelled groundwater CFC concentrations for all wells within the domain. Ranks computed from the combined absolute relative errors and sorted in increasing order from low to high ranks. Wells are grouped by the depth to their midpoint.

Name	Rel. err. CFC-11	Rel. err. CFC-12	Rel. err. CFC-113	Rank	Group
w37UpA1	0.055	0.034	0.032	2	shallow
w39UpA1	0.129	0.022	0.066	4	shallow
w41A1	0.157	0.023	0.042	4	intermediate
w39UpA2	0.081	0.063	0.079	5	shallow
w43	0.06	0.042	0.72	5	intermediate
w201	0.113	0.099	0.197	6	intermediate
w42UpA1	0.157	0.11	0.095	7	shallow
w40UpA1	-0.064	-0.231	-0.23	7	intermediate
w38UpA1	-0.052	1.277	6.161	11	deep
w39LowA1	-0.394	-0.538	-0.584	11	deep
w42UpB1	0.166	0.13	8.305	12	shallow
w39LowB1	-0.305	-0.378	3.646	12	deep
w39UpB1	0.314	0.284	10.309	13	shallow
w38LowA1	-0.943	-0.944	-0.838	13	deep
w41B2	2.894	0.122	3.698	13	deep
w37LowA1	-1	-1	-1	14	deep
w302	1.781	1.694	1.529	15	intermediate

In [Table 2](#) above, the shallow well w37UpA1 has the lowest rank, while the deep well w37LowA1 has the second highest. Both intermediate wells w43 and w40UpA1 are ranked in the upper half. With the exception of w42UpB1, w39UpB1 and w302, the shallow and intermediate wells always rank above the deep wells. Notably, the B well samples always perform worse than their corresponding A well samples.

To examine possible connections between well performance and the way each well is implemented in the model, the relative errors are compared against a set of well attributes (see [Appendix 4f](#)). The attributes are: the depth to the midpoint of the well, the difference between modelled water table and measured water table during sampling, the distance to the stream, and the date the groundwater sample was taken. Of these attributes, only the depth to the midpoint of the well shows a pronounced correlation with the relative error, consistent across all three CFC species. This highlights the importance of well depth for model performance.

In [Figure 29](#) below, the flux-averaged transit times of the well samples are scattered against the depth to their midpoint and are coloured by the relative error between simulation and measurement for each CFC species and the mean of all three species (see [App. Tab. 10](#)).

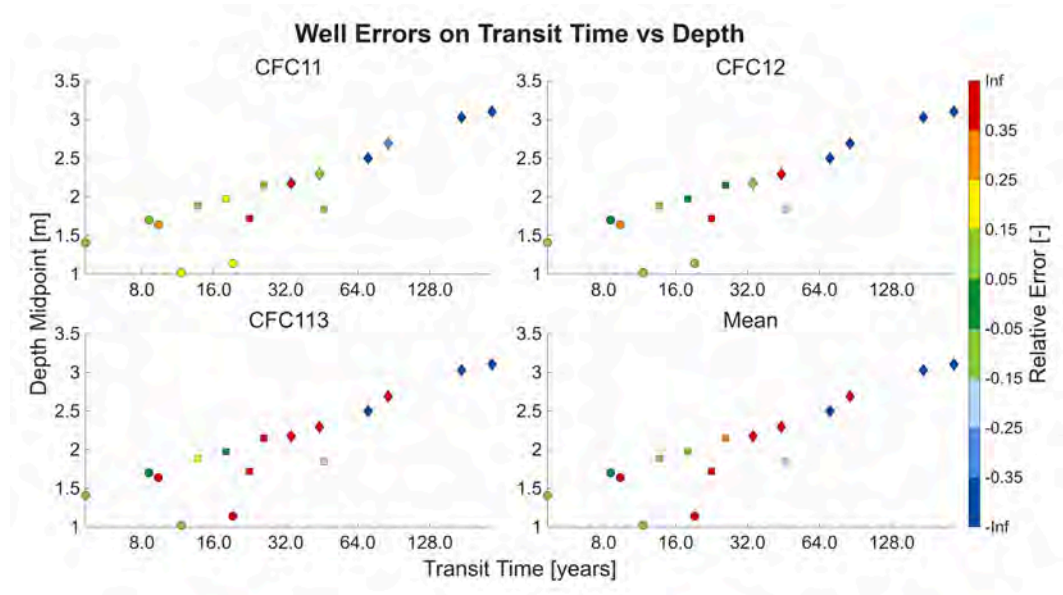


Figure 29: Flux-averaged transit time (x-axis, logarithmic) scattered against depth to the midpoint (y-axis) for the well samples. Points are coloured by their relative error for each CFC species, and by the mean relative error of all three species (bottom right). Reds indicate simulated concentrations higher than measured, while blues indicate simulated concentrations lower than measured. Well markers are circles for shallow wells, squares for intermediate wells and diamonds for deep wells.

Many wells are close or inside the $\pm 15\%$ error range for CFC-11 and CFC-12, displaying good to acceptable performance for the shallow and intermediate wells (comp. [Table 2](#) until rank 7). However, for CFC-113 the relative errors are overall higher, with only a few wells of good performance. Consequently, low errors are

not consistent across all three CFC species for a given well sample. Striking in Figure 29 is the poor performance of the deep wells, with relative error outside the $\pm 35\%$ error range.

The estimated ages (i.e. flux-averaged transit times) are compared to previous results from Kolbe and Bishop (2024) in Figure 30 below. Therein, the piston flow model was used to estimate groundwater ages from measured CFC concentrations in groundwater samples.

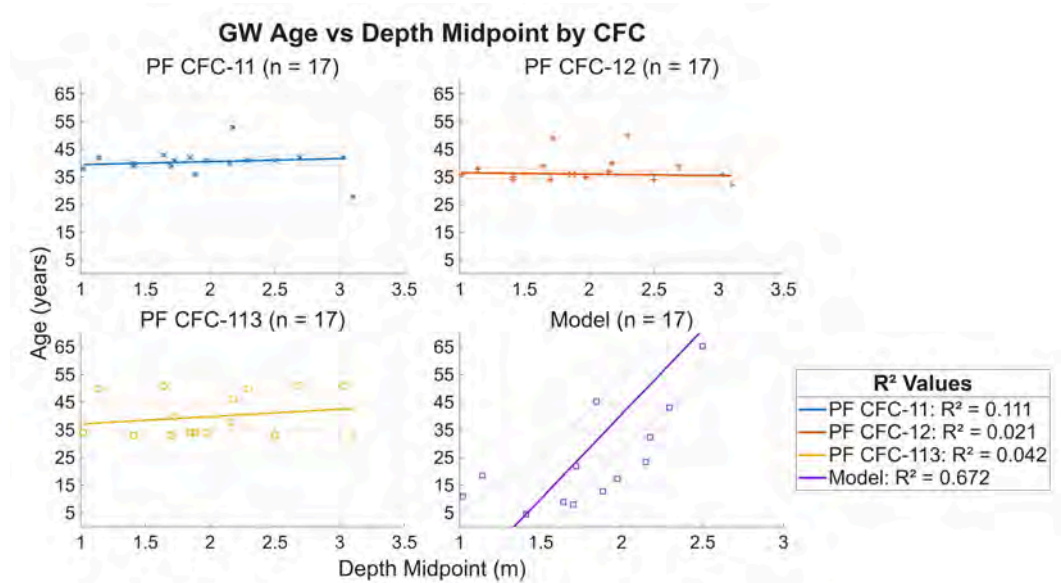


Figure 30: Estimated groundwater ages with a piston flow model (PF) from Kolbe and Bishop (2024) for each CFC species and the flux-averaged transit time estimated here (Model), against the depth to the midpoint of the sampling well. Linear regression lines in solid, 95% confidence intervals dotted, R^2 values of the linear regressions to the data points.

The groundwater age estimates of the piston flow model (Kolbe and Bishop, 2024) plotted against the sampling depth reveal low to no correlation (top left, top right and bottom left in Figure 30). In contrast, the model applied here produces a strong increase in age with depth (bottom right in Figure 30). The groundwater age pattern found here is also displayed in Figure 13, with ages of one year or younger at the groundwater table. The underlying data points of Figure 30 are shown in App. Tab. 11. Kolbe and Bishop (2024) also gave age estimates for groundwater wells outside the C2 catchment. This full sample record of estimated groundwater ages plotted against their sampling depth is given in App. Fig. 42.

4.4 Stream Results

The pathlines to the C2 stream are computed forward, i.e. from surface to stream (see Section 3.2). Below in Figure 31, the results for the assumed steady-state condition are shown. Particles are seeded at the surface and only a selection of pathlines from all seeded particles is shown.

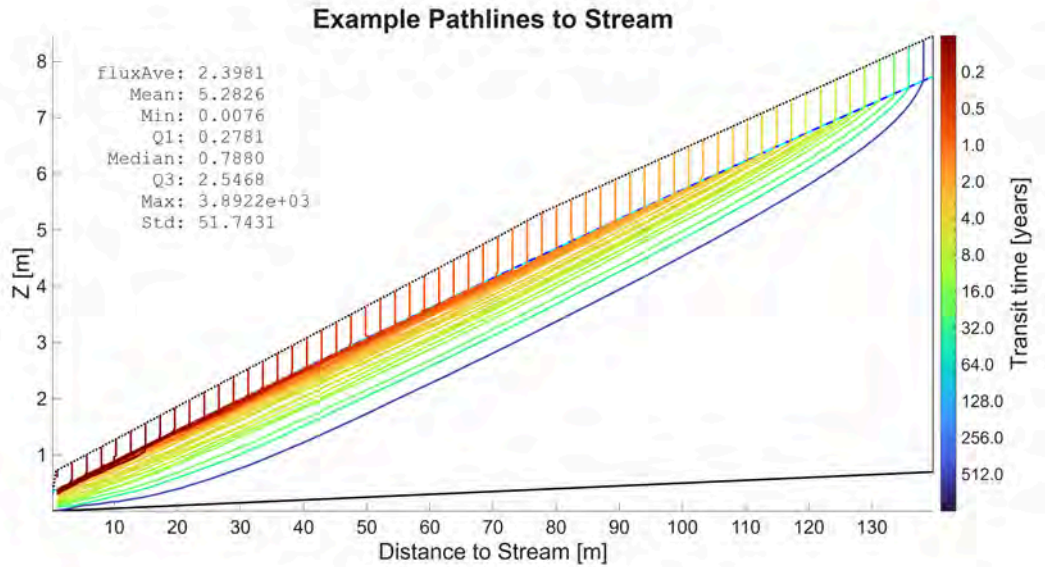


Figure 31: Pathlines computed forward from the surface to the stream with 10,000 particles, seeded uniformly across the surface and coloured by their transit time. The surface is a black dotted line, bottom and right no-flow boundaries are black solid lines, the water table is a blue line and the capillary fringe is a dashed light blue line. Summary statistics are given in the inset, in years. The “fluxAve” is the flux-averaged mean of the particle-wise transit times.

Striking is the absence of deeper pathlines in Figure 31. Deep pathlines are exclusively found for particles seeded very close (≤ 1 m) to the right no-flow boundary. Noteworthy, the colouring of the pathlines reveals a shallow transmissive layer. Particles with a transit time ≤ 4 years travel exclusively in this shallow zone just beneath the capillary fringe. This is emphasized in Figure 32, where particles are scattered by their starting position against the average travel depth of their pathlines and particles are coloured again by their transit time.

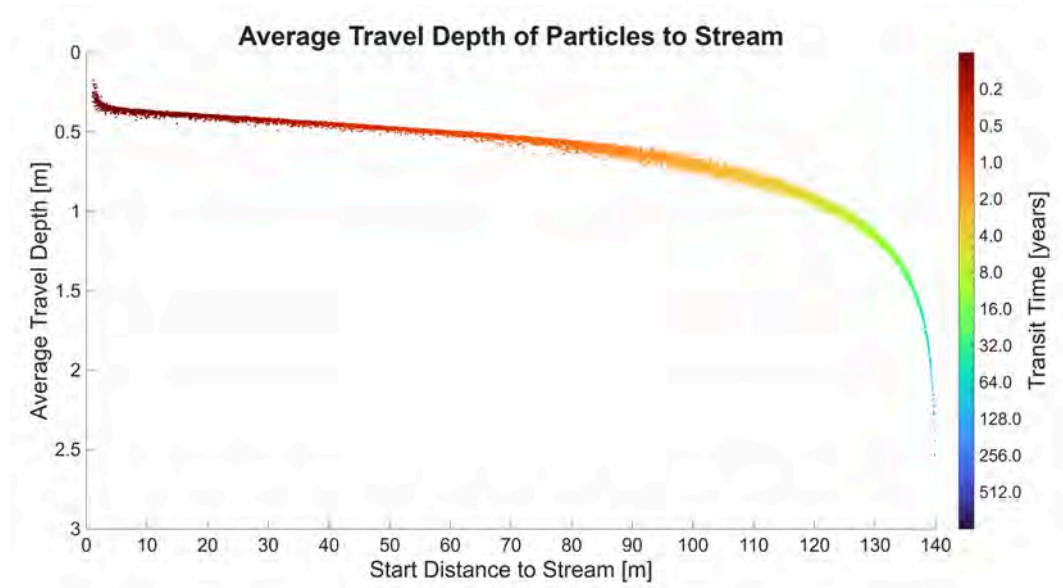


Figure 32: Particles ($n=10,000$) are plotted by their start distance to the stream (x-axis) and their average travel depth beneath the surface (y-axis), and coloured by their transit time. Particles are seeded uniformly along the surface, accordingly, a start distance of 70 m on the x-axis represents 50 % of the particles, and 105 m represents 75 %

Striking in Figure 32 is the plateau of particles from 0–100 m and an average travel depth of 0.6–0.8 m. This is followed by a rapid decline in average travel depth and transit times, with increasing distance to the stream. Clearly visualizing the shallow transmissive layer pointed out above.

In Figure 33 below, the transit times of the 10,000 particles are resampled by their flux weights and binned (see Section 3.5). The Lognormal distribution is displayed with the histogram, as it provides the best fit under Akaike’s Information Criterion, with a difference of $\Delta \text{AIC}=745$ between the best and second best fit. (see App. Tab. 15). The distribution of resampled transit times is right-skewed and bin heights declining rapidly with increasing transit time. Notably, the quantiles of the resampled transit time distribution in Figure 33 differ from those of the raw particle-wise transit times in Figure 31.

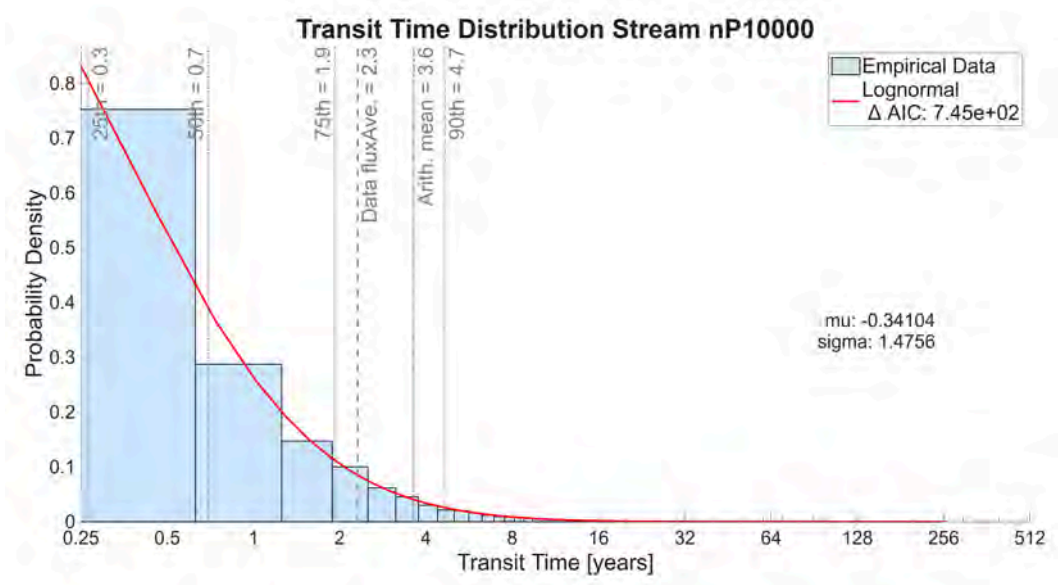


Figure 33: Estimated transit time distribution for the stream with 10,000 particles. Resampled transit time data as bars ($n=400$). Best fitting distribution under Akaike's Information Criterion in red, Δ AIC is the difference between the best and second best fit. Parameters of the fitted distribution inside the plot. Flux average transit time in gray dashed. The arithmetic mean (which neglects flux weights) in gray dash-dotted. Percentiles in gray dotted.

From the transit times of the 10,000 particles the ^{18}O signal in the stream is derived (see Section 3.6). In Figure 34 below, the time series of simulated and measured ^{18}O in the stream is displayed. The Goodness-of-Fit between simulation and measurements is estimated with the NSE and given inside the figure. Measurements of ^{18}O in the stream are only available for the time period shown.

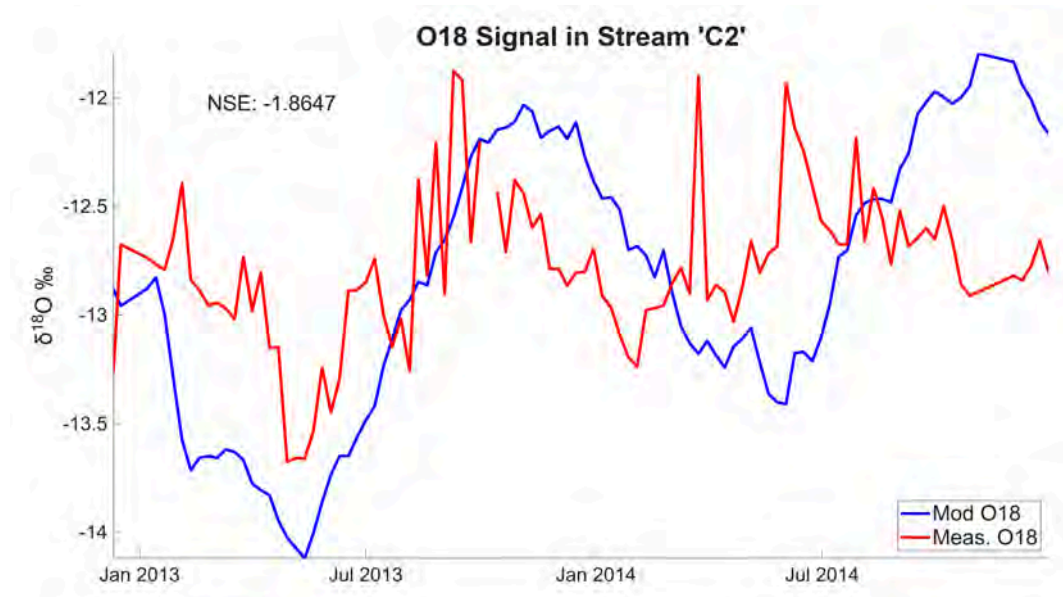


Figure 34: Modelled and measured ^{18}O signal in the stream. Measurements available only for shown time period. Nash-Sutcliffe-Efficiency between modelled and measured data given inside the figure.

Obvious from Figure 34 is the poor representation of measurements by the simulation. This is confirmed by the $\text{NSE} > 1$. Noteworthy though, the broader pattern of measured ^{18}O in the stream, seems to be resembled by the model. Referring to the general periodicity of the measured ^{18}O . However, the detail is clearly not represented.

As for the ^{18}O signal in stream, the CFC concentrations in the stream are derived from the computed transit times, and are displayed in Figure 35 below. The stream was sampled once and the measured values are highlighted as crossmarks. The stream sample was taken on the 2023-05-15, which is highlighted as a vertical dashed line. Simulated concentrations at the sampling date are highlighted as horizontal dashed lines. The relative errors between simulated concentrations and measured ones are given in the figure. A relative error below 5 % is highlighted in green.

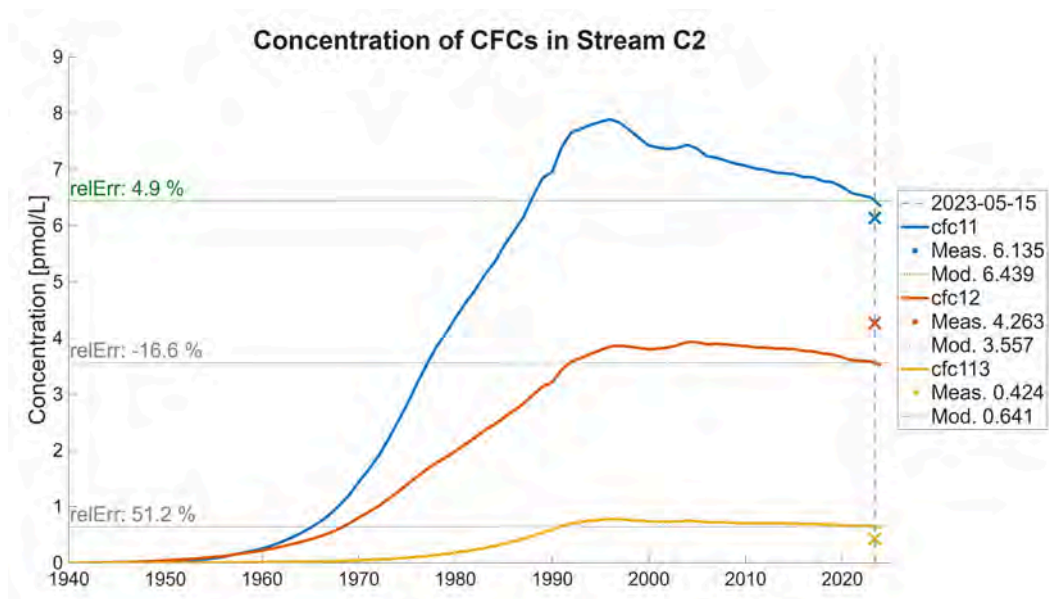


Figure 35: Time series of simulated CFC concentrations in stream C2. Concentrations as flux averages; shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations and their relative errors.

The simulated time series of CFC concentrations in the stream resembles the shape of the estimated recharge concentrations (comp. Figure 11). In Figure 35, all three CFC compounds reach their peak before the year 2000, followed by a slow decline in concentrations, which is most rapid for CFC-11. Striking is the very low relative error for CFC-11, while the errors increase for CFC-12 and CFC-113. Noteworthy, the measured concentrations of CFC-11 and CFC-12 differ by less than observed for the well samples (comp. Figure 25 until Figure 27).

Stream samples have potentially partially or fully equilibrated with the atmosphere, because the stream is in contact with the atmosphere. Therefore, the estimated recharge concentrations, which represent the solubility equilibrium between atmosphere and water (see Section 3.1), are compared to the measured concentrations in stream.

Due to the dynamic flow system of a stream, it is not clear to which temperature the equilibrium progressed. Therefore, air and soil temperature equilibrium concentrations will be presented below.

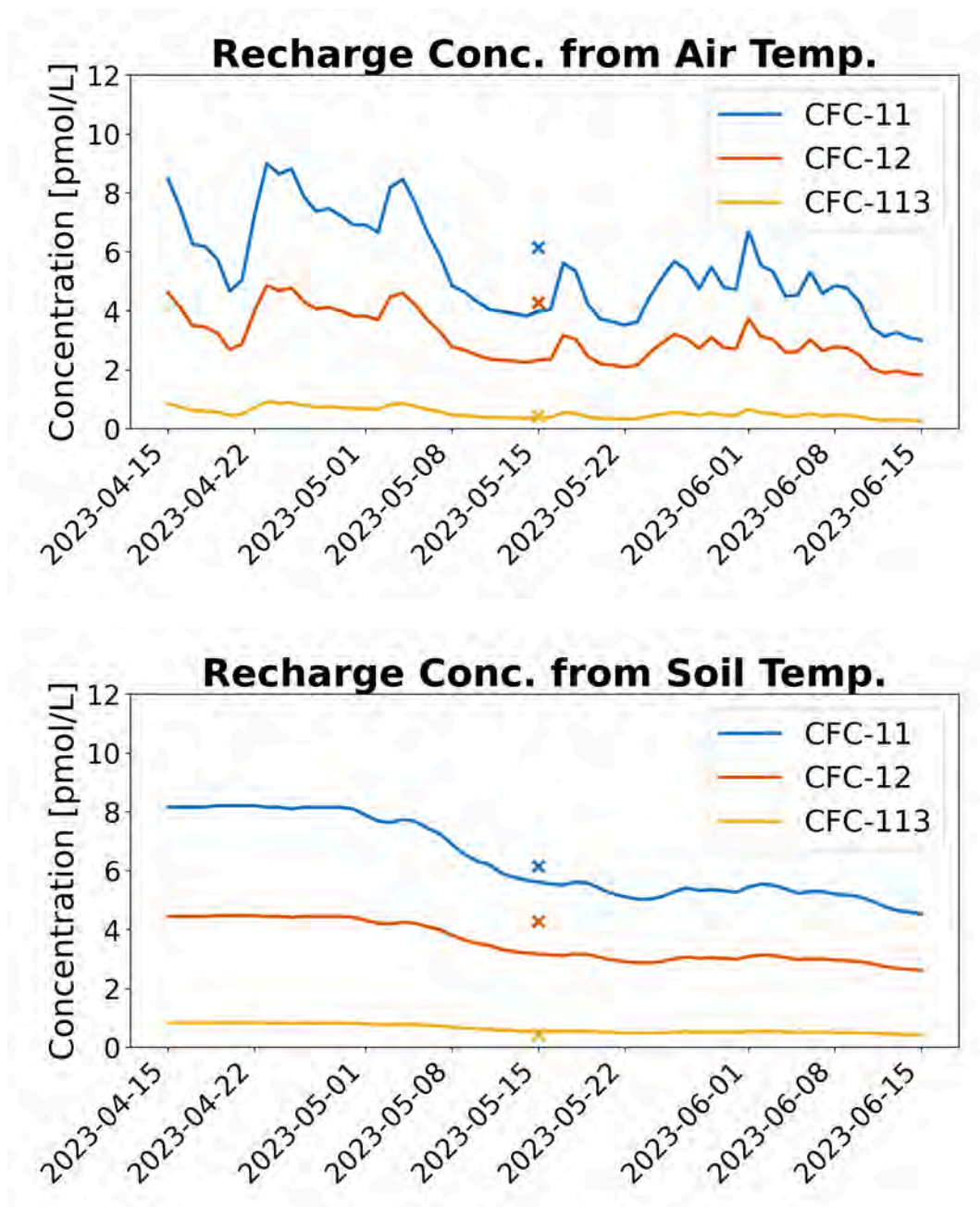


Figure 36: Equilibrium concentrations under local air temperature (upper figure) and soil temperature (lower figure). Measured CFC concentrations in the stream C2 as crossmarks. Samples were taken on the 2023-05-15 (Kolbe and Bishop, 2024). Time series is displayed from one month before until on month after the sampling date.

Striking in Figure 36 is the smoothing effect of soil temperature on the equilibrium concentrations. Notably, the measured concentrations are visibly closer to the soil temperature equilibrium concentrations than for the air temperature. However, the measured CFC-11 and CFC-12 concentrations are above the estimated equilib-

rium concentrations at the sampling time, for both are and soil temperature. For stream C2 only one sample with measured concentrations was available.

5 Discussion

The research presented examines two major assumptions. One is whether the recharge and transport of the CFCs in the groundwater behave as expected; and the second is the validity of the hydrological model in accordance with the observed CFC concentrations and ^{18}O signal. Both assumptions are strongly intertwined in the results presented, but an effort is made to separate their influences and comment on the validity of the assumptions.

5.1 Assumption on Recharge Concentrations and Conservative Transport of CFCs

The process of CFCs reaching the groundwater is described by a conceptual model in its own right. The main assumption is, that recharging water from the unsaturated zone is in equilibrium with the soil air, and for shallow aquifers that the concentrations of CFCs in the soil air are equal to the concentrations of the atmosphere. (Kazemi, 2004; IAEA, 2006). In this study, the equilibrium concentrations and therefore the concentrations of the CFCs in recharging groundwater are determined with the soil temperature at 20 cm depth to account for the insulating effect of the snow cover at the site. Generally accepted guidelines also suggest to use the long-term mean annual air temperature (because temperature at recharge time is often unknown), while also highlight the potential influences of a snow cover (IAEA, 2006).

