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Estimating groundwater and stream water ages with chlorofluorocarbons

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Abstract

The chlorofluorocarbon (CFC) concentrations in water were sampled to estimate the age of the groundwater and stream water at difference locations in a landscape with unconfined till aquifers. A "piston-flow model" was used for age estimation, with age values from three different CFCs used to get an estimate of uncertainty in the age estimates. An earlier study with CFC tracers in the landscape revealed a pattern of increasing age (three to six decades) with depth in the saturated zone of the aquifer. An intriguing feature of that initial study was that the most superficial groundwater, sometimes just two or three meters below the ground surface, was already three decades old. This report presents the result of three CFC sampling campaigns (2021, 2022 and 2023) in the Krycklan Catchment and Degerö Stormyr, both near Vindeln in Västerbotten. New groundwater locations were sampled to represent more of the landscape, including areas closer to the water divide and the riparian zone. Some groundwater locations were resampled, and stream water from several locations was sampled during high and low flow conditions. The new groundwater data revealed the same general pattern of increasing groundwater age with depth, with the youngest ages at the top of the groundwater column already being several decades old. This pattern was found even at local water divides, which is a feature that groundwater models will need to account for. The groundwater ages at resampled sites tended to be several years older when resampled. The piston-flow model yielded stream water ages ranging from 35 to 55 years. The estimated stream water ages at high flows and in smaller catchments tended to be at the younger end of this scale. The report concludes with suggestions for how to exploit the possibilities provided by CFC water age dating to deepen the understanding of hydrology in till landscapes.

Sammanfattning

Halterna av klorfluorkarboner (CFC) i vatten har provtagits för att uppskatta åldern på grundvattnet och bäckvattnet på olika platser i ett landskap med morän-akvifärer. En ”kolvflödesmodell” användes för åldersskattning, där åldersvärden från tre olika CFC användes för en uppskattning av osäkerheten i åldersbestämningarna. En tidigare studie med CFC-spårämnen i landskapet visade ett mönster av ökande ålder (tre till sex decennier) med djup i den mättade zonen i akvifärerna. Ett intressant fynd i den första studien var att det mest ytliga grundvattnet, ibland bara två eller tre meter under markytan, redan var tre decennier gammalt. I denna rapport redovisas resultatet av tre CFC-provtagningskampanjer (2021, 2022 och 2023) i Krycklans avrinningsområde och Degerö Stormyr, båda i närheten av Vindeln i Västerbotten. Nya grundvattenområden provtogs för att representera mer av landskapet, inklusive områden närmare vattendelarna och strandzonen. Vissa grundvattenrör provtogs för första gången, och bäckvatten från flera platser provtogs under hög- och lågflödesförhållanden. De nya grundvattenmätningarna visade samma allmänna mönster av ökande grundvattenålder med djupet, där de yngsta åldrarna högst upp i grundvattenpelaren redan var flera decennier gamla. Detta mönster hittades även vid lokala vattendelare, vilket är något som grundvattenmodeller bör ta hänsyn till. Grundvattnets ålder tenderade att vara flera år äldre när de provtogs igen på samma plats som tidigare. Kolvflödesmodellen indikerade att bäckvattnets ålder varierade från 35 till 55 år. Bäckvattnets ålder vid höga flöden och i mindre avrinningsområden tenderade att ligga i den yngre änden av denna skala. Rapporten avslutas med förslag på hur man kan utnyttja de möjligheter som CFC-vattenålder ger för att fördjupa förståelsen för hydrologin i moränlandskap.

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1 Introduction

This document presents the data obtained from three CFC water sampling campaigns, conducted between 2021 and 2023, at the Krycklan research catchment in northern Sweden. Both ground- and surface water were sampled during these campaigns. CFCs are particularly useful groundwater tracers for determining relatively "young" groundwater of 0-50 years old, Plummer and Busenberg (2000). A recent study by Kolbe et al. (2020) indicated that CFCs were also capable of detecting a depth-dependent stratification of groundwater ages. The capability of CFCs to provide more info regarding the depth-dependent nature of groundwater ages is of particular interest to SKB as an additional method to help calibrate and validate its 3D, physically based, numerical hydrological models historically used in its safety assessments (Werner et al., 2013, Bosson et al., 2009, Bosson et al., 2008).

1.1 The 2017 CFC Study: Lagged rejuvenation of groundwater ages in shallow till aquifers

In September 2017, with support from SKB, groundwater was sampled for chlorofluorocarbon (CFC) age dating from nine piezometers within the shallow till aquifer of the Svartberget catchment near Vindeln (subcatchment C7 in the Krycklan Catchment Study (Laudon et al., 2013)). The samples were taken at depths ranging from of 2 m to 18 m below ground (Figure 1-1, upper left panel). All sampling locations were located in glacial till at distances between 20 m and 80 m from the stream network. The unsaturated zone was between 0.9 m and 2.7 m during the sampling campaign as deduced by the groundwater level measurements taken during the sampling campaign. Results showed an overall pattern with an unexpected relationship between CFC-based groundwater age and depth (Figure 1-1, upper right panel). CFC-based groundwater ages were already 30 years immediately below the water table and then increased with depth. By representing the entire catchment as a 2-Dimensional hillslope, a groundwater flow model could reproduce the observed groundwater age stratification (Kolbe et al., 2020). This model is based on a hypothesis about groundwater flow patterns which could be tested (Figure 1-1, lower left and lower right panels). The groundwater age of 30 years at the water table indicated a lag of rejuvenation. This phenomenon was possible to explain as return flow of groundwater at a subsurface discharge zone along the interface between the two different till soil types. This lag of rejuvenation is a strong indicator for the extent and structure of the subsurface discharge zone. By analysing the CFC-based groundwater age versus depth relationship, an overall pattern of groundwater recharge could be estimated for the catchment.

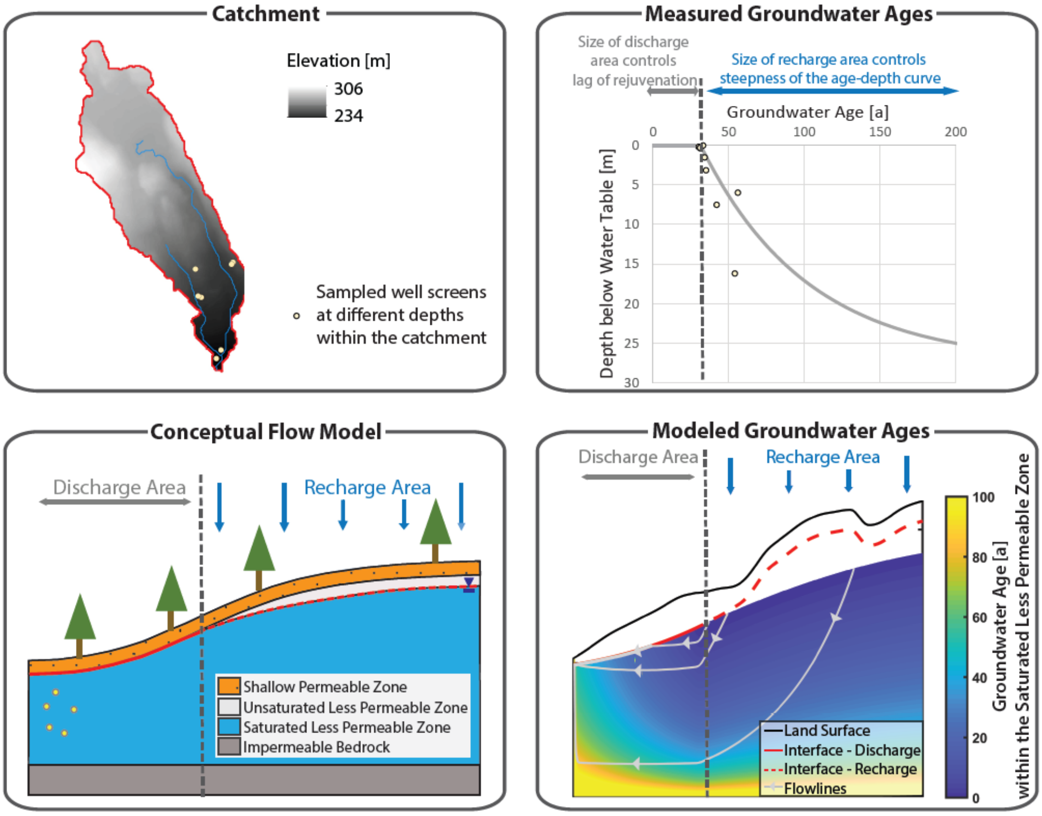

Figure 1-1 *The graphical abstract from Kolbe et al. (2020). The upper left panel shows the subcatchment C7, the topography and sampling locations. The upper right panel is the measured CFC-based groundwater ages versus depth, and an analytical approximation of this relationship. The lower left figure presents the resulting conceptual model used to explain the observations. The lower right figure shows the distribution of groundwater ages within the aquifer derived from the hs1d model. Note that the CFC-dated groundwater ages available for calibrating this model were all collected in the downslope discharge area of the conceptual flow model (lower left panel). Between 2021 and 2023, SKB financed sampling of groundwater even in the catchment recharge area as a test of the model presented in Kolbe et al., (2020)*

The initial study on CFC-based groundwater age within the aquifer was explained as a lag of rejuvenation in locations close to the stream network (20 m to 80 m). These areas were defined as “subsurface discharge zones”. The motivation for this study is to allow for testing of the conclusions arrived at in Kolbe et al. (2020) by sampling groundwater CFCs in subsurface recharge zones as well as subsurface discharge zones. This extended measurement campaign was made possible due to the installation of a more extensive network of groundwater wells in 2018 (Erdbrügger et al. 2023). In total, 75 wells were placed in subcatchments C6 (54 wells) and C7 (21 wells). In addition to sampling from upslope “recharge zones”, we wanted to test the consistence of CFC groundwater ages by repeated sampling at the same groundwater locations. Furthermore, there was an interest in exploring the possibility of using CFC dating to estimate surface water ages.

