GeoERA GROUNDWATER

Hydrogeological processes and Geological Settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystems - HOVER

Deliverable 6.4

Investigation of age distributions in water supply wells and recommendations for application of tracers and models mainly for estimating groundwater ages between 100 and 1000 years

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SUMMARY

Drinking water supplies all over Europe are at risk to contamination by nitrate, pesticides, and emerging contaminants that have been released into the environment by humans over the last century. Understanding groundwater age distributions of water supply wells significantly improve the management of well fields and knowledge of contaminant transport, fate and history. This report describes the application of new tracer and modelling techniques for estimation of groundwater age distributions in the age range of 100-1000 years in water supply wells.

For a number of pilot sites in the Netherlands and Denmark, we present a chapter with a description of the water supply wells available, the hydrogeological setting and the age distributions that were previously assessed. Next, we added newly acquired data from these water supply wells, including data on the ^{39}Ar age tracer, which enables us to further refine the age distributions, especially for the age window 100-1000 years. The results of the study help to define time lags involved in the transport of nitrate and pesticides and the attenuating processes during the transport.

The report contains a brief synthesis chapter which covers the similarities and disharmonies between the Dutch and Danish approaches which contains recommendations for application of tracers and models mainly for estimating groundwater ages for well fields that pump substantial water aged between 100 and 1000 years.

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1 EXECUTIVE SUMMARY

The present document is deliverable D6.4 "Investigation of age distributions in water supply wells and recommendations for application of tracers and models mainly for estimating groundwater ages between 10 and 1000 years" of the HOVER project "*Hydrogeological processes and Geological Settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystems*".

Work package 6 of the HOVER project aims to demonstrate the use of groundwater age distributions for design and assessment of monitoring programmes, pollution trends and history and the evolution of groundwater quality (chemical status), and specifically for task 6.4 to test and develop new techniques for estimating age distributions of groundwater bodies with residence times mainly in the age range of 10 to 1000 years. Under Task 6.4, we evaluate age distributions for water supply wells in the Netherlands and Denmark as proxies for well fields in other parts of Europe.

Tracer results help constrain the age distribution of well fields and provide calibration targets for the numerical flow models that are needed to model the age in the aquifer more generally. Following the results of the current study, we strongly recommend the use of multiple tracers for assessing age distribution of well fields and pumping wells. Including the advanced ^{39}Ar age tracer has shown to provide very valuable information about groundwater flow dynamics and groundwater age and travel time distributions. The half-life of ^{39}Ar of 267 years forms a complementary value between the ^{3}H tracer (half-life of 12.3 years) and $^{14}C_{DIC}$ (half-life of 5730 years). The case studies that are presented in this report demonstrate the merits of the additional tracer; adding the ^{39}Ar tracer enables the distinction between fractions of water in the age ranges 100-300 years and 300-1,000 years and helps to further constrain the fraction of water aged less than 100 years. This is beneficial because well fields with large proportion of the age class 100-300 years are susceptible in the operational time frame of a production well field, especially because the tracer derived age might be the result of a non-stationary flow and transport situation.; the proportion of younger water may further increase with time as the age distribution might not have reached a stable state and younger water is still approaching deeper layers.

Currently, the analyses of ^{39}Ar are still rather costly and laboratories capacity is limited worldwide. It is, however, anticipated that capacity will increase with time and prices will be reduced in the future. Relative to the costs of drilling new wells, the analytical costs are limited, which makes lab capacity the most important hurdle of large-scale application in groundwater. The technique, however, promises a new step in assessing the vulnerability of well fields, and new demonstration studies are running in the Netherlands and Denmark in cooperation with drinking water suppliers.

2 INTRODUCTION

One of the aims of Work Package 6 of HOVER project is to assess the effectiveness of new tracer and modelling techniques for estimation of groundwater age distributions in the age range of 100-1000 years in water supply wells. Within Task 6.4 we tested new techniques for estimating age distributions of groundwater bodies with residence times mainly in the age range of 100 to 1000 years and evaluated age distributions for water supply wells in the Netherlands and Denmark as proxies for well fields in other parts of Europe (see Table 2.1).

Table 2.1 The following case studies are presented in the subsequent chapters of this deliverable:

Case Study	Region	Previous age dating results	New 39Ar measurements
Netherlands	Well fields of Seppe and Veghel (Noord-Brabant province)	Yes	Yes
Denmark	Well fields of Aarhus Vand, VCS Denmark and TREFOR	Yes	Yes

The results of the assessment are described in chapters for each of the two pilot areas.

This deliverable focuses on groundwater age *distributions* rather than on discrete groundwater ages because water supply wells typically mix water of different ages by the process of pumping itself. As groundwater generally ages with depth - certainly in areas with unconsolidated aquifers, such as the pilot areas in Denmark and the Netherlands (e.g. Broers, 2004) – pumping water simultaneously from different depths leads to mixing of water of different ages. For the amount of mixing, we may distinguish 4 situations (see also GeoERA HOVER deliverable 5.2: Broers et al., 2020, section 12.2):

1. Long-screened well, pumped: mixing mainly by pumping from layers at different depth, plus drawing water from above and below the screened depth;
2. Long-screened well, not pumped: considerable mixing expected from water of different depth and age, but negligible amounts of water from above and below the screened depth;
3. Shorter screen but intensively pumped: mixing over the shorter screened depth interval but also drawing water from layers above and below, depending on the pump discharge and hydrogeological buildup;
4. Short-screened well, not pumped: here we expect a more or less a discrete age for a specific thin layer of water which can be approximated by the apparent age of age tracers such as $^{3}H/^{3}He$, CFCs or ^{39}Ar.

Conceptually, one may argue that even the discrete age of situation 4. at a short monitoring screen may be regarded as an 'age distribution' (Weissmann et al., 2002) but for practical approaches this is often ignored without a loss of significant information (Visser et al., 2007; Hansen et al., 2010; Bohlke, 2002). However, once the monitoring screen has a substantial length and is pumped, the concept under type 3 is valid and the transit time should be regarded as a distribution of mixed water over the length of the monitoring screen

The current deliverable deals with the first three situations. As groundwater mixes at the pump, the transit time cannot be described by a singular age but conceptually needs to be described by a distribution (Maloziewski & Zuber, 1982; Broers & van Geer, 2005, Jurgens et al., 2012; Eberts et al., 2012). In order to assess these kinds of distributions one either needs a set of age tracers with complementary properties representing different age ranges (Visser et al., 2013; Massoudieh et al., 2014; Kolbe et al. 2018; Leray et al., 2012) or groundwater flow models that describe age or transport (Troldborg et al., 2008; Velde et al., 2010; Kaandorp et al., 2019/2020).

3 CASE STUDY BRABANT (THE NETHERLANDS)

3.1 Previous work on age distributions in the region

3.1.1 Holten public water supply wells

In a number of previous studies, we assessed age distributions of public water supply wells (Broers et al. 2012, 2015, 2021, Visser et al. 2013, Massoudieh et al. 2014).

Broers et al. 2012, Visser et al. 2013 and Massoudieh et al. 2014 focused on a set of pumping wells of the public water supply at Holten, in the province of Overijssel, the Netherlands. The results of that study are summarized in an earlier HOVER deliverable D6.2 “Collection of use cases including good practice guidance and age indicator sampling guide” by Szocs et al. (2020), see Appendix I for details. The well field Holten consists of a number of shallower and deeper pumping wells, and one of the important findings of the study was that those compete for catchment area and for the age of the pumped groundwater. Shallower wells tend to pump the younger aged groundwater, whereas deeper wells draw the older water from the distribution. Evidence for that process came from the multi-tracer study, involving ^{3}H, ^{3}He, ^{39}Ar and ^{85}Kr. The measurement of the two latter tracers was a first in the Netherlands at the time and depended on the good cooperation with Roland Purtschert of the University of Bern.

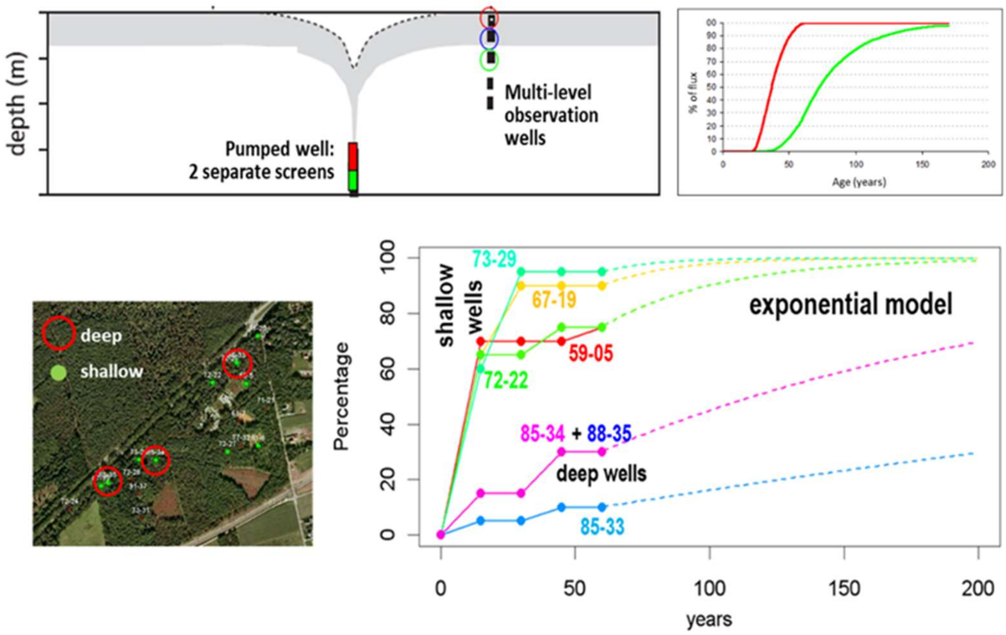

Figure 3.1 Example of age distributions at the Holten well fields based on ^{3}H, ^{3}He, ^{39}Ar and ^{85}Kr tracer data.

Figure 3.1 clearly shows that the deeper wells 85-33, 85-34 and 88-35 have a smaller contribution of water age less than 50 years. These wells pump water with 51, 77 and 74 pm Ar (percent modern Ar), respectively, whereas the shallower wells pump 93-104 pm Ar indicating modern-post 1950 waters. Unfortunately, we did not measure $^{14}C_{DIC}$ during that study, which would have enabled a further characterization of the groundwater ages.

3.1.2 Noord-Brabant public water supply wells

Broers et al. (2015) and Broers et al. (2021) assessed groundwater age distributions for 39 well fields in the Noord-Brabant region, based on a multi-tracer study including ^{3}H, ^{3}He, $^{14}C_{DIC}$, $^{4}He_{rad}$ and the Noble Gas Temperature (NGT). Instead of sampling individual pumping wells, we sampled "raw water branches" that collect the water of a set of pumping wells. Further details are available in the Water Resources Research paper (Broers et al. 2021) that was published as an outcome of the H3O-PLUS work package of the GeoERA RESOURCE project.

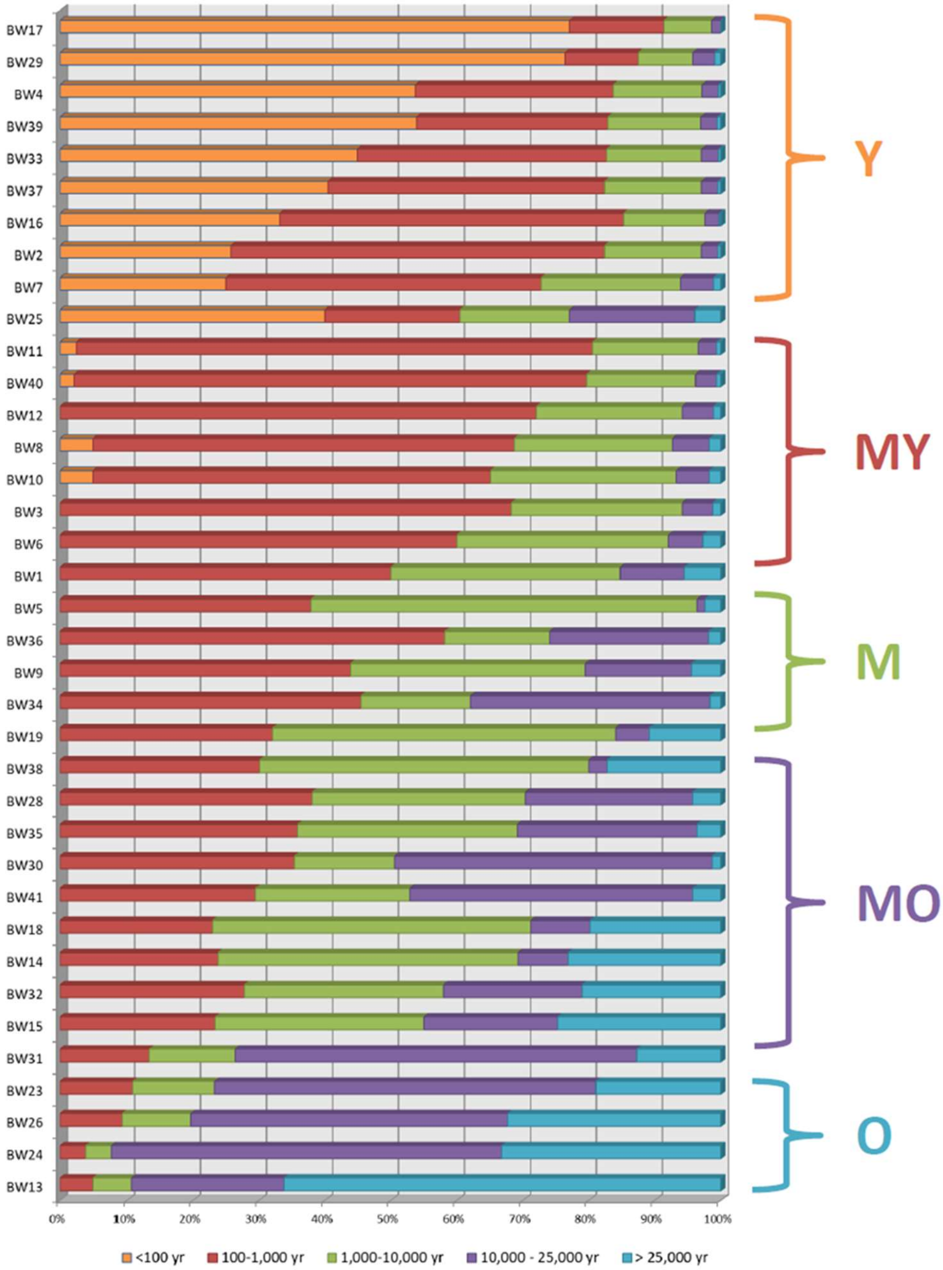

Figure 3.2 Age distributions of 37 well fields based on a multi-tracer study involving ^{3}H, ^{3}He, $^{14}C_{DIC}$, $^{4}He_{rad}$ and NGT (source: Broers et al. 2021)

In the Brabant study, a shape-free age distribution model was applied which estimate the contribution of water over 5 age classes: 0-100, 100-1,000, 1,000-10.000, 10,000-25,000 and > 25,000 years (see Figure 3.2). Subsequently, the well fields were grouped in so-called "age groups": Y, MY, M, MO, and O years (see Figure 3.2). The study concludes: "*Clearly, further constraints of the proportion of water aged between 100 and 1,000 years in the Y, MY and M groups would benefit from the analysis of ^{39}Ar as an additional tracer (Oeschger 1974, Loosli 1983, Corcho-Avarado et al. 2007, Sültenfuß et al. 2011, Visser et al. 2013, McCallum et al. 2017). For example, an analysis of ^{39}Ar or the sampling of multi-level observation wells over the complete depth range, as was previously done in Holten (Visser et al. 2013) would be required to confirm or reject our hypothesis that the water pumped in the MY age group integrates over the whole depth range of the available aquifers in this region. Currently, the lab capacity for analyzing a large set of samples for ^{39}Ar is limited worldwide, but this may change during the coming decade*".

In the current GeoERA study we started addressing this challenge by incorporating the ^{39}Ar tracer for two well fields that were part of the Brabant study: BW10 and BW27 (see Figure 3.3).

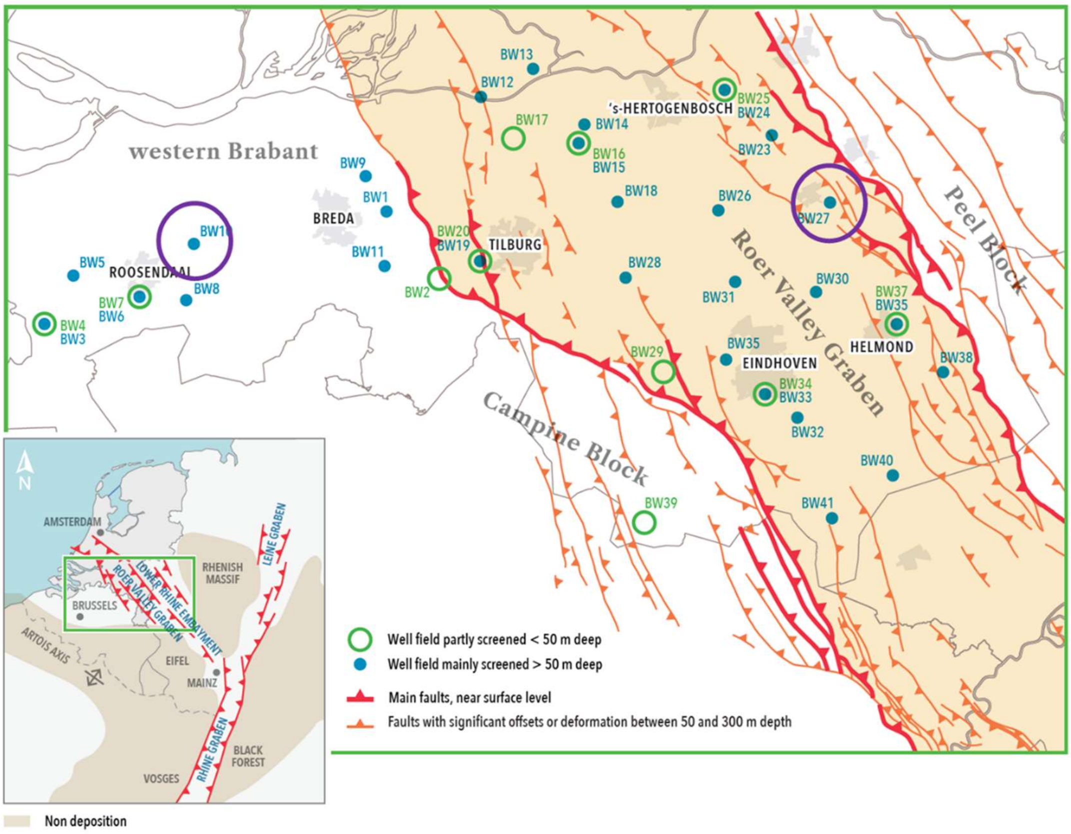

Figure 3.3 Location of the two well fields where additional measurements have been done (source: Broers et al. 2021).