Due to the single steady-state of the model, which reflects the long-term annual median of hydrological effective rainfall (see Section 2.2), yearly recharge concentrations are most reasonable. However, daily soil temperature observations allow estimating recharge concentrations on a much finer temporal scale, revealing the highly dynamic input of CFCs during the course of a year (see Figure 11). Daily estimates of CFC recharge concentrations were aggregated to yearly estimates, with possible errors (see Section 4.1). Noteworthy, already with monthly values, potential aggregation errors could be avoided (see Section 4.1).

Significant differences between the aggregation methods for yearly average recharge concentrations were found (see Figure 10). The recharge concentrations estimated with the long-term annual mean air temperature (1.8 °C, see Section 2.1.3) are similar to the yearly median concentrations. This similarity may be a coincidence, but it highlights the importance of the aggregation method and

of the seasonal snow cover at the site. The median represents the most common conditions and, for a long-term steady-state model, this could be more robust than the mean. However, the common but low soil temperatures occur during the snow cover period (i.e. December–March, [App. Fig. 39](#)), when groundwater recharge is negligible (see [Figure 4](#), [Figure 5](#)). Therefore, the median does not represent the conditions under which recharge actually occurs. This is confirmed by the volume-weighted averages, which weight by recharge and are similar to the yearly mean rather than the median. Since the mean also requires less input data than the volume-weighted average, it was chosen here as the aggregation method.

Another potential source of error is the flow system, i.e. the dominance of shallow flowpaths. For such a shallow flow system, contact with the soil air along the flowpaths can be assumed. Consequently, potential effects of equilibration could influence CFC concentrations as water moves through the subsurface. The short transit times of these shallow flowpaths (≤ 1 year, see [Figure 31](#)) emphasize this possibility. Over the course of a year, changes in equilibrium concentration are large due to intra-annual temperature variations (see [Figure 11](#)).

The modelled CFC concentrations in the stream (see [Figure 35](#)) and in the shallow and intermediate groundwater wells (see [Table 2](#), [Figure 29](#)) show relative errors of $\approx 15\%$ or lower, with few exceptions. This good agreement between simulated and measured concentrations for CFC-11 and CFC-12 suggests that both are behaving as reasonably conservative tracers. This conclusion is most robust for the shared screening depth interval of shallow and intermediate wells, i.e. 0.52 m–2.89 m beneath the surface (comp. [App. Tab. 8](#)).

However, with only a single measurement available, such a presumably good approximation for most wells might not be sufficient to validate the model application. This limitation is especially important for the shallow and intermediate wells, which can show slowly declining or stagnating CFC concentrations after the CFCs peak (see [Appendix 4e](#)). This shows that CFC tracers are most reliable for water that was recharged approximately between 1960 and 1990, i.e. during the steep increase in atmospheric CFC concentrations (see [Figure 7](#)).

Interestingly, low errors between modelled and measured CFC concentrations are not consistently found for all three CFCs inside a well. For most wells the errors for CFC-11 and CFC-12 are similar (comp. [Table 2](#), e.g. w43, w38UpA1, w42UpB1, w41B2). Notably, measured CFC-113 concentrations can approach the quantification limit of 0.1 pmol L^{-1} , for which errors of up to $\pm 20\%$ are possible ([Labasque et](#)

al., 2014; Kolbe and Bishop, 2024). Coinciding results of CFC-11 and CFC-12 are in accordance with the conclusions from the literature, suggesting both compounds as more reliable than CFC-113 (Labasque *et al.*, 2014; Kolbe *et al.*, 2020).

Contradicting the good agreement of simulation and measurement in the shallow groundwater wells, the simulated CFC concentrations in the deep wells (see Table 2) are consistently too low, with large errors. This is caused by the long transit times to the deeper wells in the model, which means that water in the wells is too old to have the observed CFC concentrations.

When dealing with such long transit times (more than a decade), diffusion is likely to have some effect. In the deeper, low- K_s region of the model domain, convection and dispersion diminish. There, diffusion could in principle drive CFC concentrations further downward than what is predicted by flow and dispersion alone. This raises the remote possibility that the modelled deeper transit times are in fact reasonable approximations, but that the absence of diffusion in the model prevents CFCs from reaching deeper groundwater ahead of the corresponding water ages. However, without site-specific constraints on diffusion, this remains a speculative alternative interpretation.

In conclusion, the model predicts CFC concentrations in accordance with the assumptions as approximately correct until a depth of about three meters below the surface (comp. Figure 14). This suggests that below this depth, water is moving too slowly in the model, with transit times too long, yielding very low CFC concentrations. This has been suspected, because K_s gets much lower than expected using the exponential K_s decline Bishop (2026). Porosity assumptions are also a model parameter and are tied to the K_s assumptions. This points to the model calibration as a bigger influence than the assumptions about how CFCs behave as tracers in the groundwater. However, errors in the flow model, as well as the fact that atmospheric CFC concentrations have declined only slowly over the past three decades, imply that small errors in the CFC assumptions are likely missed here.

Important is, that the model parameters of the steady-state solution were not subject to any calibration on CFC concentrations, highlighting potential for improvements. Nevertheless, the good approximation of CFCs in the shallow and intermediate wells, modelled with the parameters used in Ameli *et al.* (2021), suggests their applicability to the aims of this study.

5.2 Flow System and Model Limitations

The second major assumption, next to the functioning of the CFCs, is the realistic representation of the flow system in the groundwater of the hillslope by the model. The parameters applied here have been used previously in [Ameli *et al.* \(2021\)](#), where a good approximation of the flow system in accordance with ^{18}O data was found for the quasi-steady-state form of the model applied here. The earlier testing of the hillslope using ^{18}O confirmed the importance of transmissivity feedback, including the rapid lateral movement of water in the shallow groundwater zone ([Ameli, McDonnell and Bishop, 2016](#); [Ameli *et al.*, 2016](#); [Bishop *et al.*, 2024](#)). This is consistent with the reasonable fit between simulated and measured CFCs for the shallow and intermediate wells (see [Table 2](#), [Figure 29](#)). Furthermore, the lack of parameter calibration in this study supports the results of the shallow flow system modelled here.

However, the shallow wells with “young” water ages of less than a decade (see [App. Tab. 10](#)) test the flow model’s performance only in the shallow groundwater zone. The intermediate and most of all the deep wells provided an opportunity to better constrain the “old” water ages, as these ages might be old enough to represent water recharge during the period of rapidly increasing atmospheric CFC concentrations (see [Figure 8](#)). The large errors in the simulated concentrations of CFCs in the deep wells (where concentrations are predicted to be lower than observations) suggest that the hydrological model is not representing the flow system in the deep groundwater zone (see [Figure 29](#)). Consequently, the CFC observations can provide an opportunity to improve the model’s representation of deeper flowpaths.

A key formulation in the model is the continuous exponential decline in K_s until the bottom no-flow boundary (see [Equation 1](#)). This is known to not be representative of reality ([Bishop, 2026](#)). In consequence of this continued exponential decline until the bottom of the flow domain, values for K_s are too low, and transit times that are too large, yielding low CFC concentrations. Similar to K_s the porosity θ_s is also represented by a continuous exponential decline until the bottom no-flow boundary (see [Equation 2](#)). As for K_s , this results in values lower than expected for Swedish till soils in the deep soil ([Bishop, 2026](#)). However, increasing θ_s would lead to lower pore water velocities and consequently longer transit times. While porosity could be represented more accurately, this will likely not explain the CFC concentrations being too low in the deeper soil.

Deep wells also receive recharging water particles from only a very small surface strip next to the right no-flow boundary (see [Appendix 4c](#)). This may be unrealistic, but it is assumed to be an artifact of the 2-D steady-state model. Deep pathlines are forced to start very close the right no-flow boundary to allow the representation of the shallow transmissive layer. Comparing deep wells to shallow wells (see [Appendix 4c](#)), highlights the difference in contributing surface length, with the representation for the shallow wells appearing more realistic. Nevertheless, assuming that the representation of deep pathlines here approximates reality, we can suggest that the recharge of deep groundwater happens only from close to the water divide. This rather little amount of water received on the small surface, when compared to the rest of the hillslope, would then supply the whole deep groundwater domain. In consequence of the little recharge, turnover is slow, transit times are long and groundwater ages are old, fitting into the general description of the double paradox described in [Kirchner \(2003\)](#).

An additional aspect can be recharging surface areas which lay further upstream (i.e. outside the 2-D representation of the hillslope transect) and can contribute recharge longitudinally to the stream for deeper groundwater. This is not included in the 2-D hillslope model. Concluding, that the deeper flowpaths of the 2-D model are likely not realistic, allows to consider a 3-D flow system in the deeper groundwater. However, the validity of that evidence depends on the changes to the deeper flowpaths for transient conditions. An improvement to the single steady-state employed here, would be the application of the 2-D quasi-steady-state of [Ameli *et al.* \(2021\)](#), which was not available for this study.

Another influence on the pathlines is the chosen steady-state condition, i.e. the recharge amount of water R (see [Section 3.3](#)). Although not formally tested and unreported here, exploratory runs with the single steady-state suggest that the structure of the deeper flowpaths is rather consistent, while the transit times along these flowpaths can significantly increase or decrease for opposite changes in R . However, this still lacks the information of a quasi-steady-state model, in which travelling particles and derived pathlines are computed from successively updated continuous Darcy flux fields. Importantly, the single steady-state is a serious limitation given the strong intra-annual variations in R . Here, the overall median of R was chosen as it better represents monthly values of R . Consequently, it was judged to better reflect the long-term steady-state of the flow system in the hillslope. The quasi-steady-state approach of [Ameli *et al.* \(2021\)](#) would overcome the difficulties in averaging R to a single steady-state condition.

One further limitation of the model is the restricted domain, mainly the bottom no-flow boundary. While this is a results of prior model optimization (Ameli *et al.*, 2016; Ameli *et al.*, 2021), it restricts the groundwater wells to 17 of originally 24 wells (see Table 1, App. Fig. 41). The wells outside either do not match with the water table (i.e. their screening top would be in the unsaturated zone in the model, where as for the sample the well started at or beneath the water table), or are deeper than the bottom no-flow boundary. During the setup of the well positions in the model domain, it was found that the placement (i.e. distance from the stream) is an important parameter for the simulated CFCs, because the distance from the stream determines the absolute depth of the well in the model domain, whereas the relative depth below the surface is known. This can strongly influences the transit times to the well and therefore the simulated concentrations of CFCs. To place the wells, groundwater flowpaths from the wells to the stream were delineated by topographic analysis (see Section 2.1). This differs from the approach in Kolbe *et al.* (2020) and resulted in increasing differences with increasing distance to the stream (see App. Tab. 5).

The comparison of the errors between simulated and measured CFC concentrations in the wells against their attributes (e.g. distance to the stream) did not reveal consistent trends for all attributes, except for relative errors scattered against the mid depth of the wells (see App. Fig. 102 until App. Fig. 104). There a strong negative trend was found, indicating the sensitivity of the model results to the derived depth. Nevertheless, this is an expected parameter of sensitivity, because deeper wells have increasing contributions of particles with drastically longer transit times due to the exponential decline in K_s . Noteworthy, for CFC-11 and CFC-12 the spread of relative errors against the well attributes is already visually less than for CFC-113 (see App. Fig. 102 until App. Fig. 104). As pointed out above, this is supported by the conclusions from literature suggesting CFC-11 and CFC-12 as more reliable tracers (Labasque *et al.*, 2014; Kolbe *et al.*, 2020).

In conclusion, the model provides a realistic representation of the shallower and intermediate flowpaths corresponding to the established process understanding of transmissivity feedback at the site. In deeper wells, the model predicts concentrations much lower than what was observed, suggesting that K_s declines too rapidly with depth. To address this problem, a revision of the model needs to be made to allow for a different representation of the relationship between depth and K_s . One possibility is a different mathematical description of the K_s to depth relationship, e.g. an asymptote (Bishop, 2026). Alternatively, one could apply a

piecewise solution, adopting a different formulation below a threshold depth of 1.5 or 2 m depth (Bishop, 2026).

5.3 Groundwater Transit Times

From the conclusions made above, transit times for shallower and intermediate wells are likely an acceptable representation of reality. Transit times to deep wells are likely too long, unless there are severe effects of diffusion, which is not included in the model here. Comparing the flux-averaged transit times (i.e. ages) obtained from the pathlines for the well samples (see Section 4.3) to the age estimates in Kolbe and Bishop (2024) reveals contrasting differences. However, a well by well comparison is not pursued here, due to differences in computation (e.g. distance to stream) and model formulation in Kolbe *et al.* (2020).

For all wells inside the model domain Kolbe and Bishop (2024) estimated groundwater ages in the range of 30–50 years. The ages computed here differ greatly to these estimates (see Figure 30 and App. Tab. 11). Shallow wells feature flux-averaged transit times from 4.5 years to 19.2 years, intermediate wells from 13.5 years to 46.2 years and deep wells from 31.7 years to 215.5 years (see App. Tab. 10, Figure 29). Note also, that there is a strongly skewed transit time distribution for the groundwater age in each well. This contradicts the existence of the lagged rejuvenation phenomenon suggested in Kolbe *et al.* (2020).

The results presented here give rise to an alternative interpretation, embedded in the concept of transmissivity feedback. Groundwater is constantly rejuvenated, but much of it moves laterally, out of the system in a few years. Then just a little deeper, the water moves already much more slowly, supporting a steep age stratification (see Figure 13). The shallow lateral flow is enabled by the exponentially declining K_s with depth. This also produces the entangled tracer signal, because the water age in the shallow and intermediate wells is “young” enough to reflect the decline in atmospheric CFC concentrations.

The contradiction of the of lagged rejuvenation phenomenon is supported by Jutebring Sterte (2026), who presented transit time estimates for the intermediate wells w43 and w302. However for both, ages below 10 years were given, conflicting with the results of this study and Kolbe and Bishop (2024).

In conclusion, the transit times obtained for the shallow and intermediate wells appear to be representative of reality. This conflicts with the ages obtained by Kolbe and Bishop (2024), who estimate ages using the piston flow model, an

approach that assumes a single, well-defined transit time. The results of this work suggest that estimating transit time distributions for these wells (see [Appendix 4d](#)) can yield a more applicable representation of groundwater ages.

The Inverse Gaussian distribution consistently provides the best fit to the age distributions predicted by the model and, by its definition, provides the same flux-averaged transit time as the model. However, the Inverse Gaussian distribution often does not visually represent the modelled distribution well (see [Appendix 4d](#)). While this could not be analysed further here, it suggests that the compared parametric functions do not capture the actual distribution of water ages.

This shortcoming is further highlighted by the limited information the flux-averaged transit time to a well provides. The non-linear input of CFCs into the groundwater prevents a direct relation of average transit time to CFC concentration for wells which include particles that carry no CFC signal (see [App. Tab. 14](#)). This mostly applies to intermediate and deep wells, which show more skewness and heavier tails in their transit time distributions than the shallow wells. Therefore, additional and more complex distribution functions need to be examined that can better represent the particle-wise transit times and could then be applied to estimate particle-wise concentrations. This reinforces the conclusion that the true age composition at the wells is more complex than a single parametric function, including piston flow, can capture.

Overall, the results indicate that the well samples were not obtained from individual pathlines, as assumed under the piston flow model. Rather, samples are always a composite of water particles or volumes of different ages that contribute differently to the measurements. This is particularly evident in the skewness of the modelled transit times of the pathlines (see [Section 4.3.1](#), [Section 4.3.2](#)) and in the considerable differences between flux-averaged transit times and mean transit times.

5.4 Stream Transit Times

The capabilities of the flow model for stream estimates have already been demonstrated by [Ameli, McDonnell and Bishop \(2016\)](#), [Ameli *et al.* \(2016\)](#) and [Bishop *et al.* \(2024\)](#). Important is, that pathlines for the stream are computed forward from surface to stream, whereas pathlines for the wells are computed backward from well to the surface. This inherently avoids deep pathlines for the stream, because particles seeded on the surface never result in dense enough numbers

next to the right no-flow boundary to reach the deepest groundwater. In addition, in forward computation intersecting pathlines are very rare as the here applied number of particles do not reach the required densities. However, for backward pathlines from deep wells intersections occur, because all pathlines converge to a small surface strip next to the right no-flow boundary. Due to the applied particle random walk scheme, which includes dispersion, intersections happen. Judging from this, the stream is significantly less sensitive to the particle-random-walk algorithm than the wells, due to the much greater seeding length on the surface and travel domain of the particles.

The model gives a good simulation of the measured CFC concentrations in the stream. Again, as for the shallow wells, the stream reflects the atmospheric CFC concentrations (see [Figure 35](#)). This is in accordance with the majority of water showing short transit times because it travels in the shallow transmissive layer (see [Figure 32](#)), which is expected under the transmissivity feedback mechanism. CFC measurements in a stream are potentially subject to equilibration with the atmosphere. For the stream C2, no strong evidence for this was found, as measurements do not resemble equilibrium concentrations for soil- nor air temperature at the sampling date (see [Figure 36](#)).

It was also attempted to replicate the application of the ^{18}O tracer input data from [Ameli et al. \(2021\)](#) in the steady-state model. The simulation of the ^{18}O signal did not compare to the ^{18}O measurements of the stream (see [Figure 34](#)). While there was seasonal variation, it was offset from the observed ^{18}O signal in the stream. The ^{18}O signal in the stream is suspected to be much more dependent on transient conditions, because the input is subject to great differences between individual events (i.e. weeks in the application here), which also differ by their hydrological condition and flowpaths. This transient behaviour can not be represented by the steady-state model applied here. Consequently, the poor simulation results for ^{18}O are expected. It can be argued that CFC recharge is much more stable, as atmospheric concentrations change slowly compared to ^{18}O input. Furthermore, soil temperature dampens changes in air temperature, and equilibration processes (i.e., dissolving or releasing CFCs) provide an additional temporal buffer and smoothing effect. This can cause CFC concentrations to be much less susceptible to transient conditions than ^{18}O . Therefore, the model may provide a good approximation of CFC concentrations while failing to predict the ^{18}O signal. However, the influence of the strong intra-annual variations in recharge concentrations (see [Figure 9](#))

on groundwater CFC concentrations would need to be examined with a model capable of simulating transient conditions.

The estimated transit time distribution for the stream (see [Figure 33](#)) is supported by the simulation of the CFC concentrations in stream, while the steady-state model fails to provide support from the ^{18}O data. The Lognormal distribution provided the best fit under Akaike's Information Criterion. The flux-averaged mean of the transit time distribution is 2.3 years, while the median is at 0.7 years. [Peralta-Tapia et al. \(2016\)](#) report mean transit times ranging from 0.8 years up to 3.8 years, which covers the estimate given here. [Ameli et al. \(2021\)](#) report a median of long-term mean stream transit time of 3.8 years. While the findings of [Ameli et al. \(2021\)](#); [Bishop et al. \(2024\)](#) support the here modelled spatial distribution of pathlines in the hillslope, the mean transit time estimates are not consistent. The shorter flux-averaged transit times simulated here, may be due to the lack of deeper pathlines, which could be enabled by the quasi-steady-state model of [Ameli et al. \(2021\)](#). Another possibility for the here shorter flux-averaged mean transit time, is the assumed steady-state condition of $R=0.031 \text{ mm day}^{-1}$, which is still higher than the monthly mean recharge condition of six months (i.e. July, August and January to April, see [Figure 4](#)).

In conclusion, the transit time distribution found for the stream is likely a good approximation of reality when considering long-term or steady-state effects. This is corroborated by the good model performance for the shallow and intermediate wells, which are located in the dominant flow zone of the groundwater and contribute most of the recharge to the stream. While this supports transit times up to 30 years, older transit times (i.e., deeper pathlines) are likely not representative of reality. It is important to note that transient influences are not captured by the model or the estimated stream transit time distribution.

6 Conclusion

The strong seasonal variation in CFC recharge concentrations with temperature, in combination with the dominance of spring snowmelt on groundwater recharge, means that there may be a systematic offset in the calculated CFC recharge concentrations. Once recharged, there was no evidence that the CFC-11 and CFC-12 were not behaving as expected (i.e. conservatively). Monthly sampling of shallow groundwater (with residence times under a year), precipitation, throughfall, and stream could provide more insight into the behaviour of CFCs as they recharge the groundwater in relation to air and soil temperatures. Assuming that there is no major error when treating CFCs as conservative, they can provide a useful tracer for water recharged into the catchment between 1960 and ca. 1990. However, the slow decline in atmospheric CFC concentrations since their peak in 1990, results in a CFC signal difficult to interpret without knowledge about the flow system. Consequently, the use of CFCs as tracers is enhanced by using other tracers (e.g., ^{18}O) and models that have been well-tested to describe explicit flowpaths. The steady-state model used here was not disproven for the shallow and intermediate flowpaths, but below about 3 m depth, it appears that waters modelled age is much too old. This is consistent with earlier suspicions, but it is only now, with the CFCs, that these suspicions are corroborated. It would be interesting to see how far recalibrating the model to reduce the rate of K_s decline below 1.5 m depth below the soil surface (and better represent estimated porosity) would affect the results.

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Popular Science Summary

It is of great interest to understand how long water remains underground before it emerges in a stream or a well. One way to investigate this is by measuring tiny amounts of certain chemicals that dissolve into water from the atmosphere. One group of these chemicals are the Chlorofluorocarbons (CFCs). By measuring how much of them remain in the water, it is possible to estimate when that water originally entered the ground. In places where most groundwater comes from melting snow in the spring, reading this chemical signature is not straightforward. The amount of CFCs in the air changes with the seasons, and because most water seeps into the ground during a short period in spring, the chemical signal in the water may be slightly skewed from the yearly average. This study checked whether CFCs remain stable once water has soaked into the ground. The results showed that CFC-11 and CFC-12 do not break down or change in unexpected ways after entering the subsurface. This means CFCs can reliably indicate water that entered the ground roughly between 1960 and 1990. CFC concentrations in the groundwater were predicted with a computer model that simulates how water moves through the ground. For the top three meters, the model matched the CFC-11 and CFC-12 measurements well. But deeper down, the water should be younger than predicted by the model. This mismatch confirms that the model needs to be adjusted specifically in how it describes the ease with which water with which water flows through the deeper soil. Overall the results of this study reconcile CFC measurements from groundwater and stream water with established process understanding of the study site.

Appendix 1

1a Recharge and Discharge Statistics

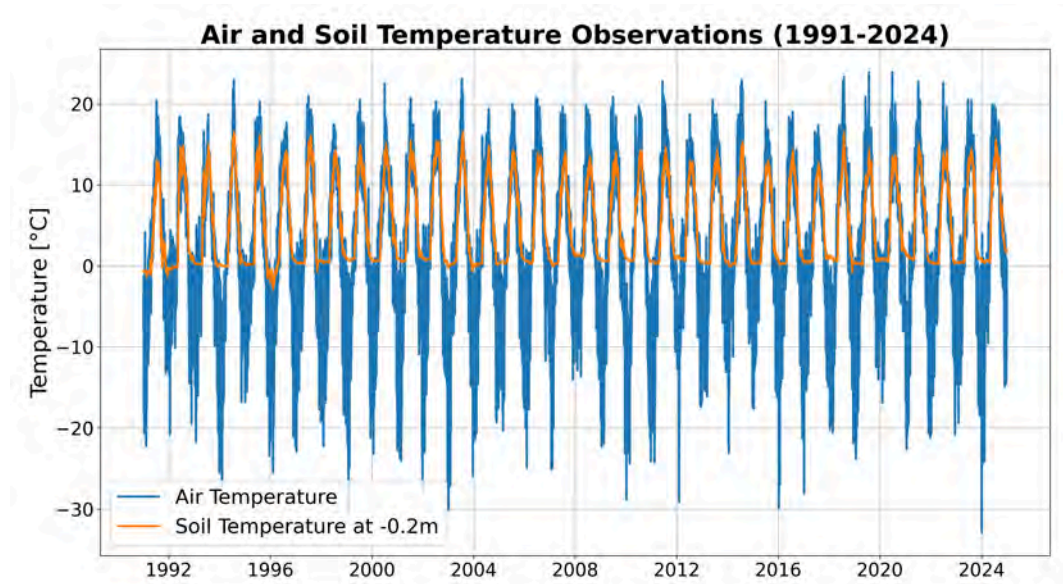
App. Tab. 3: Summary statistics of hydrologically effective rainfall used in [Ameli et al. \(2021\)](#) and obtained from personal correspondence with Ali Ameli.

	Eff. rainfall mm d ⁻¹
count	1925.000000
mean	0.769574
min	0.000000
10%	0.060200
25%	0.131600
50%	0.305800
75%	0.851500
90%	1.893660
max	10.657100
std	1.257654

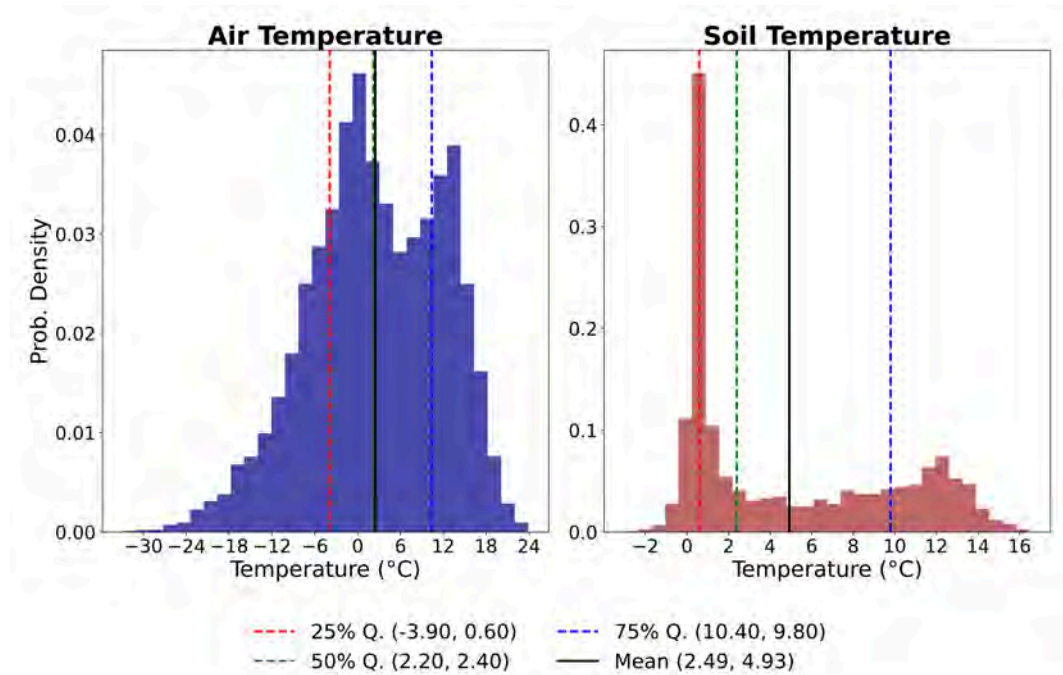
App. Tab. 4: Summary statistics for stream flow observation in the Västrabäcken stream. Catchment area is 0.119 km² Data obtained from the SITES data portal ([Water Balance - Stream Water Level and Discharge from Västrabäcken, Catchment 2, 2005-04-06–2024-09-03, 2024](#)).