The report presents the CFC data collected with SKB support during three CFC sampling campaigns conducted in 2021, 2022 and 2023. In 2021, 44 samples were taken from 28 of groundwater wells. Surface water was also sampled the outlet of two subcatchments to test the applicability of method in this region. In 2022, additional groundwater samples were taken (3 samples) in deeper wells within the Krycklan catchment. Data was complemented with measurements from riparian wells (3 samples) and within the Degerö Mire (5 samples) and nine streams on two occasions to test the distribution of water ages during baseflow and peakflow conditions (18 samples). In 2023, surface water was sampled again to see how concentrations vary for different flow conditions (29 samples). Coordinates of all sampling locations are presented in Appendix B.

The purpose of this report is to present the data gathered during the three sampling campaings in order to make it available for further analyses. An in-depth analysis of the sampling data is not undertaken in this report.

2 Methods

2.1 Chlorofluorocarbons (CFCs) as water age tracers

2.1.1 Water age definition

Water ages are key descriptors for flow dynamics that control the transport and transformation of contaminants, carbon, weathering products and other biogeochemical elements.

The **groundwater age** is defined in this study as the time that water needs for traveling from entry points at the water table to the sampling location. It is assumed that there is no mixing of different ages (piston flow assumption; Suckow 2014).

The **stream water age** is here defined as the time that water needs for traveling from the entry point at the water table to the sampling location at a stream outlet. It is assumed that there is no mixing of different ages (piston flow assumption; Suckow 2014).

2.1.2 Background on CFCs

Chlorofluorocarbons (CFCs) are industrial products that were used as refrigerants, working liquids in air-conditioning systems, blowing agents for foam and plastics, aerosol propellants, etc. (Lovelock 1971). Their industrial use started in the 1930s for CFC-12, in the 1950s for CFC-11 and in the 1970s for CFC-113. These compounds have since entered the hydrological cycle. Restrictions on CFC use following the Montreal Protocol (1987) have led to slow declines in atmospheric concentrations. This has created some ambiguity for interpretation of CFC measurements made in groundwater or surface water after 1990. This ambiguity is similar to the situation faced when using tritium as a groundwater age tracer after the cessation of atmospheric nuclear weapons testing in 1963.

Atmospheric concentrations are measured at a few stations worldwide. The monitoring is managed by the Climate Monitoring and Diagnostics Laboratory of the National Oceanic and Atmospheric Administration (NOAA), U.S. Department of Commerce, and the ALE/GAGE/AGAGE network (Cunnold et al. 1997). Monitoring started in 1976 and prior CFC mixing ratios were reconstructed from production data (IAEA 2006). Measurements show little variations between stations (10% between average concentrations in Ireland, Oregon, Barbados, Samoa and Tasmania; Cook and Solomon 1997).

The use of CFCs for dating groundwater started in the 1990s (Busenberg and Plummer 1992). Since then, CFCs have become established tracers for groundwater dating. Several case studies (Kolbe et al. 2016; Kolbe et al. 2020; Ayraud et al. 2008), reports (IAEA 2006), review publications (Höhener et al. 2003) and textbooks (Kazemi 2006; Cook 2001) have been published for dating groundwater with CFCs. Their use in streams is limited as CFCs partially re-equilibrate with the ambient atmospheric concentration within hours. The stream water CFC concentration is then somewhere between that representing the age of the discharging groundwater and the value for equilibrium with the atmosphere (Sanford et al. 2015).

2.1.3 Sampling and analysis

The sampling and analysis of CFCs used in this study follows practical advices and guidelines as implemented by the The Laboratory for Hydrology and Field Hydrogeology Experiments (LETH2) at the University of Rennes, France (IAEA 2006; Busenberg and Plummer 1992; Kazemi 2006).

While sampling CFCs, care must be taken to avoid contact with the atmosphere. Samples can be taken by (1) cap glass bottles (125 ml or 1 l) closed with a special foil-lined cap (details are given by the USGS: http://water.usgs.gov/lab/chlorofluorocarbons/sampling/bottles/), (2) glass bottles (500 ml) closed by ground-glass stoppers which are stored in a specific metallic box full of additional sampling water through the analysis, (3) steel cylinders consisting of Swagelock cylinders (40, 300 and 500 ml) closed by two Swagelock ball valves (Labasque et al. 2014). While sampling using methods (1) and (2), bottles are placed in a beaker which is continuously overflowing with pumped water in order to avoid atmospheric contamination. When applying sampling method (3), the steel cylinders are directly connected to the pumping tube in order to avoid atmospheric contamination. All sampling containers are rinsed with at least three times their volumes using water pumped from the sample point before sampling takes place.

For the analysis of CFC concentrations, the following analytical systems are used: gas extraction system (sparge system, headspace or purge and trap) and electron capture detector gas chromatography. The main analytical systems used worldwide are listed in Table 3-1 of Labasque et al. (2014). Standard calibration gases are needed for the procedure. These are provided by a limited institutions (Labasque et al. 2014). CFC concentrations are reported in pg/kg of water or in pptv.

Labasque et al. (2014) discusses the influence of method uncertainties, uncertainties related to the sampling system and the shape of the atmospheric input function on groundwater dating.

2.1.4 Dating Water

Principles on dating groundwater with CFCs can be found in: Kazemi (2006), IAEA (2006) and Plummer and Busenberg (2000). Dating principles for groundwater can be transferred to surface waters (Sanford et al. 2015). CFC concentrations measured in the aquifer might be affected by transport and chemical processes (see. 1.1.5), so assumptions are made regarding transport and chemical processes. The simplest applied assumption regarding transport processes is the piston flow assumption that assumes that CFC concentrations are not altered by transport (see 2.6). Chemical processes are usually not accounted for.

The procedure to date water with CFCs:

1. Measurement of CFC concentrations in the water sample (usually less than 400 pg/kg).
2. Determination of air temperature at which recharge occurred.
3. Calculation of solubility of the CFCs at the considered temperature based on Henry's law solubility (Warner and Weiss 1985). Solubilities are available in a number of textbooks, e.g. Plummer and Busenberg (2000).
4. Calculation of equivalent atmospheric concentration (EAC) of CFCs

$$\mathrm{EAC} = \frac{CFC}{\mathrm{S} \times \mathrm{MW}}$$

   with S the solubility in mol kg^{-1} atm^{-1} and MW the molecular weight of CFCs with unit of g/mol (137 for CFC-11, 121 for CFC-12 and 187 for CFC-113).

5. Under the assumption of piston flow the EAC is then compared to atmospheric CFC concentrations and the year of recharge is determined.

2.1.5 Limitations and potential errors

Besides the potential contamination by the contact with air, there are several processes that can affect CFC concentrations and consequently their interpretation. Below are the most important processes and their effects on CFC based water ages. Limitations are extensively discussed in the literature (Busenberg and Plummer 1992; Cook and Solomon 1997; Kazemi 2006; IAEA 2006).

Error in estimating of recharge temperature

If the recharge temperature is over- or underestimated, then solubility of CFCs calculated is greater or smaller than real values (± 2°C: ≤ 1970 ± 1 year or less; ± 2°C: 1970-1990 ± 1-3 years; ± 2°C: > 1990 > 3 years). The larger error for water classified as younger than 1990 is due to the possibility that water younger than 1990 has been incorrectly classified as older than 1990. To rule out this possibility would be require a more detailed error analysis than we have undertaken so far. Environments with shallow water tables are most affected. This is likely to be relevant for the situation in this study with shallow, unconfined aquifers in Swedish till soils where the groundwater table is generally less that ten meters below the soil surface, and more often less than five meters.

Excess air

If excess air is trapped during recharge, the CFCs of this trapped air dissolve in groundwater leading to a rise of CFC concentrations. The environments most likely to be affected have rapid, focused recharge or fractured rocks. This is not expected to be an issue in this study.

Thick unsaturated zone (more than 5 meters)

CFC dating is based on the assumption that CFC concentrations above the water table are the same as the CFC concentrations in the air. For thick unsaturated zones (> 5 m) with high soil water content this assumption is not valid leading to an overestimation of CFC based water ages. For unsaturated zones with a thickness of less than 2 meters, the error in CFC based groundwater ages is less than 2 years. We do not think this is significant for the purposes of this study. For unsaturated zones with a thickness of 30 m, the error is between 8-12 years. This uncertainty should be kept in mind when interpreting the results.