3.2 Adding information about the age window of 100-1,000 years

3.2.1 Methods

3.2.1.1 Field and lab work

For BW10 and BW27 we resampled the mixed raw water from the well field in 2019 for the same set of tracers as for the Brabant study (Broers et al. 2021) but including ^{39}Ar. For BW10, we additionally sampled 3 individual pumping wells for the same set. The idea is to reconfirm and refine the age distributions that were assessed, adding detail in the age range of 100-1,000 years. For the project, we cooperated closely with Prof. Werner Aeschbach, Timo Metz and Florian Freundt of Heidelberg University, who performed the ^{39}Ar measurements at the new ATTA facility and the noble gas, $^{14}C_{DIC}$ and $^{13}C_{DIC}$ measurements (Figure 3.4).

Figure 3.4 Sampling for noble gases and 39Ar around BW10

The samples for ^{39}Ar were collected using a contactor setup which was developed and tested in cooperation with Heidelberg University (Figure 3.5)

Figure 3.5 Sampling water from a 'raw water branch' for 39Ar with the new contactor setup (left). Gas samples were compressed and stored in stainless steel cylinders (right) using a combined vacuum/compression pump (middle).

3.2.1.2 Discrete Age Distribution Modelling

The original DTTDM model used for the Brabant study (Broers et al. 2021) was adapted to include the additional tracer ^{39}Ar. As ^{39}Ar gives additional information on the age class 100-1,000 years, given its half-life of 267 years, the original age class was subdivided into two section: 100-300 years and 300-1,000 years. Combining 5 tracers and 6 age classes in the DTTDM model yields a number of 53,130 alternative age distributions for which the proportions of the age classes were assessed, compared to 10,626 alternative distributions in the original DTTDM model. From these 53,150 possible solutions, the 50 models with the least square's solutions (i.e., the 50 best models) were selected for the determination of the age distributions and the standard deviations that quantify the uncertainty. The outcome is an age distribution with 6 classes, based on a maximum of 5 age tracers for the age classes 0-100, 100-300, 300-1,000, 1,000-10.000, 10,000-25,000 and > 25,000 years.

Table 3.1 lists the average tracer concentrations which were used to calculate the model tracer concentrations for the 53,150 alternative age distributions. The method is similar to the method described in Broers et al. (2021) except for the subdivision of age class 100-1,000 into two new age classes 100-300 years and 300-1,000 years.

Table 3.1 Average tracer concentrations for the 5 age tracers which are used in the DTTDM model. For 4He$_{rad}$, we distinguished different productions rates for shallower and deeper well fields, in line with Broers et al. (2021)

Age class	0-100	100-300	300-1000	1000-10,000	10,000-25,000	> 25,000
^{3}H (TU)	7	0.01	0	0	0	0
^{14}C_age (years)	50	200	650	5500	17,500	37,500
NGT (°C)	10	9.2	9.3	9.6	2.2	5
^{39}Ar (pmAr)	88.3	60.2	21.2	0.3	0	0
^{4}He_deep (cc STP g^{-1})	2.38E-09	9.50E-09	3.09E-08	2.52E-07	8.40E-07	1.78E-06
^{4}He_shallow (cc STP g^{-1})	7.50E-10	3.00E-09	9.75E-09	7.96E-08	2.65E-07	5.63E-07

3.2.2 Results for well field BW10

3.2.2.1 Original assessment

The age distribution as it was assessed in the original study is depicted in Figure 3.6.

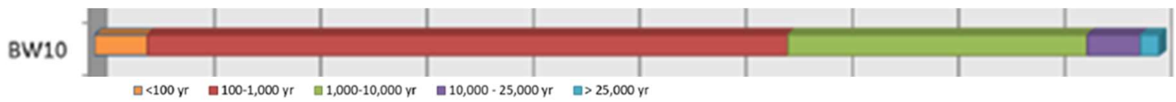

Figure 3.6 Original Age distribution of BW10.

The well field was grouped in the MY group, which indicates that the centroid of the distribution is in the 100-1,000 years age range. The contribution of this age class was estimated to be 60% (SD between 41 and 79%). As 28% contribution of older water age between 1,000 and 10,000 years was estimated with a large uncertainty of 6-50%. The contributions of even older water were estimated to be below 7%, with a good possibility of 0% (SD's between 0-10% and 0-4% for the age classes 10,000-25,000 and >25,000 years, respectively). The age distribution and associated uncertainty of the base model is depicted in Figure 3.7.

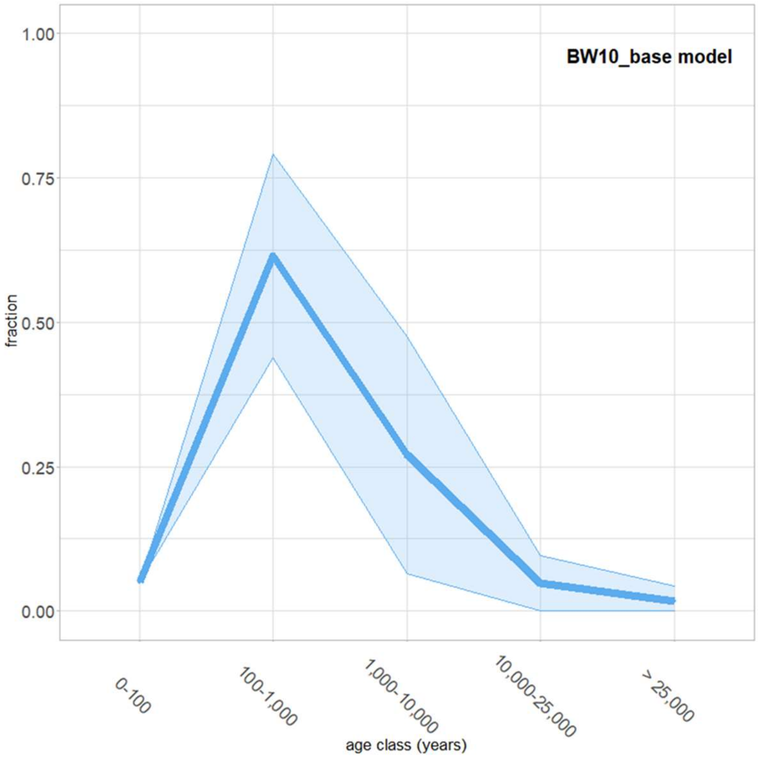

Figure 3.7 Age distribution for BW10, with uncertainty band for the base case model (blue) as reported in the WRR paper (Broers et al. 2021). The original DTTDM model distinguishes 5 age classes at the X-axis.

Figure 3.7 will function as the base case for the further analysis of the age distribution in the remaining of the chapter. The interesting phenomenon at well field BW10 is the somewhat elevated tritium concentration of 0.22 TU, which is indicating that a small part of the water infiltrated after the nuclear bomb spikes of the 50's and 60's. The contribution is estimated to be small (5%) but significant, as many other well fields in the study showed tritium at levels of 0.01 to 0.03 TU. The small contribution of modern water, together with the large proportion of water that is aged between 100 and 1,000 years made BW10 an interesting case to find out whether this small contribution is the start of the breakthrough of modern water and whether it is restricted to a number of vulnerable pumping wells, or a more general feature at the public water supply station. The idea was that ^{39}Ar may help to unravel the situation, quantifying whether the 100-1,000 years fractions is either rather young (100-300 years) or older (300-1,000 years). It would definitely change the desired protection regime for the well field if the fraction of water younger than 300 years is substantial.

Thus, we resampled the "raw water branch" for the complete suite of tracers, including 39Ar, and additionally selected a number of individual wells that showed contrasting major chemistry: PP6, PP11 and PP21.

3.2.2.2 New data on chemical processes

As a first step in the new assessment, more information about the chemical processes and hydrochemical patterns were analysed for well field BW10. Figure 3.8 shows concentration-depth profiles for methane (left) and sulphate (right).

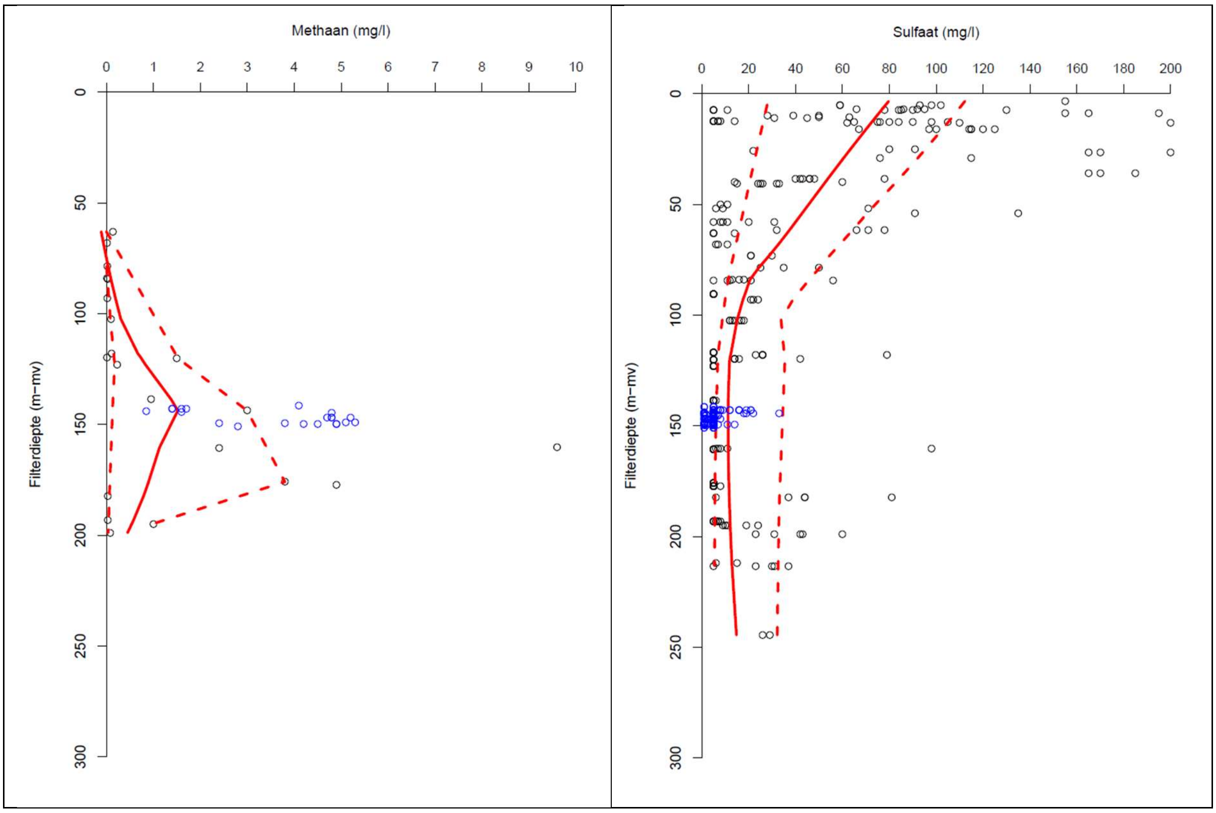

Figure 3.8 Concentration-depth (m below surface level) profiles for methane and sulphate for the surroundings of well field BW10. Black open dots represent measurements in short-screened multi-level observation wells around the well field. Blue open dots represent measurements of the pumped water in the 21 pumping wells.

The new data give rise to a new hypothesis of the hydrogeochemical evolution of the water in the aquifers pumped at BW10. Clearly, elevated methane concentrations only start below 120 m depth, which indicates that methanogenesis takes place in the deeper aquifers, using aquifer organic matter as source. In line with that observation sulphate is below the detection limit of 5 mg/l in most of the pumping wells; methanogenesis typically starts when all sulphate has been consumed. It was noticed that a number of pumping wells show a small increase in sulphate over the last 20 years, from < 5 mg/l tot maximum 33 mg/l. It was most remarkable for pumping wells PP5, PP6 and PP7. Looking at the concentration-depth profiles, two main sources of sulphate are possible: sulphate from the upper aquifers that show concentrations up to 200 mg/l which are clearly related to agricultural land use (Visser et al. 2007). Or sulphate from deeper parts of the subsurface which may be related to pockets of relict brackish water in marine Formations.

3.2.2.3 New assessment of ^{14}C apparent ages

The depth profiles changed our understanding of one of the main hydrochemical processes around the well field. In the base case mode, a ^{14}C apparent age was estimated based on the premise of a Holocene peat bog (see Figure 3.9). It means that we assumed that methanogenesis took place in the upper aquifers and methane was subsequently transported downward. Assuming deep methanogenesis was considered for this well field and would decrease the estimated 14C apparent age as calculated in the 2021 study (Broers et al. 2021, Supplementary Information). Applying the "deep methanogenesis" scenario for BW10 yields an estimated 14C apparent age for the mixture of 1000± 400 years, instead of 3250± 1000 years (Figure 3.9).

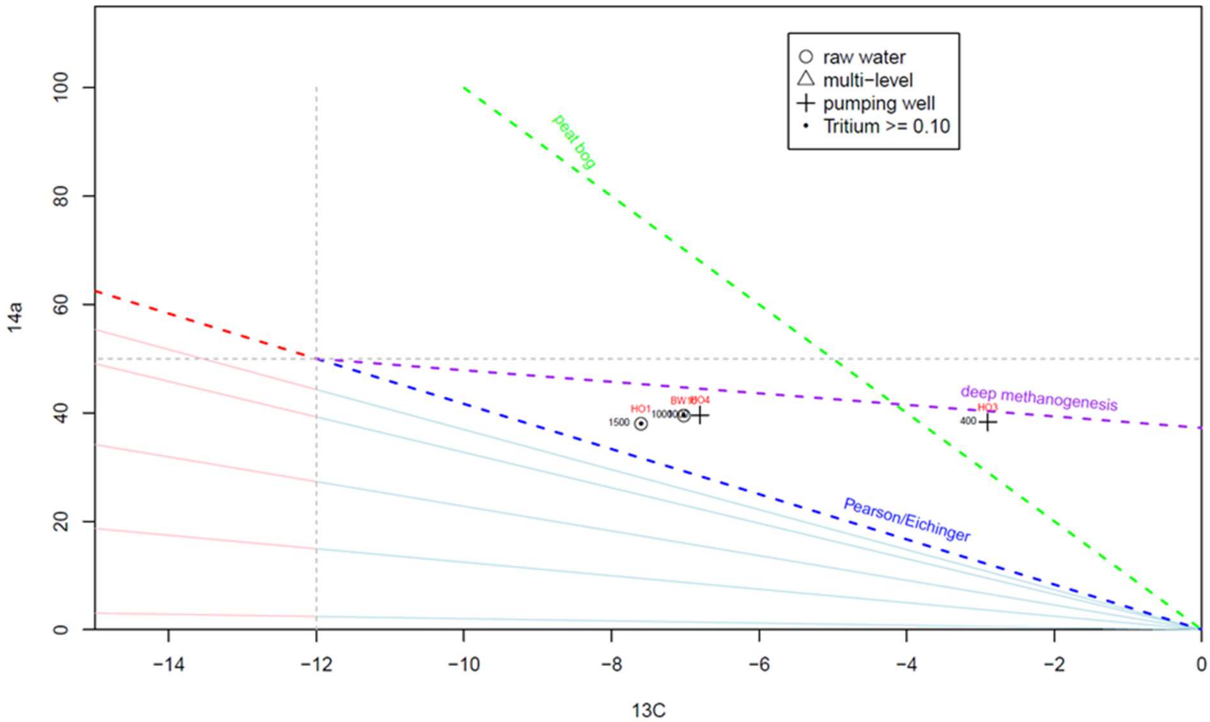

Figure 3.9 Han-Plummer plot for the samples BW10, HO1, HO3 and HO4 (see Table 3.3 for actual data)

Therefore, we reran the DTTDM model to find out whether this would change the age distribution. We learned that the differences were rather insignificant as the other tracers dominantly constrained the age distributions. The proportion of age class 100-1,000 years changed from 60% for the base model, towards 62% for the deep methane model and the resulting average age decreased from 3300 to 2750 years. Given the clear hydrochemical patterns, we choose to keep the deep methanogenesis model for each of the subsequent model runs (see next sections).