	Level [m]	Discharge [m ³ d ⁻¹]
count	5884.000000	5884.000000
mean	0.039182	86.665778
min	-0.018400	0.000000
10%	0.013800	0.000000
25%	0.021600	8.640000
50%	0.032800	34.560000
75%	0.051600	95.040000
90%	0.074000	216.000000
max	0.190700	2384.640000
std	0.026485	159.283038

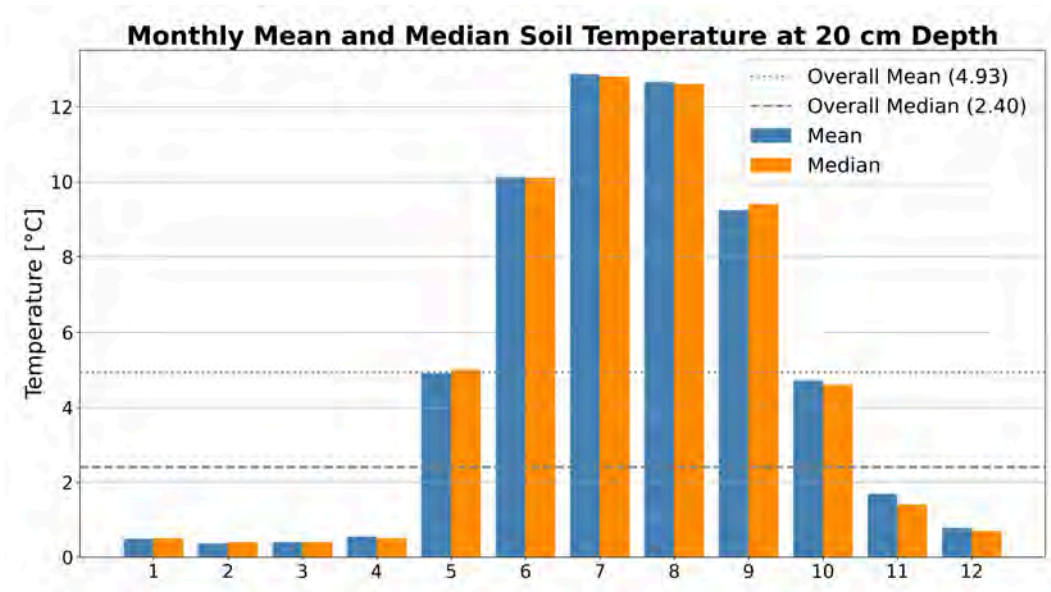
1b Temperature Observations



App. Fig. 37: Observations of air temperature and soil temperature at 20 cm depth in Svartberget from 1991 to 2024 (2025a); (2025b); (2025c).

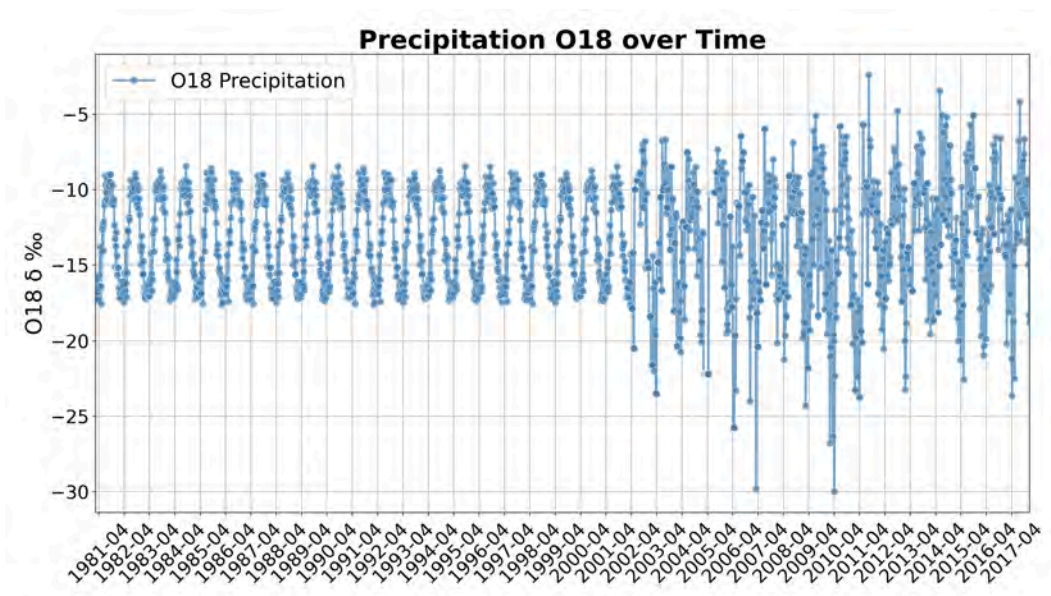


App. Fig. 38: Histograms of air temperature and soil temperature at 20 cm depth in Svartberget from 1991 to 2024 (2025a); (2025b); (2025c). Quantiles as vertical dashed lines colored according to the legend, the mean in solid black. Values in brackets for air and soil temperature, respectively.



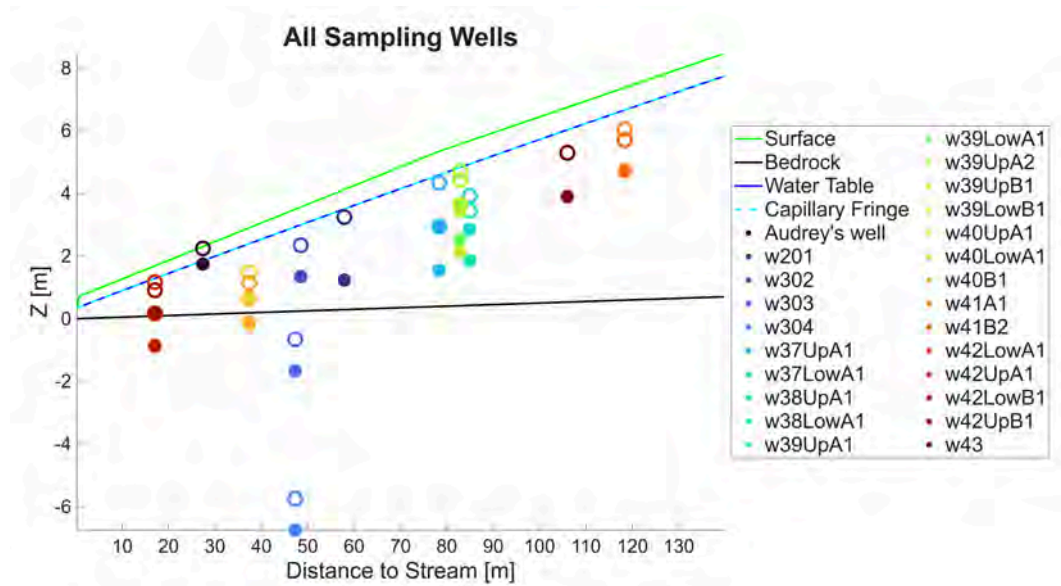
App. Fig. 39: Long-term monthly mean and median of soil temperature observations at 20 cm depth (2025a); (2025b); (2025c).

1c ^{18}O Input Data

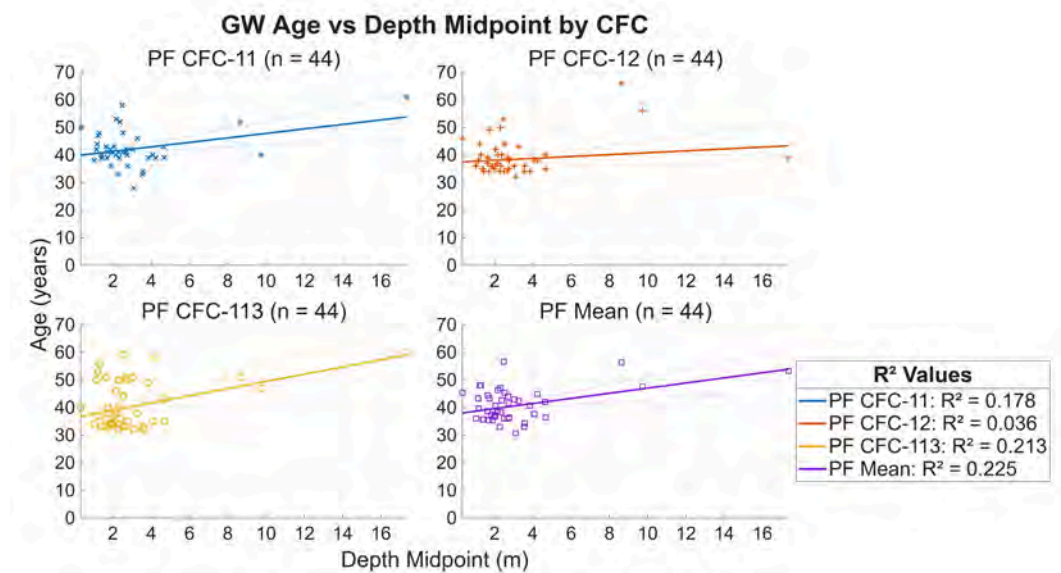


App. Fig. 40: Full time series of weekly average hydrologically effective rainfall (Teutschbein et al., 2015; Ameli et al., 2021). Effective rainfall is shown in blue, the linear trend is shown as a red line. Note, that this time series is a modelling product.

1d Groundwater CFC Samples



App. Fig. 41: All sampling wells from [Kolbe and Bishop \(2024\)](#) projected on the representative hillslope transect. Wells are mapped into the transect by their groundwater flowpaths. Screening top as hollow circles and screening bottom as filled circles, both colored the same for a given well.



App. Fig. 42: Groundwater ages estimates given in [Kolbe and Bishop \(2024\)](#) scattered against the depth to the midpoint of the sampling well. Linear regression lines in solid, 95% confidence interval as dotted lines.

App. Tab. 5: Comparison of flow distances from groundwater wells to the stream, estimated in this study by topographic analysis and in [Kolbe et al. \(2020\)](#). Distances in meter.

Well sam- ple	Topographic flow dis- tance	Kolbe <i>et</i> <i>al.</i> (2020)	Differ- ence
w42UpA1	17.1	17.1	0
w42UpB1	17.1	17.1	0
w40UpA1	37.4	37.1	0.3
w302	48.5	68.3	-19.8
w201	57.9	50.4	7.5
w37UpA1	78.3	124.5	-46.2
w37LowA1	78.3	124.5	-46.2
w39UpA1	82.9	58.3	24.6
w39UpA2	82.9	58.3	24.6
w39UpB1	82.9	58.3	24.6
w39LowA1	82.9	58.3	24.6
w39LowB1	82.9	58.3	24.6
w38LowA1	84.9	129.5	-44.6
w38UpA1	84.9	129.5	-44.6
w43	106	238.1	-132.2
w41A1	118.3	260.2	-141.9
w41B2	118.3	260.2	-141.9

Appendix 2

Extended information for the employed equations for recharge concentrations and the model formulation.

2a EAC Method

Recharge concentrations are estimated according to the EAC method described in [Kazemi \(2004\)](#) with the following equations.

$$\text{EAC} = \frac{\text{CFC}_{\text{S}_{\text{gw}}}}{\text{S} \cdot \text{MW}} \quad (13)$$

“Where EAC is the equivalent atmospheric concentration, $\text{CFC}_{\text{S}_{\text{gw}}}$ is the concentration of CFCs in the groundwater, S is the solubility in $\text{mol kg}^{-1} \text{atm}^{-1}$, and MW is the molecular weight of CFCs with unit of g/mol (137 for CFC-11, 121 for CFC-12, and 187 for CFC-113).” ([Kazemi, 2004, p. 110](#))

Here, the the molecular weights of 137.37 for CFC-11, 120.91 for CFC-12, and 187.38 for CFC-113 in $\left[\frac{\text{g}}{\text{mol}}\right]$ are applied ([IAEA, 2006](#)). To obtain recharge concentrations, i.e., concentrations under solubility equilibrium with a given atmospheric concentration EAC [App. Eq. 13](#) is solved for CFC_{gw} . Note that concentrations are calculated in $\left[\frac{\text{pmol}}{\text{L}}\right]$. The solubility parameters already account for the unit choice via the coefficients in [App. Eq. 14](#), so molecular weights are not needed for unit conversion.

[Kazemi \(2004\)](#) suggests “[...] to calculate the solubility of the CFCs at the considered temperature (summer, winter or annual) with the use of the Warner and Weiss (1985) relationship.” ([Warner and Weiss, 1985; Kazemi, 2004, p. 110](#))

$$\ln(S) = a_1 + a_2 \left(\frac{100}{T} \right) + a_3 \ln \left(\frac{T}{100} \right) + a_4 \left(\frac{T}{100} \right)^2 + I \left[b_1 + b_2 \left(\frac{T}{100} \right) + b_3 \left(\frac{T}{100} \right)^2 \right] \quad (14)$$

Where:

- S = Solubility, either $\left[\frac{\text{mol}}{\text{kg}}\right]$ or $\left[\frac{\text{mol}}{\text{L}}\right]$
- T = Temperature $[K]$
- I = Salinity $[ppt]$, i.e. $[‰]$

Here, Salinity I is disregarded as a parameter due to the very low salinity values of the groundwater, i.e., between 19.7 and 76.5 $\mu S\ cm^{-1}$. The coefficients depend on the CFC type and desired output units are given in [App. Tab. 6](#) below.

App. Tab. 6: Solubility coefficients depend on the CFC type and desired output. Values for CFC-11 and CFC-12 from (Warner and Weiss, 1985) and for CFC-113 from (Bu and Warner, 1995).

Parameter	Units	CFC-11	CFC-12	CFC-113
a_1	mol/kg	-232.0411	-220.2120	-231.902
a_2	mol/kg	322.5546	301.8695	322.915
a_3	mol/kg	120.4956	114.8533	119.111
a_4	mol/kg	-1.39165	-1.39165	-1.3917
b_1	mol/kg	-0.146531	-0.147718	-0.02547
b_2	mol/kg	0.093621	0.093175	0.004540
b_3	mol/kg	-0.0160693	-0.0157340	0.0002708
a_1	mol/L	-229.9261	-218.0971	-230.016
a_2	mol/L	319.6552	298.9702	320.338
a_3	mol/L	119.4471	113.8049	118.173
a_4	mol/L	-1.39165	-1.39165	-1.3917
b_1	mol/L	-0.142382	-0.143566	-0.02425
b_2	mol/L	0.091459	0.091015	0.004381
b_3	mol/L	-0.0157274	-0.0153924	0.0002708

2b Model Equations

The model formulations given in [Ameli, McDonnell and Bishop \(2016\)](#) and [Ameli et al. \(2021\)](#) are repeated here in brief (see [Appendix 2b](#) for details).

A 2-D transect of a hillslope is chosen as a representation, creating a domain in (x, z) coordinates $[L, L]$, where z represents elevation. This 2-D domain is a coordinate transform of the hillslope transect, presented in [Section 2.1.2](#), to ensure an orthogonal decline in saturated hydraulic conductivity with depth from the surface. The domain features an unsaturated zone (from the surface until the water table) and a saturated zone (from the water table until the bedrock). The whole

domain is assumed to be in steady-state, i.e., there are no changes in the storage of the domain, i.e. the water content does not change and input fluxes equal the output fluxes.

The saturated zone is described with the discharge potential ϕ_s [$L^2 T^{-1}$]:

$$\phi_s(x, z) = K_{s0} h_s(x, z) \quad (15)$$

Where:

- K_{s0} = Saturated hydraulic conductivity at the soil surface [$L T^{-1}$]
- $h_s(x, z)$ = Total hydraulic head [L] at point (x, z)

The unsaturated zone is described with the *Kirchhoff* potential ϕ_u [$L^2 T^{-1}$]:

$$\phi_u(\varphi(x, z)) = \frac{K_{s0} \exp(\beta(\varphi - \varphi^e))}{\beta} \quad (16)$$

Where:

- $\varphi(x, z)$ = Suction pressure head [L] at point (x, z)
- K_{s0} = Saturated hydraulic conductivity at the soil surface [$L T^{-1}$]
- β = Gardner's sorptive number [L^{-1}]
- φ^e = Gardner's air entry pressure [L]

The saturated hydraulic conductivity $K_s(x, z)$ [$L T^{-1}$] declines exponentially with depth (comp. [Equation 1](#)):

$$K_s(x, z) = K_{s0} \exp(\alpha(z - Z_t(x))) \quad (17)$$

Where:

- K_{s0} = Saturated hydraulic conductivity at the soil surface [$L T^{-1}$]
- α = Exponential relationship parameter [-]
- $Z_t(x)$ = Topographic surface elevation [L]

K_{s0} is set to 100 m day^{-1} , α is set to 2.5 and $Z_t(x)$ is derived from the coordinate transformed topographic surface of the hillslope transect (see [Figure 2](#)) ([Ameli et al., 2021](#)).

The unsaturated hydraulic conductivity $K_u(x, z)$ is described with Gardner's constitutive function ([Gardner, 1958](#)):

$$K_u(\varphi, x, z) = K_s(x, z) \exp(\beta(\varphi - \varphi^e)) \quad (18)$$

Where:

- $\varphi(x, z)$ = Suction pressure head [L] at point (x, z)
- $K_s(x, z)$ = Saturated hydraulic conductivity [$L T^{-1}$] at point (x, z)

- β = Gardner's sorptive number [L^{-1}]
- φ^e = Garner's air entry pressure [L]

Here, β is set to 2.5 m^{-1} and φ^e is set to 0.0 m to ensure a numerically stable solution in the least square scheme for the boundary conditions applied here (see below [App. Eq. 29](#)).

The formulations of ϕ_s , ϕ_u , K_s and K_u allows the linearization of the steady-state form of *Richard's Equation* (see [App. Eq. 19](#)) yielding separate linear differential equations for the saturated zone (see [App. Eq. 20](#)) and the unsaturated zone (see [App. Eq. 21](#)) ([Bakker and Nieber, 2004](#); [Ameli, Craig and Wong, 2013](#)).

$$\frac{\partial}{\partial x} \left(K(\varphi) \frac{\partial \varphi}{\partial x} \right) + \frac{\partial}{\partial z} \left(K(\varphi) \frac{\partial \varphi}{\partial z} \right) + \frac{\partial}{\partial z} K(\varphi) = 0 \quad (19)$$

Where:

- $K(\varphi)$ = Suction dependent hydraulic conductivity [$L \text{ T}^{-1}$], $K(\varphi)$ is adapted from K_u
- φ = Suction pressure head [L]
- θ = Water content [$L \text{ L}^{-3}$]
- t = Time [T]

The saturated zone is described in with the following linearized differential equation in terms of the Discharge potential ϕ_s :

$$\frac{\partial^2 \phi_s}{\partial x^2} + \alpha \frac{\partial \phi_s}{\partial z} + \frac{\partial^2 \phi_s}{\partial z^2} = 0 \quad (20)$$

Where:

- ϕ_s = Discharge potential [$L^2 \text{ T}^{-1}$]
- α = Parameter [-] of the exponential decline of K_s

The unsaturated zone is described in with the following linearized differential equation in terms of the *Kirchhoff* potential ϕ_u :

$$\frac{\partial^2 \phi_u}{\partial x^2} + \frac{\partial^2 \phi_u}{\partial z^2} (\alpha + \beta) \frac{\partial \phi_u}{\partial z} + (\alpha\beta) \phi_u = 0 \quad (21)$$

Where:

- ϕ_u = *Kirchhoff* potential [$L^2 \text{ T}^{-1}$]
- α = Parameter [-] of the exponential decline of K_s
- β = Gardner's sorptive number [L^{-1}]

ϕ_s and ϕ_u are then solved as a *Fourier-Series* type solution (Ameli, Craig and Wong, 2013).

$$\phi_s(x, z) = A_0 + \sum_{n=1}^N \left[A_n \cos\left(\frac{n\pi}{L}x\right) \exp(\gamma_n z) + B_n \cos\left(\frac{n\pi}{L}x\right) \exp(\bar{\gamma}_n z) \right] \quad (22)$$

$$\gamma_n = -\frac{\alpha}{2} + \frac{1}{2} \sqrt{\alpha^2 + \left(\frac{2n\pi}{L}\right)^2}; \quad \bar{\gamma}_n = -\frac{\alpha}{2} - \frac{1}{2} \sqrt{\alpha^2 + \left(\frac{2n\pi}{L}\right)^2} \quad (23)$$

Where:

- A_n, B_n = Series coefficients
- N = Number of series terms
- L = Aquifer length [L]
- α = Parameter [-] of the exponential decline of K_s

$$\phi_u(x, z) = C_0 [\exp(-\beta z)] - \sum_{m=1}^M \left[C_m \cos\left(\frac{m\pi}{L}x\right) \exp(\xi_m z) \frac{\xi_m}{\frac{m\pi}{L}} + D_m \cos\left(\frac{m\pi}{L}x\right) \exp(\bar{\xi}_m z) \frac{\bar{\xi}_m}{\frac{m\pi}{L}} \right] \quad (24)$$

$$\xi_m = -\frac{\alpha + \beta}{2} + \frac{1}{2} \sqrt{(\alpha + \beta)^2 - 4\alpha\beta + \left(\frac{2n\pi}{L}\right)^2};$$

$$\bar{\xi}_m = -\frac{\alpha + \beta}{2} - \frac{1}{2} \sqrt{(\alpha + \beta)^2 - 4\alpha\beta + \left(\frac{2n\pi}{L}\right)^2} \quad (25)$$

Where:

- C_n, D_n = Series coefficients
- M = Number of series terms
- L = Aquifer length [L]
- β = Gardner's sorptive number [L^{-1}], see App. Eq. 18
- α = Parameter [-] of the exponential decline of K_s

The derivatives of ϕ_s and ϕ_u with respect to x and z yield Darcy flux vectors in x, z directions for every point in the hillslope.

$$q_{sx}(x, z) = \exp(\alpha(z - Z_t(x))) \frac{d\phi_s(x, z)}{dx};$$

$$q_{sz}(x, z) = \exp(\alpha(z - Z_t(x))) \frac{d\phi_s(x, z)}{dz} \quad (26)$$

$$\begin{aligned}
q_{ux}(x, z) &= \exp(\alpha(z - Z_t(x))) \frac{d\phi_u(x, z)}{dx}; \\
q_{uz}(x, z) &= \exp(\alpha(z - Z_t(x))) \left[\frac{d\phi_u(x, z)}{dz} + \beta\phi_u(x, z) \right]
\end{aligned} \tag{27}$$

$$q_{sx}(x, z) = -e^{\alpha(z-z_t)} \sum_{n=1}^N \left[\frac{n\pi}{L} \left(A_n \sin\left(\frac{n\pi}{L}x\right) \exp(\gamma_n z) + B_n \sin\left(\frac{n\pi}{L}x\right) \exp(\bar{\gamma}_n z) \right) \right]; \tag{28}$$

$$q_{sz}(x, z) = e^{\alpha(z-z_t)} \sum_{n=1}^N \left[\gamma_n A_n \cos\left(\frac{n\pi}{L}x\right) \exp(\gamma_n z) + \bar{\gamma}_n B_n \cos\left(\frac{n\pi}{L}x\right) \exp(\bar{\gamma}_n z) \right]$$

$$q_{ux}(x, z) = e^{\alpha(z-z_t)} \sum_{m=1}^M \left[C_m \sin\left(\frac{m\pi}{L}x\right) \exp(\xi_m z) \xi_m + D_m \sin\left(\frac{m\pi}{L}x\right) \exp(\bar{\xi}_m z) \bar{\xi}_m \right]; \tag{29}$$

$$q_{uz}(x, z) = e^{\alpha(z-z_t)} \sum_{m=1}^M \left[\frac{m\pi}{L} \left(C_m \cos\left(\frac{m\pi}{L}x\right) \exp(\xi_m z) + D_m \cos\left(\frac{m\pi}{L}x\right) \exp(\bar{\xi}_m z) \right) \right]$$

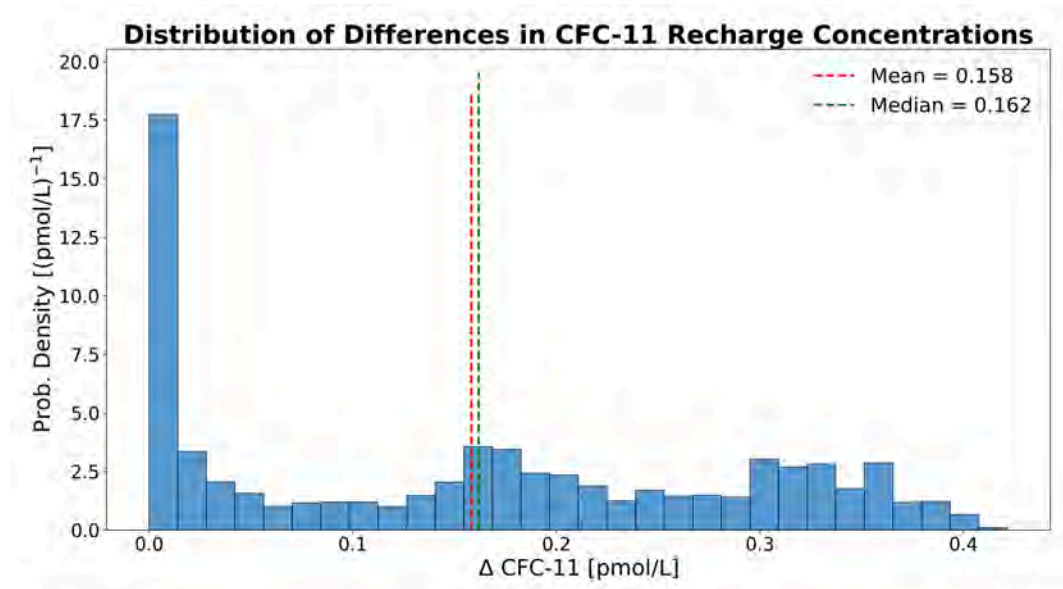
The remaining unknown series coefficients (A_n, B_n, C_n, D_n) in the series solutions of ϕ_s, ϕ_u and the Darcy fluxes are solved in a least square scheme for 280 control points located every 0.5 m along each interface (i.e., soil surface, water table, bottom no-flow) (Ameli, McDonnell and Bishop, 2016; Ameli *et al.*, 2021). To solve the least square scheme, here the boundary conditions of Ameli *et al.* (2021) are assumed:

- The infiltration rate at the surface equals the hydrologically effective rainfall
- The right side of the domain, i.e. the water divide, is a no-flow boundary;
- The bottom of the domain, i.e. the bedrock, is a no-flow boundary;
- The surface of the water course is represented by uniform hydraulic head;
- Continuity of flux and pressure head at the interface of unsaturated and saturated zone.

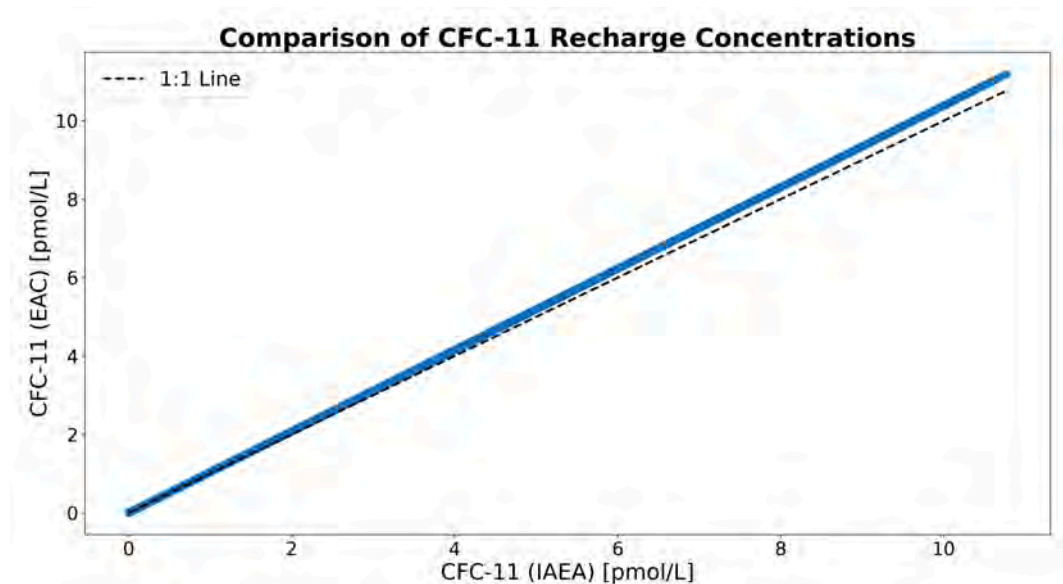
Appendix 3

Extended information on the estimated recharge concentrations.