Microbial degradation

Microbial degradation is the most common problem for using CFCs. This has been reported in anaerobic environments as well as in sulphate-reducing and methanogenic environments. CFC concentrations affected by degradation yield age estimates that are older than the real ages. The greater the microbial degradation, the greater the error. Since when microbial degradation removes CFC, it looks like the air concentration at the time of GW recharge was lower. And since levels of the CFC are generally lower further back in time, the error appears to be older.

Depending on the microbial activity, each of the different CFCs degrade at different rates. Therefore, the comparison between different CFCs helps to identify microbial degradation.

Sorption

CFCs tend to sorb onto particulate organic carbon and mineral surfaces in organic-rich sediments and peat soils. The CFC based groundwater age is then overestimated. CFC-11, CFC-12 and CFC-113 have different sorption characteristics, so that the comparison among the CFCs can help identify the extent to which adsorption may have affected the measurement of aqueous CFC concentrations.

Uncertainty in the estimation of atmospheric input function

Depending on the distance of the study site from atmospheric CFCs measurement stations, historical concentrations of CFCs might be underestimated or overestimated. Since measurement stations show nearly homogeneous concentrations of CFC, the uncertainty is expected to be low.

2.2 Krycklan - Study site description

Krycklan is a boreal, long-term monitoring and research catchment in northern Sweden (Laudon et al. 2013; Laudon et al. 2021). Initial CFC measurements in groundwater took place the Svartberget (C7; 0.47 km^2; Figure 2-1), a subcatchment of the Krycklan catchment (Kolbe et al. 2020). The topography is characterized by gentle slopes with an elevation ranging from 234 m to 306 m. At the time of the CFC sampling (between 2017 and 2023), mean temperature at the site was 1.8 °C with an average snow cover of 168 days per year. Mean annual precipitation and runoff was 614 mm and 321 mm, respectively. The area is mainly forested (82%) consisting of pine and spruce forest. The dominant soil type is glacial till that covers 65 % of the area with the remainder consisting of peat (18 %) and are thin soils (16 %) (Laudon et al. 2013). Within the glacial till area, two till types are found: A shallow (< 3 m deep from groundwater surface) ablation till and an underlying basal till that is limited by the bedrock (Nyberg et al. 2001). The mean depth of the soil to the bedrock is 11.5 m, varying between 0 m and 22 m (Lindqvist et al. 1989). The ablation till is more permeable than the basal till (Pinder and Celia 2006). The gneiss bedrock is poorly weathered and contains horizons of biotite-plagioclase and graphite-sulphide schists (Grabs et al. 2009; Mason 1990).

2.3 CFC sampling

Water samples were taken using a stainless-steel flask for CFC analysis (CFC-11, CFC-12 and CFC-113; see Appendix A). This corresponds to method #3 in Section 2.1.3. Glass bottles were used for sampling SF-6 and noble gases (Appendix A). Each of the sampling containers were rinsed 3 times before taking the sample.

Before groundwater samples were taken in the wells, the water table was measured and one well volume was purged before taking the sample.

For the surface water sampling, the pumping tube was placed closed to the streambed to sample discharging groundwater and to avoid sampling water that has re-equilibrated with atmospheric concentrations. This sampling was done immediately upstream from the weir structures measuring discharge at the subcatchment outlets. The stream discharge is measured continuously at these subcatchment outlets (see monitoring program and online data: https://www.slu.se/en/departments/forest-ecology-management/environment/krycklan/data/, accessed 20240518). The amount of inflow per unit length of stream reach does vary. The sampling points were not selected to get higher amounts of GW input. Instead, we are assuming that there is limited vertical mixing of waters in the stream, so the degree of equilibration with the atmosphere will be limited by sampling near the streambed, regardless of the local rate of inflowing water from the hillslope.

2.3.1 Sampling campaign 2021

We took 44 groundwater samples in 28 wells within the C6 and C7 subcatchment (Figure 2-1). Some of these samples were taken from locations sampled previously in 2017. Other samples were taken from the new network of groundwater wells installed in 2018 (Erdbrügger et al. 2023). Nine of the 44 samples were taken repeated samples from a well, but at from different times or different depths using a packer-system. Surface water was also sampled at the outlet of C2 and C7 to test CFCs for surface water dating at the site (Figure 2-1).

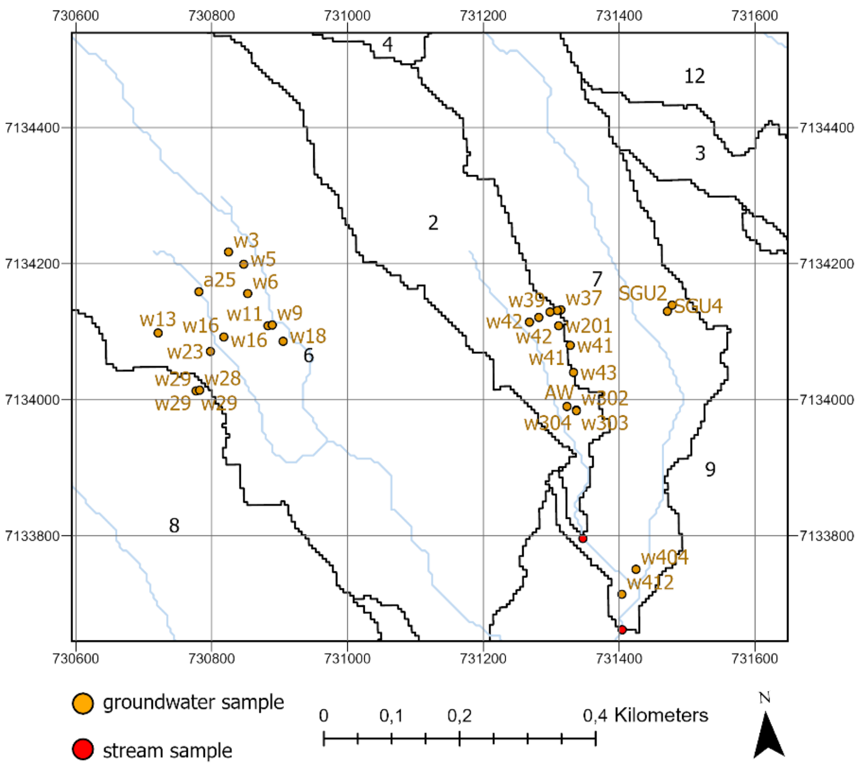

Figure 2-1 *Groundwater sampling locations within the C6 and C7 subcatchment (orange). Stream water sampling locations at the C2 and C7 outlet (red).*

2.3.2 Sampling campaign 2022

We took 3 groundwater samples at deep wells within the Krycklan catchment (W511 and W512; Nydahl et al. 2020; and tap water from a 80 m deep well at the site "field station"; Figure 2-2) that haven't been sampled during previous campaigns. To get a better understanding on groundwater dynamics in Krycklan, we sampled groundwater in riparian wells (R504, R505 and R507; Ploum et al. 2021) along the stream in C6 (Figure 2-2), we took 5 groundwater samples at the Degerö Mire (Campeau et al. 2017) and we sampled stream water twice at the subcatchment outlets (in total 18 samples; Figure 2-2). The locations and descriptions of the Degerö Mire sites can be found in Campeau et al. (2017).

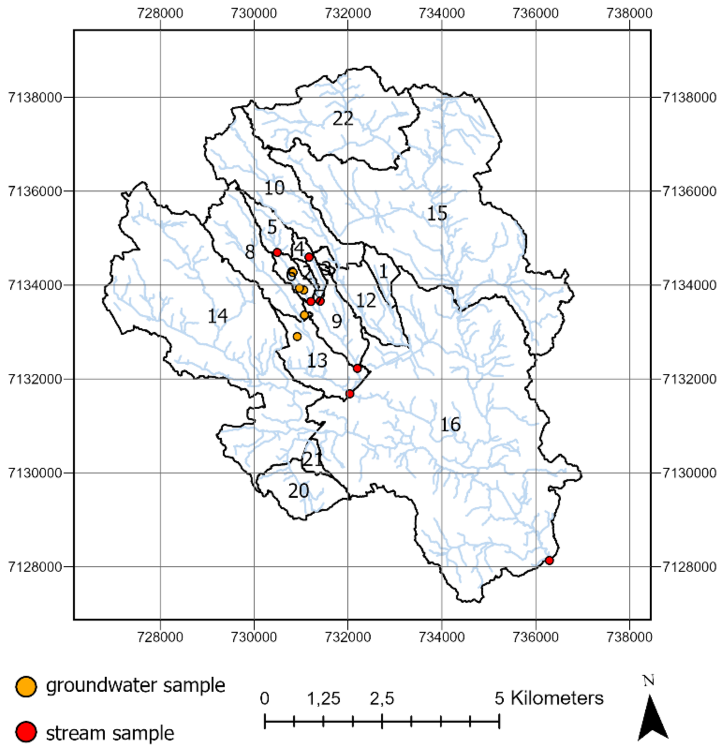

__Figure 2-2__ Groundwater and stream water sampling locations during the sampling campaign in 2022.

2.3.3 Sampling campaign 2023

We took 29 CFC samples at 12 stream outlets within the Krycklan catchment and at two stream outlets within the Degerö Mire (four sampling periods at different flow conditions; Figure 2-3). C17 and C18 are located at the outlet of Degerö Stormyr (6.5 km2, of which two thirds is peatland). Information about sites C17 and C18 can be found in Campeau et al. (2017).