3.2.2.4 New assessment of the proportions of the 6 age classes for 5 tracers

Table 3.2 lists the 2014 and 2020 measurements of the "raw water branch" BW10. Most measurements are similar, except for NGT. The newly derived NGT is subject for further investigation and a duplicate sample will be measured in order to check the deviation. New is the ^{39}Ar measurement which yields 59% of present modern Ar. If we would expect this to be a sample with a discrete single age, this would yield an apparent age of approximately 200 years. However, we know the ^{39}Ar is the result of mixing over a large age range, which we will quantify using the DTTDM model.

Table 3.2 Measurements of tracers and estimated ^{14}C apparent age. BW10 is original data of the 2014 sampling campaign. HO1 is the new data, from the same “raw water branch” of the 2020 sampling campaign.

BWNR	NGT °C	^{3}H (TU)	$^{4}He_{rad}$ cc STP g-1	pH	$^{14}C_{DIC}$ pmC	δ^{13}C ‰	^{39}Ar pmAr	CH_4 mg/l	Cl mg/l	SO_4 mg/l	HCO_3 mg/l	^{14}C apparent age (years)
BW10	9.4 ± 0.4	0.22 ± 0.02	4.61E-08	7.28	39.5	-7.02	-	3.5	17.9	6.0	330	1000 ± 400
HO1	7.6 ± 0.3	0.25 ± 0.05	4.80E-08	7.40	38.0	-7.60	59 ± 13	3.3	20.0	2.5	320	1500 ± 500

Using the newly derived data, we ran the DTTDM model with the 6 age classes 0-100, 100-300, 300-1,000, 1,000-10.000, 10,000-25,000 and > 25,000 years and the 5 tracers ^{3}H, ^{39}Ar, NGT, $^{4}He_{rad}$ and ^{14}C apparent age. For sample HO1, 2020 sample taken from the same "raw water branch" as BW10, the resulting age distribution and uncertainty bands are shown in Figure 3.10.

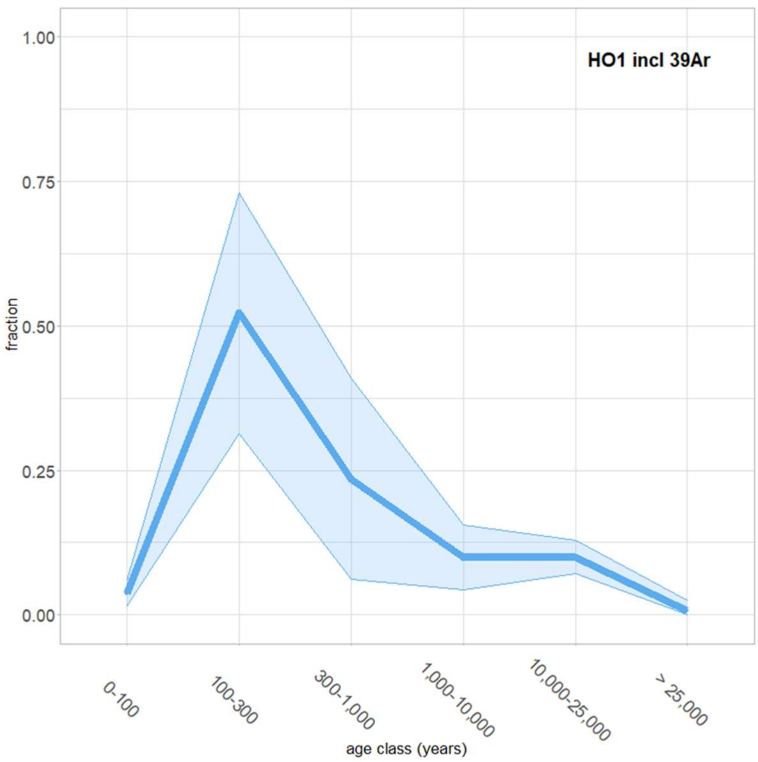

Figure 3.10 Groundwater age distribution of HO1 (former BW10) based on 5 tracers and 6 age classes on the X-axis. Please note that the X-axis changed relative to Figure 3.7

The newly derived age distribution differs from the original base model of BW10:

- the age class 100-1,000 years is now divided in the classes 100-300 and 300-1,000
- the total percentage over the original class 100-1,000 years increased from 62% (original, including deep methanogenesis) to 76% in the new model
- Of this 76%, the dominant part of 52% is attributed to the class 100-300 years
- The contribution of the class 1,000-10.000 years dropped from 28% to 10 ± 6%, but another 10% ± 3% is now attributed to water ages 10,000-25,000 years.

Overall, the new distribution tends to overall younger ages, with a mean age of 2800 years instead of 3300 years for the original model. Especially the large contribution of water age between 100 and 300 years is an important new finding. It may mean that the first breakthrough of modern water (5% contribution of ages < 100 years) may indicate a first signal of the front with young water moving towards the pumping wells.

We ran a brief sensitivity analysis to investigate how the uncertainty of the ^{39}Ar measurement influences the outcomes. If we assume that we have a more precise estimate of the 59% pmAr (59 ± 5% instead of 59 ± 13%), then the percentage of water age 100-300 year would further increase to 71% instead of 52%. In that case, the model is better able to mimic the ^{39}Ar concentration. The best fit models predict 39% pmAr for the model depicted in Figure 3.10, whereas a more precise estimate would enable the model to mimic the measured 59% better: 48% as a model result in that case.

3.2.2.5 Analysis of individual pumping wells PP6, PP11 and PP21

Additional to the analysis of the mixed raw water at BW10, a number of 3 individual pumping wells were sampled for the same suite of tracers. Table 3.3 lists the most important components that we used for the age distribution modelling. Here, BW10 and HO1 represent the mix water as it was sampled in 2014 and 2020, respectively. Unfortunately, the sample bottle for carbon isotopes was broken for the PP6 pumping well, so we miss information from this specific well. However, the tracer concentrations and major chemistry tell most of the story, and the DTTDM model was run for this sample, with exclusion of the ^{14}C tracer, which still gives a valid result.

Table 3.3 Measurements of tracers and estimated ^{14}C apparent age

BWNR	NGT °C	^{3}H (TU)	$^{4}He_{rad}$ cc STP g-1	pH	$^{14}C_{DIC}$ pmC	$\delta^{13}C$ ‰	^{39}Ar pmAr	CH_4 mg/l	Cl mg/l	SO_4 mg/l	HCO_3 mg/l	^{14}C apparent age (years)
BW10: raw	9.4± 0.4	0.22 ± 0.02	4.61E-08	7.28	39.52	-7.02	±	3.5	17.9	6	330	1000 ± 400
HO1: raw	7.6 ± 0.4	0.25 ± 0.05	4.80E-08	7.4	38	-7.6	59 ± 13	3.3	20	2.5	320	1500 ± 500
HO2: PP6	7.8 ± 0.4	1.16 ± 0.10	1.62 E-08	7.55	-	-	77 ± 14	1.1	34	40	240	-
HO3: PP11	8.3 ± 0.4	0.01 ± 0.05	5.73E-08	7.32	38.3	-2.9	32 ± 9	5.1	20	2.5	370	400 ± 400
HO4: PP21	7.1± 0.4	0.01 ± 0.05	1.44E-08	7.32	39.6	-6.8	33 ± 9	2.8	13	2.5	350	1000 ± 400

From Table 3.3 we may easily conclude that PP6 is different from the pumping wells PP11 and PP21. PP6 shows a much higher ^{3}H concentration (1.16 TU compared with 0.01 TU), substantially elevated ^{39}Ar (77% versus 32%) and also contrasting major chemistry: lower methane and higher sulphate and chloride concentrations. The higher ^{3}H and ^{39}Ar give conclusive evidence that the chloride and sulphate concentrations are derived from younger groundwater, which is present in the shallower aquifer of the BW10 well field (see Figure 3.8). The lower methane can be explained by the same mechanism; drawing water from shallower layers relative to the other pumping wells which draw a larger proportion of water from the 140-160 m depth interval. Typically, the raw water has tracer and major chemistry concentrations which lie somewhere between the concentrations of PP6 and PP11/PP21 respectively. This is no wonder as the water of wells PP6, PP11 and PP21 is mixed at the "raw water branch": the mix is actually made of water from the 3 sampled pumping wells PP6, PP11 and PP21, and another 4 wells: PP9, PP14, PP15 and PP19.

Figure 3.11 also confirms the mixing of water of the 3 individual pumping wells, illustrating the Ne/He ratio vs the $^{3}He/^{4}He$ ratio for the 4 samples. HO1, HO3 (PP11) and HO4 (PP21) all lie on a mixing line between atmospheric ratios and the mantle/crust ratio that was observed previously in the Brabant study (Broers et al. 2021). Sample HO2 (PP6) clearly deviates from this line, indicating tritium decay which increase the ^{3}He concentrations. The mixture of the HO1 raw water seems most related to the HO3 (PP11) sample, and we may thus expect that the pumping wells PP9, 14, 15 and 19 will resemble these characteristics. We may assume that the ^{3}H concentration of the raw water (0.25 TU) is then mainly due to the contribution of pumping well PP6 (1.16 TU). If this would be true, PP6 would contribute 21% of the mix and the other 6 wells would yield the remainder 79%.

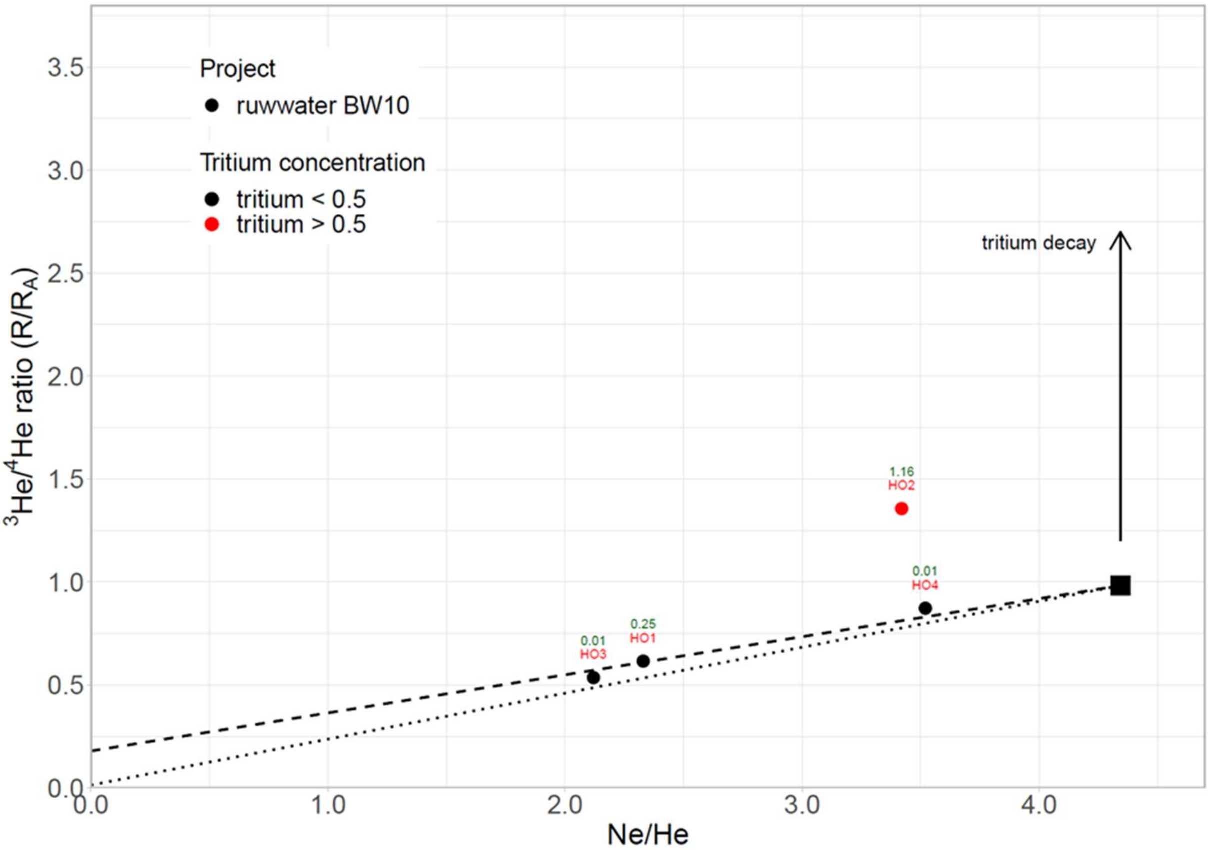

Figure 3.11 Ne/He ratio vs $^{3}He/^{4}He$ ratio for the 3 individual pumping wells and the mixed raw water of well field BW10. Green labels denote the ^{3}H concentrations.

Using the DTTDM model that was described earlier, the age distributions for the 3 individual pumping wells were estimated (see Figure 3.12). Here, the age distribution for PP6 was calculated for only 4 tracers, as we did not have the ^{14}C apparent age available due to loss of the sample.
For PP6 our best estimate indicates that 16% ± 5% of the water is less than 100 years old, 51% ± 17% is between 100 and 300 years old, and 88% of the water is younger than 1000 years (Figure 3.12b). This makes PP6 rather vulnerable for diffuse contamination, as is already expressed by increasing concentrations of chloride and sulphate that is apparently drawn from the shallower aquifer above the pumped interval. The most sensible explanation is that the semi-confined Oosterhout Formation aquifer is not well protected by the aquitard at the top of this Formation.

The age distributions for PP11 and PP21 are rather similar, with 83% of the water, which is less than 1,000 years old, 0% of modern post-1950 water and rather large contribution of water aged 100-300 years (38% ± 16%) and 300-1,000 years (45 ± 18%).

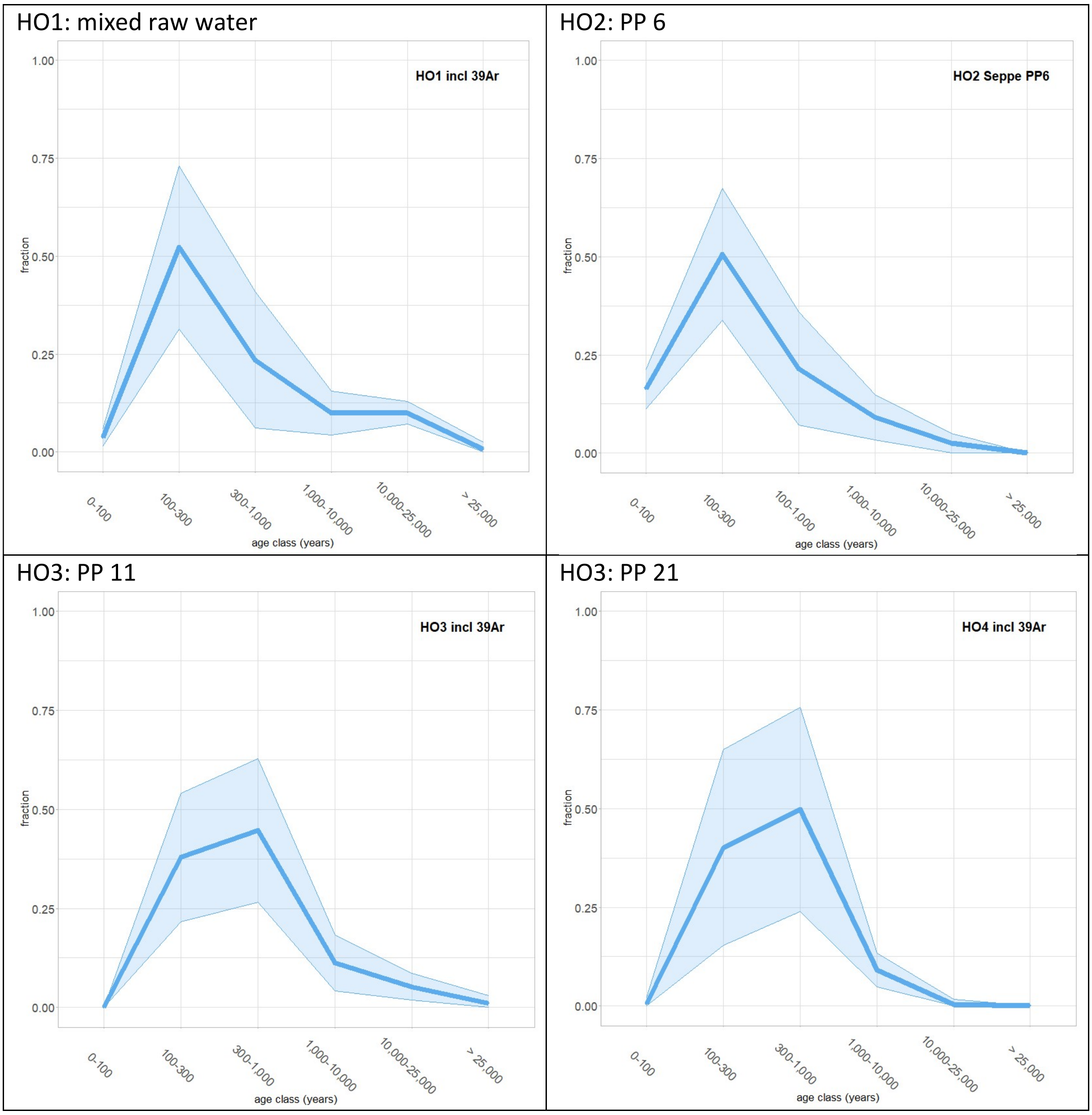

Figure 3.12 DTTDM age distributions for HO1 (mixed raw water), HO2 Pumping well PP 6, HO3 Pumping well PP 11 and HO4 Pumping well PP 21.

Overall, these age distributions are younger than previously expected with a large proportion of water aged between 100 and 300 years at both the wells PP11 and PP21 and in the raw water. The question is whether the breakthrough of chloride and sulphate is a signal for further breakthrough in the other wells, or that the well construction of PP6 shows failures. This would then also affect the wells PP5 and PP7 that also show increasing concentrations of these constituents. It is known that the well construction of PP7 has been altered some decades ago, because the original pumps ran dry, and failures of the PVC liners has occurred. If this is related to the sulphate and chloride is not known, and further investigations are recommended.