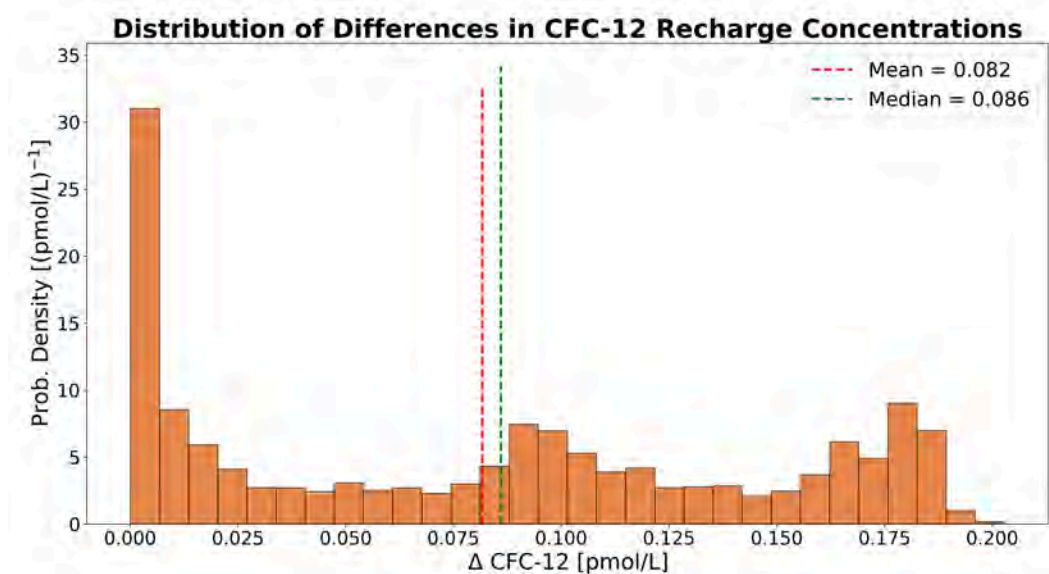
3a EAC vs IAEA Recharge Concentrations



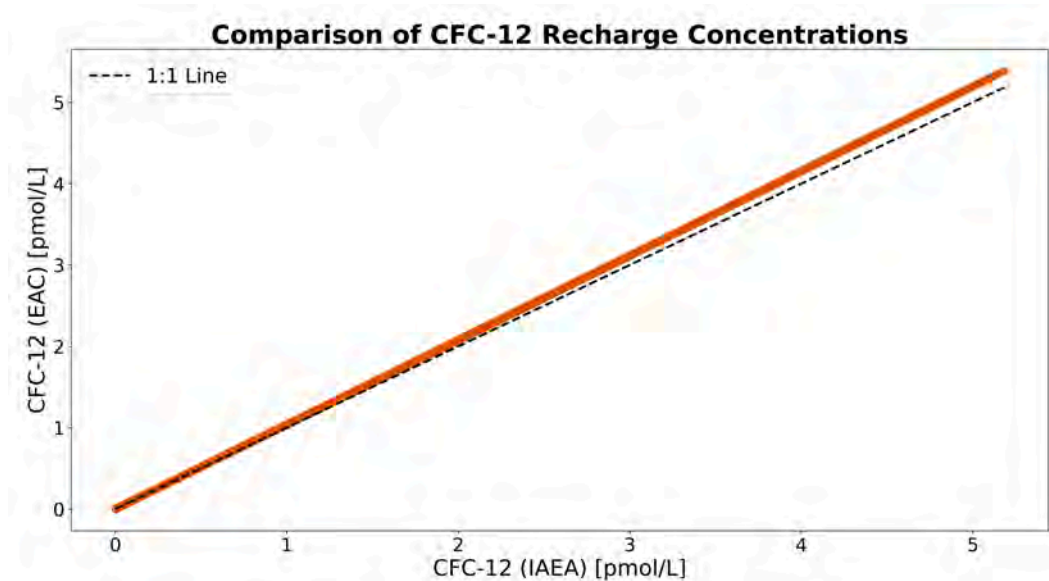
App. Fig. 43: Histogramm of the differences between the EAC and IAEA methods for estimating equilibrium solubility concentrations for CFC-11 in water. Differences computed as $\Delta \text{CFC-11} = \text{EAC} - \text{IAEA}$.



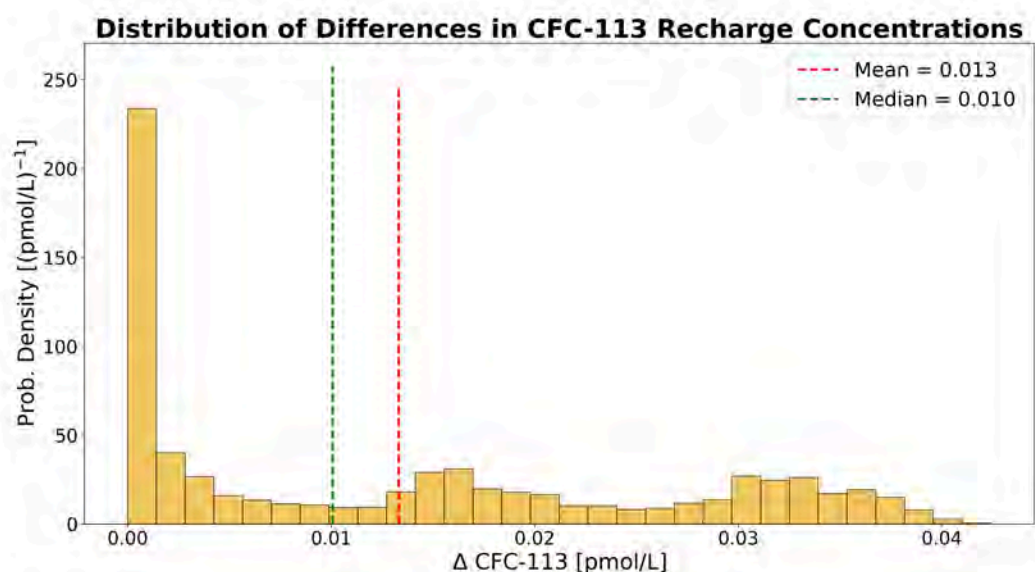
App. Fig. 44: QQplot of the estimated equilibrium solubility concentrations with the EAC and IAEA method.



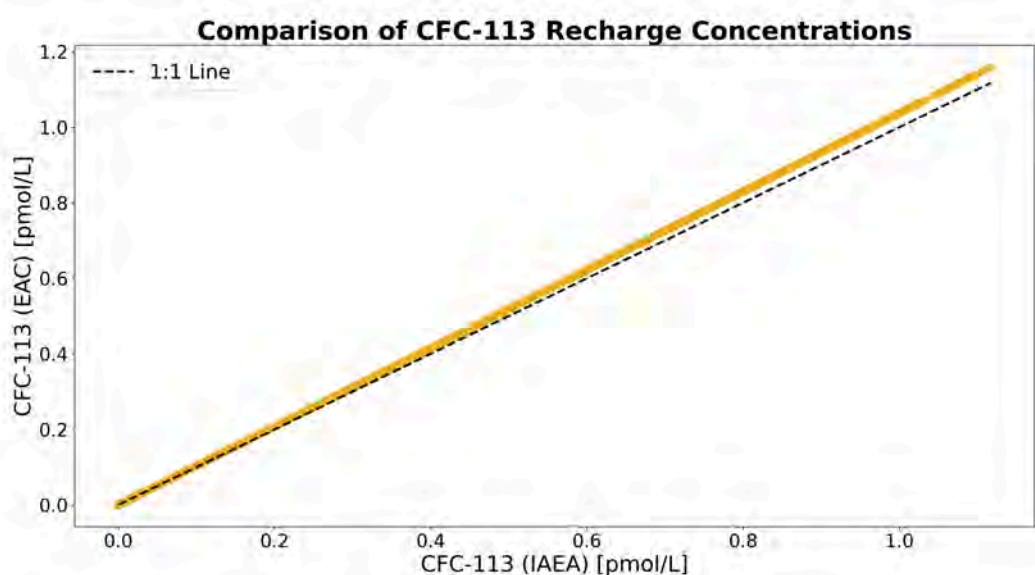
App. Fig. 45: Histogramm of the differences between the EAC and IAEA methods for estimating equilibrium solubility concentrations for CFC-12 in water. Differences computed as $\Delta \text{CFC-12} = \text{EAC} - \text{IAEA}$.



App. Fig. 46: QQplot of the estimated equilibrium solubility concentrations with the EAC and IAEA method.



App. Fig. 47: Histogramm of the differences between the EAC and IAEA methods for estimating equilibrium solubility concentrations for CFC-113 in water. Differences computed as $\Delta \text{CFC-113} = \text{EAC} - \text{IAEA}$.



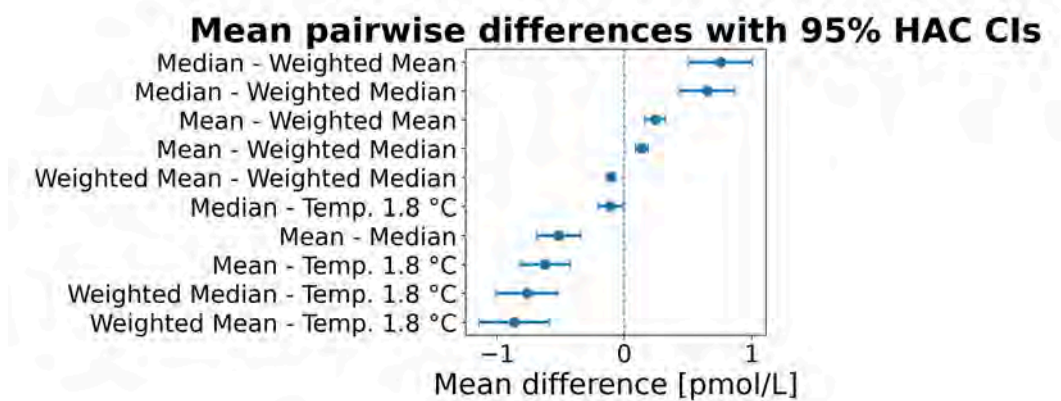
App. Fig. 48: QQplot of the estimated equilibrium solubility concentrations with the EAC and IAEA method.

3b Aggregations of Daily Recharge Concentrations

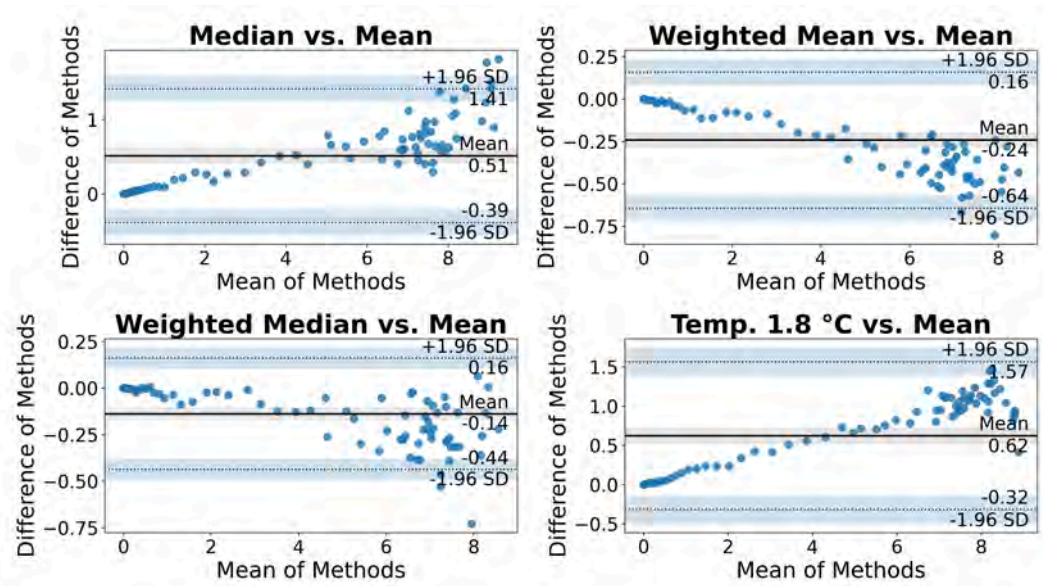
App. Tab. 7: Results of the Ljung-Box test for autocorrelation of the estimated yearly recharge concentrations of CFC-11.

Aggr. Method	Lag	LB stat	LB p-value
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Mean	1	85.4	85.432
Mean	2	168.9	168.93
Mean	3	250	250.021
Median	1	84.8	84.795
Median	2	167.6	167.645
Median	3	247.6	247.609
Weighted Mean	1	85.2	85.247
Weighted Mean	2	168.6	168.562
Weighted Mean	3	249.5	249.525
Weighted Median	1	85.2	85.16
Weighted Median	2	168.4	168.357
Weighted Median	3	249.2	249.219
Annual 1.8 °C	1	85.5	85.533
Annual 1.8 °C	2	169.1	169.13
Annual 1.8 °C	3	250.3	250.339



App. Fig. 49: Pairwise HAC/Newey-West differences with CI 95% for yearly aggregates of daily data estimated with soil temperature, except ‘Temp 1.8 °C’ (long-term annual mean air temperature). Means computed as arithmetic means. Weighted averages computed with mean and median monthly weights of hydrologically effective rainfall.



App. Fig. 50: Pairwise Blandaltman comparison for the different methods of aggregation of daily data estimated with soil temperature against the yearly estimates from the long-term annual mean air temperature of 1.8 °C. Daily data of CFC-11 aggregated to yearly values by their mean, median and weighted averages with monthly mean weights and monthly median weights.

Appendix 4

Extended information on the simulation of the groundwater wells.

4a Well Summary Tables

App. Tab. 8: Overview of all attributes of all wells placed inside the domain. Depth to the screening top, bottom and midpoint in meters. Difference between the water table in the steady-state model and during sampling (ΔWT) also in meters. Distance to stream derived from topographic analysis, also in meter. Wells grouped by the depth to their midpoint, to three groups of equal size.

Well sam- ple	Sampling data	Depth top	Depth bot	Depth mid	ΔWT	dist. Stream	Group
w37UpA1	18/06/2021	1	2.4	1.7	0.25	78.32	shallow
w39UpA1	17/06/2021	0.86	1.96	1.41	0.12	82.86	shallow
w39UpA2	17/06/2021	0.86	1.96	1.41	0.12	82.86	shallow
w39UpB1	31/08/2021	1.14	2.14	1.64	0.4	82.86	shallow
w42UpA1	21/06/2021	0.52	1.52	1.02	0.12	17.07	shallow
w42UpB1	31/08/2021	0.78	1.5	1.14	0.38	17.07	shallow
w201	31/05/2021	0.88	2.89	1.885	0.27	57.89	inter- mediate
w302	31/05/2021	1.22	2.22	1.72	0.19	48.51	inter- mediate
w40UpA1	24/06/2021	1.435	2.255	1.845	0.93	37.36	inter- mediate
w41A1	08/06/2021	1.33	2.62	1.975	0.63	118.32	inter- mediate
w43	13/09/2021	1.45	2.85	2.15	0.74	105.98	inter- mediate
w37LowA1	18/06/2021	2.4	3.805	3.1025	0.25	78.32	deep
w38LowA1	20/08/2021	2.23	3.83	3.03	1.03	84.94	deep
w38UpA1	20/08/2021	1.76	2.83	2.295	1.03	84.94	deep
w39LowA1	17/06/2021	1.96	3.04	2.5	0.12	82.86	deep
w39LowB1	31/08/2021	1.94	3.44	2.69	0.4	82.86	deep

w41B2	02/09/2021	1.67	2.68	2.175	0.97	118.32	deep
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App. Tab. 9: Overview of measured and modelled CFC concentrations at the groundwater wells placed inside the model domain. Concentrations in pmol/l. Measured values from [Kolbe and Bishop \(2024\)](#).

Well sam- ple	meas. CFC-11	meas. CFC-12	meas. CFC-113	mod. CFC-11	mod. CFC-12	mod. CFC-113	Group
w37UpA1	6.44	3.58	0.66	6.8	3.7	0.68	shallow
w39UpA1	6.03	3.65	0.64	6.81	3.73	0.69	shallow
w39UpA2	6.31	3.51	0.64	6.81	3.73	0.69	shallow
w39UpB1	5.31	2.95	0.06	6.98	3.79	0.7	shallow
w42UpA1	5.76	3.27	0.61	6.67	3.63	0.66	shallow
w42UpB1	5.65	3.13	0.07	6.58	3.54	0.65	shallow
w201	5.93	3.26	0.55	6.6	3.59	0.66	inter- mediate
w302	2.36	1.29	0.25	6.56	3.48	0.64	inter- mediate
w40UpA1	5.5	3.31	0.59	5.14	2.54	0.46	inter- mediate
w41A1	5.71	3.48	0.63	6.61	3.56	0.65	inter- mediate
w43	5.97	3.25	0.36	6.33	3.38	0.62	inter- mediate
w37LowA1	6.69	4.01	0.77	0	0	0	deep
w38LowA1	5.6	3.41	0.07	0.32	0.19	0.01	deep
w38UpA1	5.75	1.21	0.07	5.45	2.76	0.5	deep
w39LowA1	5.91	3.66	0.66	3.58	1.69	0.27	deep
w39LowB1	5.44	2.9	0.07	3.78	1.81	0.31	deep
w41B2	1.55	2.78	0.12	6.02	3.12	0.57	deep

App. Tab. 10: Overview of particle tracking results for mean and median transit times for all wells placed inside the model domain. Mean transit times computed as the flux average. Transit times in years. Dist. stream and depths in meters.

Well sam- ple	CFC-11 rel. err.	CFC-12 rel. err.	Flux ave. TT	Me- dian TT	Dist. stream	Top depth	Bot depth	Group
w42UpA1	0.16	0.11	11.7	6	17.1	0.5	1.5	shal- low
w42UpB1	0.17	0.13	19.2	12.2	17.1	0.8	1.5	shal- low
w39UpA1	0.13	0.02	4.7	2.9	82.9	0.9	2	shal- low
w39UpA2	0.08	0.06	4.7	2.8	82.9	0.9	2	shal- low
w39UpB1	0.31	0.28	9.4	6.6	82.9	1.1	2.1	shal- low
w37UpA1	0.05	0.03	8.6	4.7	78.3	1	2.4	shal- low
w302	1.78	1.69	22.6	16.5	48.5	1.2	2.2	inter- medi- ate
w40UpA1	-0.06	-0.23	46.3	35.1	37.4	1.4	2.3	inter- medi- ate
w201	0.11	0.1	13.7	5.9	57.9	0.9	2.9	inter- medi- ate
w41A1	0.16	0.02	18	11.1	118.3	1.3	2.6	inter- medi- ate
w43	0.06	0.04	25.9	15.4	106	1.5	2.9	inter- medi- ate
w41B2	2.89	0.12	33.7	24.6	118.3	1.7	2.7	deep
w38UpA1	-0.05	1.28	44.3	31.5	84.9	1.8	2.8	deep
w39LowA1	-0.39	-0.54	70.6	49.9	82.9	2	3	deep
w39LowB1	-0.31	-0.38	85.7	49.9	82.9	1.9	3.4	deep
w38LowA1	-0.94	-0.94	173.8	97.8	84.9	2.2	3.8	deep
w37LowA1	-1	-1	233.4	141.7	78.3	2.4	3.8	deep

App. Tab. 11: Overview of groundwater ages estimated in [Kolbe and Bishop \(2024\)](#) with the Piston-Flow model and the particle tracking results for flux-average and median transit times for all wells placed inside the model domain. Ages and transit times in years. The error rank is derived from model results against the combined absolute relative errors of all three simulated CFC compounds.

Well sam- ple	CFC-11 PFM age	CFC-12 PFM age	CFC-113 PFM age	Flux ave. TT	Me- dian TT	Error rank	Group
w42UpA1	38	36	34	11.7	6	7	shallow
w42UpB1	42	38	50	19.2	12.2	12	shallow
w39UpA1	40	34	33	4.7	2.9	4	shallow
w39UpA2	39	35	33	4.7	2.8	5	shallow
w39UpB1	43	39	51	9.4	6.6	13	shallow
w37UpA1	39	34	33	8.6	4.7	2	shallow
w302	41	49	40	22.6	16.5	15	intermediate
w40UpA1	42	36	34	46.3	35.1	7	intermediate
w201	36	36	34	13.7	5.9	6	intermediate
w41A1	41	35	34	18	11.1	4	intermediate
w43	40	37	38	25.9	15.4	5	intermediate
w41B2	53	40	46	33.7	24.6	13	deep
w38UpA1	41	50	50	44.3	31.5	11	deep
w39LowA1	41	34	33	70.6	49.9	11	deep
w39LowB1	42	39	51	85.7	49.9	12	deep
w38LowA1	42	36	51	173.8	97.8	13	deep
w37LowA1	28	32	32	233.4	141.7	14	deep

4b Fitting results for transit time distributions

The Akaike's Information Criterion is used here to decide which fitted distribution provides the better fit.

App. Tab. 12: AIC values for the distributions fitted to the flux weighted transit times estimated from the pathlines for every well sample. Δ AIC is the difference between the best and second best AIC.

Well sam- ple	Gamma AIC	In- verse Gauss- ian AIC	Log- nor- mal AIC	Weibull AIC	BestFit	Δ AIC
w201	14472	13295	13405	14341	InverseGaussian	110
w302	15699	15274	15336	15948	InverseGaussian	62
w37UpA1	12521	11792	11911	12583	InverseGaussian	119
w37LowA1	25498	24785	24847	25696	InverseGaussian	62
w38UpA1	18399	17943	18002	18662	InverseGaussian	59
w38LowA1	24471	23620	23680	24609	InverseGaussian	60
w39UpA1	10047	9604	9706	10113	InverseGaussian	102
w39LowA1	20256	19796	19853	20525	InverseGaussian	57
w39UpA2	10046	9582	9692	10115	InverseGaussian	110
w39UpB1	12368	11946	12022	12568	InverseGaussian	76
w39LowB1	21584	20807	20872	21747	InverseGaussian	66
w40UpA1	18301	17935	17987	18579	InverseGaussian	52
w41A1	15255	14622	14705	15429	InverseGaussian	83
w41B2	17204	16792	16849	17470	InverseGaussian	57
w42UpA1	13825	12952	13068	13833	InverseGaussian	116
w42UpB1	15454	14869	14945	15644	InverseGaussian	76
w43	16776	16065	16145	16936	InverseGaussian	80

App. Tab. 13: Parameters estimates of the best AIC distribution fitted to the modelled transit time data. “Mean” and “Median” transit time estimates of the distribution and of the underlying resampled data. Transit times in years.

Well sam- ple	Best Fit	λ	μ	Mean Fit	Median Fit	Mean Model	Median Model
w201	In- verseGauss- ian	8.2909	13.7413	13.7	7.7	13.7	5.9
w302	In- verseGauss- ian	51.0885	22.6032	22.6	18.6	22.6	16.5

w37UpA1	In-verseGaussian	7.8382	8.5521	8.6	5.6	8.6	4.7
w37LowA1	In-verseGaussian	353.0597	233.3596	233.4	176.8	233.4	141.7
w38UpA1	In-verseGaussian	100.4473	44.2669	44.3	36.4	44.3	31.5
w38LowA1	In-verseGaussian	216.6246	173.8277	173.8	125.4	173.8	97.8
w39UpA1	In-verseGaussian	4.1329	4.6528	4.7	3	4.7	2.9
w39LowA1	In-verseGaussian	162.5728	70.6383	70.6	58.3	70.6	49.9
w39UpA2	In-verseGaussian	4.2365	4.6581	4.7	3.1	4.7	2.8
w39UpB1	In-verseGaussian	17.4316	9.3816	9.4	7.4	9.4	6.6
w39LowB1	In-verseGaussian	115.2921	85.7229	85.7	63.1	85.7	49.9
w40UpA1	In-verseGaussian	129.524	46.2885	46.3	39.4	46.3	35.1
w41A1	In-verseGaussian	25.8093	17.9881	18	13.5	18	11.1
w41B2	In-verseGaussian	82.9599	33.7241	33.7	28.1	33.7	24.6
w42UpA1	In-verseGaussian	9.1724	11.6948	11.7	7.3	11.7	6

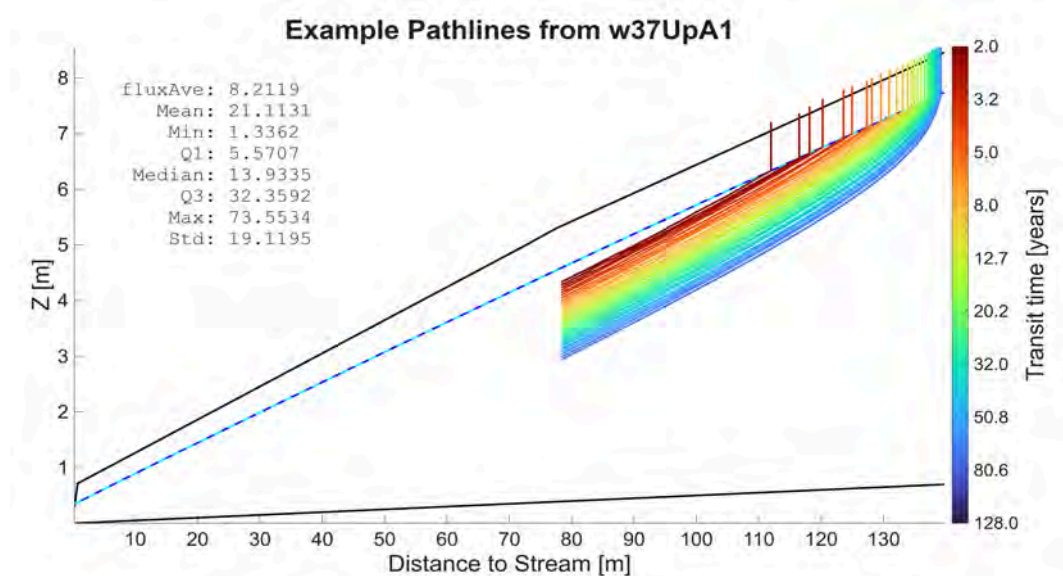
w42UpB1	In-verseGaussian	29.6299	19.2194	19.2	14.6	19.2	12.2
w43	In-verseGaussian	34.6666	25.8761	25.9	19	25.9	15.4

App. Tab. 14: Relative error of CFC-11 concentrations in the wells for the modelled concentration (flux-averaged particle-wise concentrations) and the concentration estimated directly from the single flux-averaged and median transit time to a well. Δ is the difference between flux-averaged or median and the modelled relative error.