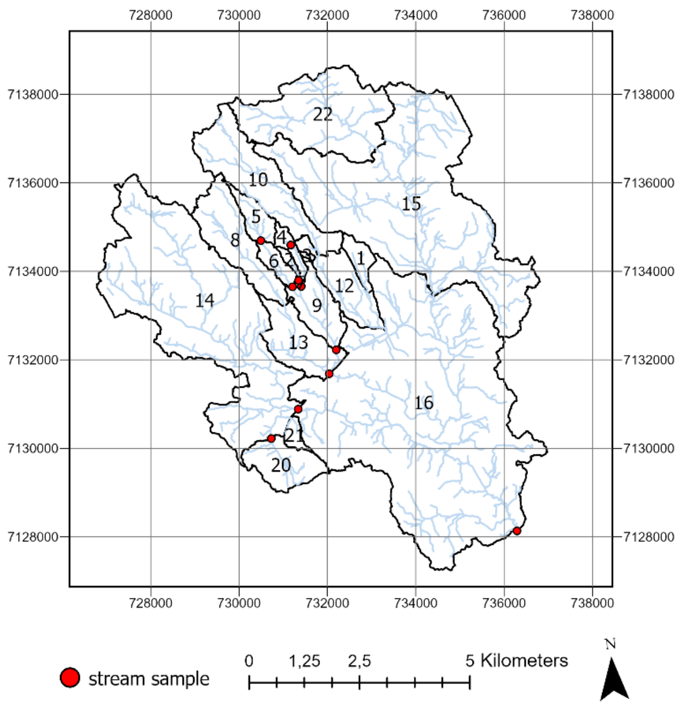

__Figure 2-3__ Stream sampling location within the Krycklan catchment during the sampling campaign 2023

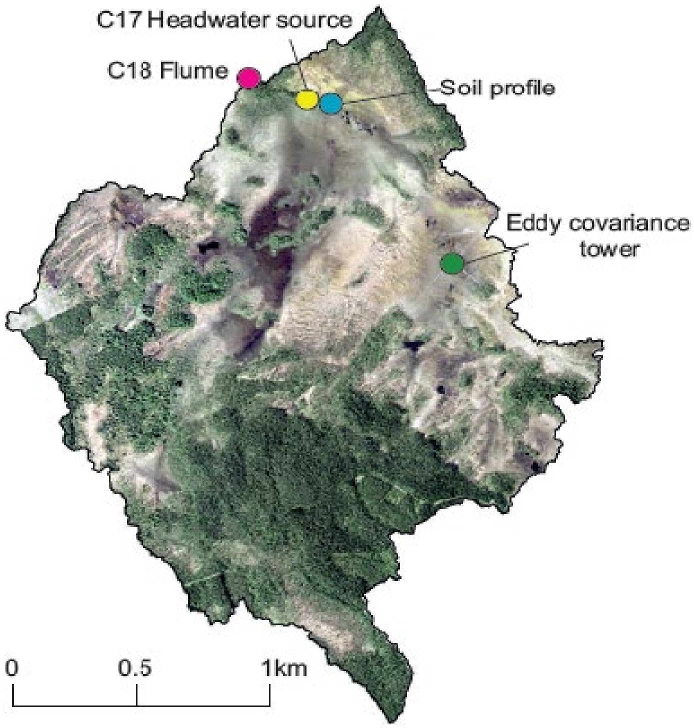

Figure 2-4 Map of the Degerö mire showing the location of stream sampling locations C18 and C17, as well as the "soil profile" in the mire where groundwater was sampled from specific depths using piezometers. Figure adapted from Campeau et al. 2017 in Global Change Biology.

2.4 CFC Data

2.4.1 CFC Laboratory analysis

Groundwater and surface water samples were analysed at the OSUR analytical platform "CONDATE Eau" in Rennes, France (Ayraud et al. 2008; Labasque et al. 2014). The analysis was performed by 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).

2.4.2 Interpretation of CFC concentrations

Groundwater samples contain a mixture of water with different recharge dates. Here, a piston flow model is applied to translate CFC concentrations to groundwater ages (Jurgens et al. 2012; Maloszewski and Zuber 1996). The piston flow model is a lumped parameter model that assumes that all water moving along a particular flow line has the same travel time. The water within the sample taken from along a particular flow line has the same age. It is assumed that CFCs are not affected by hydrodynamic dispersion or mixing And that they are transported conservatively through the subsurface with a constant flow field. The piston flow model is described by only one parameter, the water age of the sample. Furthermore, the piston flow model assumes transport occurs within an idealized unconfined aquifer with homogeneous thickness and uniform groundwater recharge (Maloszewski and Zuber 1996).

By knowing the atmospheric CFC concentrations over time, the measured concentration can be used to determine the recharge date and therefore the water age can be calculated by subtracting the sampling date from the recharge date.

Other lumped parameter models also exist: exponential flow model, linear model, combined piston flow and exponential model, combined linear flow and piston flow model and dispersion model. These lumped parameter models depend on two or more parameters (Maloszewski and Zuber 1996). All lumped parameter models provide insights about general patterns of water ages and have been useful in solving practical problems (IAEA 2006). However, these models are not applied in this study.

A comparison among the measured CFCs (CFC-11, CFC- 12 and CFC-113) gives insight into their conservative nature and potential degradation, sorption or contamination. The most reliable results are obtained when the groundwater ages of all three CFC compounds agree. In the case that a deviation is observed, this may be an indication that CFC compounds may have degraded or samples may have been contaminated; a closer look at the derived CFC-based ages is needed in these cases (IAEA 2006). For example, if the CFC-11 based age and CFC-12 based age are equal and older than the CFC-113 based age, then mixing of old and young water has likely occurred. Or if the CFC-12 based age and the CFC-113 based age are equal and younger than the CFC-11 based age, then the CFC-11 based age is most likely degraded. If the CFC-12 based age is younger than the CFC-113 based age and both are younger than the CFC-11 based age, then it most likely that CFC-11 and CFC-113 have been affected by degradation. CFC-12 is the most stable of the CFCs (IAEA 2006).

3 Results

3.1 2021 Sampling – More groundwater locations and repeating some of the 2017 locations

Table 3-1 shows an overview of measured CFC concentrations and derived CFC-based groundwater ages. The coefficient of variation indicates how consistent determined groundwater age are between CFC-11, CFC-12 and CFC-113. Some of the sites were sampled at different depths the same day. Table 3-2 indicates sampling depths below the water, unsaturated zone thickness and CFC-based groundwater ages.

Table 3-1 CFC-11, CFC-12 and CFC-113 for each of the groundwater samples. Mean CFC-based groundwater and surface water ages, the standard deviation (SD) and the coefficient of variation (CV) are also given.

Site	Date	CFC-12 [pptv]	CFC-12 age [years]	CFC-11 [pptv]	CFC-11 age [years]	CFC-113 [pptv]	CFC-113 age [years]	mean CFC age [years]	SD [years]	CV
w412	01.06.	342.2	39	10.1	61	1.5	60	53.3	12.4	23%
w404	01.06.	19.0	66	13.4	52	5.0	51	56.3	8.4	15%
w201	31.05.	387.7	36	173.4	36	49.8	34	35.3	1.2	3%
w302	31.05.	153.4	49	69.0	41	22.8	40	43.3	4.9	11%
w303	31.05.	330.9	40	17.9	43	17.1	43	42.0	1.7	4%
SGU4	03.06.	358.1	38	137.1	36	43.0	35	36.3	1.5	4%
SGU2	03.06.	425.4	34	184.4	33	62.8	32	33.0	1.0	3%
w41	08.06.	413.4	35	167.1	41	56.7	34	36.7	3.8	10%
w39	17.06.	433.7	34	176.5	40	58.3	33	35.7	3.8	11%
w42	21.06.	402.7	36	172.8	41	53.8	34	37.0	3.6	10%
w40	24.06.	393.1	36	160.8	42	53.6	34	37.3	4.2	11%
w39	17.06.	435.0	34	172.8	41	59.5	33	36.0	4.4	12%
w42	21.06.	387.9	36	168.6	38	55.0	34	36.0	2.0	6%
w37	18.06.	424.9	34	188.5	39	59.6	33	35.3	3.2	9%
w40	24.06.	446.6	34	168.7	41	58.7	33	36.0	4.4	12%
w37	18.06.	476.7	32	195.8	28	69.6	32	30.7	2.3	8%
w39	17.06.	416.9	35	184.5	39	57.6	33	35.7	3.1	9%
w41	02.09.	330.5	40	45.2	53	10.9	46	46.3	6.5	14%
w40	02.09.	324.5	40	48.1	52	41.2	36	42.7	8.3	20%
w38	20.08.	144.0	50	168.3	41	6.3	50	47.0	5.2	11%
w38	20.08.	404.4	36	163.9	42	6.0	51	43.0	7.5	18%
w39	31.08.	350.9	39	155.4	43	5.6	51	44.3	6.1	14%
w42	31.08.	309.9	42	154.3	43	37.3	37	40.7	3.2	8%
w304	06.08.	72.0	56	177.5	40	11.0	47	47.7	8.0	17%
w42	31.08.	372.0	38	165.2	42	6.3	50	43.3	6.1	14%
w39	31.08.	344.9	39	159.1	42	6.0	51	44.0	6.2	14%
AC	18.08.	224.3	46	68.7	50	24.4	40	45.3	5.0	11%
w43	13.09.	385.7	37	174.7	40	32.6	38	38.3	1.5	4%
w28	07.06.	431.3	34	216.4	33	64.2	32	33.0	1.0	3%
w11	08.06.	413.8	35	182.1	39	57.4	33	35.7	3.1	9%