In summary, for well field BW10, the benefits of additional ^{39}Ar age dating are clear; the extra tracer helps to gain insight in a crucial age range and the proportions of water that are now estimated to be 100-300 years old are substantial for the specific well field. Moreover, the older components (> 1,000 years) are clearly less important relative to the water that has ages < 1,000 years. It is noteworthy that calculation of the ^{14}C apparent age might give a false impression of rather old water and may overestimate the proportion of this older water. This might be partially related to the increasing in DIC concentrations with depth at this particular well field.

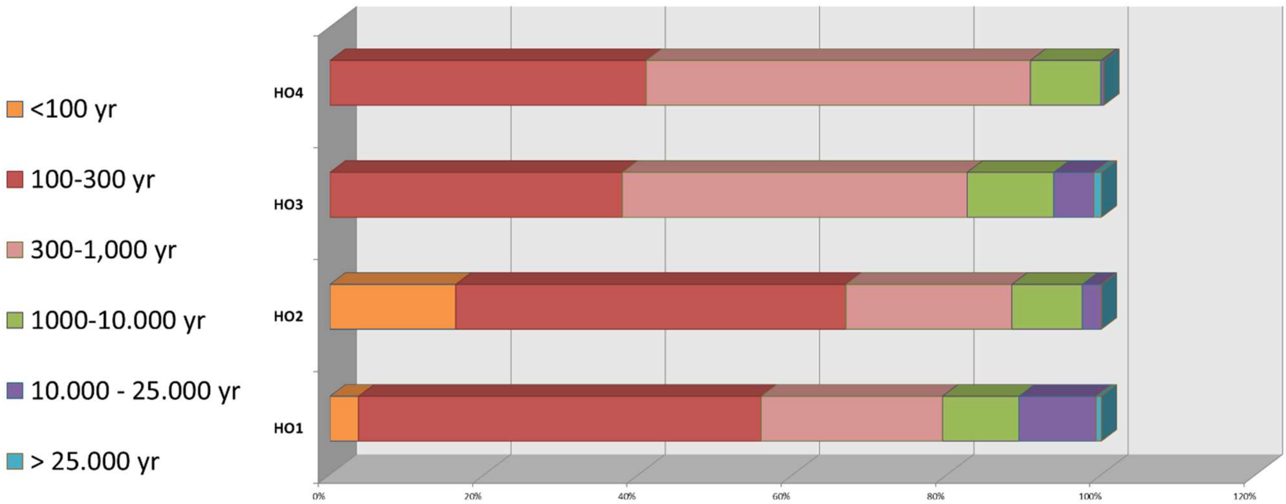

Figure 3.13 Visualisation of the age distributions for the samples VO1 (BW27 raw water), VO2 (Pumping well PP8), HO3 (pumping well PP11) and HO4 (pumping well PP21).

3.2.3 Results for well field BW27

3.2.3.1 Original assessment

For well field BW27, no age distribution was assessed in the Broers et al. (2021) study because the NGT could not be established due to problems with the duplicate samples. For BW27, we resampled the same "raw water branch" of 2014 for the complete suite of tracers, and additionally selected a number of individual wells that showed contrasting major chemistry: PP1, PP8, PP14, PP17 and PP29. We took samples for ^{39}Ar for the raw mixed water (VO1-raw) and for the pumping wells PP1 (VO2) and PP8 (VO3). At the moment of writing, only the ^{39}Ar sample of VO1 (raw mixed water) is available.

3.2.3.2 New data on chemical processes

As a first step in the new assessment, more information about the chemical processes and hydrochemical patterns were also analysed for well field BW27 (resampled as VO1-raw). Figure 3.14 shows concentration-depth profiles for methane and sulphate.

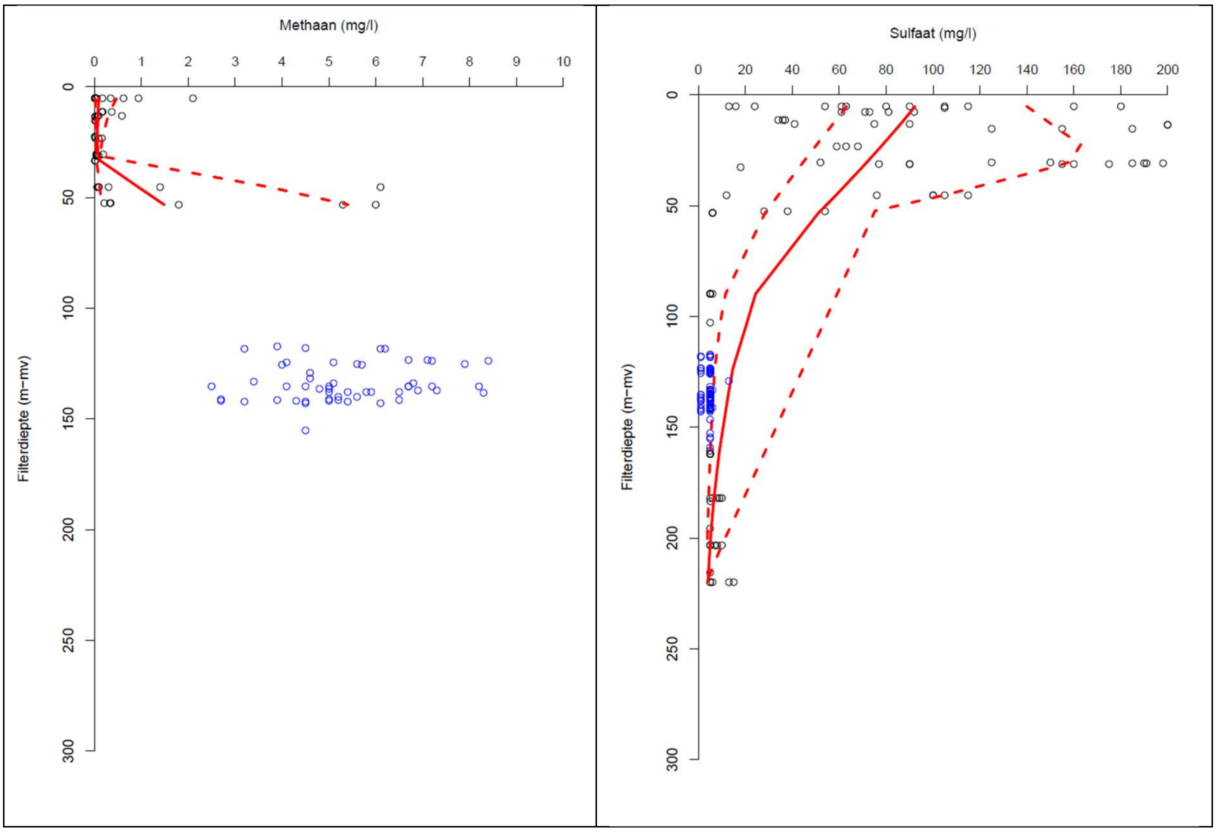

Figure 3.14 Concentration-depth (average screen depth m-slvl) profiles for methane and sulphate for the surroundings of well field BW27. Black open dots represent measurements in short-screened multi-level observation wells around the well field. Blue open dots represent measurements of the pumped water of all available pumping wells.

The new data confirms the original hypothesis about the hydrogeochemical evolution of the water in the aquifers pumped at BW27. Clearly, methane concentrations are elevated in the depth interval of the pumping wells between 100 and 150 m depth, and indications for very shallow production of methane are absent. In line with that observation sulphate is below the detection limit of 5 mg/l in almost all of the pumping wells; methanogenesis typically starts when all sulphate has been consumed, presumably below 100 m depth. There are no indications for increasing sulphate concentrations at well field BW27.

3.2.3.3 *Overview of the new data for well field BW27*

The newly acquired data is listed in Table 3.4. The new sample for the mixed raw water (VO1-raw) is very similar to the original BW27 sample for most of the tracers and the apparent age that was calculated under the assumption of deep methanogenesis is in the same range. A small deviation occurs for tritium: ^{3}H for VO1 is a little higher than for BW27: 0.09 vs 0.02. It is unknown whether this is a significant difference, as the lab results have a little less accuracy for the new runs (pers. Comm. Jürgen Sültenfuß). The first ^{39}Ar sample which is available for this well field at VO1-raw gives some indication that a small contribution of younger water (post-1950 or from the 100-1,000 years age range) may be present at the well field. The new NGT of 4.1°C indicates that quite a large proportion of Pleistocene water should be present at the well field, which will further be quantified in the next sections.

Table 3.4 Measurements of tracers and estimated ^{14}C apparent age for well field BW27

BWNR	NGT °C	^{3}H (TU)	$^{4}He_{rad}$ cc STP g-1	pH	$^{14}C_{DIC}$ pmC	$\delta^{13}C$ ‰	^{39}Ar pmAr	CH_4 mg/l	Cl mg/l	SO_4 mg/l	HCO_3 mg/l	^{14}C apparent age (years)
BW27-raw		0.02 ± 0.01	1.67E-06	7.16	15.0	-8.5	-	6.1	51.3	< 5	350	9300 ± 930
VO1-raw	4.1± 0.3	0.09 ± 0.05	1.61E-06	7.15	13.9	-9.1	9 ± 5	5.4	49	< 5	350	10100 ± 1010
VO2-PP1	1.7± 0.3	0.10 ± 0.05	1.75E-06	7.19	10.1	-10.6	-	4	75	< 5	370	13000 ± 1300
VO3-PP8	7.2± 0.3	0.12 ± 0.05	7.15E-07	7.23	21.3	-5.3	-	7.7	29	< 5	340	5800 ± 580
VO4-PP14	4.8 ± 0.3	0.02 ± 0.05	1.70E-06	7.29	-	-	-	4.6	68	< 5	360	-
VO5-PP17	5.9± 0.3	0.01 ± 0.05	2.15E-06	7.3	15.6	-9.7	-	5.3	59	< 5	350	9200 ± 920
VO6-PP29	5.3± 0.3	0.01± 0.05	6.51E-07	7.28	13.8	-8.1	-	4.1	11	2< 5	370	9900 ± 990

The tracer results from the individual pumping wells show rather large ranges indicating different catchment areas for the 5 selected pumping wells. A relatively high $^{4}He_{rad}$, a low NGT and low ^{14}C activity and correspondingly high ^{14}C apparent age found for VO2-PP1, which are indications for a large contribution of older groundwater of Pleistocene age. VO3-PP8 seems to cover the other end of the spectrum, with a trace of ^{3}H (0.12 TU), relatively low $^{4}He_{rad}$ and a predominantly Holocene ^{14}C apparent age corresponding with higher NGT and elevated CH_4 and $\delta^{13}C_{DIC}$ (Figure 3.15). The other pumping wells have tracer concentrations in between. Higher $^{4}He_{rad}$ concentrations correlate with higher chloride concentrations, indicating that the older water is richer in chloride. This leads to the hypothesis that the older water is drawn from deeper layers that are known to have elevated chloride concentrations (Figure 3.16).

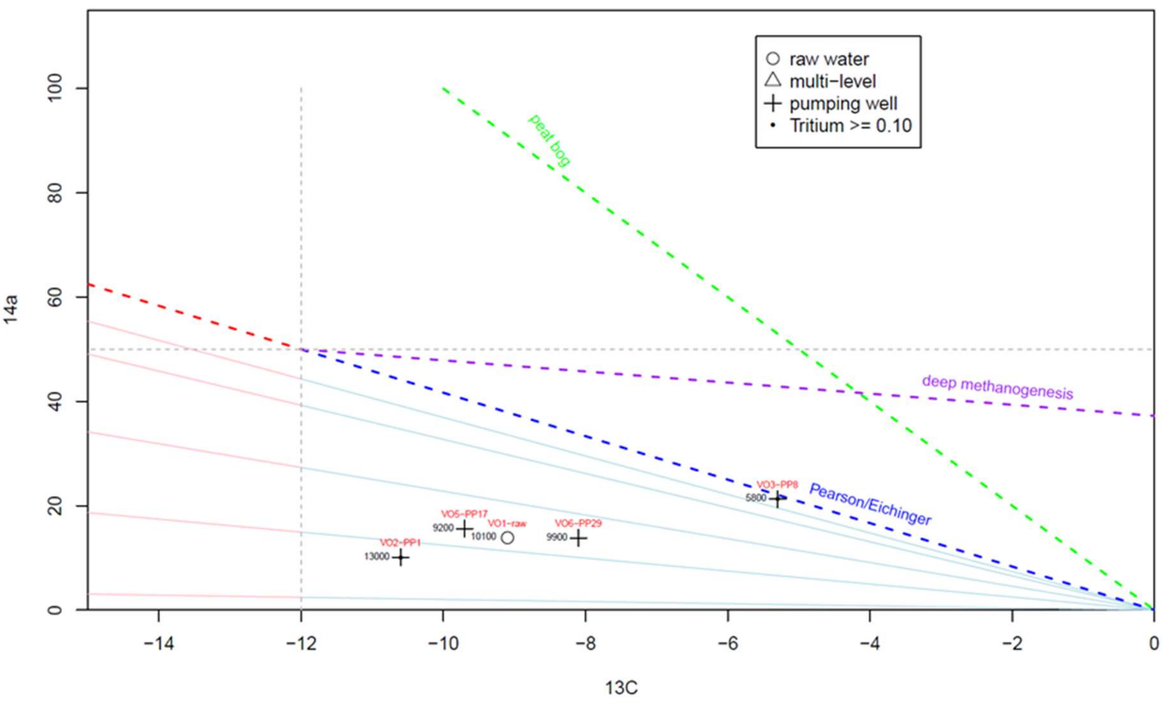

Figure 3.15 Han-Plummer plot for the samples of well field BW27

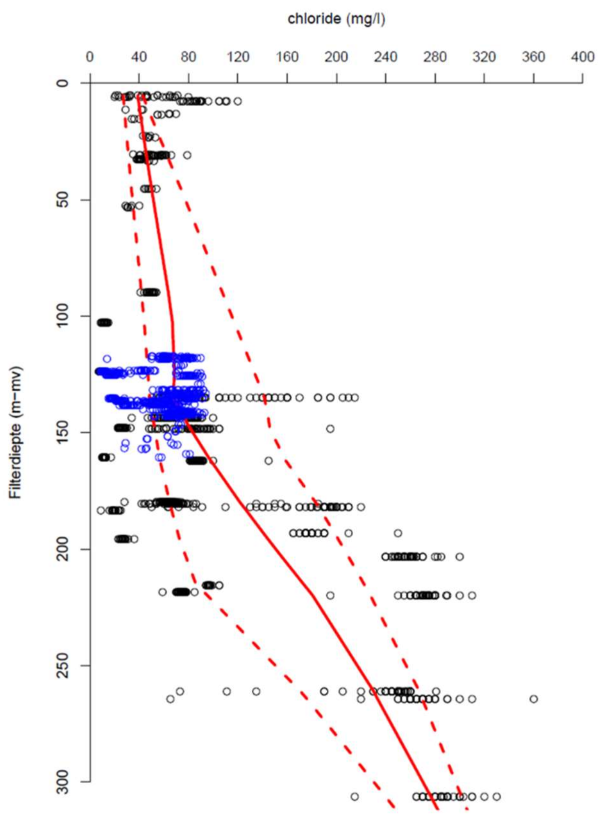

Figure 3.16 Concentration-depth profile for chloride. Blue dots indicate pumping wells, black dots indicate samples from multi-level observation wells

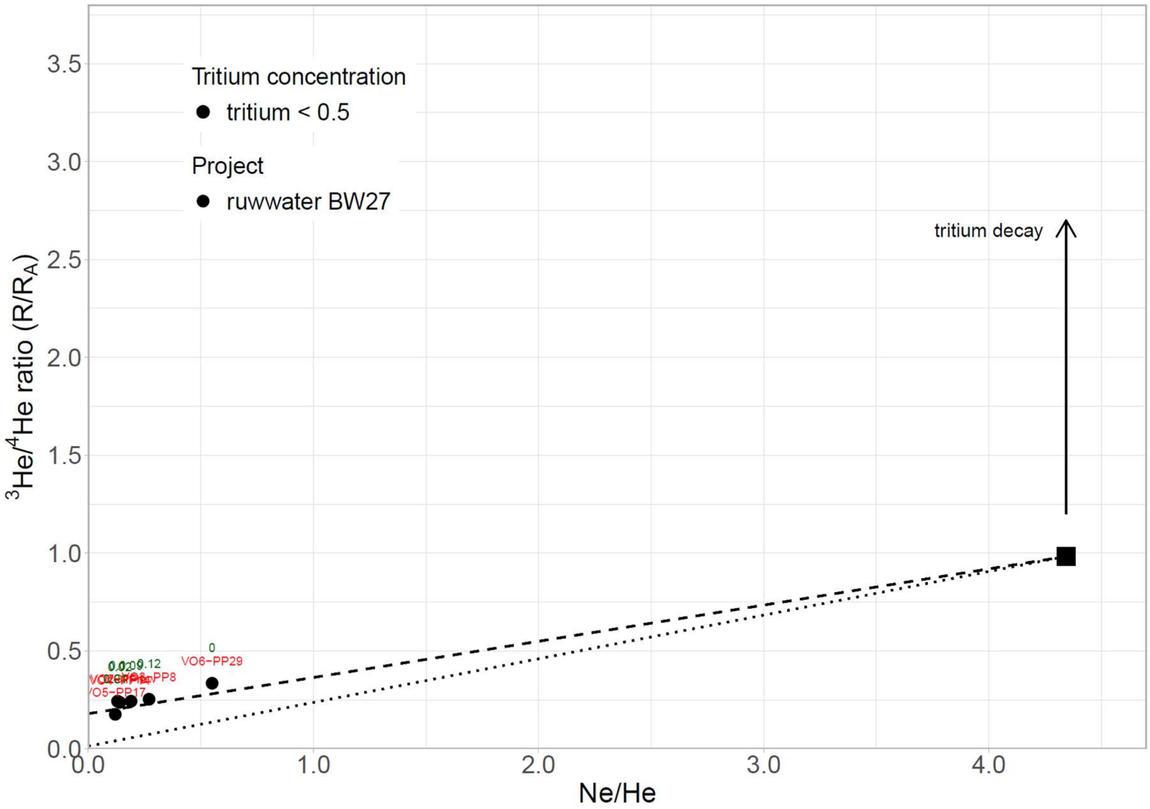

Figure 3.17 Ne/He ratio vs $^{3}He/^{4}He$ ratio for the 6 individual pumping wells and the mixed raw water of well field BW27. Green labels denote the ^{3}H concentrations. Samples VO2-PP8 and VO6-PP29 plot to the right of the rest of the group. All samples plot far from the atmospheric equilibrium point and close to the Mantle/Crust mixing line of the Broers et al. (2021) study.