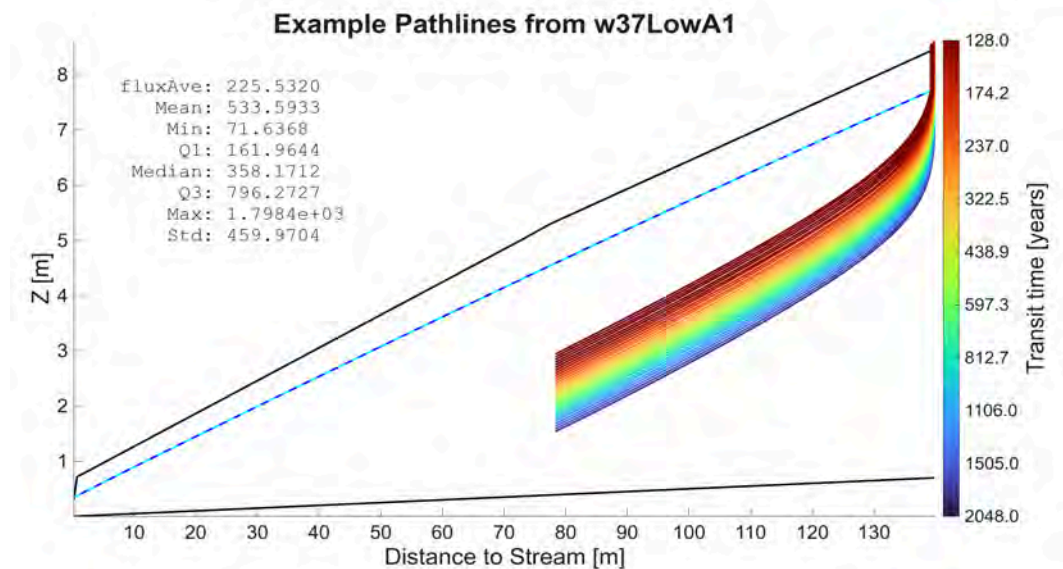
Well sam- ple	Rel.Err. Mod. CFC-11	Rel.Err. Flux-ave. CFC-11	Δ Flux-ave.	Rel.Err. Median TT CFC-11	Δ Median	Group
w37UpA1	0.05	0.07	0.02	0.07	0.02	shallow
w39UpA1	0.13	0.14	0.01	0.12	-0.01	shallow
w39UpA2	0.08	0.09	0.01	0.07	-0.01	shallow
w39UpB1	0.31	0.32	0.01	0.3	-0.01	shallow
w42UpA1	0.16	0.23	0.07	0.19	0.03	shallow
w42UpB1	0.17	0.33	0.16	0.26	0.09	shallow
w201	0.11	0.21	0.1	0.16	0.05	intermediate
w302	1.78	2.23	0.45	2.12	0.34	intermediate
w40UpA1	-0.06	-0.34	-0.28	0.22	0.28	intermediate
w41A1	0.16	0.33	0.17	0.24	0.08	intermediate
w43	0.06	0.39	0.33	0.21	0.15	intermediate
w37LowA1	-1	-1	0	-1	0	deep
w38LowA1	-0.94	-1	-0.06	-1	-0.06	deep
w38UpA1	-0.05	-0.23	-0.18	0.33	0.38	deep
w39LowA1	-0.39	-0.99	-0.6	-0.62	-0.23	deep
w39LowB1	-0.31	-1	-0.69	-0.57	-0.26	deep

w41B2	2.89	3.8	0.91	4.16	1.27	deep
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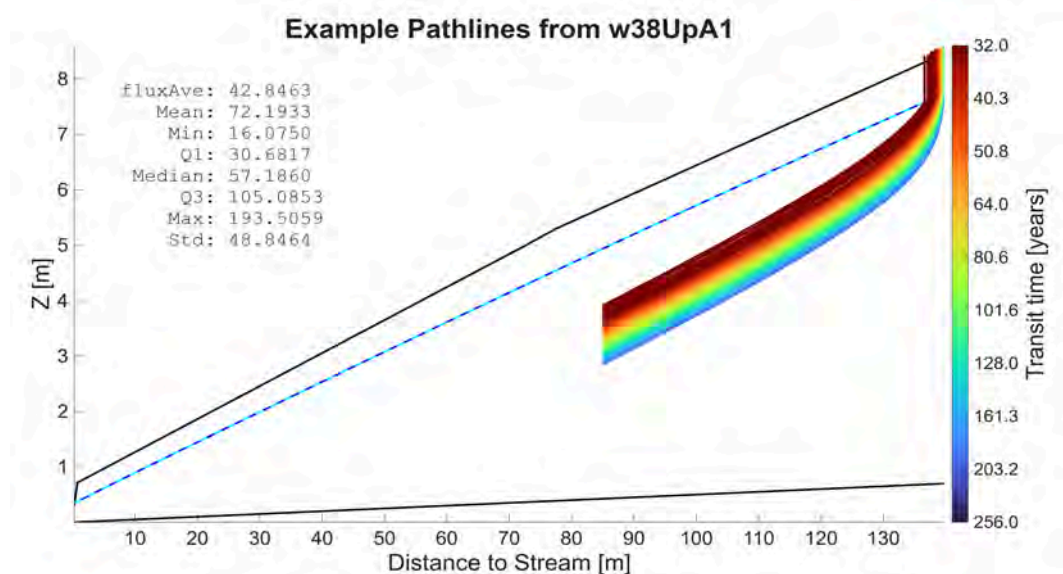
4c Pathlines for all wells inside the domain



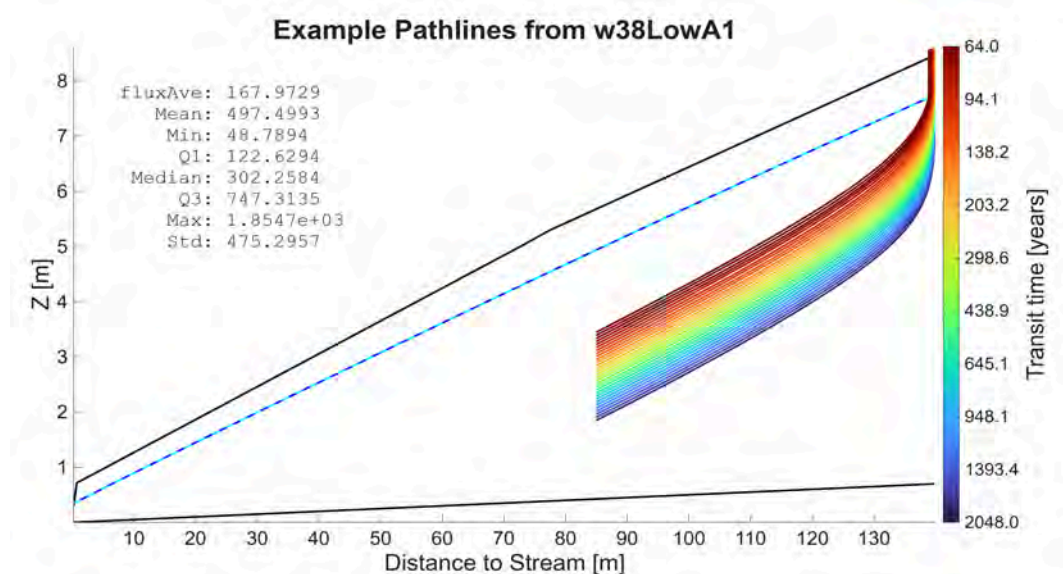
App. Fig. 51: Pathlines computed backwards from “w37UpA1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



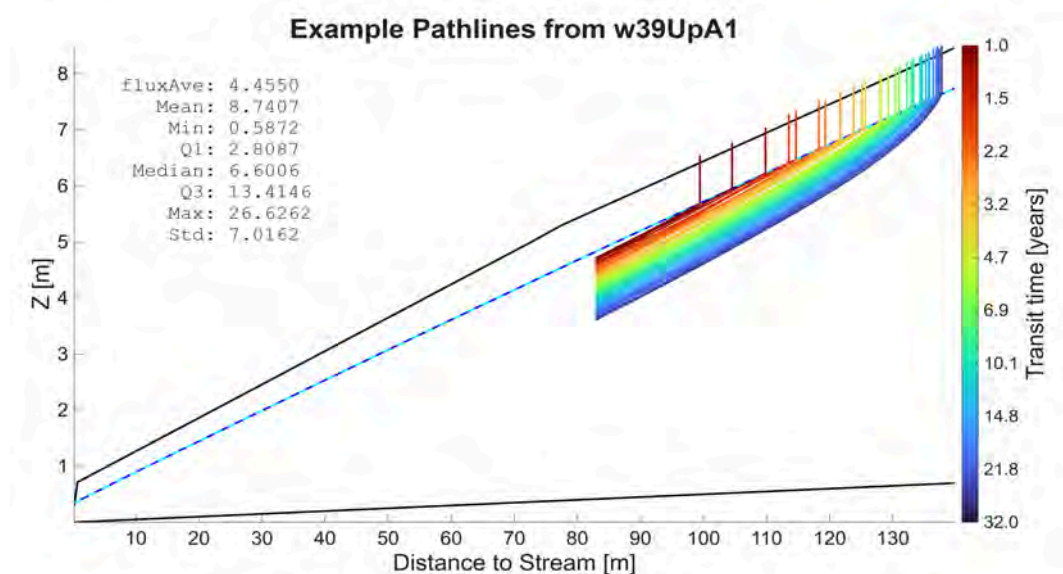
App. Fig. 52: Pathlines computed backwards from “w37LowA1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



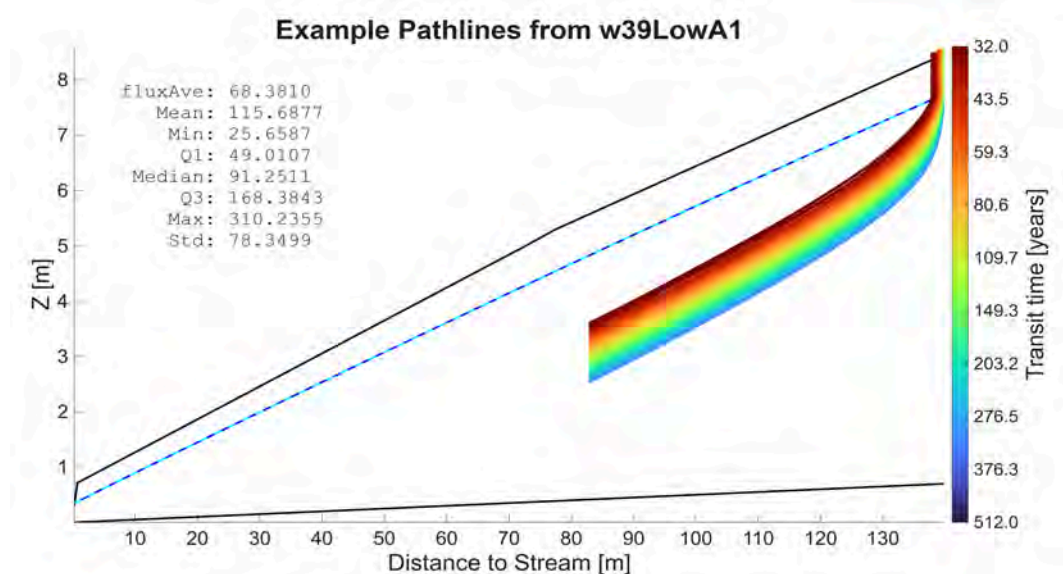
App. Fig. 53: Pathlines computed backwards from “w38UpA1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



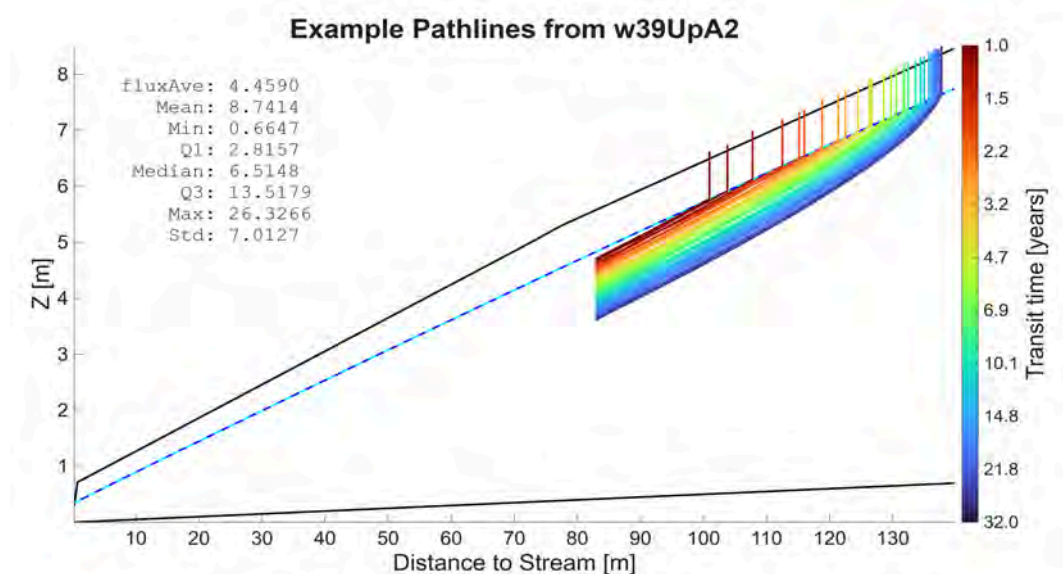
App. Fig. 54: Pathlines computed backwards from “w38LowA1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



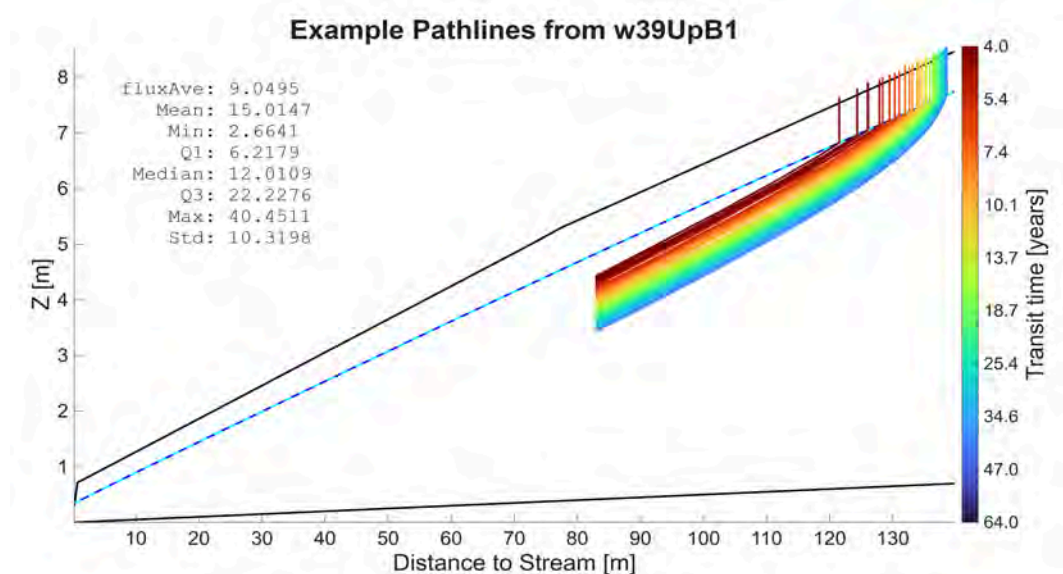
App. Fig. 55: Pathlines computed backwards from “w39UpA1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



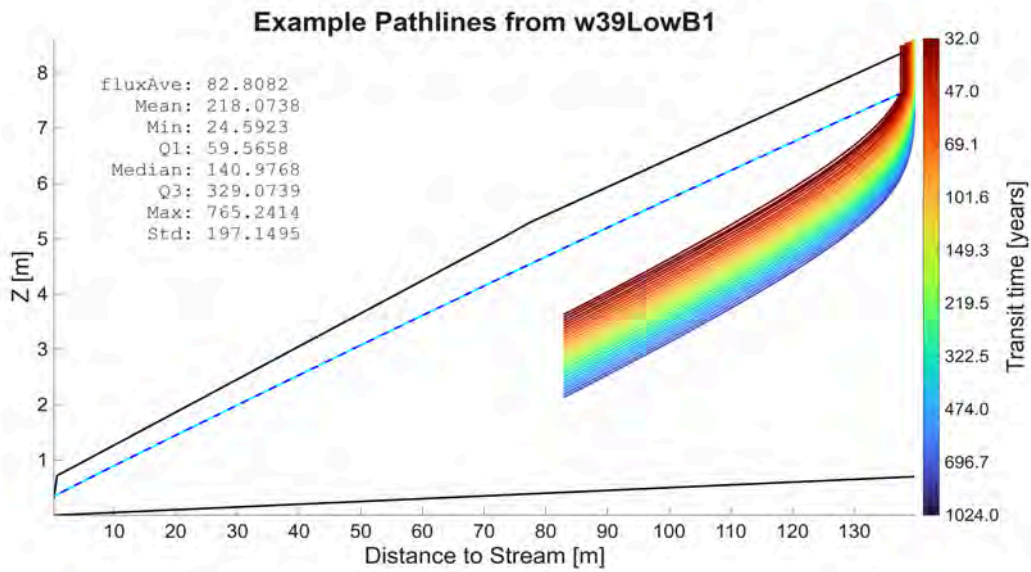
App. Fig. 56: Pathlines computed backwards from “w39LowA1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



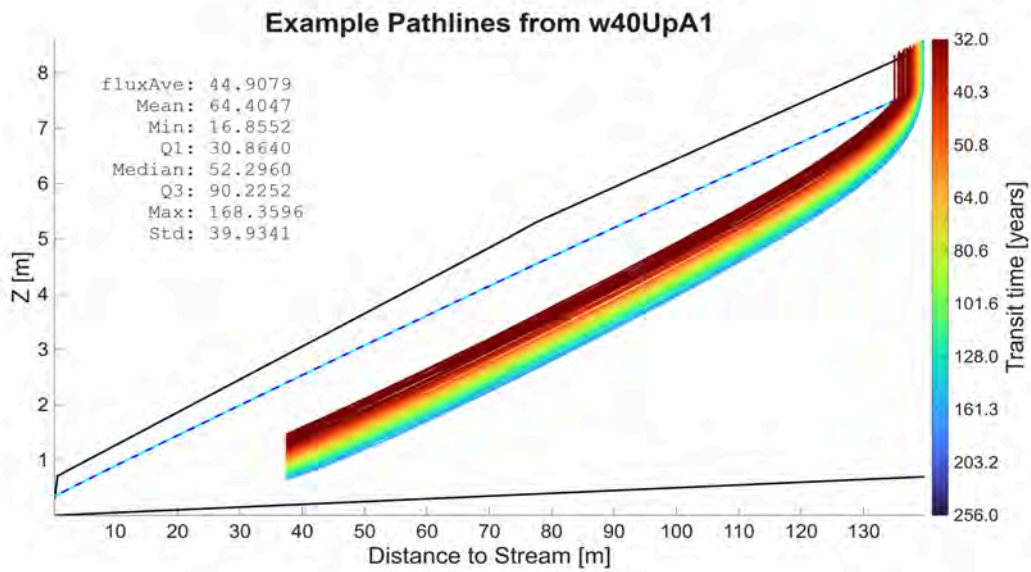
App. Fig. 57: Pathlines computed backwards from “w39UpA2” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



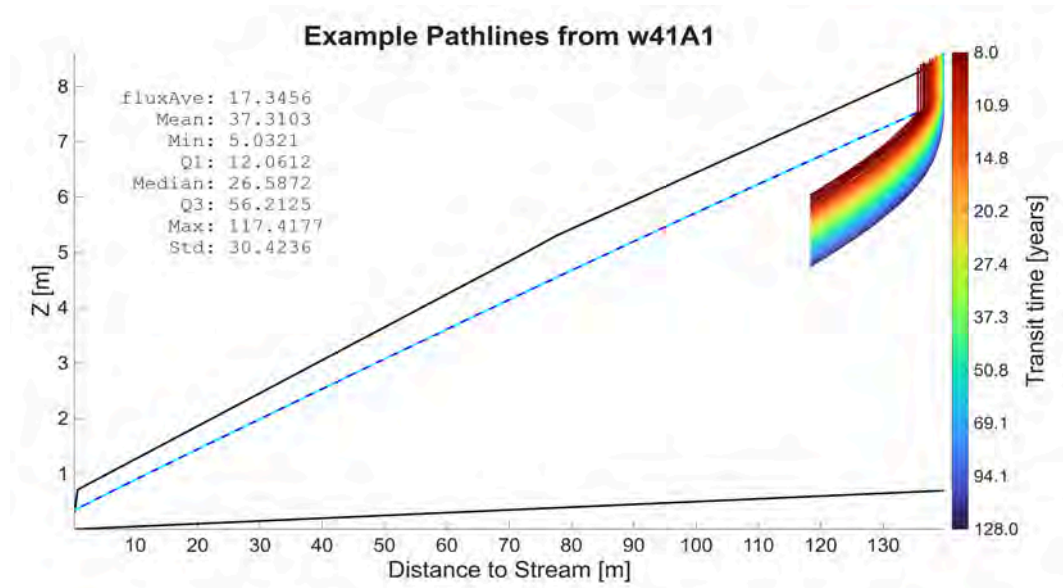
App. Fig. 58: Pathlines computed backwards from “w39UpB1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



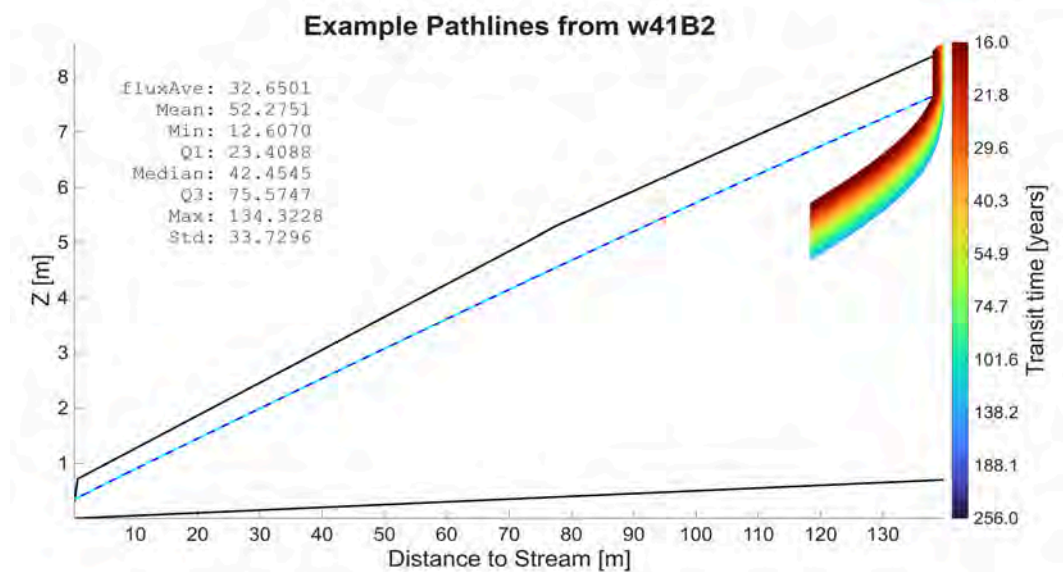
App. Fig. 59: Pathlines computed backwards from “w39LowB1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



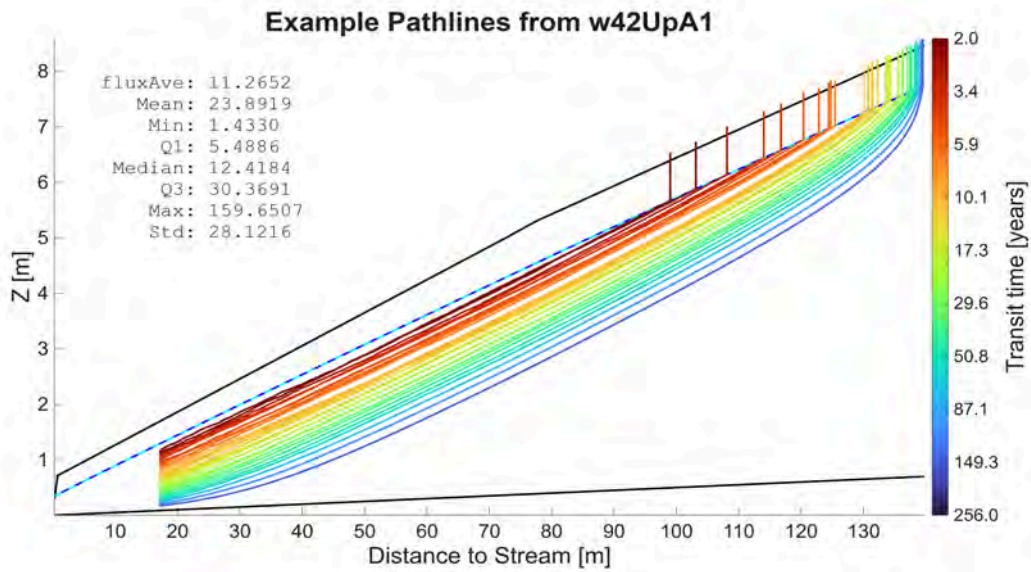
App. Fig. 60: Pathlines computed backwards from “w40UpA1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



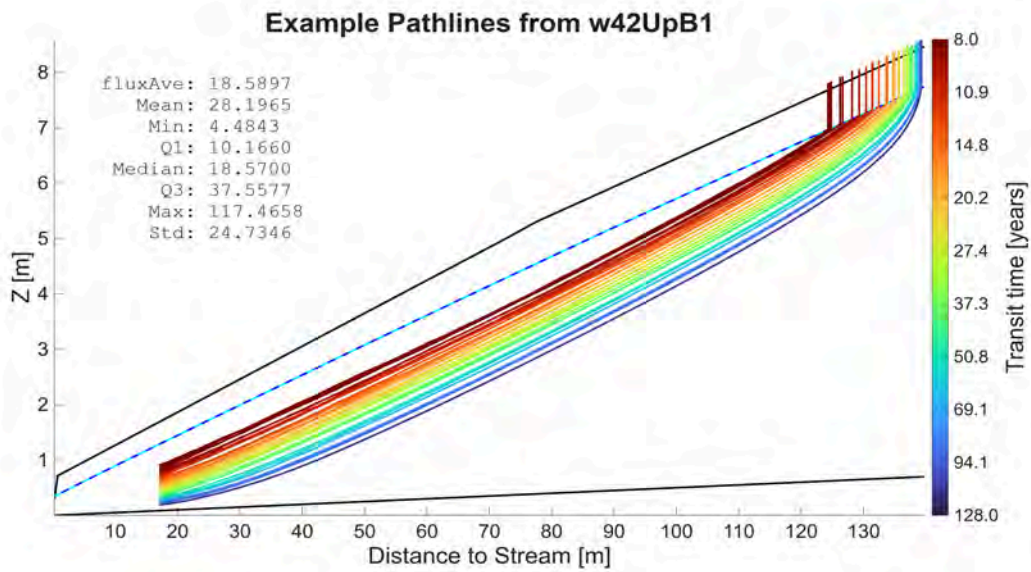
App. Fig. 61: Pathlines computed backwards from “w41A1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



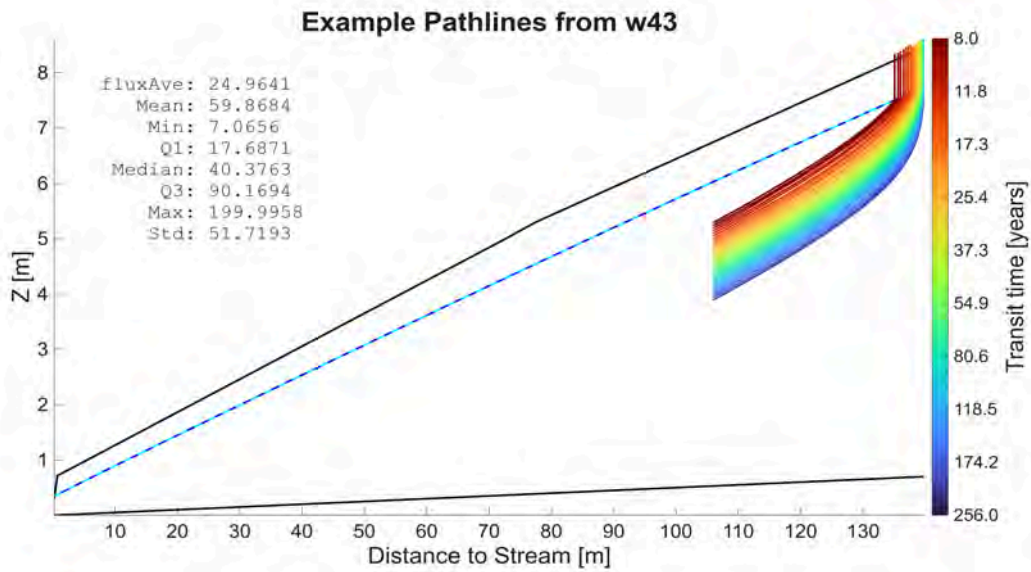
App. Fig. 62: Pathlines computed backwards from “w41B2” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



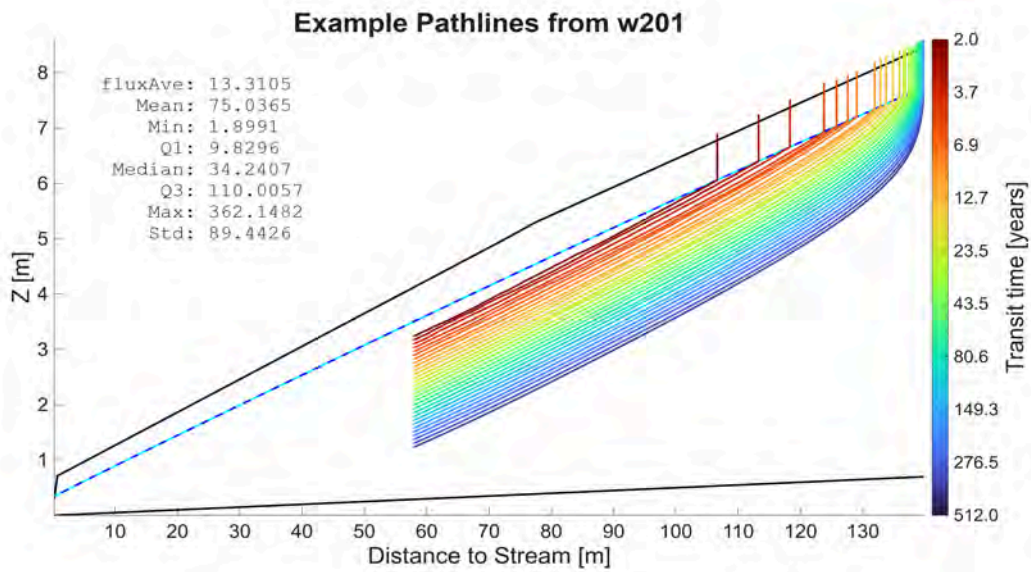
App. Fig. 63: Pathlines computed backwards from “w42UpA1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



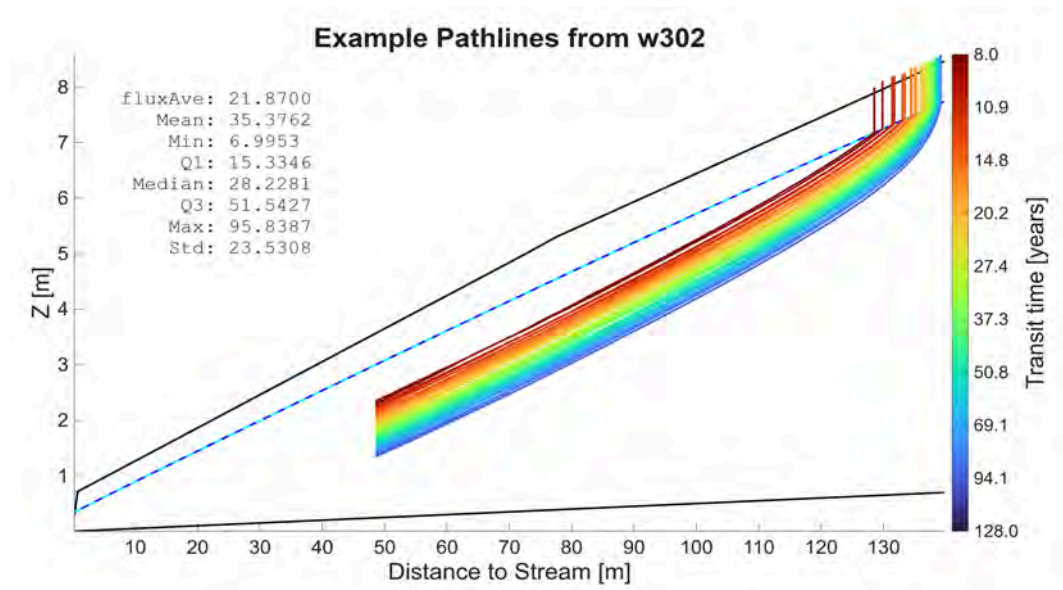
App. Fig. 64: Pathlines computed backwards from “w42UpB1” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.