Site	Date	CFC-12 [pptv]	CFC-12 age [years]	CFC-11 [pptv]	CFC-11 age [years]	CFC-113 [pptv]	CFC-113 age [years]	mean CFC age [years]	SD [years]	CV
w29	08.06.	400.5	36	178.1	34	58.9	33	34.3	1.5	4%
w29	30.08.	440.7	34	189.3	39	7.2	49	40.7	7.6	19%
w29	30.08.	416.7	35	187.0	39	48.8	35	36.3	2.3	6%
w6	18.08.	418.4	35	180.7	40	6.4	50	41.7	7.6	18%
w16	20.08.	271.7	44	87.0	48	16.0	44	45.3	2.3	5%
w16	20.08.	322.2	40	89.9	48	2.7	56	48.0	8.0	17%
w9	18.08.	375.5	37	148.4	43	40.8	36	38.7	3.8	10%
a25	01.09.	269.3	44	110.9	47	4.4	53	48.0	4.6	10%
w23	09.08.	286.4	43	119.2	46	33.9	38	42.3	4.0	10%
w13	06.08.	362.0	38	185.5	39	2.0	58	45.0	11.3	25%
w3	12.08.	94.6	53	22.3	58	1.8	59	56.7	3.2	6%
w28	02.08.	361.6	38	180.2	40	47.2	35	37.7	2.5	7%
w18	18.08.	356.1	38	147.9	44	38.3	37	39.7	3.8	10%
w5	10.09.	397.6	36	185.1	39	26.4	40	38.3	2.1	5%
C2	03.06.	559.3	20	166.4	34	56.9	33	29	8	27%
C7	03.06.	353.9	38	167.5	35	50.4	34	36	2	6%

Table 3-2 CFC-based groundwater age and sampling depths for each of the sampling locations.

Site	Date	CFC-12 age [years]	CFC-11 age [years]	CFC-113 age [years]	water table below ground [m]	sampling top below water table [m]	sampling bottom below water table [m]
w412	01.06.	39	61	60	0.9	15.9	16.9
w404	01.06.	66	52	51	2.2	6.0	7.0
w201	31.05.	36	36	34	0.9	0.0	2.0
w302	31.05.	49	41	40	0.8	0.5	1.5
w303	31.05.	40	43	43	0.6	3.6	4.6
SGU4	03.06.	38	36	35	0.6	1.7	2.7
SGU2	03.06.	34	33	32	1.0	0.8	1.8
w41	08.06.	35	41	34	1.3	0.0	1.3
w39	17.06.	34	40	33	0.9	0.0	1.1
w42	21.06.	36	41	34	0.5	1.0	2.0
w40	24.06.	36	42	34	1.4	0.0	0.8
w39	17.06.	34	41	33	0.9	1.1	2.2
w42	21.06.	36	38	34	0.5	0.0	1.0
w37	18.06.	34	39	33	1.0	0.0	1.4
w40	24.06.	34	41	33	1.4	0.8	1.6
w37	18.06.	32	28	32	1.0	1.4	2.8
w39	17.06.	35	39	33	0.9	0.0	1.1

Site	Date	CFC-12 age [years]	CFC-11 age [years]	CFC-113 age [years]	water table below ground [m]	sampling top below water table [m]	sampling bottom below water table [m]
w41	02.09.	40	53	46	1.7	0.0	1.0
w40	02.09.	40	52	36	1.8	0.0	1.2
w38	20.08.	50	41	50	1.8	0.0	1.1
w38	20.08.	36	42	51	1.8	0.5	2.1
w39	31.08.	39	43	51	1.1	0.0	1.0
w42	31.08.	42	43	37	0.8	0.7	1.8
w304	06.08.	56	40	47	1.3	8.0	9.0
w42	31.08.	38	42	50	0.8	0.0	0.7
w39	31.08.	39	42	51	1.1	0.8	2.3
AC	18.08.	46	50	40	0.1	0.0	0.5
w43	13.09.	37	40	38	1.5	0.0	1.4
w28	07.06.	34	33	32	2.4	0.0	2.3
w11	08.06.	35	39	33	0.4	0.0	1.9
w29	08.06.	36	34	33	1.7	0.0	3.7
w29	30.08.	34	39	49	3.3	0.0	1.1
w29	30.08.	35	39	35	3.3	0.6	2.1
w6	18.08.	35	40	50	1.8	0.0	1.8
w16	20.08.	44	48	44	0.7	1.3	2.3
w16	20.08.	40	48	56	0.7	0.0	1.2
w9	18.08.	37	43	36	0.9	0.0	1.5
a25	01.09.	44	47	53	0.8	0.0	0.8
w23	09.08.	43	46	38	2.5	0.0	1.5
w13	06.08.	38	39	58	2.7	0.0	3.1
w3	12.08.	53	58	59	1.3	0.5	2.0
w28	02.08.	38	40	35	3.5	0.0	1.2
w18	18.08.	38	44	37	0.2	0.0	2.0
w5	10.09.	36	39	40	1.5	0.0	1.6

CFC-12 based groundwater ages are plotted versus depth (Fig. 6). CFC-12 is the most stable compound of the three CFCs and used in Kolbe et al. (2020). Figure 3-1 shows CFC-12 based groundwater ages against depth below water table for the 44 sampling points within the C7 and C6 subcatchment. All samples have a groundwater age of 30 years or more.

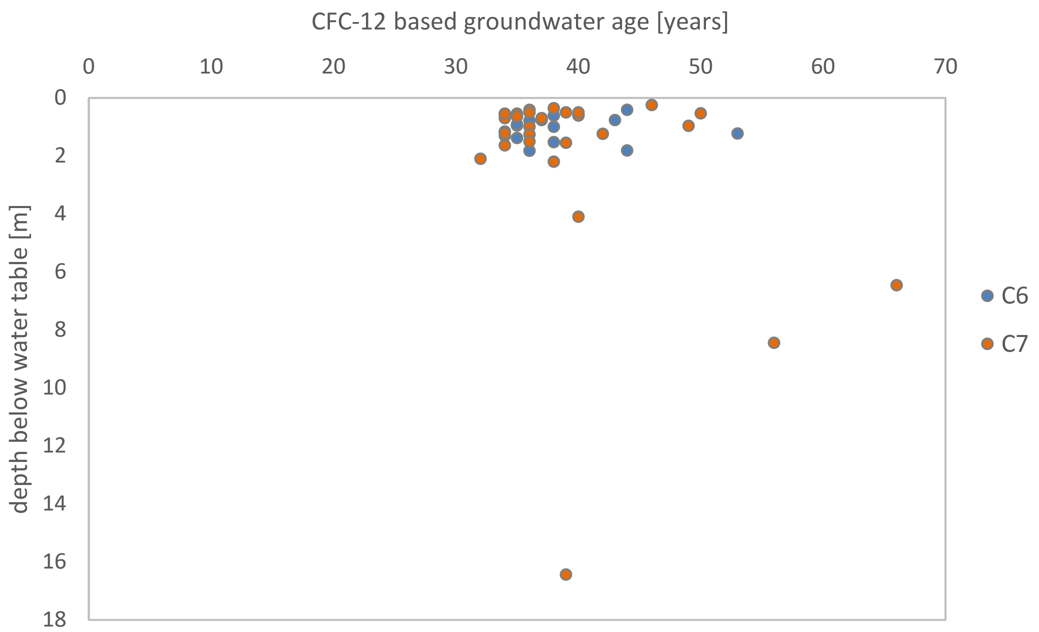

Figure 3-1 *CFC-12 based groundwater ages with depth below the water table.*

Comparing the CFC-based groundwater ages between the two sampling dates in 2017 and 2021, we see that groundwater ages show the same pattern (Figure 3-2) and that groundwater ages are older in 2021 than in 2017 (Figure 3-3). The ages sampled in 2021 are generally five to ten years older sampled that the ages than in 2017.