Figure 3.17 show the position of the samples from BW27 along the in the Ne/He ratio vs the $^{3}He/^{4}He$ ratio diagram. The samples lie far to the left relatively to the samples of the BW10 well field that was discussed previously (see Figure 3.11). The samples lie close to the mixing line between atmospheric ratios and the mantle/crust ratio that was observed previously in the Brabant study (Broers et al. 2021). Sample VO2-PP8 and VO6-PP29 plot most to the right, indicating slightly younger ages of the groundwater or mixture with water from shallower aquifers.

3.2.3.4 Age distributions for the BW27 well field

Using the DTTDM model that was described earlier, the age distributions for 4 individual pumping wells were estimated together with the mixed raw water sample (see Figure 3.18). Here, the age distribution for VO1-raw includes the complete set of tracers, thus including the ^{39}Ar tracer. The other 4 samples were modelled in the same model setup, however leaving out the ^{39}Ar tracer. For sample VO4-PP14 no age distribution was calculated, as only 3 tracers were available.

Figure 3.18 DTTDM age distributions for VO1 (mixed raw water), VO2 Pumping well PP 1, VO3 Pumping well PP 8, VO5 Pumping well PP 17 and VO6 Pumping well PP 29.

From Figure 3.18, it becomes clear that the mixed raw water of VO1 pumps a dominant fraction from the 10,000—25,000 years Pleistocene age range (67% ± 6%). In the age grouping that was applied in the Broers et al. (2021) paper this would classify the well field as age group "MO". The available ^{39}Ar measurement seems to imply that a fraction of either 100-300 or 300-1,000 years old water is present in the mixture. The uncertainty of these fractions is rather high, 10 ± 10% and 8 ± 5% respectively, thus varying between 0 and maximum 20%.

Pumping well PP1 shows the most prominent peak in the 10,000-25,000 years age range (85% ± 6%), with possible small fractions of the 1,000-10,000 and/or >25,000 years age ranges. These fractions could, however, also be 0% each. Thus, PP1 pumps the oldest water from a limited age window.

Contrary, VO3-PP8 covers a much broader age range, but with high uncertainty for the fractions 100-300 years, 300-1,000 years and 1,000-10,000 years. The age distribution will definitely be better constrained when the ^{39}Ar results come available.

The other pumping wells VO5-PP17 and VO6-PP29 show intermediate age distribution with a clear peak in the 10,000-25,000 years age range. Unfortunately, no ^{39}Ar measurements will come available from this study.

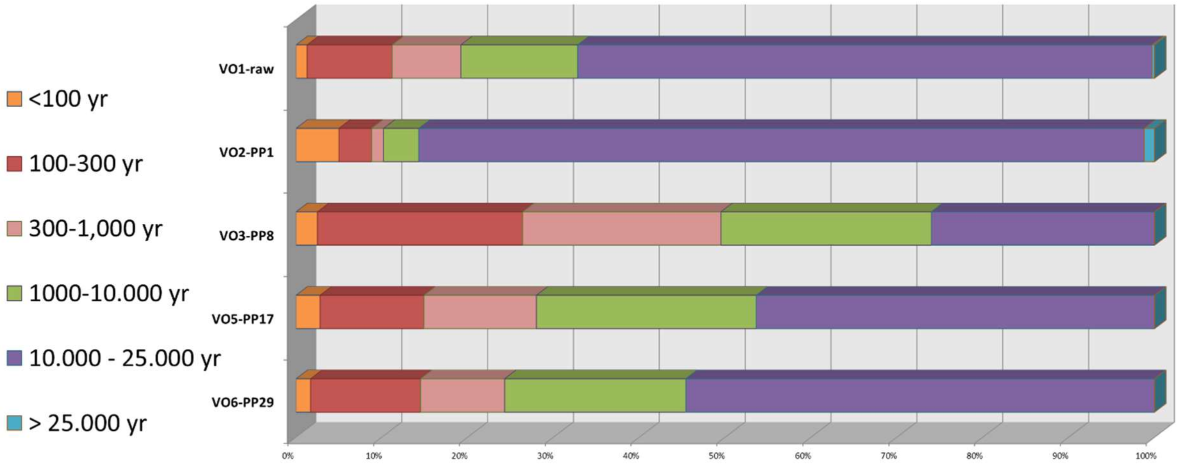

Figure 3.19 Visualisation of the age distributions for the samples VO1 (BW27 raw water), VO2 (pumping well PP1), VO3 (pumping well PP8), VO5 (pumping well PP17) and V06 (pumping well PP29).

The age distributions are summarized in the diagram of Figure 3.19. Overall, these age distributions are within the range of expectations from the Broers et al. (2021) study. Interesting is the measurable ^{39}Ar concentration in the mixed raw water of VO1. It might imply that water from shallower aquifers is approaching the pumped wells, presumably concentrated in the corners of the well field at PP8 and PP29. The ^{39}Ar data for PP8 will be revealing once the come available. There is a clear link between chloride and the ages of the water; PP1 pumps the oldest water and has the highest chloride concentrations. It confirms the hypothesis that this particular pumping well draws water from the deeper parts of the aquifers, meaning there is some salinization going on.

3.3 Conclusions and recommendations

One of the aims of Work Package 6 of HOVER project is to assess the effectiveness of new tracer and modelling techniques for estimation of groundwater age distributions in the age range 100-1,000 years in water supply wells. Within Task 6.4 we tested how the ^{39}Ar tracer may help revealing patterns in the age distributions of groundwater with residence times mainly in the age range of 100 to 1,000 years. For this purpose, we evaluated age distributions for water supply wells in the Netherlands as a proxy for well fields in other parts of Europe for which existing analyses of age distributions were previously done.

For well field BW10, which contains a large fraction of water in the targeted age range of 100-1,000 years, the benefits of additional ^{39}Ar age dating are clear; the extra tracer helps to gain insight in a crucial age range and the proportions of water. The additional ^{39}Ar tracer proves that a significant fraction of the water is between 100 and 300 years old, which gives rises to questions about the long-term susceptibility of the well field. For the BW27 well field, there is slight indication that water from the age ranges of 100-300 or 300-1000 years is part of the raw water mixture. We expect additional data on 2 pumping wells which may confirm this finding in the near future.

In the current situation, ^{39}Ar measurements are not readily available as the lab capacity is still limited worldwide. However, the technique promises to be highly beneficial for the evaluation of the vulnerability of well fields and will eventually help to improve water quality projections for public water supply.

4 CASE STUDY DENMARK

4.1 Previous work on age distributions in the region

Travel times and transport of environmental tracers in unsaturated zones (Andersen and Sevel, 1967, Engesgaard et al., 2004) and sandy aquifers (Hinsby et al., 2007) or complex glacial aquifer systems (Corcho Alvarado et al., 2005; Hinsby et al., 2006; Troldborg et al., 2008) have been studied in Denmark for several decades in order to understand the vulnerability, characteristics and groundwater flow dynamics of Danish aquifers since the late Pleistocene (Hinsby et al., 2001; Sonnenborg et al., 2016; Meyer et al, 2018) including the advance of potentially polluted young groundwater in Denmark and Europe (Hinsby et al., 2001b).

Figure 4.1 illustrates groundwater age distributions simulated under different assumptions in three different water supply wells located in a complex aquifer system of glacial deposits typical for Denmark. The simulations demonstrate rather different age distributions in similar water supply wells in the same aquifer system, which may have uni-, bi- or even multi-modal age distributions.

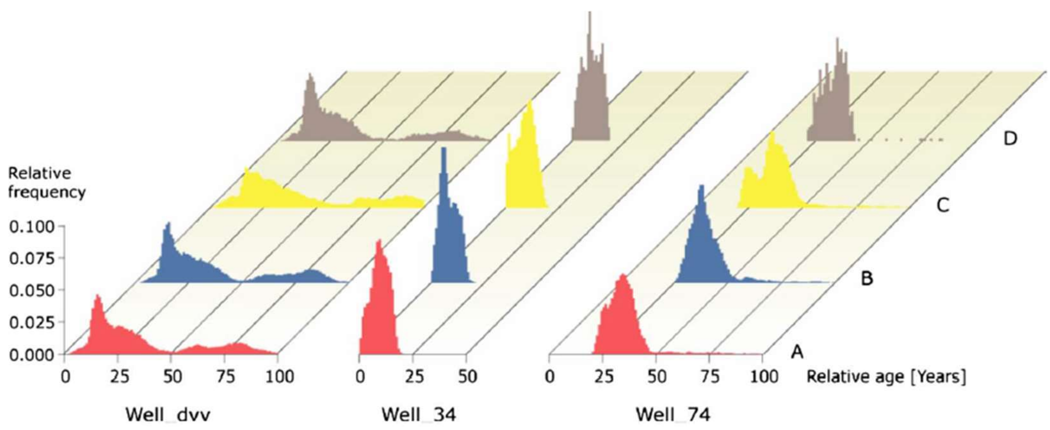

Figure 4.1 Simulated groundwater age distributions: A) age distribution from steady-state simulations; B) age distribution from transient simulation; C) age distribution using steady-state flow and distributed porosity; and D) age distribution simulated by using steady-state flow and registration point as substitute for registration radius (Troldborg et al., 2008)

More recently, groundwater ages have been used for assessment and evaluation of contaminant trends in monitoring wells (Hansen et al., 2012, 2019) and investigation of groundwater age distributions and mixing of groundwater of different ages in a long-screened water supply well contaminated by pesticides. The history and fate of the two observed pesticides were investigated by the use of multiple tracers including ^{39}Ar for age dating of groundwater primarily in the age range of 100-1000 years (Jakobsen et al., 2020). Both applications are relatively new and promising research fields, enabling significantly improved understanding of the transport and fate of contaminants in the subsurface and the vulnerability / susceptibility of wells towards pollution from the surface (Solder et al., 2020).

While groundwater flow models have the benefit of being able to delineate the possible source areas for contamination, the tracers have the benefit of identifying contamination resulting from poorly developed or damaged wells and identify exactly in which part of the screen the contamination enters the well.

As an example of this is the study by Jakobsen et al. (2020) that investigate the occurrence, history and fate of the two pesticides bentazon and dichlorprop in a water supply well which is screened at an interval between 13 and 25 meter below surface. Mixed samples from the well showed elevated concentrations of both pesticides in several samples since around 2011 (Figure 4.2).

The simulation of groundwater age distributions based on the multi-tracer measurements ($^{3}H/^{3}He$; ^{85}Kr, ^{39}Ar) in level-specific samples collected in the top and bottom of the screen, clearly demonstrate that the two pesticides, which were measured in mixed samples from the whole screen flowed to the well at different depths, and that they have infiltrated to the water table at different points in time (Figure 4.4) .

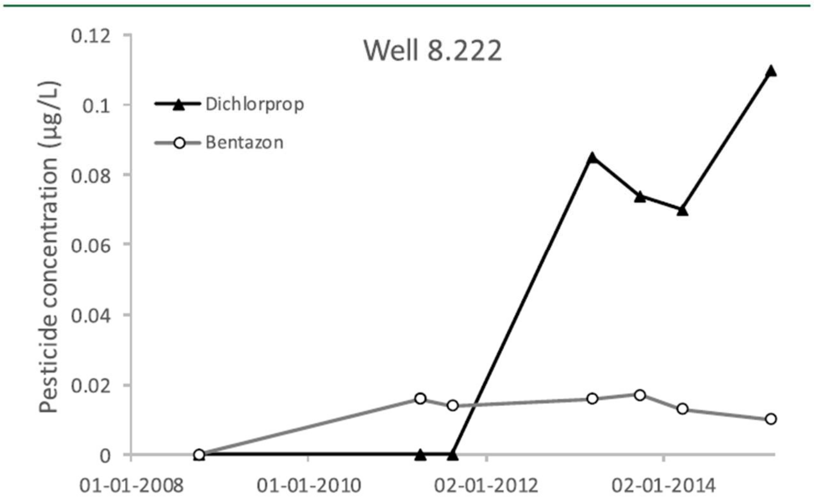

Figure 4.2 Monitoring trends in concentrations of the pesticides dichlorprop and bentazon in a Danish water supply well. (Jakobsen et al., 2020).

The sample collected at the top of the screen contained bentazon, but no dichlorprop, while the sample collected at the bottom contained dichlorprop, but no bentazon (Figure 4.3) .

The simulation of the groundwater age distributions in the top and the bottom of the screen of the water supply well performed either by TracerLPM simulations (Jurgens et al., 2012, 2016; Jakobsen et al., 2020) or particle tracking by groundwater flow models (Jakobsen et al., 2020) are shown in Figure 4.4.

The age distributions simulated by the two independent methods differ considerably, but they agree that a significant amount of the groundwater pumped from the top of the screen is less than 20 years old (about 33% according to the simulated tracers and 68 % according to the particle tracking simulations), while all of the groundwater pumped from the lower part of the screen is older than 20 years according to both types of simulations. 85 % is older than 100 years according to the tracer simulations, while 95 % is older than 100 years according to the particle tracking simulations.

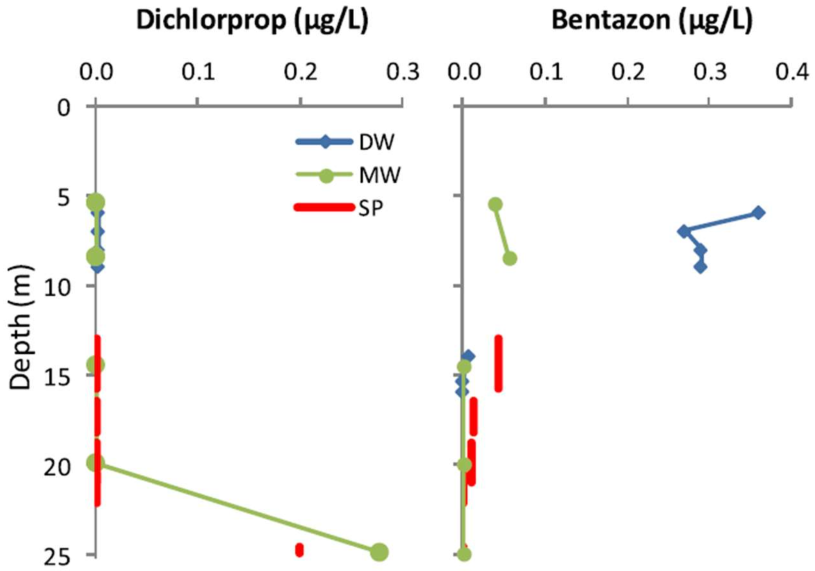

Figure 4.3 Dichlorprop and bentazon concentrations measured in the water supply well (SP = 12 m screen), permanent monitoring wells around the supply well (MW = 1 m screens) and temporary driven wells / drive points (DW = 0.1 m screens). After Jakobsen et al. 2020.

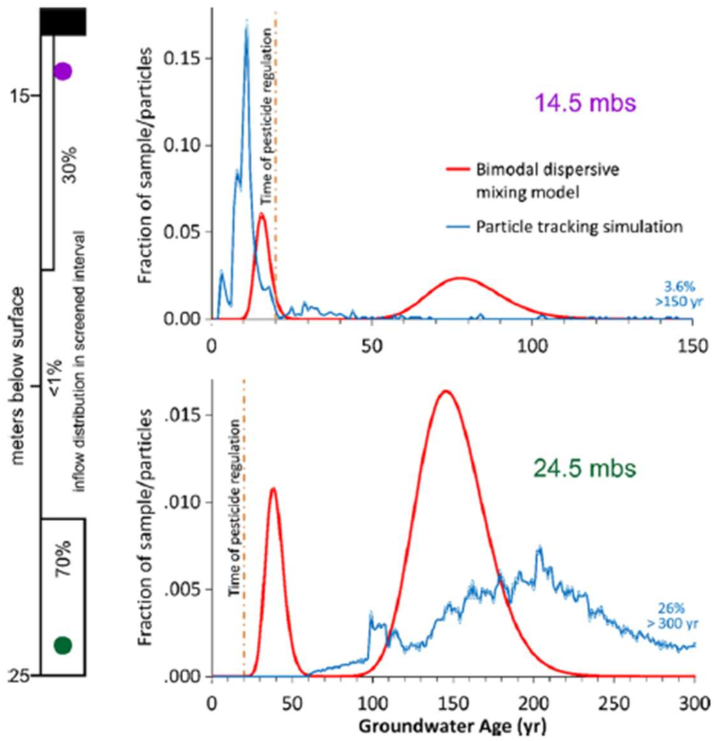

Figure 4.4 Distribution of age (travel time) for groundwater entering the top and bottom of the drinking water well determined by either TracerLPM (bimodal dispersive mixing model shown in red) or particle-tracking simulations (shown in blue) (Jakobsen et al., 2020)

The study concludes that the two pesticides bentazon and dichlorprop originates from two different sources most probably a point source related to a nearby golf course and a former corn field to the south of the water supply well, respectively. It is also shows that bentazon contamination occurred after bentazon was regulated in Denmark in 1995, and that the dichlorprop contamination occurred most probably 10-20 years before that. The Jakobsen et al. (2020) study illustrates how the simulation of groundwater age distributions e.g. in long-screened water supply wells can help identifying pesticide sources and help resolving the history and fate of the pesticides in groundwater. The introduction of ^{39}Ar as a groundwater dating tracer for groundwater within the age range of <100 - > 1000 years enables the estimation of the mixing fractions of both young (< 60 and < 100 years) and old groundwater (> 100 years), and a much better understanding of the vulnerability (susceptibility, Solder et al., 2020) of e.g. water supply wells towards contamination from the surface.