App. Fig. 65: Pathlines computed backwards from “w43” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.

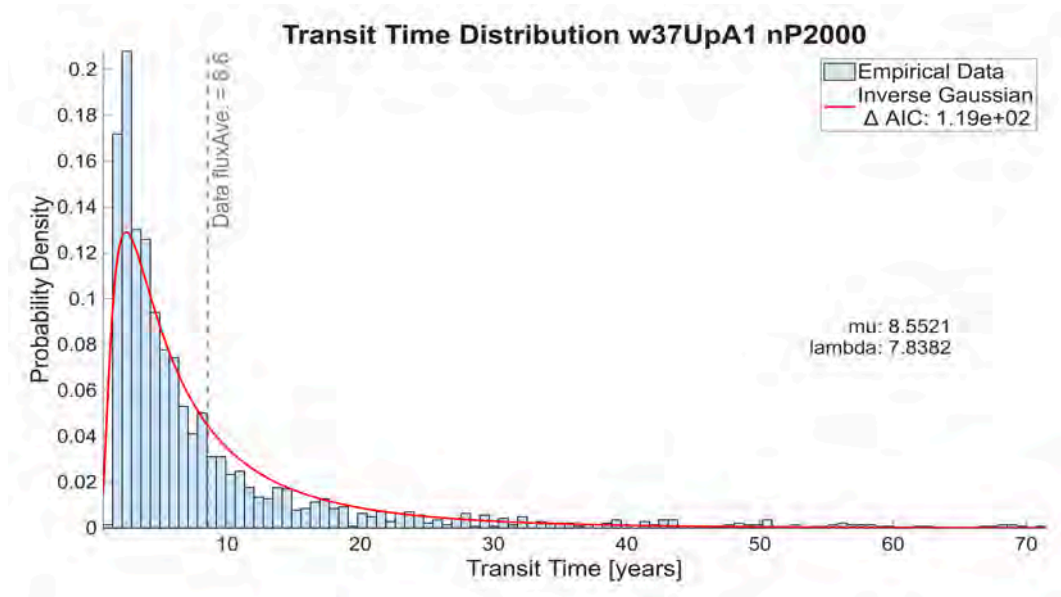


App. Fig. 66: Pathlines computed backwards from “w201” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.

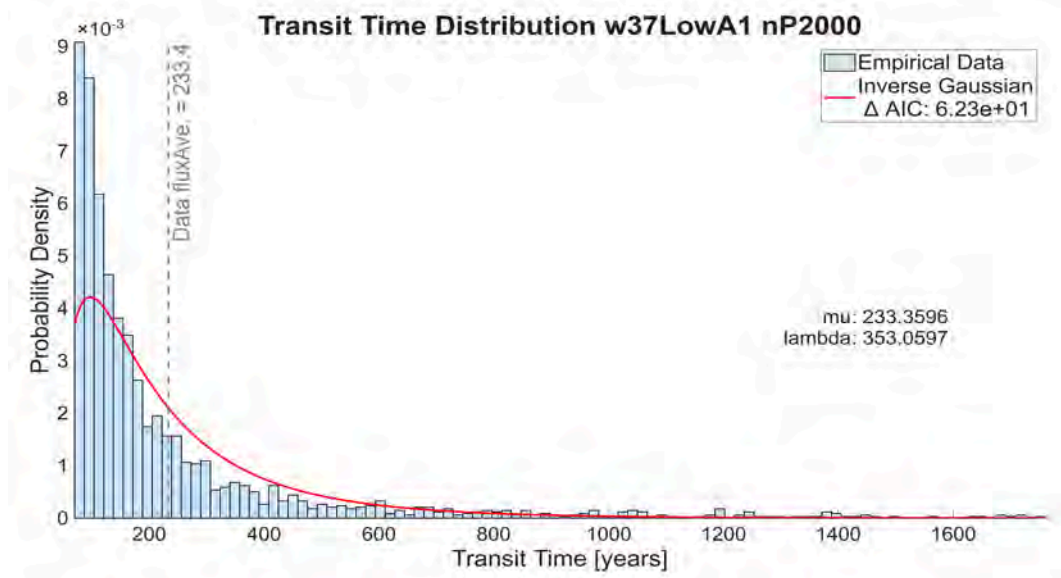


App. Fig. 67: Pathlines computed backwards from “w302” with 2,000 particles, seeded uniformly across the screening depth. Pathlines coloured by their transit time. Summary statistics given in the inset, note that only the “fluxAve” metric weights the particles by their flux at the well.

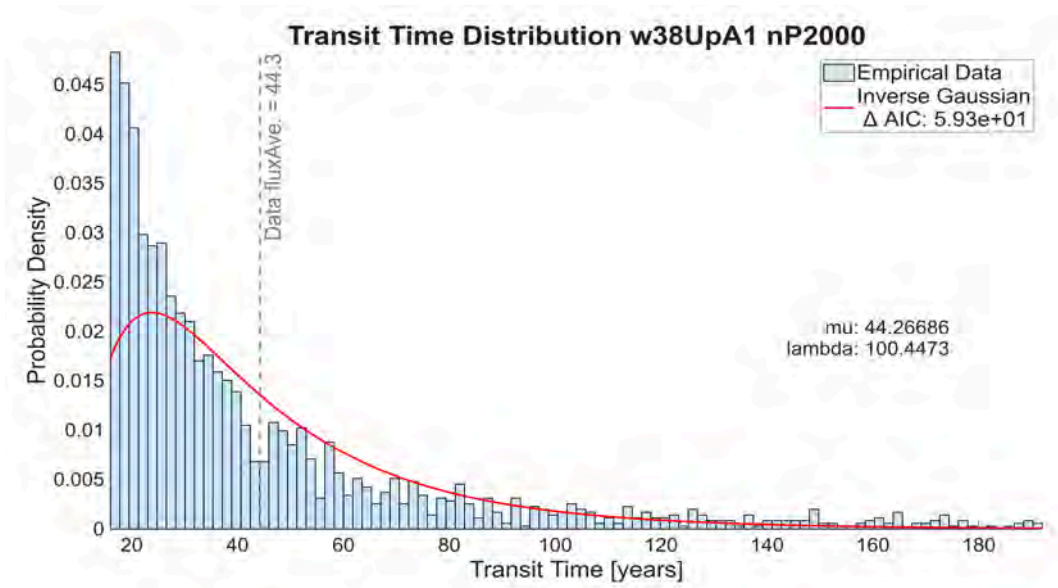
4d Fitted distribution for all wells inside the domain



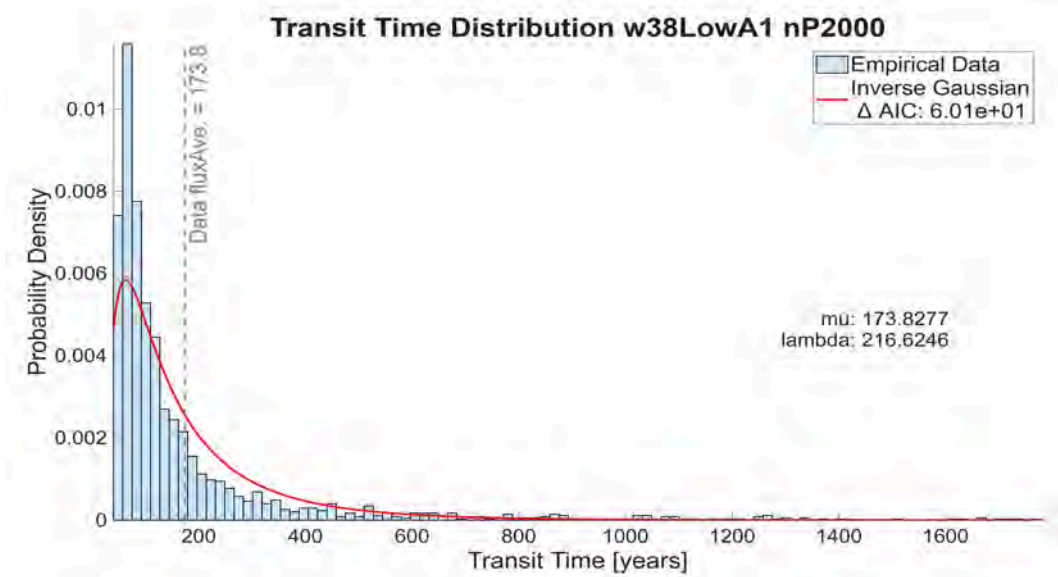
App. Fig. 68: Estimated transit time distribution for well “w37UpA1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



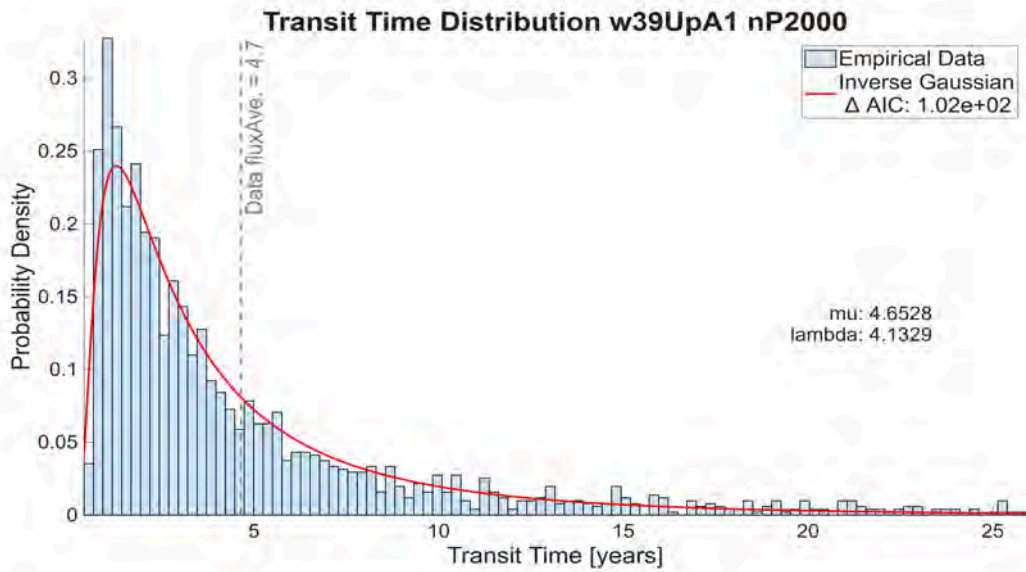
App. Fig. 69: Estimated transit time distribution for well “w37LowA1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



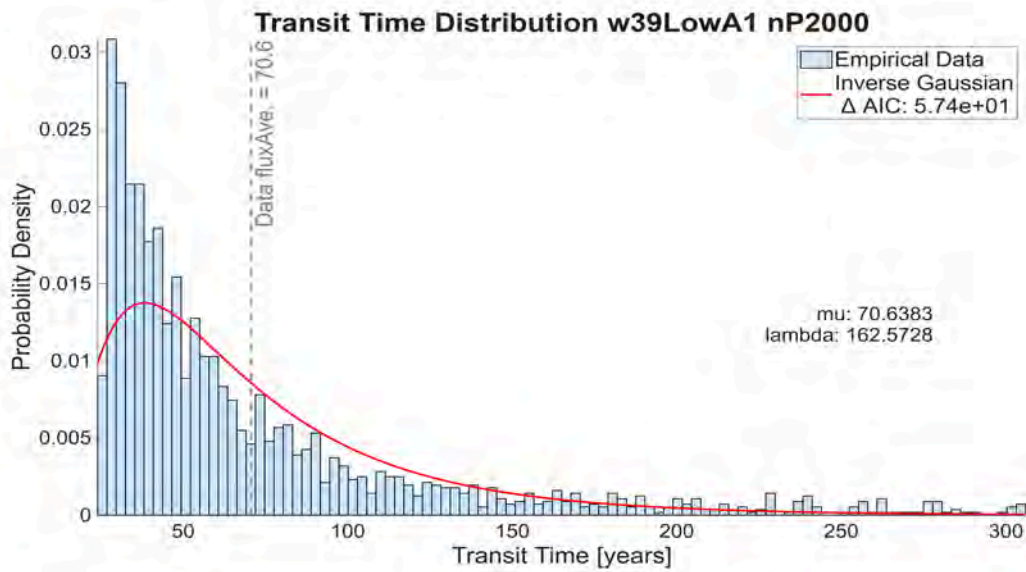
App. Fig. 70: Estimated transit time distribution for well “w38UpA1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



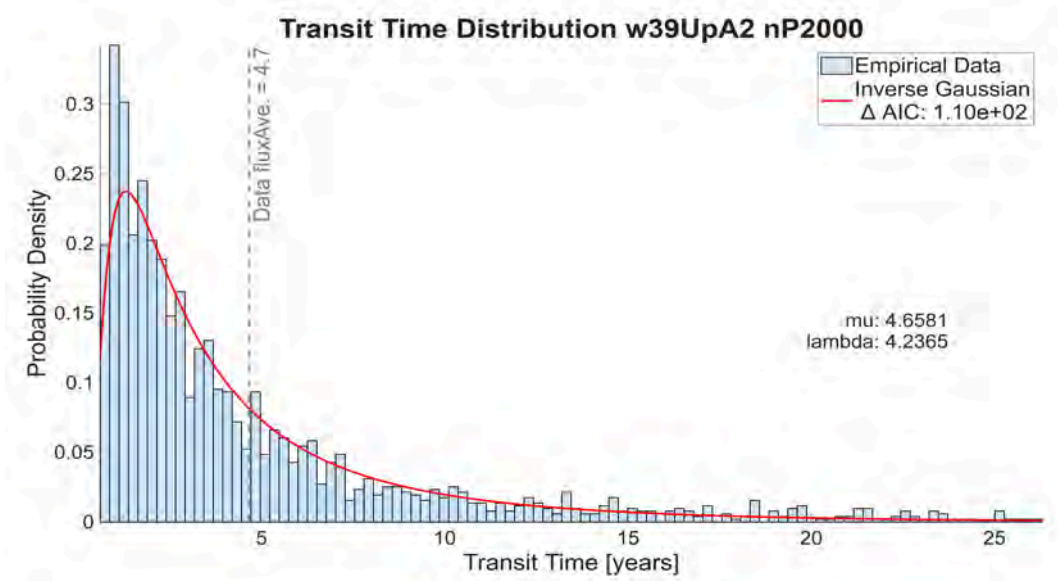
App. Fig. 71: Estimated transit time distribution for well “w38LowA1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



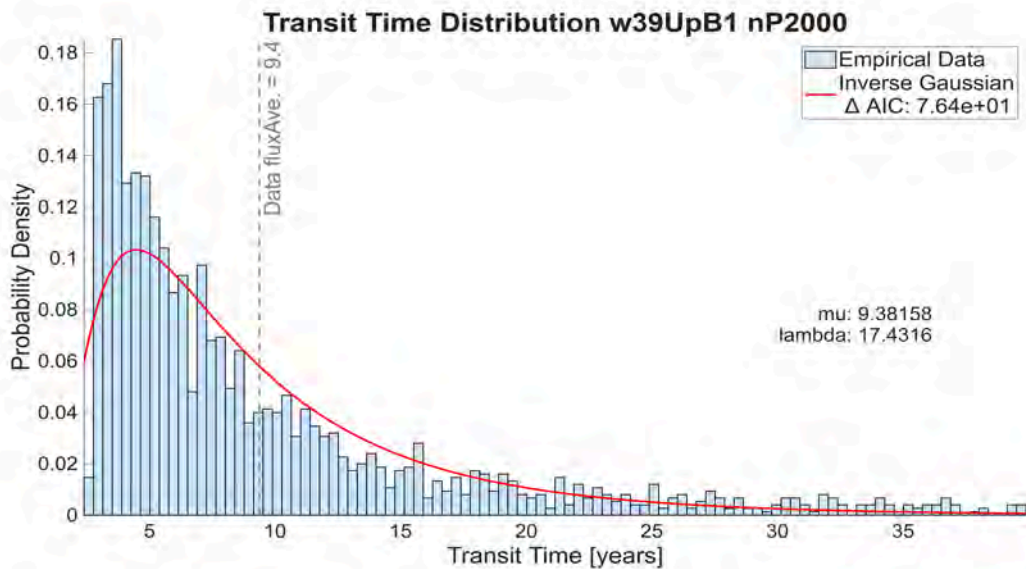
App. Fig. 72: Estimated transit time distribution for well “w39UpA1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



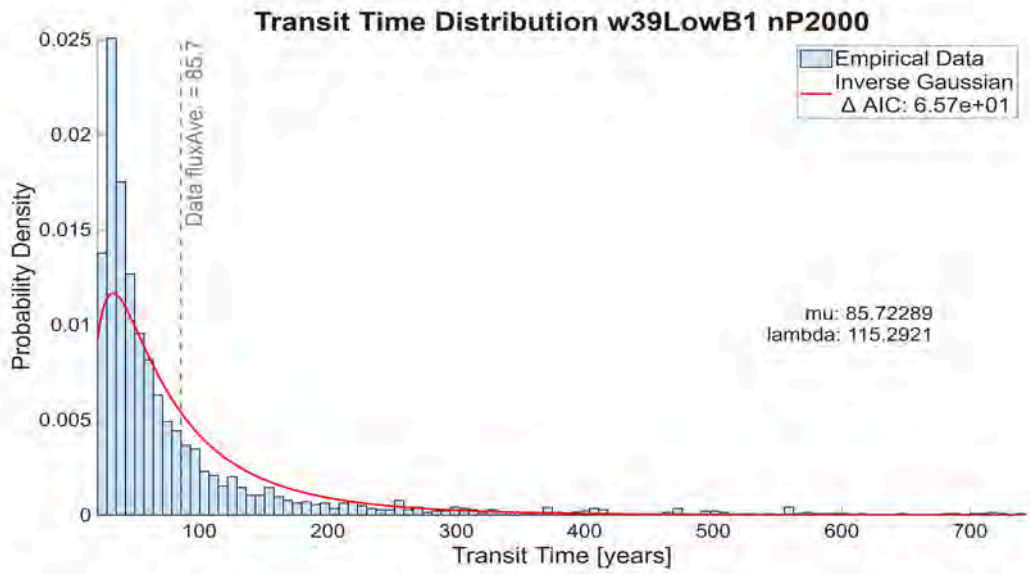
App. Fig. 73: Estimated transit time distribution for well “w39LowA1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



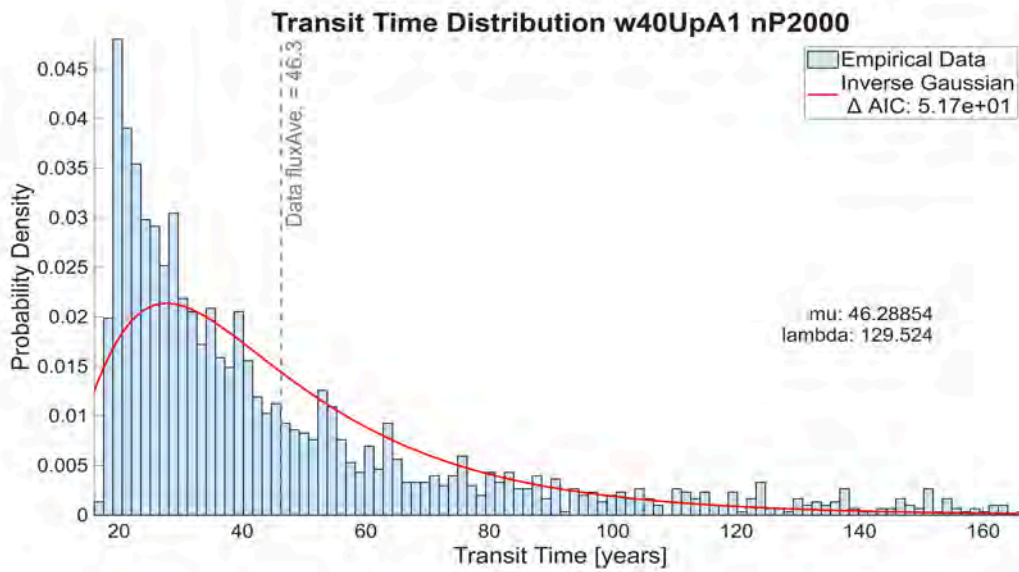
App. Fig. 74: Estimated transit time distribution for well “w39UpA2”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



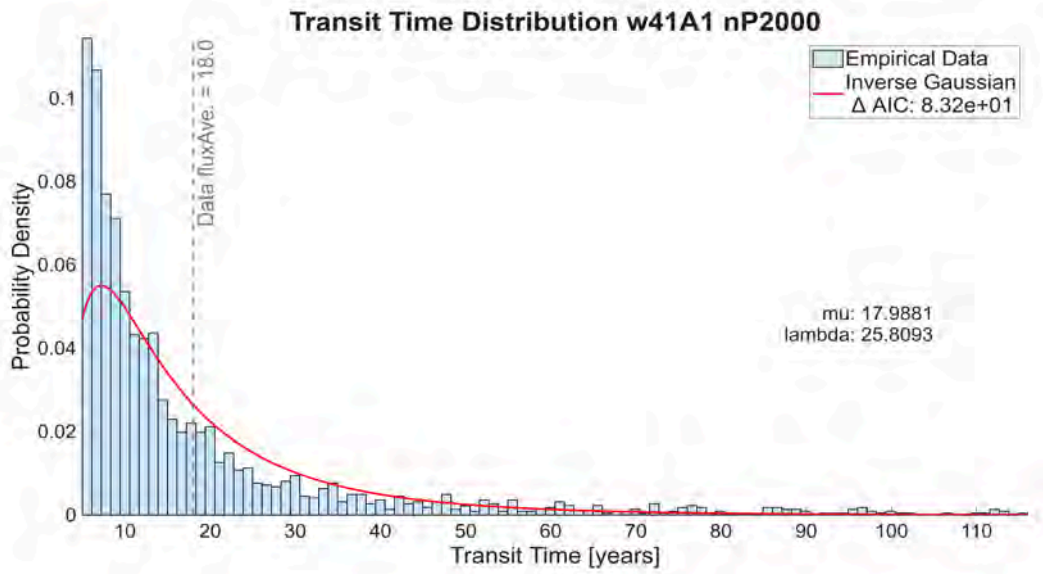
App. Fig. 75: Estimated transit time distribution for well “w39UpB1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



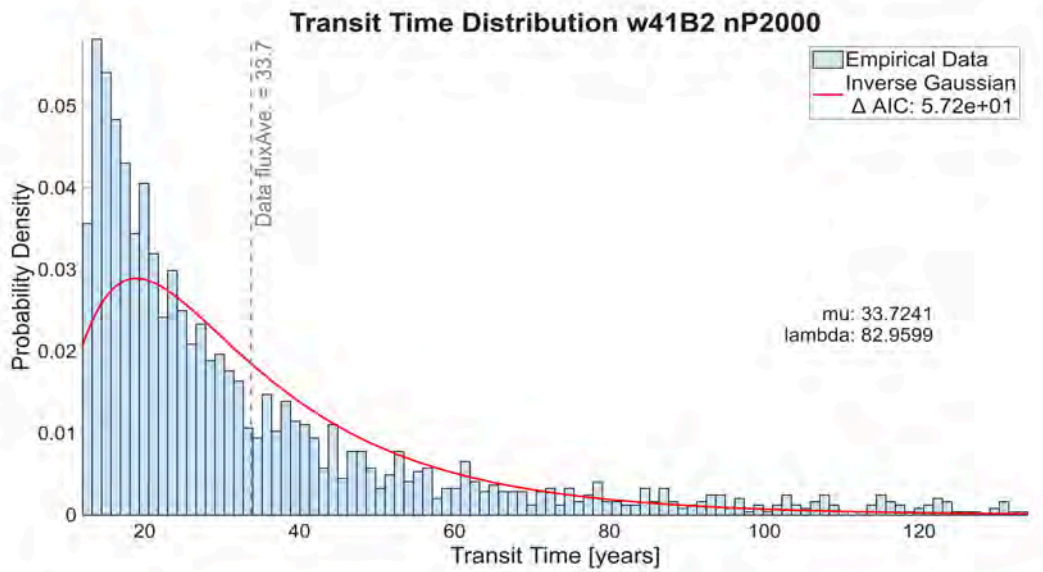
App. Fig. 76: Estimated transit time distribution for well “w39LowB1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