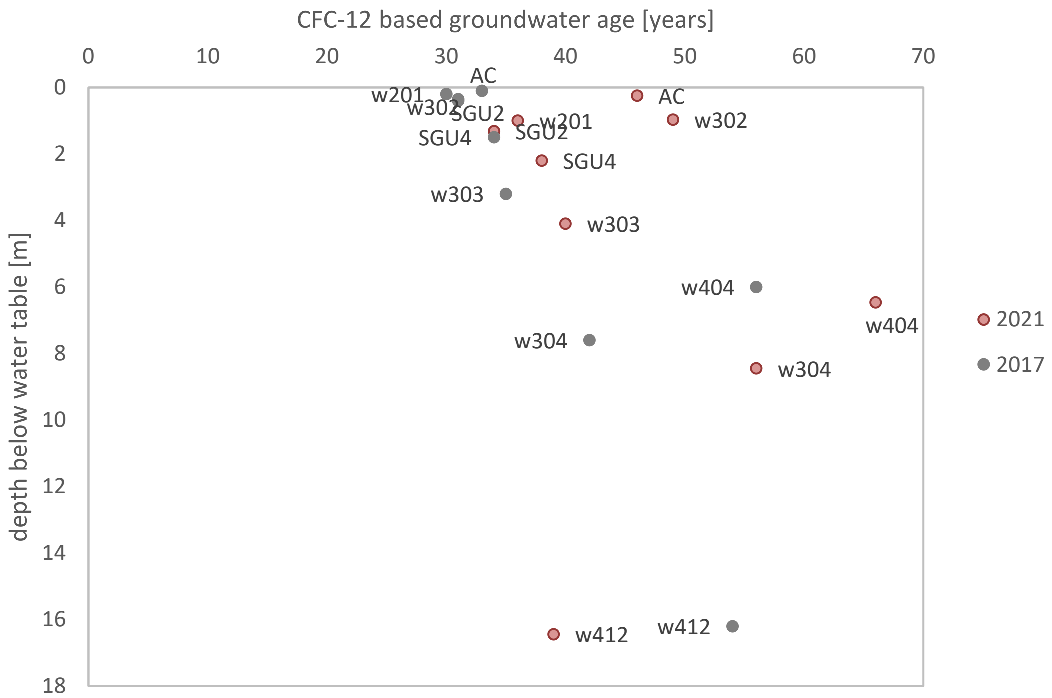

Figure 3-2 *Comparison of CFC-12 based groundwater age with depth below water table. Circles in grey and orange are results from 2017 and 2021, respectively.*

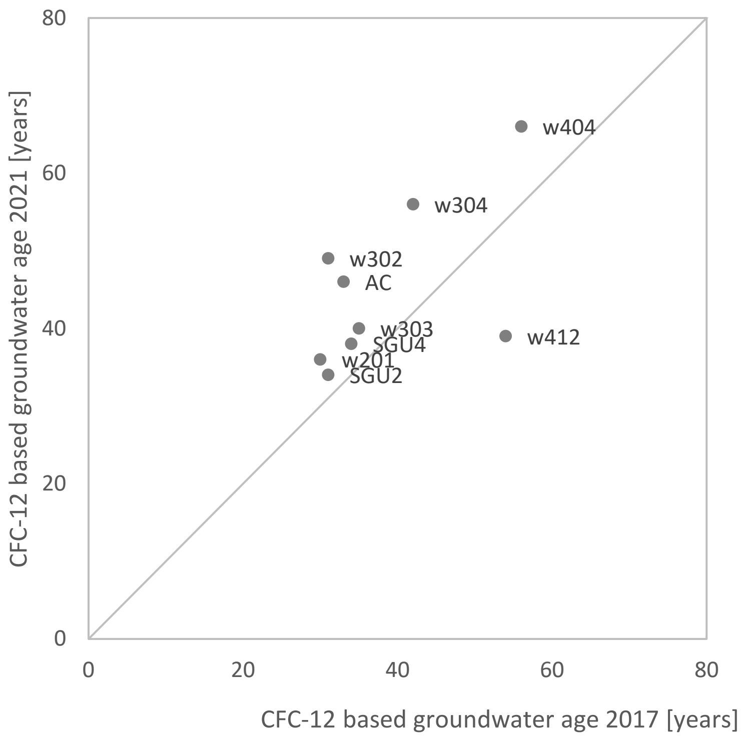

Figure 3-3 *CFC-12 based groundwater age from 2017 vs 2021.*

3.2 2022 Sampling – Stream water, mire and riparian groundwaters

Table 3-3 gives an overview of the CFC concentrations and derived CFC-based groundwater and surface water ages.

Table 3-3 CFC-11, CFC-12 and CFC-113 for each of the samples. Mean CFC-based groundwater and surface water ages, the standard deviation (SD) and the coefficient of variation (CV) are also given

Site	Date	CFC-12 [pptv]	CFC-12 age [years]	CFC-11 [pptv]	CFC-11 age [years]	CFC-113 [pptv]	CFC-113 age [years]	mean age [years]	SD [years]	CV
C4	12.05.	399.1	37	185.7	40	33.4	39	39	2	4%
C5	12.05.	362.3	39	150.3	44	25.6	41	41	3	6%
C6	09.05.	426.0	35	193.1	39	31.4	39	38	2	6%
C7	09.05.	455.5	34	214.8	37	40.0	37	36	2	5%
C9	09.05.	455.4	34	223.8	36	43.3	37	36	2	4%
C13	09.05.	435.7	35	197.0	39	31.3	39	38	2	6%
C16	10.05.	416.0	36	194.8	39	35.2	38	38	2	4%
C17	10.05.	372.8	38	130.4	46	23.3	42	42	4	10%
C18	10.05.	348.4	40	137.1	45	25.3	41	42	3	6%
field station	09.05.	27.6	64	13.1	61	7.4	50	58	7	13%
R504	12.05.	464.1	34	134.8	46	25.5	41	40	6	15%
R505	13.05.	142.8	51	2.8	68	1.0	64	61	9	15%
R507	12.05.	427.1	35	175.1	41	29.7	40	39	3	8%

Site	Date	CFC-12 [pptv]	CFC-12 age [years]	CFC-11 [pptv]	CFC-11 age [years]	CFC-113 [pptv]	CFC-113 age [years]	mean age [years]	SD [years]	CV
W511	11.05.	451.6	34	90.8	49	25.4	41	41	8	18%
W512	13.05.	116.1	53	3.8	67	1.1	64	61	7	12%
W1 Degerö	15..06	117.3	53	11.7	61	4.1	54	56	4	8%
W2 Degerö	15.06.	66.5	57	20.3	58	10.1	48	54	6	10%
W3 Degerö	15.06.	30.9	63	11.4	61	3.1	56	60	4	6%
W4 Degerö	15.06.	197.8	58	62.3	52	14.7	45	52	7	13%
W5 Degerö	15.06.	168.3	59	55.0	52	9.4	48	53	6	11%
C4	20.07.	268.9	44	91.5	49	32.4	39	44	5	11%
C5	20.07.	233.6	47	95.1	49	19.0	44	47	3	5%
C6	20.07.	260.8	45	112.0	47	33.2	39	44	4	10%
C7	-	-	-	-	-	-	-	-	-	-
C9	-	-	-	-	-	-	-	-	-	-
C13	20.07.	274.5	44	113.8	47	32.8	39	43	4	9%
C16	20.07.	291.5	44	123.2	46	32.8	39	43	4	8%
C17	20.07.	177.0	49	23.8	58	9.8	48	52	6	11%
C18	20.07	229.4	47	66.2	51	20.5	43	47	4	9%

*Field station is tap water from the Svartberget field station. We do not know the location of the well, or its depth. We assume it is a drilled borehole from nearby the station.

Figure 3-4 shows CFC-12 based groundwater ages measured in 2017, 2021 and 2022. CFC-12 based groundwater ages measured in 2022 are even older than the groundwater ages measured in earlier years.

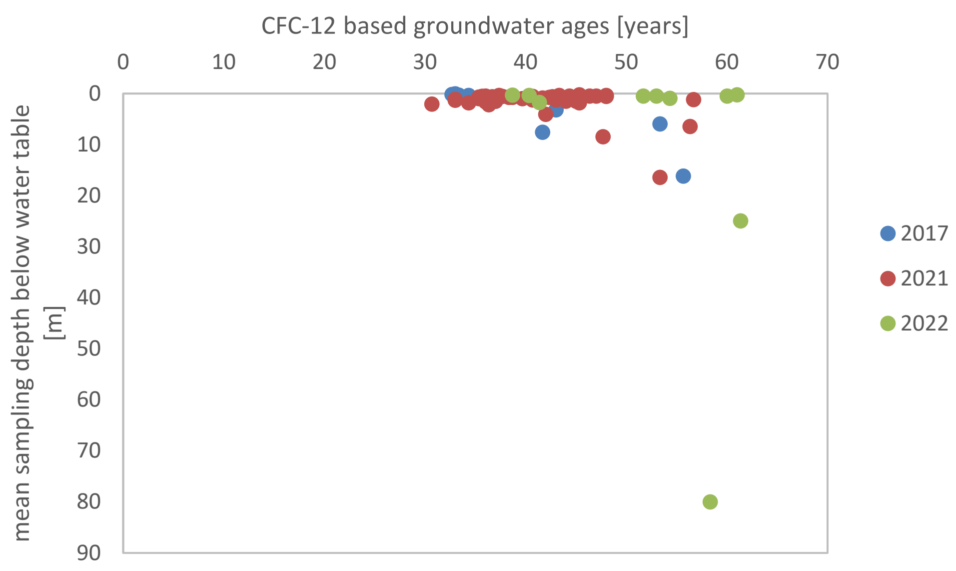

Figure 3-4 *Overview off all CFC based mean groundwater ages sampled in 2017, 2021 and 2022.*