This study by Jakobsen et al. (2020) inspired and resulted in additional funding for further studies on groundwater age distributions in about 25 Danish water supply and monitoring wells in the HOVER project. The study was enabled by additional funding from Innovation Fund Denmark to the GeoERA program specifically for sampling and analysing multiple tracers incl. ^{39}Ar for the estimation of groundwater age distributions in specific water supply wells of three major Danish water companies and a few monitoring wells of a regional authority.

The results of the study are not yet published, and some preliminary results are only briefly presented in the following to illustrate the type and application of the obtained data.

4.2 Adding information about the age window of 100-1000 years – work conducted in HOVER

4.2.1 Methods

Twenty-eight samples were collected from 23 water supply wells, four monitoring wells (88.1942, 88.1979-1; 88.1979-2, 88.1421-1) and one remediation well (88.1580) in or around main well fields of three of the major Danish water companies: Aarhus Vand, VCS Denmark and TREFOR. The samples for tracer analyses were collected in collaboration with the tracer laboratories at University of Bern (Roland Purtschert), University of Bremen (Jürgen Sültenfuss) and University of Heidelberg (Werner Aeschbach).

Two water supply wells, four monitoring wells and a remediation well were sampled for Aarhus Vand and Region Midtjylland close to the city of Aarhus. All samples collected for the TREFOR and VCS Denmark water companies were collected in water supply wells with screen lengths between 5 and 29 meters.

Samples collected from Aarhus Vand and TREFOR wells were analysed for ^{3}H/^{3}He, ^{85}Kr, and ^{39}Ar. In addition to these tracers the VCS Denmark wells were also analysed for ^{14}C, δ^{13}C, SF_6 and CFC-gases. The industrial gases, CFCs and SF6, however, were either affected by degradation in aquifers (Hinsby et al., 2007) or contamination, and were not used in simulation of the groundwater age and travel time distributions. Tracers that appeared to be free from contamination or degradation issues, which were mainly ^{3}H/^{3}He, ^{85}Kr, ^{39}Ar and ^{14}C, where used in the simulation of groundwater age and travel time distributions by TracerLPM developed by USGS (Jurgens, 2016). TracerLPM simulations were conducted by the USGS (Bryant Jurgens).

The water supply wells, monitoring and remediation wells are all screened at various intervals between 22 – 150 mbs with screen lengths varying between 2 and 36 meters. The four monitoring wells, which are not pumped, have screen lengths between 2 and 6 meter. The water supply pumping wells are screened at intervals between 5 and 36 mbs, and the remediation pumping well (88.1580) has a screen length of 12 m.

The location of the wells around the cities of primarily Aarhus, Vejle and Odense are shown in Figure 4.5.

Figure 4.5 Upper left: Location of the investigated 25 water supply and monitoring wells in central Denmark (The Island of Funen and eastern Jutland) around the cities of Aarhus, Vejle and Odense. Upper right: sampling $^{14}C_{DIC}$ at well 136.218 near Odense. Lower middle: the author of this chapter explaining the groundwater study to the local press.

4.2.2 Selected Results

4.2.2.1 Water supply, monitoring and remediation wells investigated for Aarhus Vand and Region Midtjylland, Denmark

Figure 4.6 shows the locations of the Aarhus set of wells. Table 4.1 provides the tracer measurements available at the Aarhus wells.

Table 4.1 Measured tracers and simulated mean ages of the investigated water supply, monitoring and remediation wells of the water supply of Aarhus / Aarhus Vand and Region Midtjylland

Well ID	Filter depth interval (mbs)	^{3}H [TU]	trit-^{3}He [TU]	^{4}He radio [Nml/kg] E-06	^{39}Ar pmAr	^{85}Kr dpm	Mean age – young fraction Years	Mean age - old fraction Years
88.969	25-37	3,38	18,75	6,66	77	5,73	32	-
88.1580	64-76	3,15	18,50	1,13	-	3,04	36	500
88.1942	38-40	4,09	5,20	4,45	-	29,79	16	-
88.1979-2	69-72	3,74	12,88	3,00	57	5,09	33	1000
88.1979-1	80-86	3,53	11,94	1,87	86	4,06	32	1000
89.1421-2	91-127	-	-	-	62	0,64	-	186
89.1421-1	145-150	-0,01	-	-	0	3,24	-	2000

Following Table 4.1, no tritium (^{3}H) could be measured in the samples collected in well 89.1421-1. Hence, 89.1421-1 do not contain a fraction of young potentially contaminated groundwater. The contents of the young tracer ^{85}Kr may be a result of contamination because of sampling difficulties in this short poorly yielding monitoring well. Unfortunately, the tritium and helium samples were missing from 89.1421-2. The water supply well that pumps groundwater primarily within an age range of 150 – 250 years old, however, shows increasing salinity (Figure 4.7) most probably as a result of up-coning from deeper more saline parts of the aquifer as indicated by the high chloride concentrations observed in the monitoring well 89.1421-1, at 145-150 meter below surface.

Samples 88.1979-1 and 88.179-2 yield somewhat ambiguous results. Overall, the modern tracers indicate that the age of the samples is primarily modern but the low ^{39}Ar results indicate that an old water must also be present, and the age of that older component needs to be quite old to offset the ^{39}Ar concentrations contributed by the modern water. Better models can be obtained for wells 88.1979-1 and 88.179-2 by including a 15 years unsaturated zone delay. We did not include unsaturated zone delays in any of the Tracer LPM models in this report because no tracer evidence for a large influence of unsaturated zone travel times was indicated in any of those wells. Including a unsaturated zone travel time of 15 years (+/-5) yields a better model fit which would give an age of the old fraction of 80 and 400 years for samples 88.1979-1 and 88.179-2, respectively. The age of the young water would then be about 42 years, which makes sense in comparison with the shallower wells that have 30 years old water.

Figure 4.6 The location of the wells sampled around the city of Aarhus for simulation of groundwater age and travel time distributions in water supply, monitoring and remediation wells.

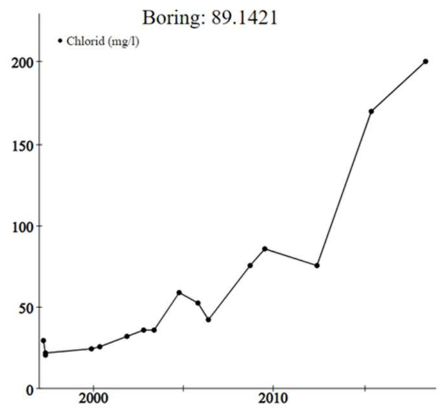

Figure 4.7 Increasing chloride concentrations approaching the drinking water standard of 250 mg/l in water supply well, 89.1421 (source: GEUS groundwater database).

Figure 4.8 illustrates the cumulative age distribution for the wells 89.1421-1 and 89.1421-2 near Aarhus. The shallower well has an apparent age of 120 years, the deeper one of 2000 years. The deeper well contains 1300 mg/l chloride and the shallower one shows the onset of salinization as well (Figure 4.7).

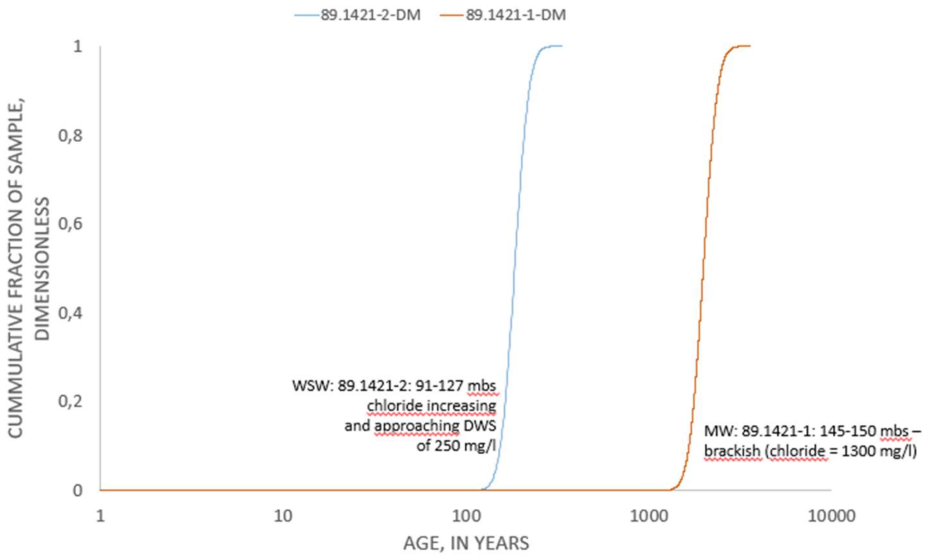

Figure 4.8 Age distributions in a water supply well (WSW 89.1421-2, screened at 91-127 mbs) and a monitoring well (MW 89.1421-1, screened at 145-150 mbs) as simulated by TracerLPM based on the contents of ^{39}Ar in samples collected from the wells.

Figure 4.9 provides the cumulative age distributions for the Åbo kildeplads west of Aarhus (Figure 4.6). These wells pump a substantial amount of water aged < 100 years. All wells contain pesticides and a fraction of young groundwater, which infiltrated later than 1953. The simulations are based on the contents of ^{3}H/^{3}He, ^{85}Kr and ^{39}Ar.

In summary, measurements of ^{39}Ar revealed that wells with screens deeper than 60 mbs have some fraction of old groundwater whereas wells shallower than 60 mbs have no water older than 50 years. Although ^{39}Ar concentrations in 1979-1 and 1979-2 suggest ages less than 500 years, the models suggest the age of the old water component is 1,000 years or more. Groundwater older than 1,000 years is necessary to dilute the concentration of modern argon contributed from the young fraction of groundwater.

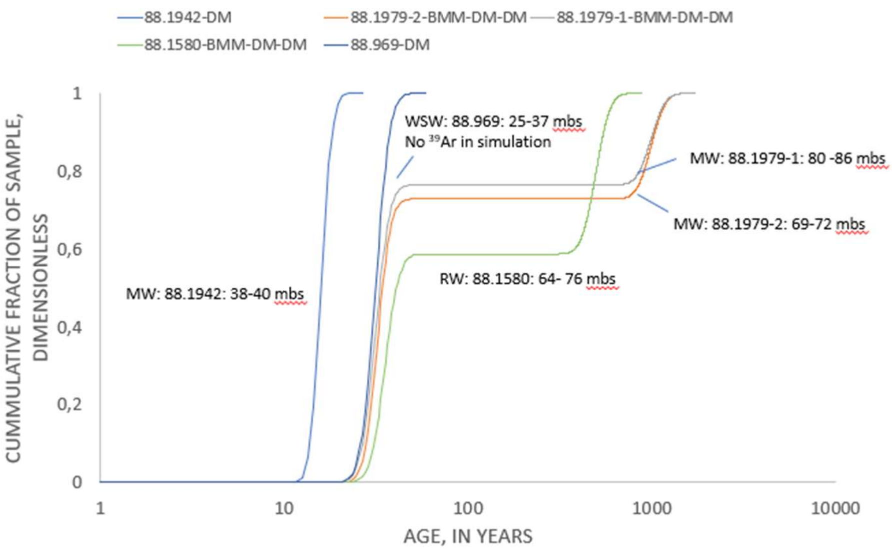

Figure 4.9 Age distribution in water supply (WS), monitoring (MW) and remediation (RW) wells of Åbo kildeplads west of Aarhus (Figure 4.6). All wells contain pesticides and a fraction of young groundwater, which infiltrated later than 1953. The simulations are based on the contents of $^{3}H/^{3}He$, ^{85}Kr and ^{39}Ar.

4.2.2.2 Water supply wells of VCS Denmark

Table 4.2 provides the tracer measurements available from the water supply of VCS, Denmark – the water supply of the City of Odense (Figure 4.10).

Table 4.2 Measured tracers and simulated mean ages of the investigated water supply wells of VCS Denmark

Well ID	Filter depth interval (mbs)	^{3}H [TU]	trit-^{3}He [TU]	^{4}He-radio Nml/kg (E-06)	^{39}Ar pmAr	^{85}Kr dpm	Mean age – young fraction Years	Mean age - old fraction Years
136.218	24-29	3,13	11,02	2,07	95	11,60	28	-
136.285	24-39	0,70	8,83	36,7	107	1,40	34	585
136.891	19,5-32,5	0,65	10,25	133		1,40	38	516
136.907	26-35	1,11	7,99	43,4		5,07	28	202
145.717	38-53		17,69	4,37	127	9,68	28	0
145.2740	44-73	1,58	16,11	78,9	64	3,30	34	357
145.3083b	80,5 - 82,5	0,23		161	45	2,89	10	618
145.3083t	64,5 - 66,5	0,56	8,10	82,4	65	3,21	20	86
145.3083m	64,5-82,5	0,38	6,66	128	30	2,40	24	537
146.490	63-103	0,03	0,14	76,8	43	3,80	-	422
146.492	29-34	2,95	28,82	17,8	95	7,20	33	-

Note! ^{14}C and $\delta^{13}C$ values exist for some VCS wells with a range of values between 37 – 63 pmC, and -12 to -14 ‰, respectively, indicating that there are no paleowaters in the investigated wells and that the ^{14}C values are affected by carbonate dissolution

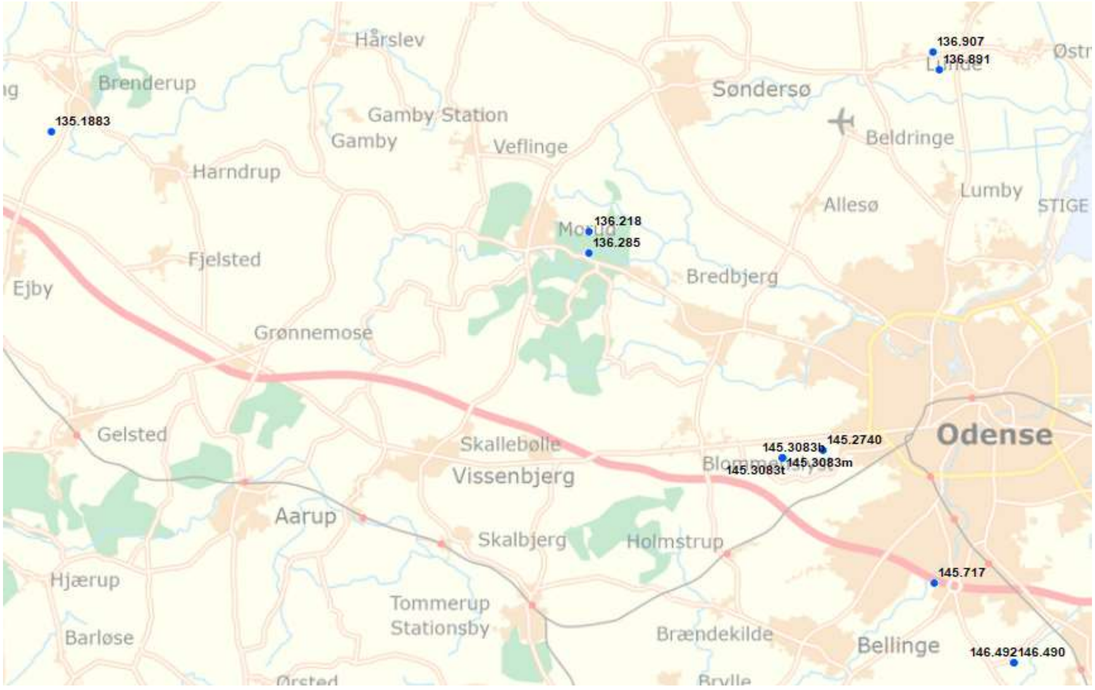

Figure 4.10. Location of the investigated water supply wells of the city of Odense.

A young, potentially contaminated fraction of the pumped groundwater was found in all except one of the investigated wells for the water company VCS Denmark, based on the $^{3}H/^{3}He$ and ^{85}Kr (Table 4.2). 4.11 show the simulated age and travel time distributions for those 11 water supply wells. Wells 147.717, 145.3082, 136.218, 136.285 all pump very young groundwater with ages < 100 years. Clearly, those wells have highest vulnerabilities for the potentially contaminated recharge of anthropogenically altered water. For the other 7 wells ^{39}Ar enabled the simulation and quantification of the fraction of "pre-development" unpolluted groundwater recharged in the period about 100 – 1000 years before present (Jurgens et al., 2016). Well 136.907 and 145.2740 combine a fraction of 40-55% fraction of the age class < 100 years, and 45-60% of the age class 100-300 years. These wells represent an intermediate vulnerability: 40-55% water aged less than 100 years indicates a substantial susceptibility as well, comparable to the Dutch Holten case from section 3.1.1. All other wells pump the dominant fraction from the age class 300-1000 years and are much less susceptible for anthropogenic alteration from diffuse superficial sources.