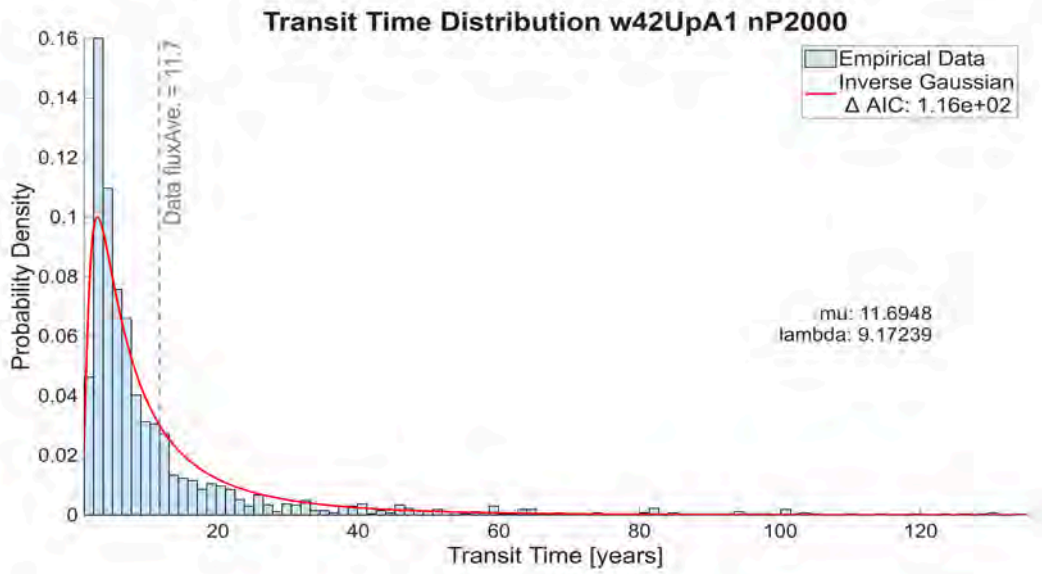
App. Fig. 77: Estimated transit time distribution for well “w40UpA1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



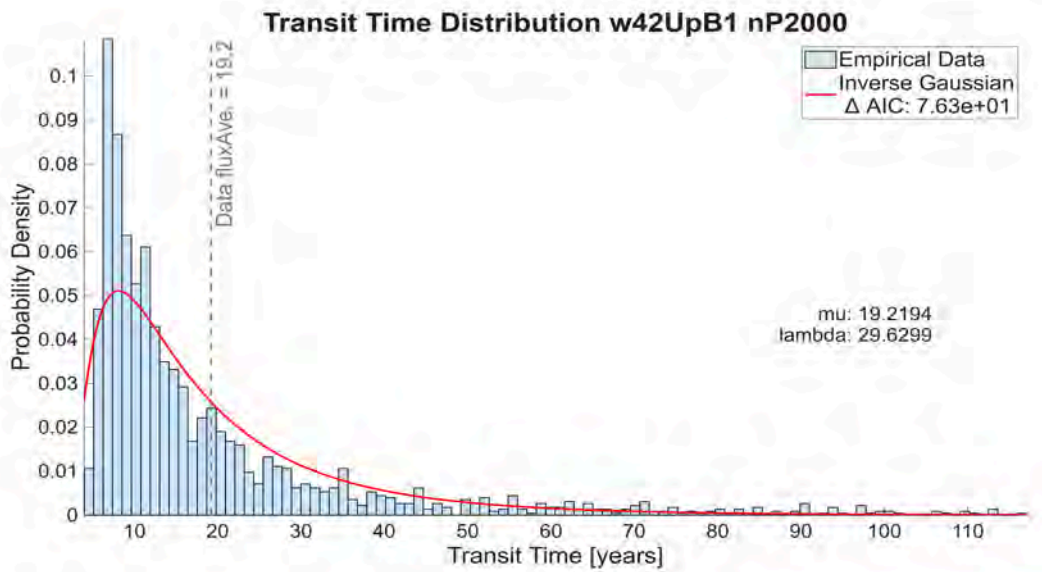
App. Fig. 78: Estimated transit time distribution for well “w41A1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



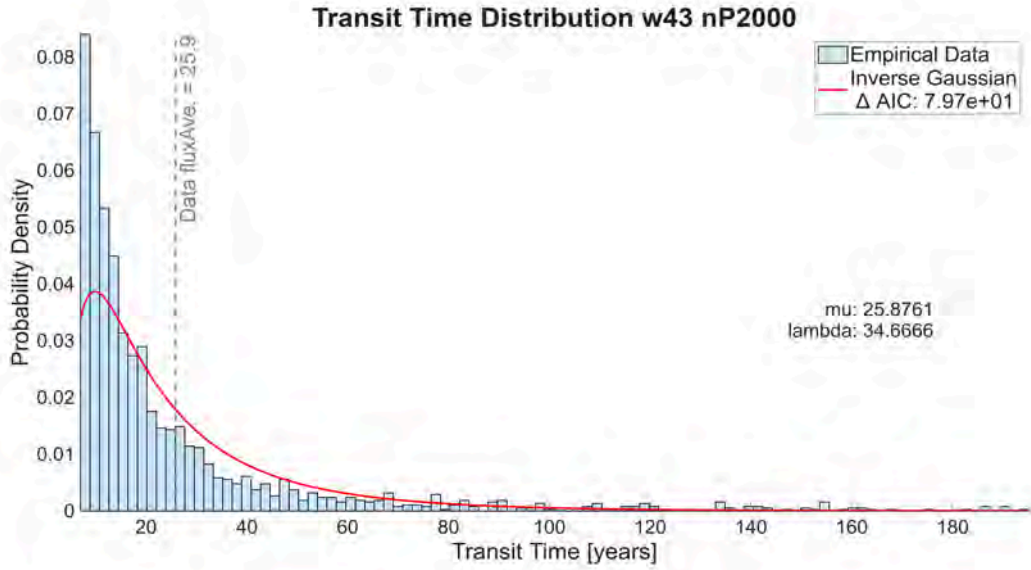
App. Fig. 79: Estimated transit time distribution for well “w41B2”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



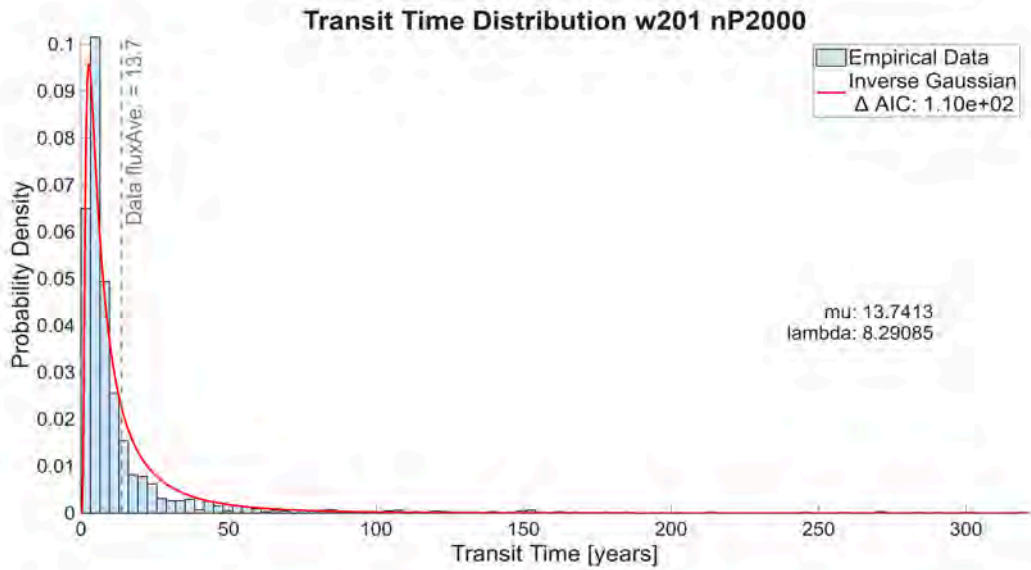
App. Fig. 80: Estimated transit time distribution for well “w42UpA1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, Δ AIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



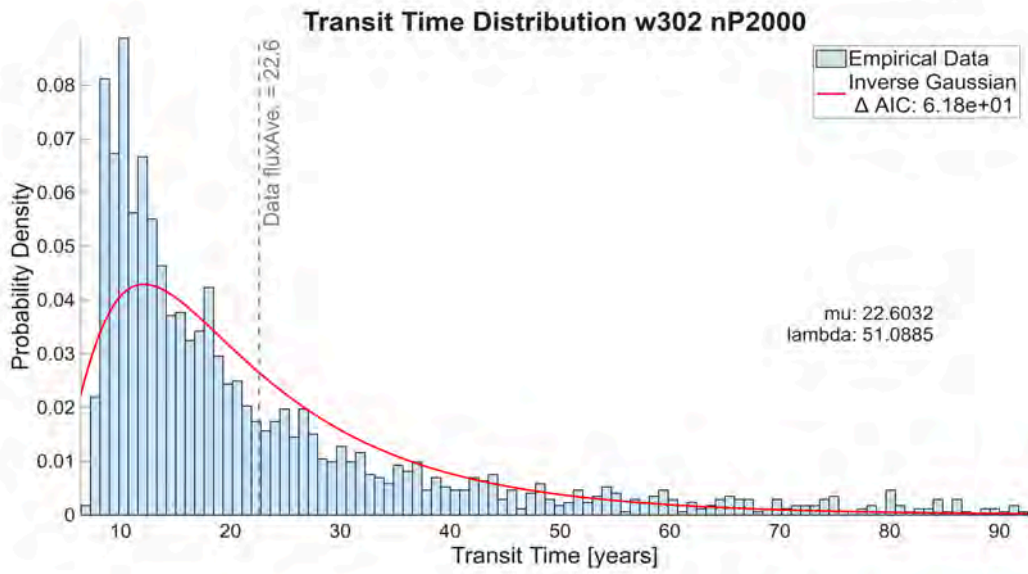
App. Fig. 81: Estimated transit time distribution for well “w42UpB1”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, Δ AIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.



App. Fig. 82: Estimated transit time distribution for well “w43”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, Δ AIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.

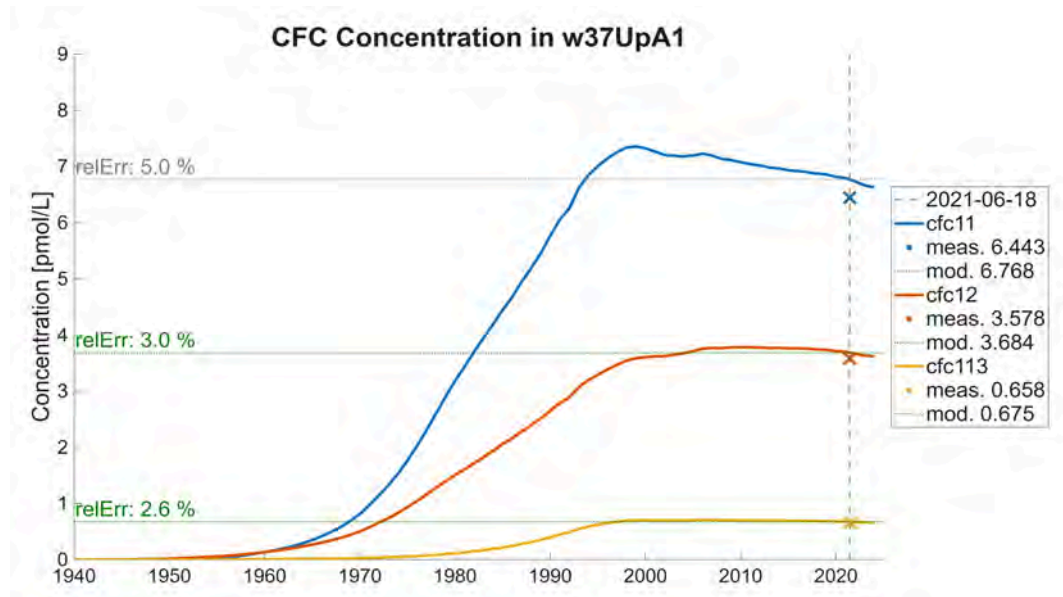


App. Fig. 83: Estimated transit time distribution for well “w201”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, Δ AIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.

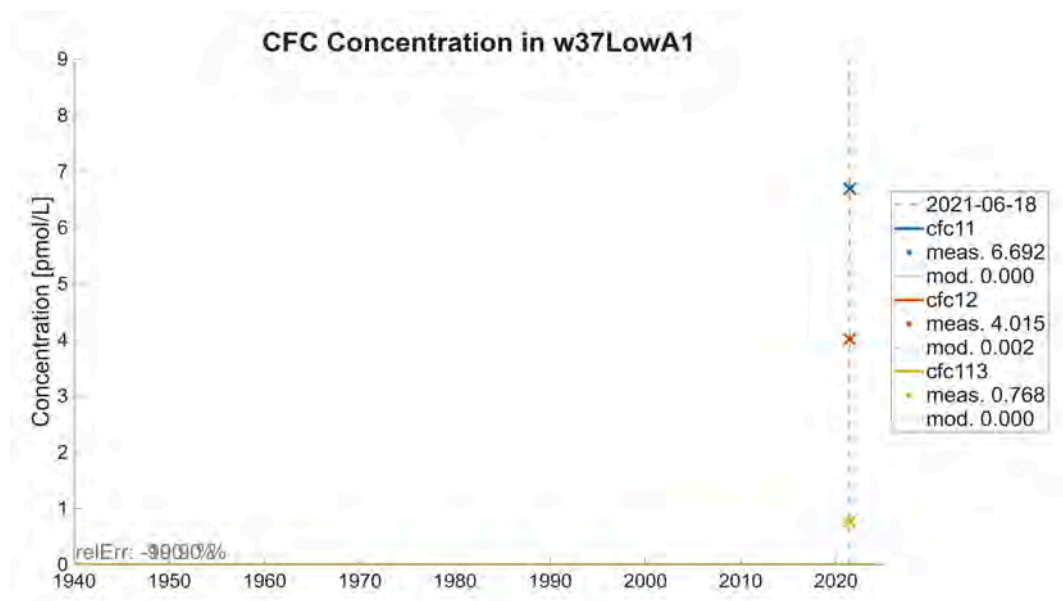


App. Fig. 84: Estimated transit time distribution for well “w302”. Transit time data as bars, flux weighted and binned ($n=100$). Fitted distribution in red, ΔAIC is the difference in AIC to the second best distribution. Parameters of the fitted distribution given inside the plot, flux average transit time of the fitted distribution in dashed grey.

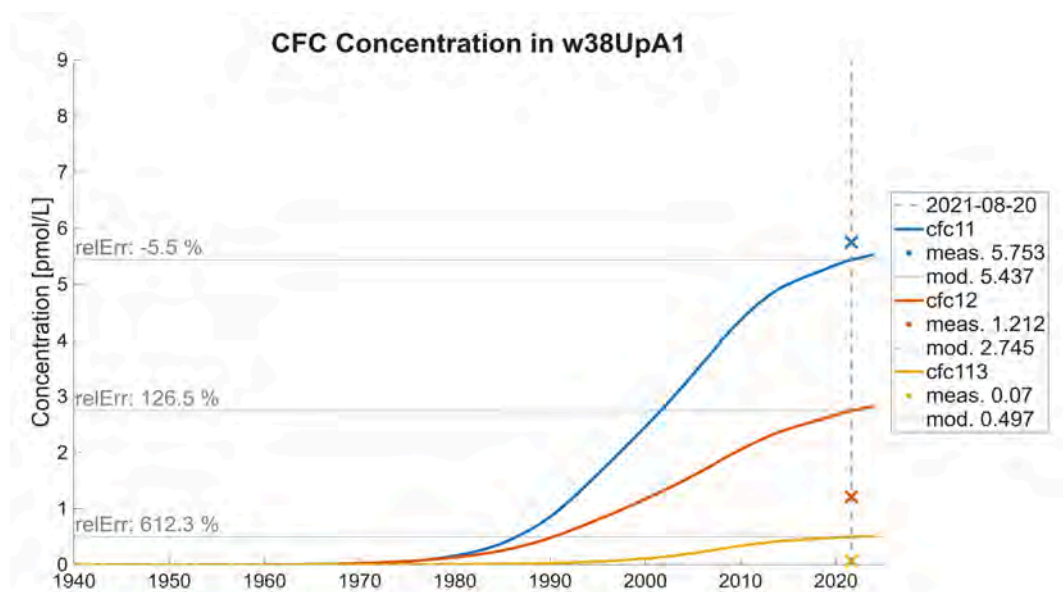
4e CFC results for all wells inside the domain



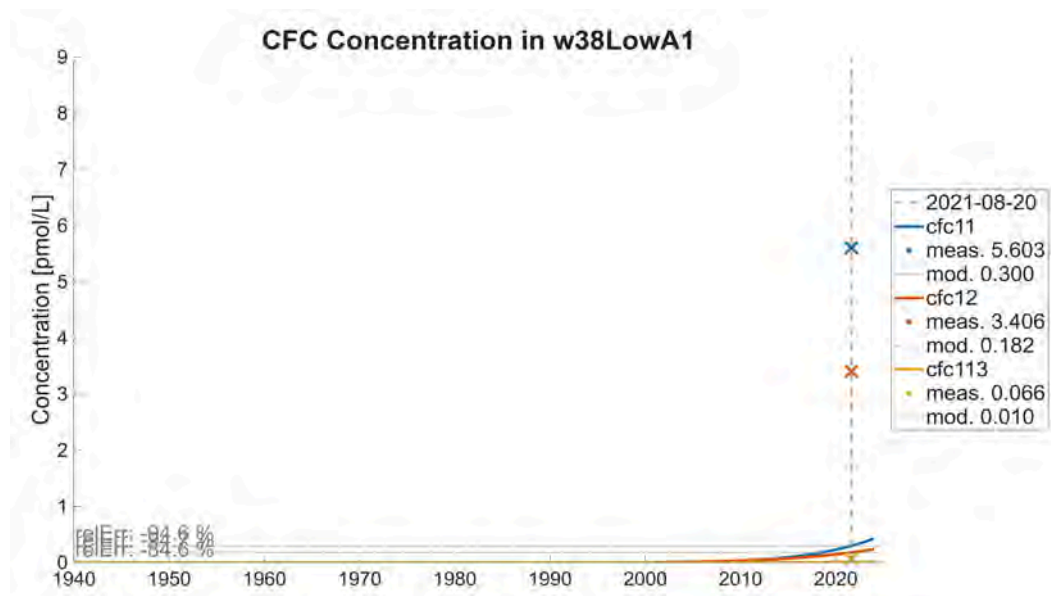
App. Fig. 85: Time series of simulated cfc concentrations at well “w37UpA1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



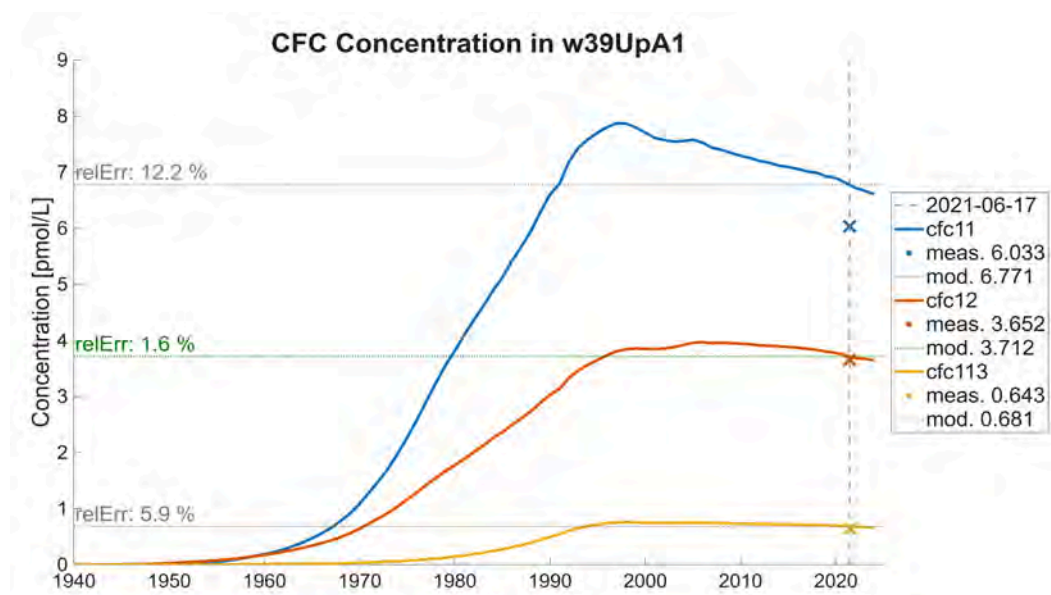
App. Fig. 86: Time series of simulated cfc concentrations at well “w37LowA1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



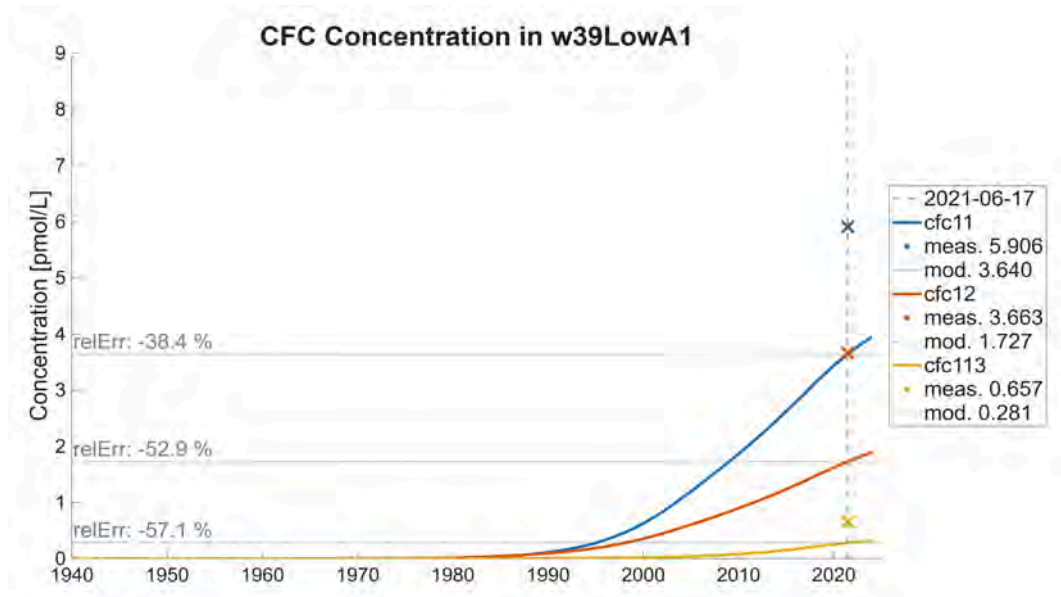
App. Fig. 87: Time series of simulated cfc concentrations at well “w38UpA1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



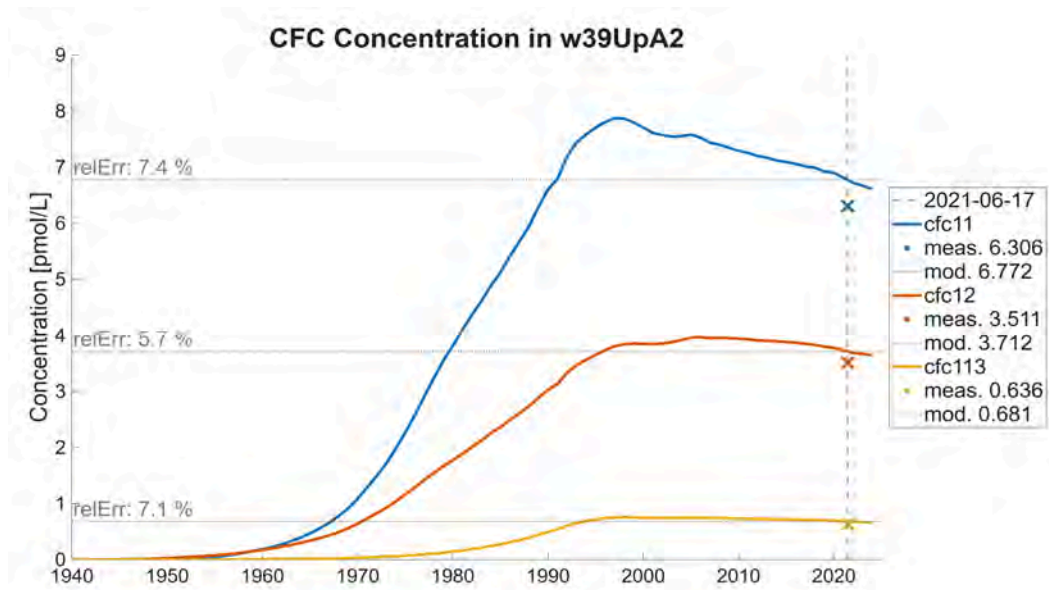
App. Fig. 88: Time series of simulated cfc concentrations at well “w38LowA1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



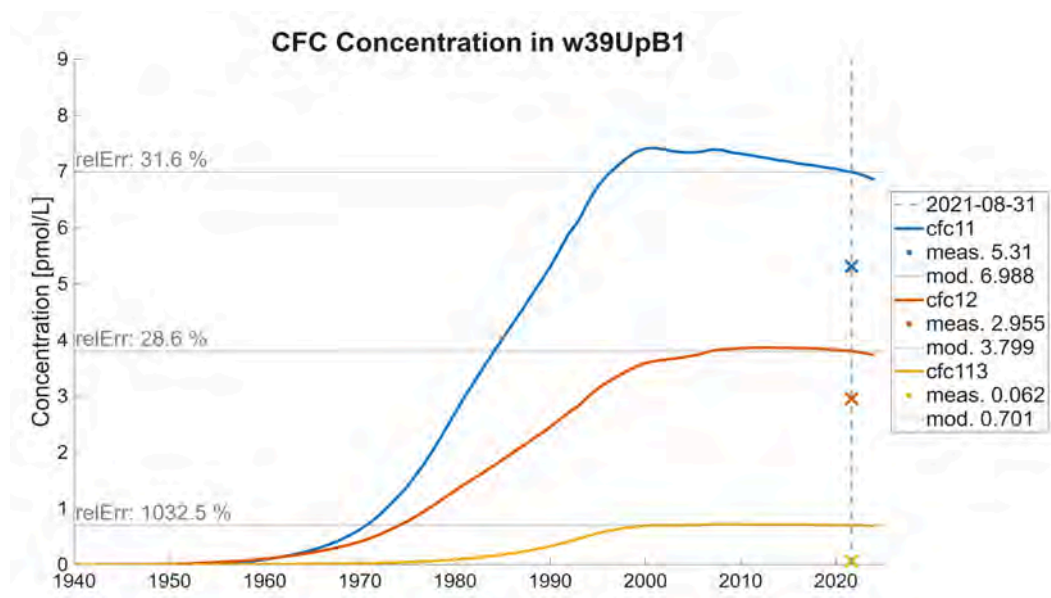
App. Fig. 89: Time series of simulated cfc concentrations at well “w39UpA1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



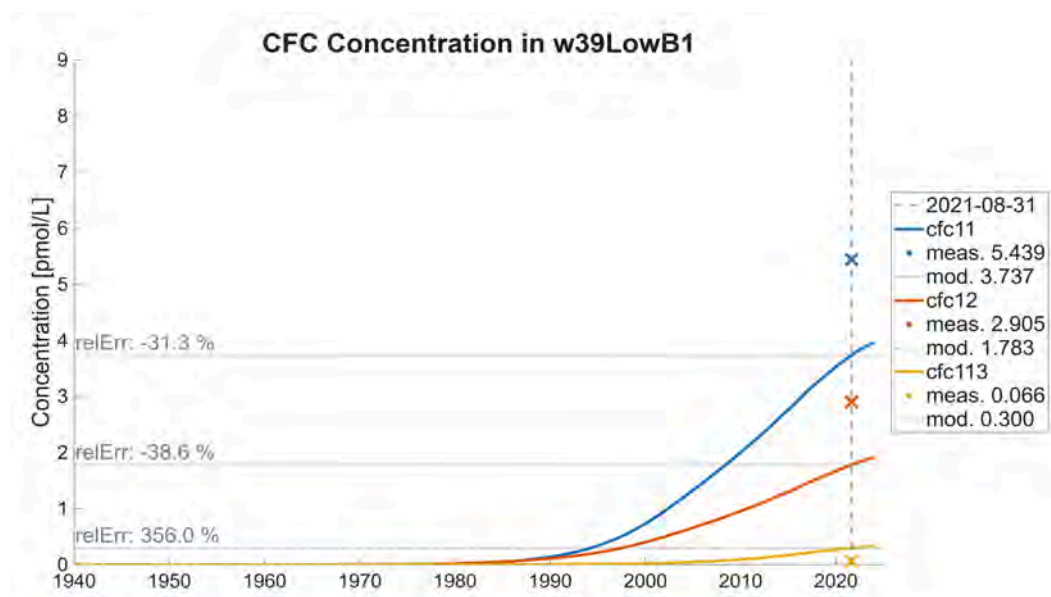
App. Fig. 90: Time series of simulated cfc concentrations at well “w39LowA1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors ≤ 5 % highlighted in green.