Mean CFC-based stream water ages vary between 36 years and 56 years, representing a similar timeframe found in groundwater. Figure 3-5 compares the mean stream water age sampled in May 2022 and July 2022. Mean stream water ages at low flow conditions (July 2022) are older than at high flow conditions (May 2022)

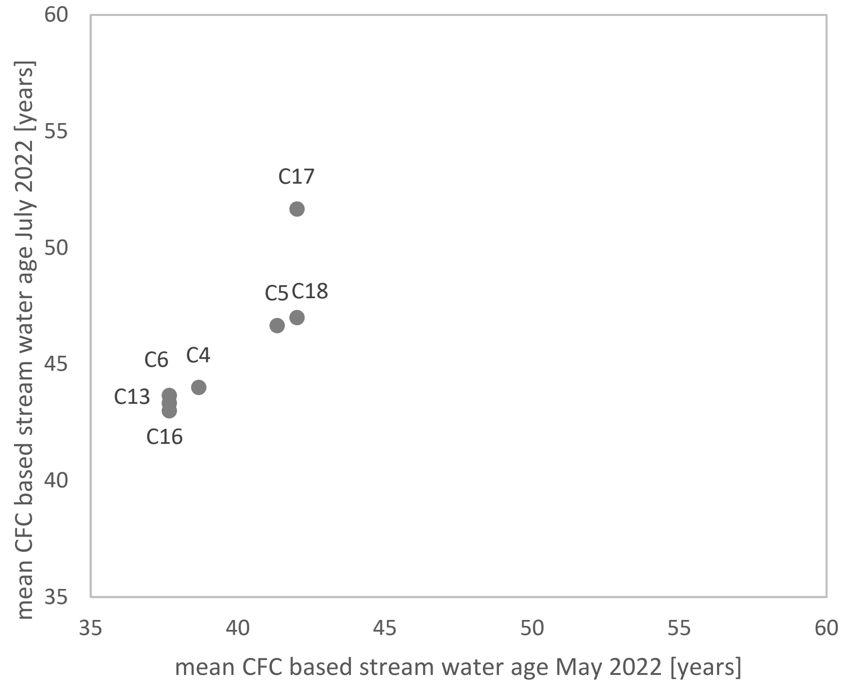

Figure 3-5 *Comparison of the two stream sampling campaigns in May 2022 and July 2022. Stream water sampled in July 2022 at low flow conditions is older than in May 2022 at high flow conditions.*

3.3 2023 sampling–Stream water

The mean CFC-based surface water ages vary between 32 and 59 years (similar range as found in groundwater). Table 3-4 gives an overview of sampling locations and measured CFC-11, CFC-12 and CFC-113 concentrations.

Table 3-4 CFC-11, CFC-12 and CFC-113 for each of the samples. Mean CFC-based surface water ages, the standard deviation (SD) and the coefficient of variation (CV) are also given

Site	Date	CFC-12 [pptv]	CFC-12 age [years]	CFC-11 [pptv]	CFC-11 age [years]	CFC-113 [pptv]	CFC-113 age [years]	mean age [years]	SD [years]	CV
C7	15.05.	486.99	33*	1790.23	-	41.74	38	35.5	3.5	10%
C13	15.05.	440.85	36	153.88	45	34.58	40	40.3	4.5	11%
C9	15.05.	431.08	36	152.09	45	34.18	40	40.3	4.5	11%
C2	15.05.	506.18	32**	179.50	42	38.44	39	37.7	5.1	14%
C6	15.05.	393.39	38	134.67	46	29.61	41	41.7	4.0	10%
C5	16.05.	304.17	43	127.64	47	28.66	41	43.7	3.1	7%
C4	15.05.	357.93	40	145.08	45	35.32	39	41.3	3.2	8%
C18	16.05.	284.91	45	94.48	49	26.46	42	45.3	3.5	8%
C17	16.05.	272.15	46	73.27	51	22.62	43	46.7	4.0	9%
C16	16.05.	364.54	40	153.26	45	32.12	40	41.7	2.9	7%

Site	Date	CFC-12 [pptv]	CFC-12 age [years]	CFC-11 [pptv]	CFC-11 age [years]	CFC-113 [pptv]	CFC-113 age [years]	mean age [years]	SD [years]	CV
C4	14.07.	165.80	51	28.06	57	14.38	46	51.3	5.5	11%
C5	14.07.	87.45	56	57.75	53	25.52	42	50.3	7.4	15%
C6	14.07.	288.07	45	117.67	48	30.72	41	44.7	3.5	8%
C7	14.07.	301.32	44	127.62	47	30.23	41	44.0	3.0	7%
C4	27.07.	225.03	48	83.32	50	26.01	42	46.7	4.2	9%
C5	27.07.	175.26	50	64.23	52	17.02	45	49.0	3.6	7%
C6	27.07.	266.03	46	117.89	48	28.42	41	45.0	3.6	8%
C7	27.07.	293.36	44	131.23	47	31.50	40	43.7	3.5	8%
C9	27.07.	276.38	45	122.84	47	32.40	40	44.0	3.6	8%
C13	27.07.	218.38	48	84.52	50	21.43	43	47.0	3.6	8%
C14	27.07.	260.04	46	113.77	48	27.66	41	45.0	3.6	8%
C16	28.07.	269.17	45	116.90	48	28.01	41	44.7	3.5	8%
C18	28.07.	256.05	46	101.18	49	24.75	42	45.7	3.5	8%
C20	27.07.	266.97	46	117.00	48	27.20	42	45.3	3.1	7%
C4	03.08.	252.80	47	87.01	50	27.01	41	46.0	4.6	10%
C5	03.08.	178.95	50	15.10	48	10.00	49	49.0	1.0	2%
C6	03.08.	262.18	46	21.88	59	14.06	46	50.3	7.5	15%
C7	03.08.	285.83	45	108.27	49	28.61	41	45.0	4.0	9%
C16	03.08.	253.56	47	106.95	49	25.94	42	46.0	3.6	8%

* CFC-12 age could be 1 year; ** CFC-12 age could be 5 years. These alternatives are due to the possibility of the groundwater age being on the "younger side" of the CFC-12 peak concentrations. We do not believe this to be likely, but call attention to the possibility.

Figure 3-6 shows the relationship between the catchment size and mean stream water age. There is a variation of stream water ages for small and large subcatchments. Figure 3-7 displays the specific discharge versus the mean stream water ages. There is a tendency that mean stream water ages decrease with increasing specific discharge.

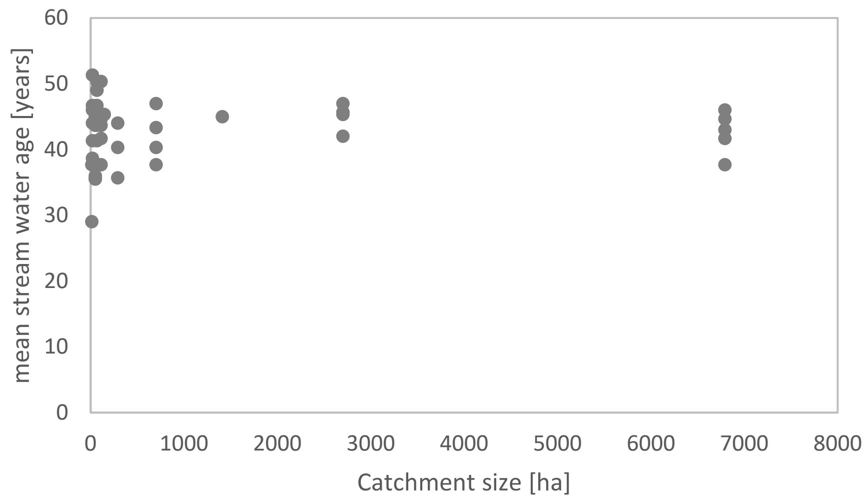

***Figure 3-6** Catchment size versus mean stream water age. Mean stream water ages from the campaign in 2021 are included.*