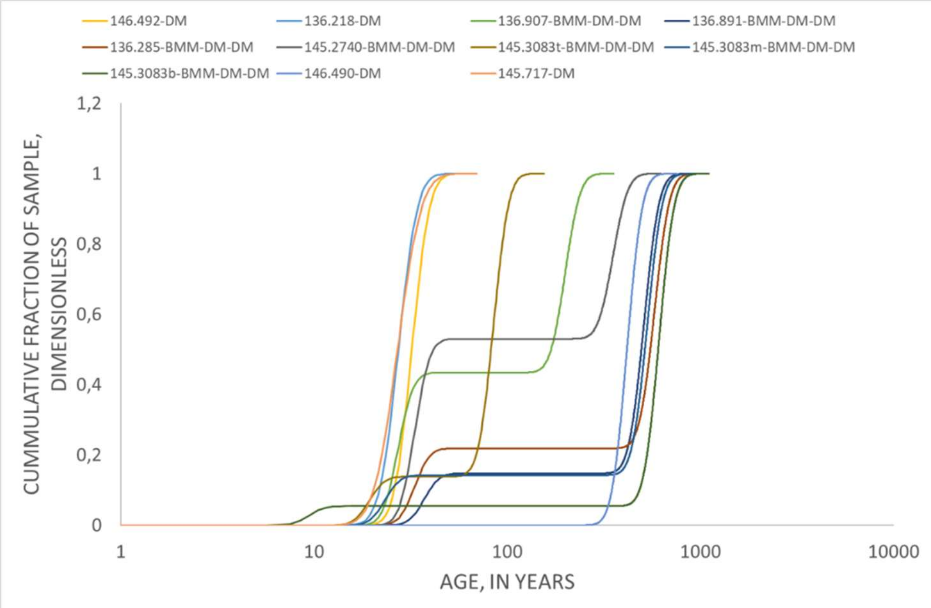

Figure 4.10 Age distributions of 11 groundwater samples collected from nine water supply wells of the water company VCS, Denmark of the city of Odense. The age distributions are simulated by TracerLPM based on the tracers: $^{3}H/^{3}He$, ^{85}Kr, ^{39}Ar and ^{14}C.

4.2.2.3 Water supply wells of TREFOR, Denmark

Figure 4.6 shows the locations of the Aarhus set of wells. Table 4.1 provides the tracer measurements available at the Aarhus wells.

Table 4.3 Measured tracers and simulated mean ages for the TREFOR wells around the cities Kolding and Vejle (Figure 4.12)

Well ID	Filter depth interval (mbs)	^{3}H [TU]	trit-^{3}He [TU]	^{4}He radio Nml/kg E-06	^{39}Ar pmAr	^{85}Kr dpm	Mean age - young fraction Years	Mean age - old fraction Years
116.153	22-35	2,05	9,56	10,9	37	6,34	26	2000
124.357	79 – 112	1,16	14,46	2,78	65	1,64	38	219
124.1019	99-117	0,00	-1,27	1,05	59	0,62	-	206
125.788	42-57	1,21	-0,05	29,1	93	5,52	16	81
125.1713	66-84	0,23	-0,70	26,6	64	1,91	16	187
133.1107	23-43	0,14	-0,14	13,9	51	0,22	4	271
133.1461	61-73	0,25	3,30	19,8	-	0,95	18	500
133.1718	68-83	0,05	0,93	223	28	0,87	38	509
133.1784	67-79	0,31	1,77	23,7	45	1,21	26	360
135.1883	51-63	0,02	3,31	169	43	3,75	4	332

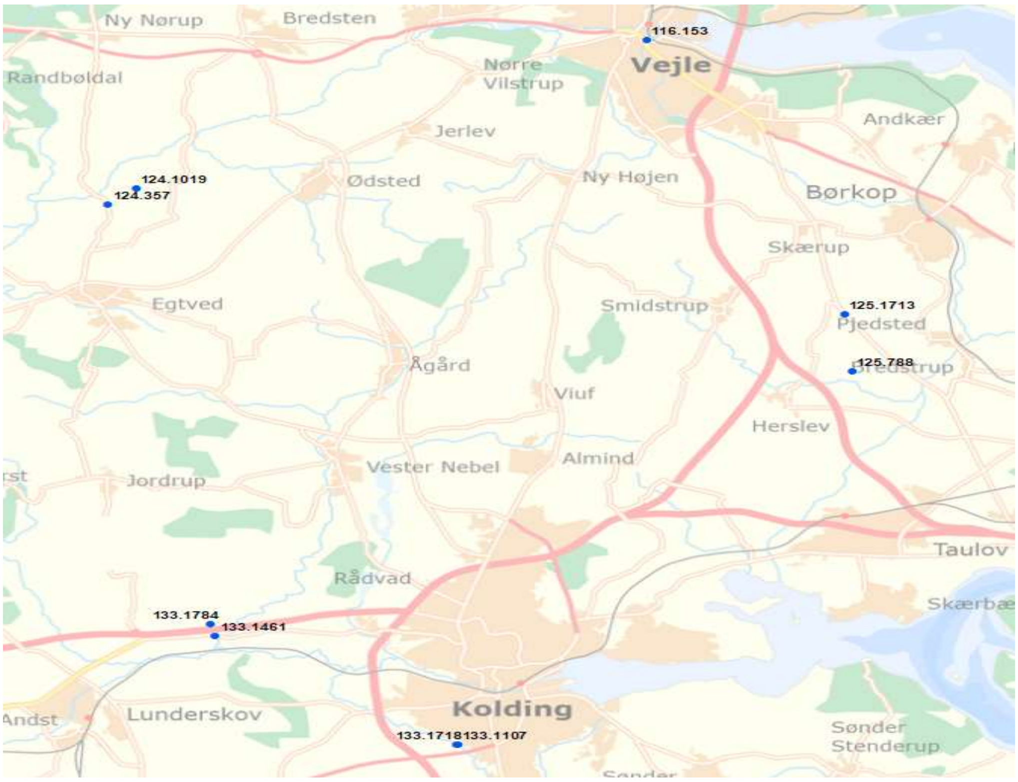

Figure 4.12 Location of the investigated TREFOR wells around the cities of Kolding and Vejle.

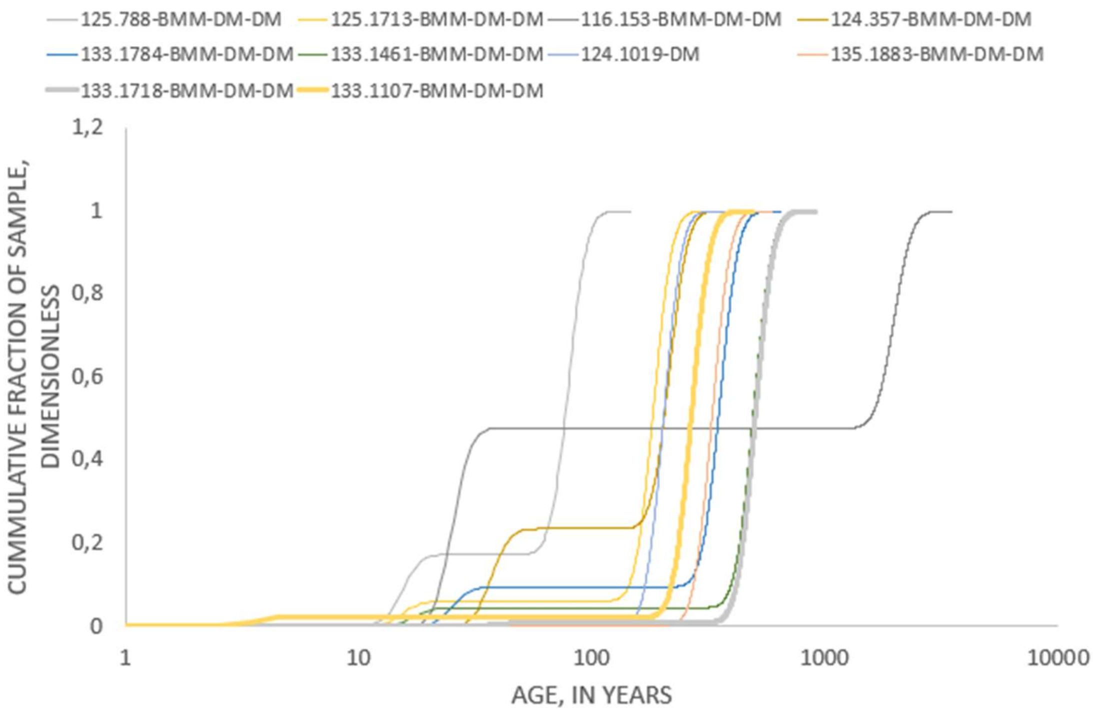

Figure 4.13 Simulated age distributions of the ten water supply wells investigated for the TREFOR water company. Preliminary data.

Figure 4.13 shows the groundwater age distributions of the ten water supply wells investigated for the TREFOR water company. Well 125.788 is estimated to have all water from the age class < 100 years, and wells 116.153, 124.357 and 133.1784 have 48%, 23% and 9% young water, respectively. Well 116.153 is known to exhibit increasing pesticide concentrations, confirming the large proportion of young water. The plot of the ages illustrates the value of the ^{39}Ar tracer in simulating the fraction of groundwater in the water samples with the age range between about 100 – 1000 very well; wells 125.1713, 124.1019, 124.357 and 133.1107 all seem to have a considerable proportion of water in the age class 100-300 years. Wells 133.1784, 135.1883,133.1718 and 133.1461 have slightly older water with age in the range of 300-500 years. For both the TREFOR and VCS Denmark samples, the additional ^{39}Ar tracer is key to understanding those age distributions. Note that the TREFOR samples are older than the VCS Denmark samples with a significant fraction of groundwater older than 1000 years in one of the wells.

A major part of the groundwater pumped from the TREFOR water supply wells are more than 100 years old and hence without contamination from the surface. Note, however, that most of the wells have a young fraction, which may result in contamination of the well even with only a very little fraction of young groundwater as e.g. observed in well no. 133.1718. This contamination maybe the result of poorly developed or damaged wells that have leakage along or through a damaged well casings.

4.3 Conclusions and recommendations

The examples show in the previous sections on groundwater age distributions in the water supply wells of the Aarhus Vand, TREFOR and VCS Denmark water companies clearly demonstrate the value of ^{39}Ar as a tracer for simulation of the fraction of groundwater within the age range of 100 – 1000 years.

Together with especially the tracers for dating of young groundwater, primarily $^{3}H/^{3}He$ and ^{85}Kr it enables simulation of groundwater age distributions in the age range from a few years and up to > 1000 years. If $^{14}C_{DIC}$ is included, it is furthermore possible to assess the amount of paleowater in the groundwater sample i.e., groundwater with an age of more than 10.000 years and dating back to the late stages of the latest glaciation. The investigated wells did not show examples of this although $^{14}C_{DIC}$ analyses were included in the analyses of the samples collected from the VCS Denmark wells (see note below Table 4.2).

Figure 4.14 summarizes the age distributions following the visualization that was introduced for the Dutch water supply wells in Broers et al. (2015, 2021) showing the discrete age classes of < 100 years, 100-300 years etc. Clearly, the Danish water supply well show a much larger proportion of water aged less than 100 years compared to the well fields sampled in the Netherlands. This is partly the case because typical the sampling depths in the southern Netherlands' aquifers are larger than in the Danish regions studied. The Danish situation resembles the situation of the Holten well field (Visser et al. 2013, Broers et al. 2012) where aquifers have more limited depths.

Besides providing valuable information relevant for assessing the vulnerability / susceptibility of water supply wells to contamination from the surface (Solder et al., 2020), the age distributions may also provide information on the sustainability of the exploitation of the aquifers and well fields (Ferguson et al., 2020).

Data of the TREFOR water company have shown that large fractions of old groundwater (>100 years) may decrease the risk of microbial growth in water distribution systems as preliminary results have shown that the contents of organic matter in the older groundwater is less reactive than in young groundwater (pers. Comm. Ole Silkjær, TREFOR now EuroFinns, unpublished data). Hence, there may be additional benefits of exploiting this resource besides reducing the risk of contamination from the surface.

Finally, other previous studies have also demonstrated the value of ^{39}Ar in combination with groundwater flow modelling for the assessment of the vulnerability of regional aquifers (Sonnenborg et al., 2016).

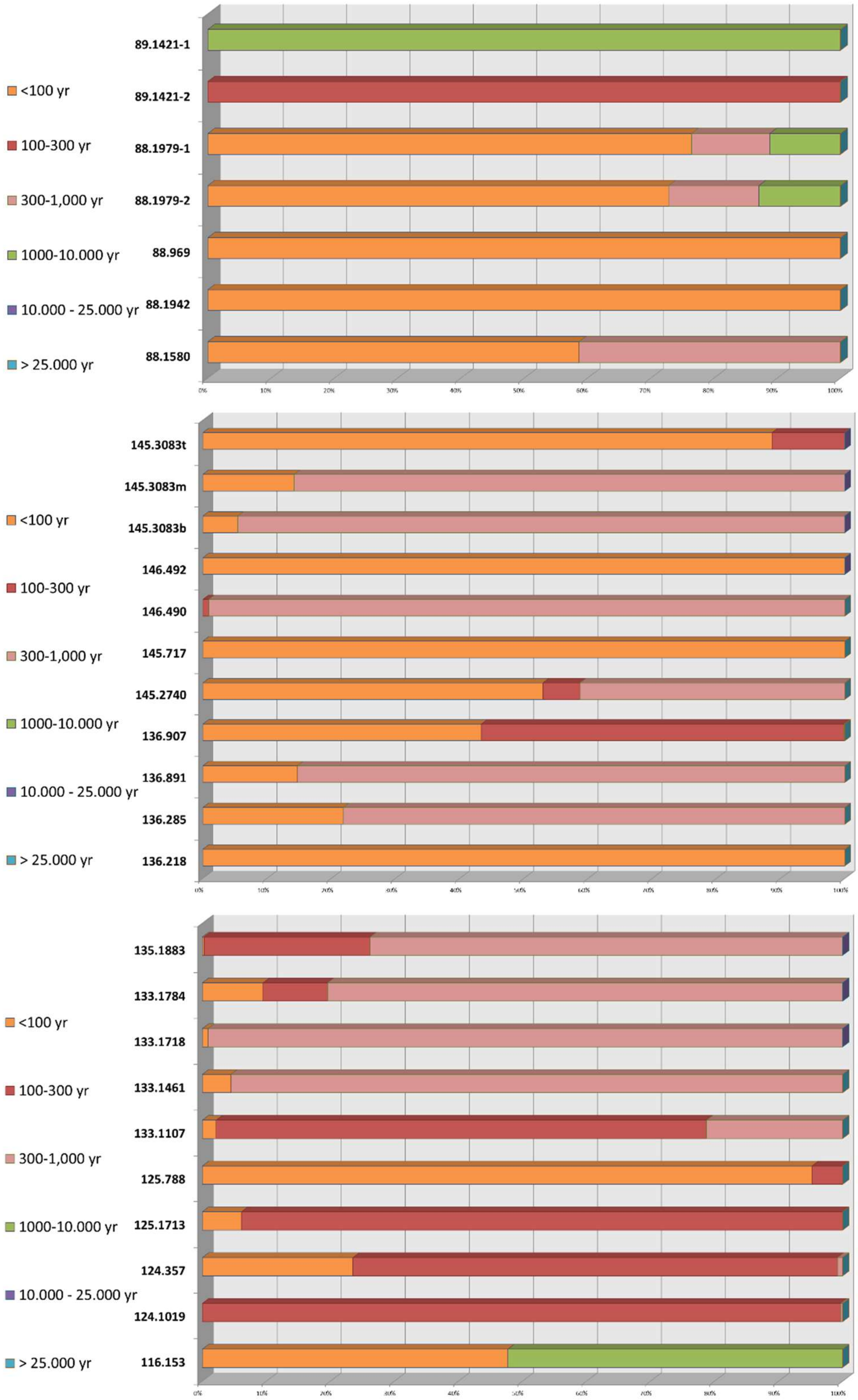

Figure 4.11 Visualization of the age distributions for the samples of Aarhus Vand (88- and 89-series), VCS Denmark (135- to 145-series) and Odense TREFOR (116- to 133-series) following the "Dutch" visualization approach using discrete age classes

5 AGGREGATION AND OUTLOOK

5.1 Introduction

One of the aims of Work Package 6 of HOVER project is to assess the effectiveness of new tracer and modelling techniques for estimation of groundwater age distributions in the age range of 100-1000 years in water supply wells. Within Task 6.4 we tested new techniques for estimating age distributions of groundwater bodies with residence times mainly in the age range of 100 to 1000 years and evaluated age distributions for water supply wells in the Netherlands and Denmark as proxies for well fields in other parts of Europe (see Table 2.1).

Table 5.1 Overview of pilot studies in HOVER WP6

Case Study	**Region**	**Individual pumped wells**	**Mixed raw water**
Netherlands	Well fields Veghel and Seppe	X	X
Denmark	Well fields of Aarhus Vand, VCS Denmark and TREFOR	X	

5.2 Lessons learned from the Dutch and Danish case studies

Table 5.2 lists the tracer sets that were used in the studies which are summarized in this report. The new tracer ^{39}Ar is mainly used in combination with $^{3}H/^{3}He$ and ^{85}Kr in Denmark. In the Netherlands, the new tracer is mainly used in combination with ^{3}H, $^{14}C_{DIC}$, $^{4}He_{rad}$ and Noble Gas Temperatures (NGT). This is partly related to the size of the well fields: overall abstraction rates of Dutch well fields are generally one order of magnitude larger than their Danish counterparts. As a result, the water is drawn from multiple aquifers and presumable a larger age range.