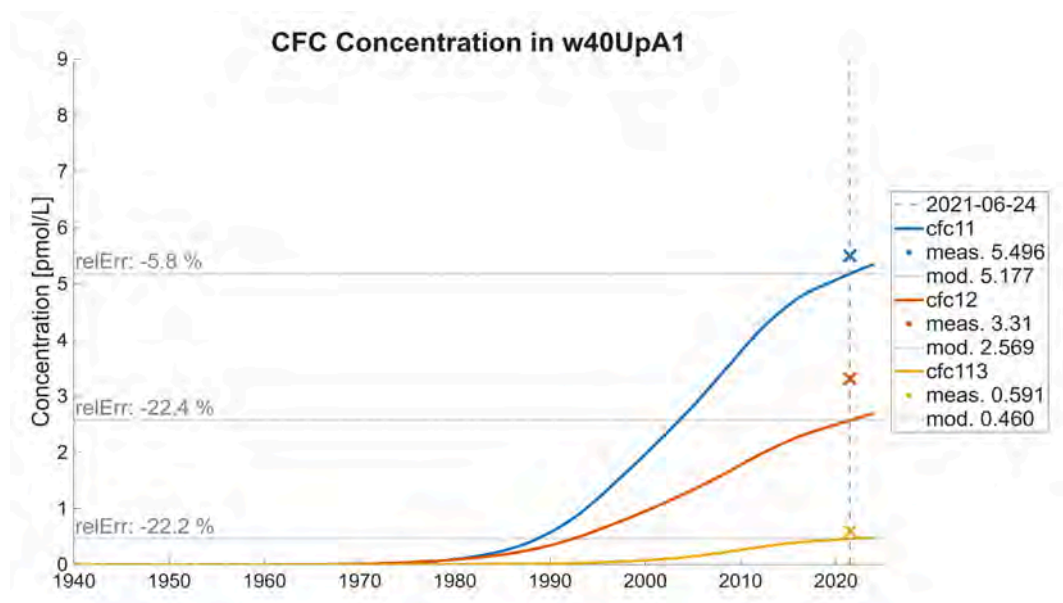
App. Fig. 91: Time series of simulated cfc concentrations at well “w39UpA2”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors ≤ 5 % highlighted in green.



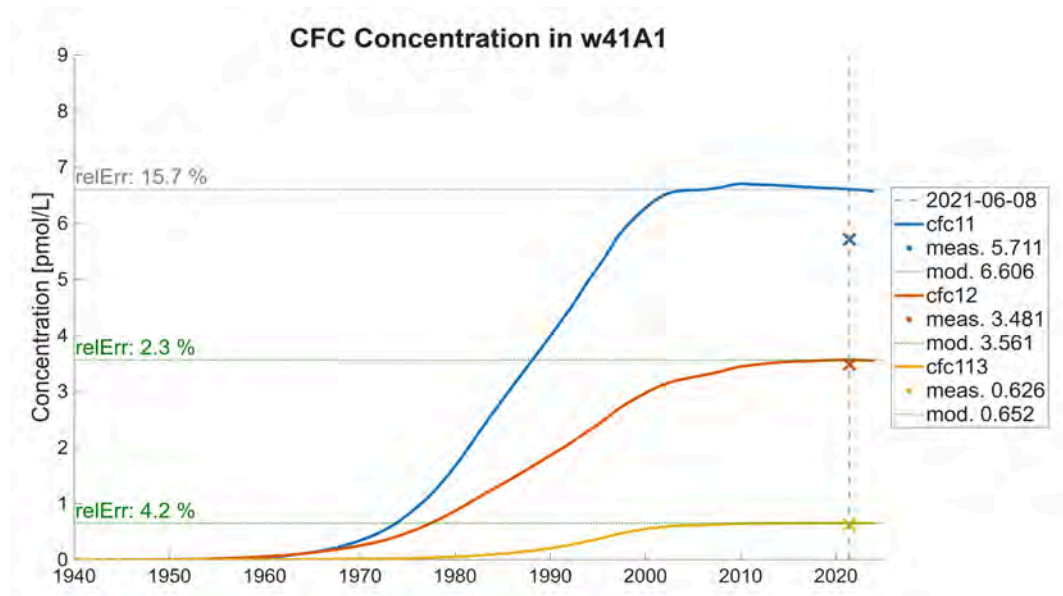
App. Fig. 92: Time series of simulated cfc concentrations at well “w39UpB1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors ≤ 5 % highlighted in green.



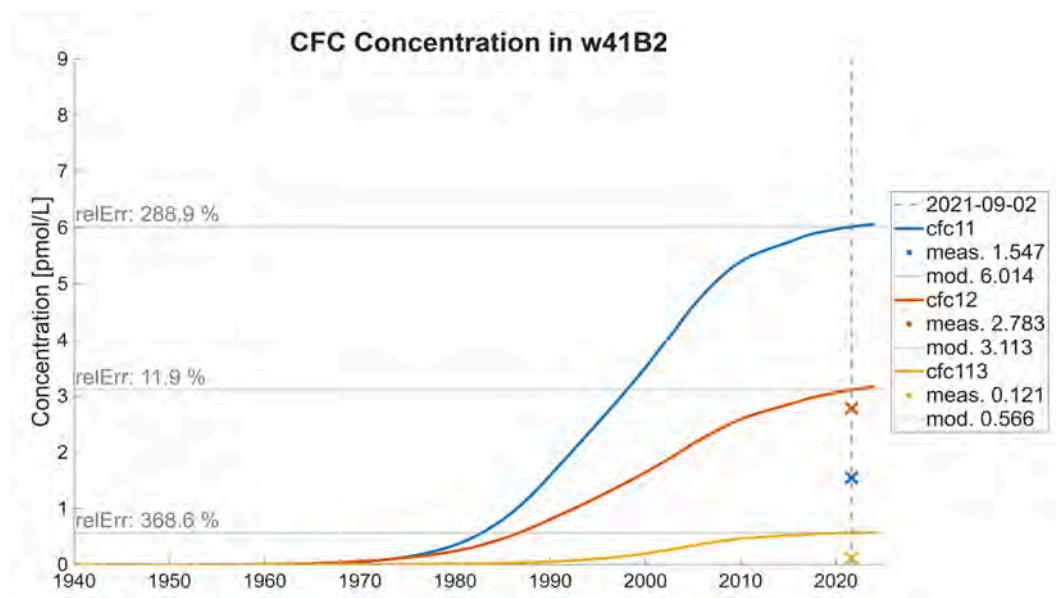
App. Fig. 93: Time series of simulated cfc concentrations at well “w39LowB1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors ≤ 5 % highlighted in green.



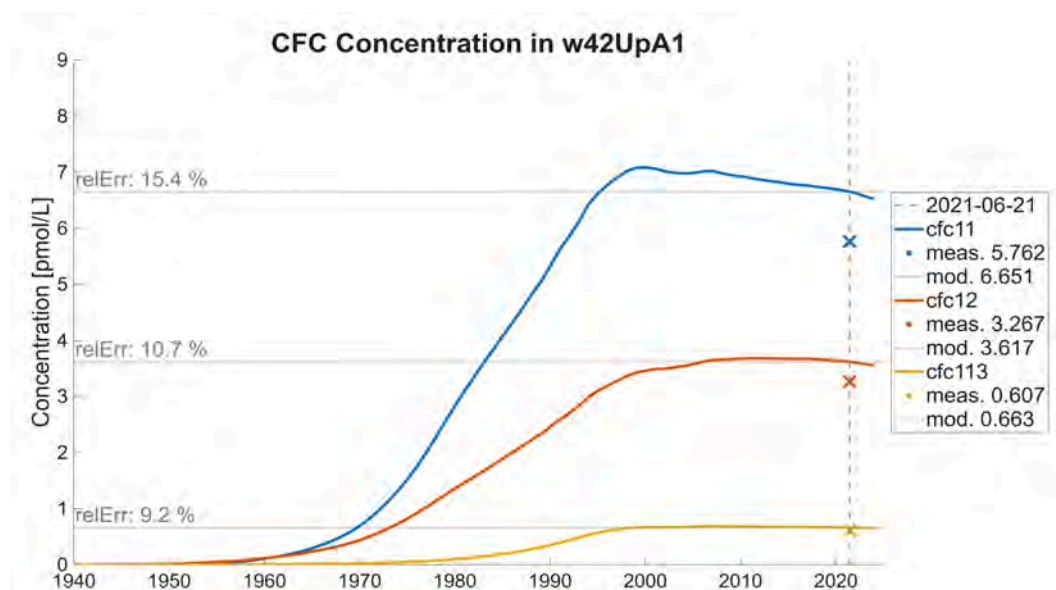
App. Fig. 94: Time series of simulated cfc concentrations at well “w40UpA1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



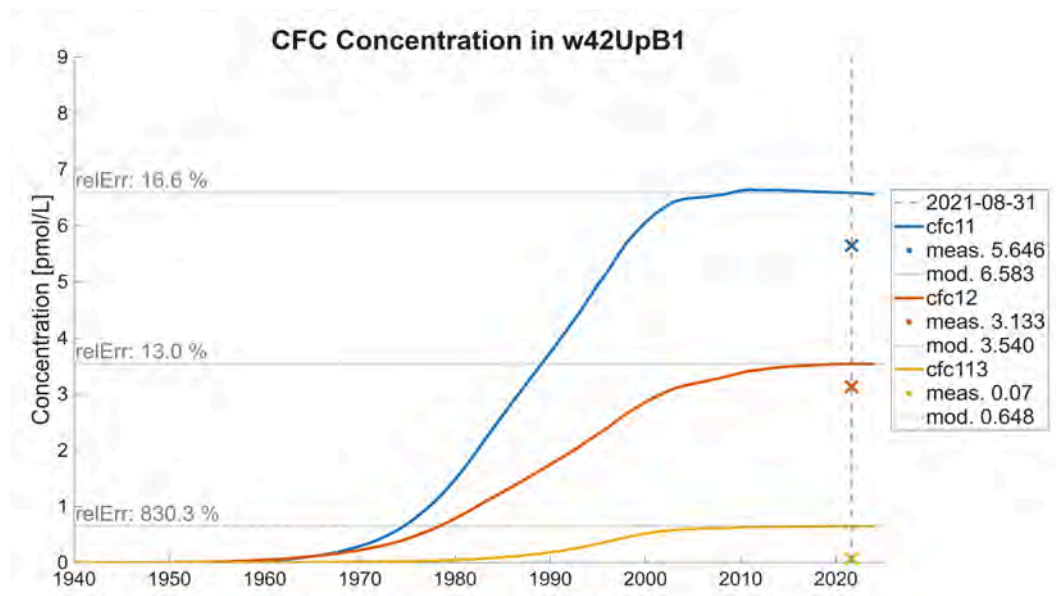
App. Fig. 95: Time series of simulated cfc concentrations at well “w41A1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



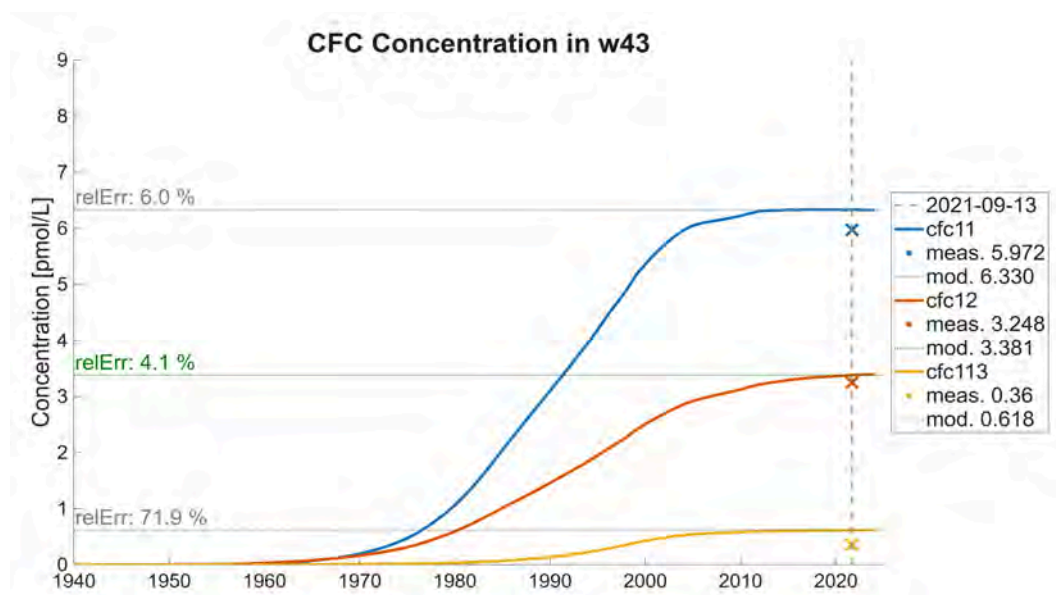
App. Fig. 96: Time series of simulated cfc concentrations at well “w41B2”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors ≤ 5 % highlighted in green.



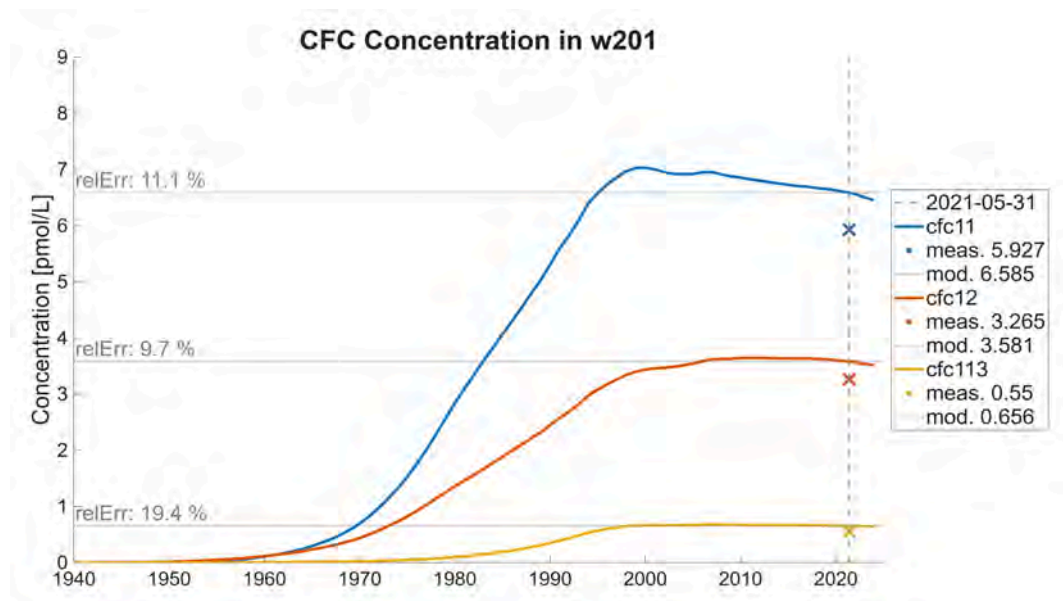
App. Fig. 97: Time series of simulated cfc concentrations at well “w42UpA1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors ≤ 5 % highlighted in green.



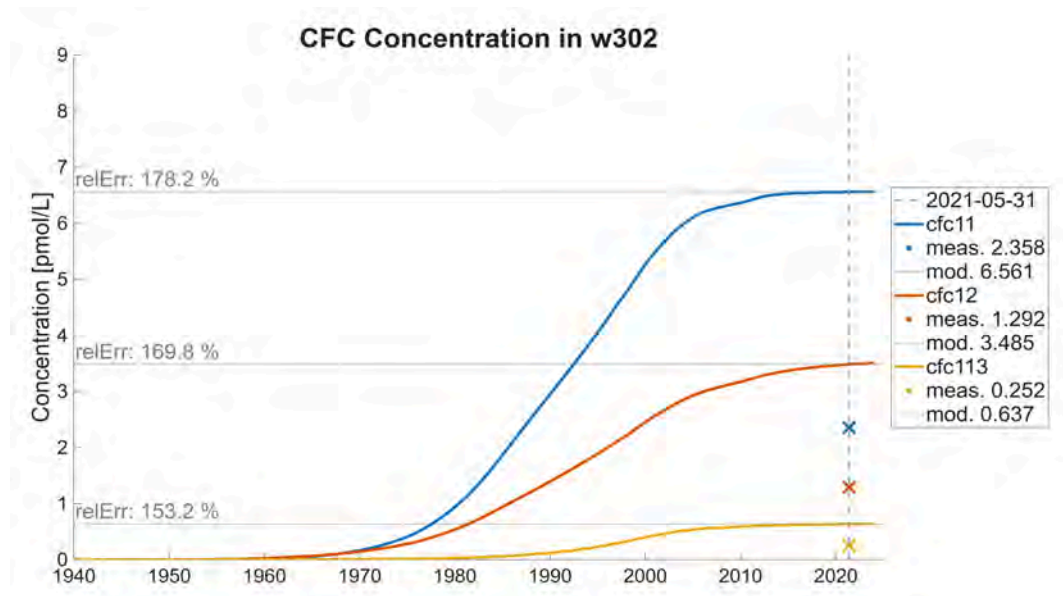
App. Fig. 98: Time series of simulated cfc concentrations at well “w42UpB1”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



App. Fig. 99: Time series of simulated cfc concentrations at well “w43”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



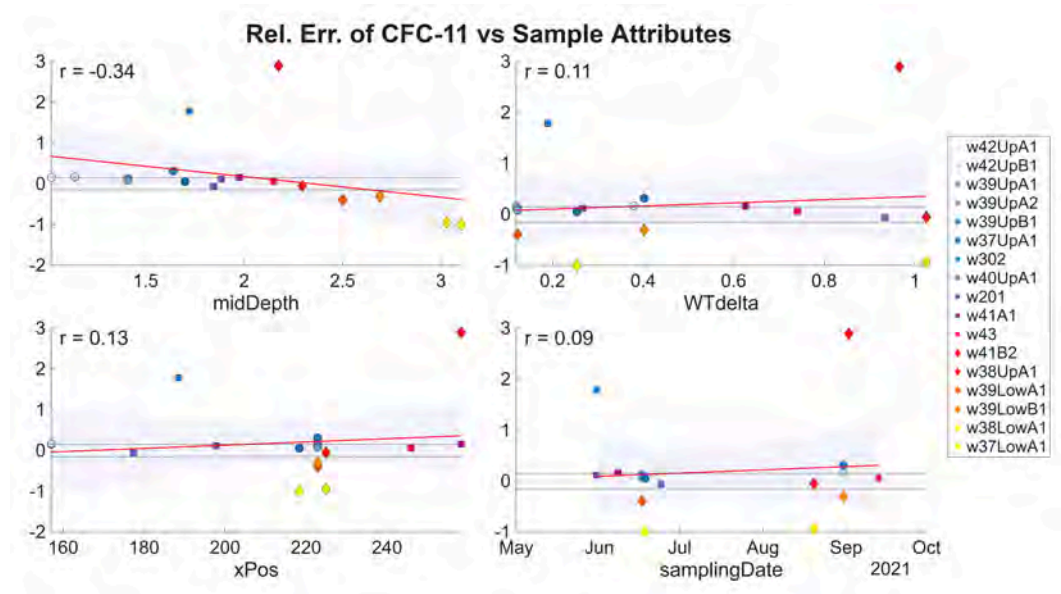
App. Fig. 100: Time series of simulated cfc concentrations at well “w201”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.



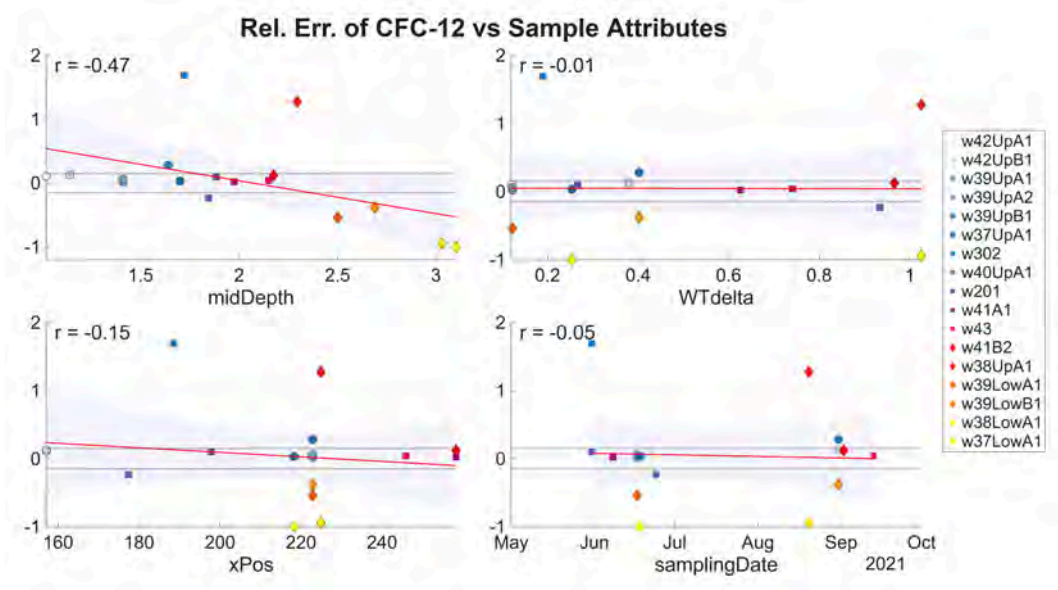
App. Fig. 101: Time series of simulated cfc concentrations at well “w302”. Concentrations as flux averages shown as solid lines and coloured by CFC. Crossmarks for sampled values, vertical dashed line is the sampling date, horizontal dashed lines emphasize simulated concentrations. Relative errors between modelled and measured concentrations given in the figure, errors $\leq 5\%$ highlighted in green.

4f Well Performance Predictors

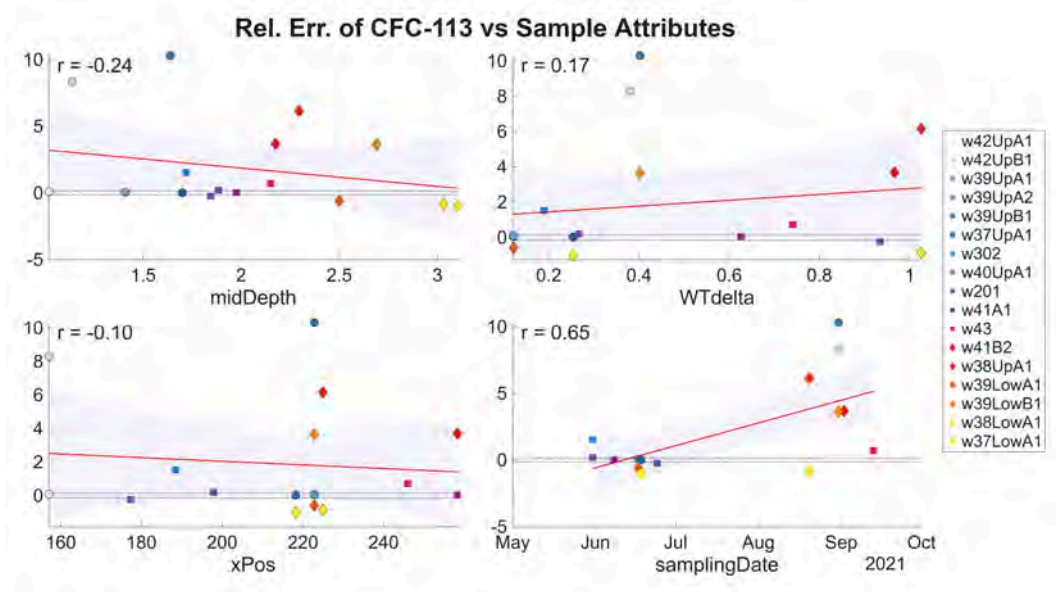
In [App. Fig. 102](#) below, the absolute relative errors of the modelled CFC-11 concentrations at all groundwater wells in the sampling year are scattered against their implementation attributes. This is repeated for CFC-12 in [App. Fig. 103](#) and CFC-113 in [App. Fig. 104](#). Wells are coloured by the depth to their midpoint from faint blue to yellow, in increasing order. Well markers are circles for shallow wells, squares for intermediate wells and diamonds for deep wells (see [Table 2](#) and [App. Tab. 8](#)).



App. Fig. 102: Relative errors of simulated CFC-11 scattered against well attributes: Depth to midpoint (midDepth); difference between water table in the model and when sampled (WTdelta); distance to the stream (xPos-140 m); sampling date (samplingDate). Linear regressions in red, 95% confidence intervals shaded, $\pm 15\%$ error bands between gray dotted lines. Well markers are circles for shallow wells, squares for intermediate wells and diamonds for deep wells.



App. Fig. 103: Relative errors of simulated CFC-12 scattered against well attributes: Depth to midpoint (midDepth); difference between water table in the model and when sampled (WTdelta); distance to the stream (xPos-140 m); sampling date (samplingDate). Linear regressions in red, 95% confidence intervals shaded, $\pm 15\%$ error bands between gray dotted lines. Well markers are circles for shallow wells, squares for intermediate wells and diamonds for deep wells.



App. Fig. 104: Relative errors of simulated CFC-113 scattered against well attributes: Depth to midpoint (midDepth); difference between water table in the model and when sampled (WTdelta); distance to the stream (xPos-140 m); sampling date (samplingDate). Linear regressions in red, 95% confidence intervals shaded, $\pm 15\%$ error bands between gray dotted lines. Well markers are circles for shallow wells, squares for intermediate wells and diamonds for deep wells.

Overall, many wells are close or inside the $\pm 15\%$ error range for CFC-11 and CFC-12 (comp. Table 2 until rank 7). However, relative errors between simulated and measured concentrations are not consistent for all CFC species. Striking in App. Fig. 102 to App. Fig. 104 are the consistent outliers “w38LowA1”, “w3LowA1”, “w302”.

The depth to the midpoint of the well results in a pronounced negative slope for the linear regression line for all three CFC species. This highlights the importance of the depth to the midpoint of the well to the simulation. CFC-11 and CFC-12 do not exhibit any trends for the other predictors, while for CFC-113 especially the sampling date provides a strong positive slope (see App. Fig. 104).

Appendix 5

Extended information on results for the stream C2.

5a Fitting results for Stream Transit Time Distributions

App. Tab. 15: Akaike's Information Criterion for the fitted distributions to the flux weighted transit times of 10,000 particles from surface to stream. "deltaAIC_next" is the difference between the best and second best AIC. Mean and median of the modelled transit times ("meanModel", "medianModel") are given next to estimates of the best distribution ("meanBestFit", "medianBestFit"). Transit times are given in years. Parameter estimates are also given for the best distribution.

Variable	Value
AIC_Gamma	32878.364
AIC_Lognormal	28957.7593
AIC_InverseGaussian	29702.6207
AIC_Weibull	31054.0706
bestFit	Lognormal
bestAIC	28957.7593
deltaAIC_next	744.8614
meanModel	2.31
meanBestFit	2.112
medianModel	0.6966
medianBestFit	0.71103
param_mu	-0.34104
param_sigma	1.4756

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