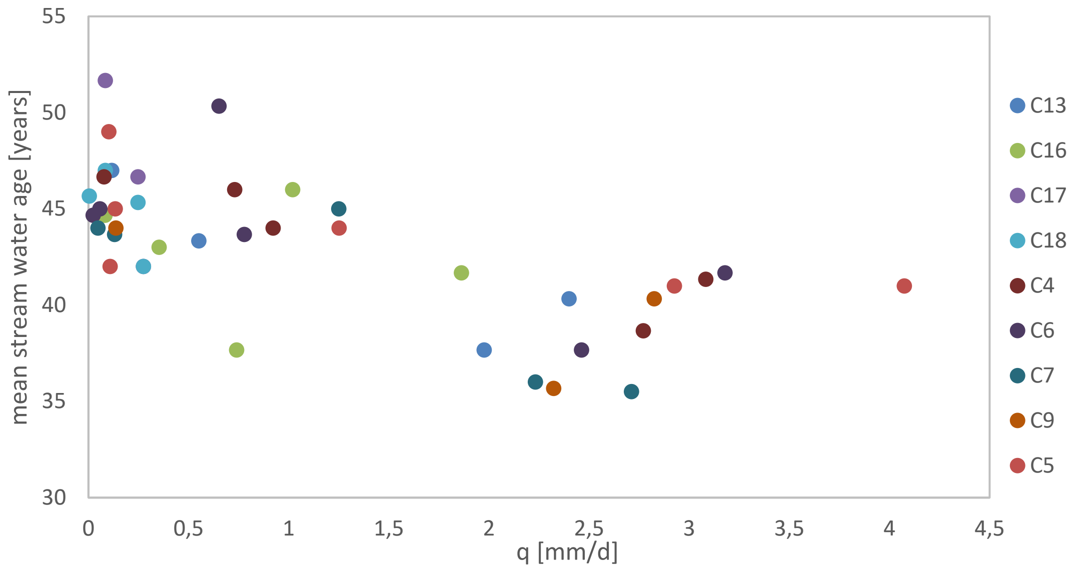

Figure 3-7 *Specific discharge versus mean stream water age for each of the outlets that have more than 2 measurements. Mean stream water ages from the campaign in 2021 are included.*

4 Suggested further work

Suggested further work involves:

1. Modeling using CFC data,
2. Combined interpretation of CFCs and stable water isotope data
3. Additional sampling on CFCs during rain events.

Modeling

So far, the data set of CFCs measured in groundwater and surface in 2021, 2022 and 2023 have "only" been interpreted with a simple lumped parameter model using the piston flow assumption. This model representation is only capable of estimating mean groundwater ages. Lumped models with 2- or 3-parameters should be tested, as well as 2D and 3D physically based numerical models. While 2D and 3D physically based numerical models are more complex and require more assumptions and calibration, these models have the ability to model individual streamlines thus being able to deliver distributions of modeled water ages rather than only estimating a mean age. This is particularly valuable for surface water samples where water from many different flow paths would be expected.

There are several intriguing features of the CFC data collected between 2021 and 2023 that are presented in this report. There appear to be systematic differences in the ages which might provide insight into the flow system which is indicated by the differences in age between the 2017 and 2021 groundwater samplings at the same locations (Figure 3-2). Another is the difference in stream age with flow rates (Figure 3-7). Finally, the groundwater collected in 2021 includes samples taken from close to local water divides. This means that the groundwater is from the upslope recharge area as conceptualized in the lower panels of Figure 1-1. Nonetheless, lagged rejuvenation is still present, with groundwater being several decades old even close to the water table. This suggests that a different approach than that presented in Figure 1-1 is needed to explain the larger set of groundwater dates available from the 2021 sampling.

Additional data on stable water isotopes

There is extensive data available at the Krycklan catchment on stable isotopes of the atoms in the water molecule (oxygen-18, deuterium). These data can provide information about water ages in the range of days to months. By combining measurements of these stable isotopes and the CFC data, new insights in the water age distributions of stream water will be provided. This mulit-tracer approach may be particularly powerful when used in particle-tracking models.

CFC sampling to get insights in flow dynamics during rain events

Stream water samples were either taken during snowmelt periods with high flow, or during baseflow conditions. CFC sampling during rainfall periods would help to understand flow dynamics at the site and how water is stored and released. So far, there are no CFC information on stream water ages during rain events from Krycklan.

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Appendix A - Sampling procedure for CFC

Sampling procedure using stainless steel vessels for sampling of CFC-11, CFC-12 and CFC-113

1. Ensure no bubbles are in the tubing connected to the pump. With pump running, raise clear tubing leaving the pump and examine tubing for bubbles. Allow all bubbles in tubing to exit the tube before sampling begins.
2. Attach flow reducer to outlet of vessel and tubing adapter to inlet of vessel.
3. Connect tubing from pump to sampling vessel while valve on sampling vessel is closed.
4. To begin sampling, first open valve on vessel inlet then open valve on vessel outlet.
5. Maintain vessel vertical and allow water to flow through the vessel for 1-2 minutes.
6. To stop sampling, first close valve at vessel outlet then close valve at vessel inlet.
7. Once sampling is completed, remove the tubing from the pump and then remove the valve levers from the sampling vessel so as to reduce the risk of the valves opening during transport.

NOTE: two stainless steel vessels need to be filled in order to sample for CFC-11, -12 and -113: one “large” vessel and one “small” vessel. The sampling procedure is the same for both vessel sizes.

Sampling procedure using glass vessels for sampling of SF-6 and noble gases.

1. Place glass sampling vessel, rubber septum or “stopper” and metal screw-cap in a bucket.
2. Over-fill glass sampling vessel with water from pump until all contents in bucket are completely submerged.
3. Continue pumping water into vessel until at least 2 liters of water spill from the bucket.
4. While keeping the bottle and septum completely submerged, place septum on bottle ensuring no air enters the bottle.
5. While keeping the bottle, septum and screw-cap completely submerged, place metal screw-cap on top of septum and screw down onto sampling vessel.
6. Invert the glass sampling vessel and examine for bubbles. If bubbles exist, repeat steps starting from step 3.

NOTE: it is advantageous to use a bucket which is dimensioned such that the sampling vessel can be submerged using a minimal amount of water as this can dramatically reduce sampling times.

Appendix B – Coordinates of all sampling locations 2021–2023

Coordinates of groundwater and stream sampling sites 2021–2023									
Site	x-coordinate	y-coordinate	elevation	Type	Comment	Sampling years			
						2017	2021	2022	2023
a25	730780.515	7134159.142		groundwater	shallow		1		
AW	731323.000	7133990.000		groundwater	shallow		1		
field station	730922.003	7132905.026		groundwater	Tapwater			1	
R504	731057.422	7133894.418		groundwater	riparian			1	
R505	730967.355	7133936.363		groundwater	riparian			1	
R507	730824.301	7134267.129		groundwater	riparian			1	
SGU2	731478.000	7134139.000		groundwater	shallow		1		
SGU4	731471.000	7134130.000		groundwater	shallow		1		
w11	730882.617	7134108.690		groundwater	shallow		1		
w13	730720.616	7134098.120		groundwater	shallow		1		
w16	730818.341	7134091.700		groundwater	shallow		1		
w18	730905.201	7134085.962		groundwater	shallow		1		
w201	731311.000	7134109.000		groundwater	shallow	1	1		
w211	731544.000	7134116.000		groundwater	shallow	1			
w213	731560.000	7134109.000		groundwater	shallow	1			
w23	730797.764	7134070.902		groundwater	shallow		1		
w28	730781.711	7134013.622		groundwater	shallow		1		
w29	730776.985	7134013.416		groundwater	shallow		1		
w3	730824.781	7134216.814		groundwater	shallow		1		
w301	731337.000	7133985.000		groundwater	shallow	1			
w302	731337.000	7133985.000		groundwater	shallow	1	1		
w303	731337.000	7133984.000		groundwater	shallow	1	1		
w304	731337.000	7133984.000		groundwater	shallow	1	1		
w37	731313.860	7134131.537		groundwater	shallow		1		
w38	731309.387	7134131.498		groundwater	shallow		1		
w39	731297.690	7134128.679		groundwater	shallow		1		
w40	731281.603	7134121.245		groundwater	shallow		1		
w404	731425.000	7133751.000		groundwater	shallow, near C2	1	1		
w41	731327.788	7134080.076		groundwater	shallow		1		
w411	731418.000	7133728.000		groundwater	near C2	1			
w412	731404.000	7133714.000		groundwater	bedrock, 18m, near C2	1	1		
w42	731268.169	7134114.137		groundwater	shallow		1		
w43	731332.658	7134040.217		groundwater	shallow		1		
w5	730846.709	7134199.081		groundwater	shallow		1		
W511	731079.105	7133353.916		groundwater	deep			1	
W512	731073.134	7133360.779		groundwater	deep			1	
w6	730853.242	7134155.675		groundwater	shallow		1		
w601	731418.000	7133728.000		groundwater	near C13	1			
w701	731418.000	7133728.000		groundwater	near C16	1			
w9	730889.010	7134110.272		groundwater	shallow		1		
C2	731423.427	7133729.536	237.6	stream	Krycklan				1
C4	731171.731	7134599.243		stream	Krycklan			1	
C5	730493.417	7134697.139		stream	Krycklan			1	
C6	731209.125	7133653.556		stream	Krycklan			1	
C7	731404.125	7133659.264		stream	Krycklan			1	
C9	732201.703	7132226.187		stream	Krycklan			1	
C13	732042.891	7131684.247		stream	Krycklan			1	
C14	731294.328	7130893.908	161.4	stream	Krycklan				1
C16	736288.417	7128133.556		stream	Krycklan			1	
C17	720577.659	7125922.478		stream	Degerö				1
C18	720577.722	7125921.588		stream	Degerö				1
C20	730744.986	7130193.593		stream	Krycklan				1