Table 5.2 Tracer sets used in the examples in this report

	^{39}Ar	$^{3}H/^{3}He$	^{85}Kr	$^{14}C_{DIC}$	$^{4}He_{rad}$	NGT
Holten (2013,2014)	X	X	X			
Brabant (2021)		X		X	X	X
BW10 well field Noord-Brabant	X	X		X	X	X
BW27 well field, Noord-Brabant	X	X		X	X	X
Aarhus Vand wells, Aarhus, Denmark	X	X	X		X	
Denmark VCS, Vejle, Denmark	X	X	X		X	
TREFOR wells, Odense, Denmark	X	X	X	X	X	

5.3 Recommendations for assessing age distributions in water supply wells

We strongly recommend the use of multiple tracers for assessing age distribution of well fields and pumping wells. Including the advanced ^{39}Ar age tracer has shown to provide very valuable information about groundwater flow dynamics and groundwater age and travel time distributions. The half-life of 267 years forms a complementary value between the ^{3}H tracer (half-life of 12.3 years) and $^{14}C_{DIC}$ (half-life 5730 years). This was first recognized for application in an oceanographic setting but is increasingly recognized in the groundwater world. The BW10 case, which is described in section 3.2.2, demonstrates the merits of the additional tracer; it was concluded in a previous study (Broers et al. 2021) that water with an age of 100-1,000 years was present in large proportions, but a more precise estimate could only be achieved adding the ^{39}Ar tracer in the multi-tracer approach. It matters much whether a large proportion of this water is between 100 and 250 years old or between 500 and 1000 years; well fields with large proportion of the first are more susceptible in the operational time frame of a production well field, especially because the tracer derived age might be the result of a non-stationary flow and transport situation; the proportion of younger water may further increase with time as the age distribution might not have reached a stable state and younger water is still approaching deeper layers. Similar findings were made in the Danish case: for example well 124.357 shows a bimodal age distribution with a mix of young water of 40 years old and older water between 100 and 200 years old. Such a situation may remain stable over the production time of the well field but may as well change with an increasing young component if an equilibrium distribution has not yet been reached.

A sound understanding of the groundwater age distributions in water pumped from contaminated water supply wells may help deciding whether wells can be renovated or the contaminated well has to be closed and a new well drilled. Hence, the relative high costs of ^{39}Ar analyses may be more than justified if they can save existing wells. A relatively small but polluted young water component may result from poor well development or damaged casings, which may be repaired, or from only the upper part of a well that may be sealed to reduce the contamination, and thereby avoid closing the well.

5.4 Outlook

A major disadvantage at the moment, is that the analyses of ^{39}Ar are still rather costly and lab capacity is limited worldwide. As an example, ^{39}Ar and ^{85}Kr were measured by the University of Bern for the Danish study, and ^{39}Ar was analyzed using the new ATTA technique at Heidelberg University for the Dutch GeoERA case study. These are the only available options in Europe, and lab capacity is still limited and only available at highly advanced physical laboratories at universities such as Heidelberg, Bern and Hefei, China and large research institutes, such as Argonne National Laboratory in Chicago. It is anticipated that capacity will increase with time and prices will be reduced in the future. Relative to the costs of drilling new wells, the analytical costs are limited, which makes lab capacity the most important hurdle of large-scale application in groundwater. The technique, however, promises a new step in assessing the vulnerability of well fields, and new demonstration studies are running in the Netherlands and Denmark in cooperation with drinking water suppliers. The application may yield clear management perspectives in producing drinking water. For example, a sound understanding of groundwater age distributions e.g. in combination with borehole flow logs may enable modifications of a contaminated abstraction well e.g. closing part of the screen allowing for continuation of the well.

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7 ACKNOWLEDGMENTS

We would like to thank Prof. Werner Aeschbach, dr. Timo Metz and dr. Florian Freundt from Heidelberg University for the fruitful cooperation in the project and the analysis of noble gases, carbon isotopes and ^{39}Ar for the Dutch sites. The same holds for dr. Jürgen Sültenfuß from Bremen University who was responsible for the ^{3}H, ^{3}He and ^{4}He data, Dr. Roland Purtchert from University of Bern who analyzed the ^{39}Ar and ^{85}Kr of the Danish samples and Dr. Bryant Jurgens, USGS for running TracerLPM simulations of groundwater age distributions of wells investigated for the Danish water companies: Aarhus Vand, TREFOR and VCS Denmark. We very much enjoyed common discussions and hope to forward this to the immediate future in new cooperations. The tracer analyses of the Danish water supply wells were primarily made possible by additional funds to GeoERA from Innovation Fund Denmark and co-funding of the province of Noord-Brabant, the province of Limburg, Brabant Water N.V. and Waterleiding Maatschappij Limburg was much appreciated for the Dutch GeoERA pilots.

APPENDIX I: DESCRIPTION OF THE HOLTEN CASE STUDY (2012-2014)

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3.18 Description of the Holten case study, The Netherlands

Title of Case Study	Holten well field
Location (region, Country)	Twente region, province of Overijssel, Netherlands
Other information	The case study summarizes 2 studies that were published in peer-reviewed journals which focus on the applications of age dating of drinking water production wells. A method was developed to determine groundwater age distributions using a discrete shape-free age distribution model.

Description of Case Study
The production well field is located near Holten, in the eastern part of the Netherlands. The area is characterized by the Holterberg, an ice-pushed ridge north of Holten, consisting of thrusted sediments reaching 70 meters above mean sea level (msl). The surface elevation in the rest of the area varies between 15 and 20 meters above msl. A phreatic groundwater system is present in the (partly ice-pushed) fluvial and periglacial deposits of 90 to 120 m thickness. The Holten well field produces 2.5 million cubic meters groundwater from a depth of 10 to 70 meters below the surface. The well field is vulnerable to contamination because of the agricultural land use and residential areas in the capture area, the sandy aquifer, expected short groundwater residence times and relatively deep groundwater levels (4-8 m below surface). Especially nitrate and agriculture related contaminants like heavy metals are the largest threat to the water quality in the production wells. The well field currently has 19 pumped wells that were mostly constructed between 1960 and 1973 and were screened between 15 and 30 m below the surface. In 1985, three additional deep wells were drilled and screened from 45 to 70 m below the surface. These wells were intended to capture deep iron-rich anoxic groundwater to prevent well clogging that occurs when shallow oxic groundwater mixes with deep anoxic groundwater

Description of problem
The evolution of water quality in the well field was difficult to understand and especially fluctuations in concentrations of agriculturally derived contaminants including nitrate and sulfate made it uncertain which management options would be preferable for sustainable water production at the site.

Methods used in the Case Study
The case study included the application of a wide range of groundwater age and paleoclimate indicators including: $^{3}H/^{3}He$, ^{85}Kr, ^{39}Ar, ^{4}He and ^{18}O. The drinking water well field is surrounded by a network of multilevel monitoring wells with short screens (1-2 m); these monitoring wells were sampled for $^{3}H/^{3}He$ in order to determine discrete apparent ages and to deduce the age stratigraphy in the aquifer. Eleven production wells were selected for sampling based on their typical production, ensuring that both shallow and deep wells in close proximity were sampled. Samples for $^{3}H/^{3}He$ analysis were collected from all eleven wells, providing over 95% of the total production. Samples for krypton-85, argon-39, dissolved gas and stable isotope analysis were collected from seven of the eleven wells, capturing 69% of the total drinking water production. To quantify a groundwater age distribution from the available age tracer data, a shape-free discrete groundwater age distribution model was applied. The model describes the

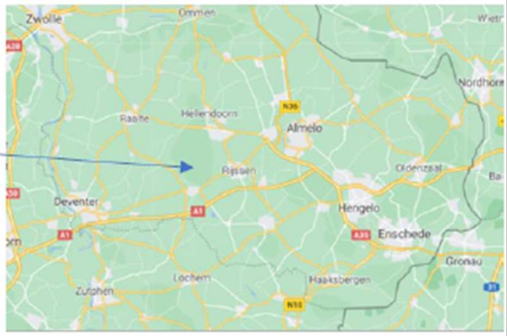
groundwater age distribution by a number of age bins with a uniform age distribution within each bin.

Results from this Case Study
The sampling of the multi-level observation wells yielded a description of the age stratigraphy of the water in the aquifers with groundwater aging with depth, which could be represented by an exponential model with a mean travel time of 15-19 years that is truncated after 30-40 years. The discrete groundwater age distribution model described the mixing from the pumped aquifers, with the shallower wells extracting a younger mix of groundwater than the deeper wells. This age distribution in the production wells appeared to be consistent with the vertical groundwater age profile in monitoring wells in the vicinity of the well field. We were able to estimate the contributions of water aged between 0-15, 15-30, 30-45, 45-60 and > 60 years using the discrete age distribution model. The shallow pumping wells produced young (0-30 y) groundwater mixed with possibly a small (15%) fraction of old groundwater. The apparent argon-39 ages in these wells suggest that the old fraction is several hundred years old at most, which is supported by low concentrations of radiogenic helium-4. Two of the three deep wells produce a mixture of 40% intermediate (15-30 y) groundwater and 60% old groundwater. The third deep well produces 90% old groundwater. The apparent age of the old groundwater component is 310 ± 90 years. The study taught us that production wells compete for capture area and age of the pumped groundwater. When shallow and deep production wells are in close vicinity, the age of the groundwater is separated into an older mix in the deeper wells and a preferential younger mix in the shallower wells. Changing the pumping regime between shallower and deeper wells therefore influences the age of the pumped water, leading to fluctuations in water composition that were not properly understood beforehand. We learned that varying well pumping rates, abandoning wells or drilling additional wells will impact the groundwater captured by existing wells and therefore also the age distribution of individual wells.

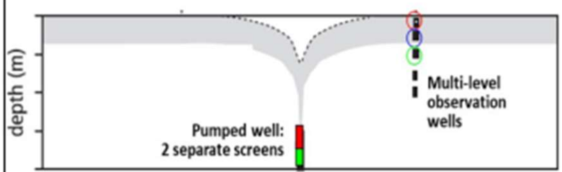
Impact - how this Case Study contributes to the overall project aims
The case study is one of the first examples for demonstrating the use of groundwater age distributions for understanding the evolution of water quality at drinking water production well fields. It also represents one of the first successful application of ^{39}Ar age dating in such a setting. The HOVER project will extend this work under task 6.4 in order test and develop new techniques for estimating age distributions of groundwater bodies with residence times mainly in the age range of 100 to 1000 years, for which a number of demonstration pilots at drinking water well fields have been sampled in 2019 and 2020. Under task 6.4, we intend to develop a common methodology for characterization of the age distribution of pumped wells by using a suite of tracers and models. The Holten study in one of the case studies to provide input for this work.

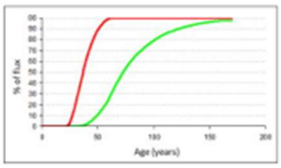
Name of pilot area / aquifers / type: Holten well field	Country: Netherlands Region: Holten well field, Overijssel, The Netherlands
Study level	Transboundary : ☐ Regional: X Local: X Single well(s): ☐
Type of observations	X Short screened observation wells (not pumped) ☐ Long screened observation wells (not pumped) X Pumped wells, long screens in one aquifer ☐ Pumped wells, long screens over multiple aquifers ☐ Springs ☐ Other (eg. research wells; indicate type and information on pumping):

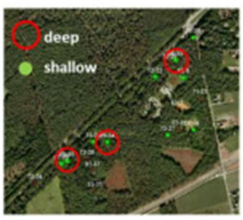
Approximate location of pilot (WGS84):
minX: 6.327500
maxX: 6.500000
minY: 52.250000
maxY: 52.310000

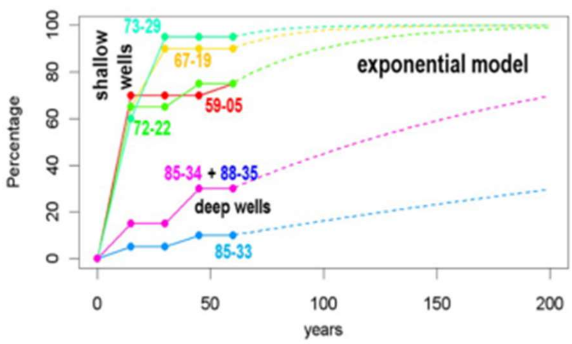


Geological cross section / conceptual model of the pilot area:









Name of Shape- / Geopackage file defining the area:	Projection to be used: WGS84 (Epsg4326)

Hydrological parameters:	**Mean annual precipitation (mm or range in mm)**	**Mean annual groundwater recharge (mm or range in mm)**	**Mean annual groundwater recharge temperature (°C)**	**Thickness of unsaturated zone (range in m)**
	750	200-300	10	< 5 m
Pumped wells only		**Typical pump discharge of sampled individual well (m^3/day): 800**		**Typical pump discharge of complete well field (m^3/day): 10,000**
List of aquifers and aquitards in pilot area		**No. of confined or semiconfined aquifers in pilot area: 2**		**No. of unconfined aquifers in pilot area: 1**
Aquifer no. (aqf): 3	**Aquifer/aquitard type and/or name**	**Lithology**	**Depth range (m)**	**GW age range (yr)**
Aqf-1:	Quaternary sands	Fluvial fine to coarse fluvioglacial sands	10	< 30
Porosity type	Porous: X	Fissured: □	Karst: □	Fissured and porous / dual porosity: □
Aqf-2:	Quaternary sands	Fluvial coarse sands	10-30	< 60
Porosity type	Porous: X	Fissured: □	Karst: □	Fissured and porous / dual porosity: □
Aqf-3:	Quaternary sands	Shallow marine fine sands	30-70	60-500
Porosity type	Porous: X	Fissured: □	Karst: □	Fissured and porous / dual porosity: □
Applied tracer age indicators (^3H, $^3H/^3He$, ^{85}Kr, ^{39}Ar) **Applied recharge temperature indicators** (^{18}O)		**Aquifer-1** $^3H/^3He$		
		Aquifer-2 ^3H, $^3H/^3He$, ^{39}Ar, ^{85}Kr, ^4He, ^{18}O		
		Aquifer-3 ^3H, $^3H/^3He$, ^{39}Ar, ^{85}Kr, ^4He, ^{18}O		
Number of sites (wells/springs) with age indicators		**Aquifer-1** **1-5: □ 5-10: □ 10-25: X >25: □**		
		Aquifer-2 **1-5: □ 5-10: □ 10-25: X >25: □**		
		Aquifer-3 **1-5: □ 5-10: X 10-25: □ >25: □**		
GW age range (GAR) **GAR-1: Modern (< 60 yr)** **GAR-2: Old (> 60 yr and 10 kyr)**		**Aquifer-1** **GAR-1: 1-10%: □ 10-25%: □ 25-50%: □ >50%: X** **GAR-2: 1-10%: X 10-25%: □ 25-50%: □ >50%: □**		

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GAR-3: Paleowaters (> 10 kyr)	GAR-3: 1-10%: 0 10-25%: □ 25-50%: □ >50%: □
	Aquifer-2 GAR-1: 1-10%: □ 10-25%: □ 25-50%: □ >50%: X GAR-2: 1-10%: X 10-25%: X 25-50%: □ >50%: □ GAR-3: 1-10%: 0 10-25%: □ 25-50%: □ >50%: □
	Aquifer-3 GAR-1: 1-10%: □ 10-25%: □ 25-50%: □ >50%: X GAR-2: 1-10%: □ 10-25%: □ 25-50%: X >50%: X GAR-3: 1-10%: 0 10-25%: □ 25-50%: □ >50%: □
Groundwater age ranges (GAR) estimated by:	Tracer based estimates

Objective of age dating studies:

Basic research or General groundwater management	Assessment of pollutant history	Assessment of the efficiency of remediation and mitigation measures	Indication of vulnerability of aquifers and water supply wells
			x

Water Usage	Water supply	Irrigation	Industry	Other
	x			

Geoenergy related activities	Shallow Geo-T	Deep Geo-T	Hydrocarbons	Nuclear waste disp.	CO_2 storage

Mining activities	Construction materials	Minerals / metals	Coal	Other

REFERENCES

OPEN Access reports and papers (PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches):	Reports and papers with restricted access:
	Visser, A., Broers, H. P., Purtschert, R., Sültenfuß, J., & de Jonge, M. (2013). Groundwater age distributions at a public drinking water supply well field derived from multiple age tracers (85Kr, 3H/3He, and 39Ar). Water Resources Research, 49(11), 7778-7796. Massoudieh, A., Visser, A., Sharifi, S., & Broers, H. P. (2014). A Bayesian modeling approach for estimation of a shape-free groundwater age distribution using multiple tracers. Applied geochemistry, 50, 252-264.

Remarks / other relevant information:

APPENDIX I: DESCRIPTION OF THE DANISH CASE STUDIES (2019-2021)

Title of Case Study	Travel time distributions in 30 long-screened water supply wells
Location (region, Country)	Eastern Jutland and Funen, Denmark
Other information	Mainly long-screened water supply wells of the three major Danish water supply companies TREFOR, VCS Denmark and Aarhus Vand were investigated in order to assess the age and travel time distributions in the wells and their vulnerability towards pollution from the surface. Many of the investigated wells are contaminated with pesticides or their degradation products.

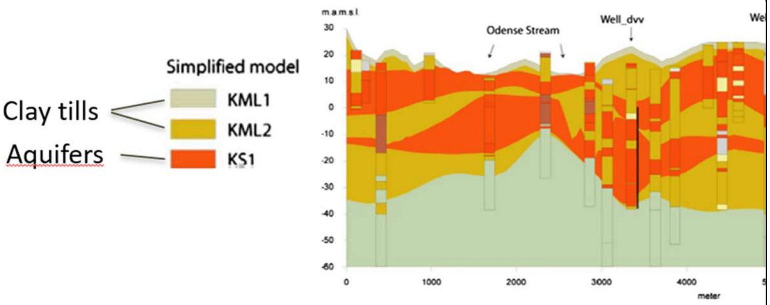
Description of Case Study (background information on the region)
Pilot study in collaboration with three major Danish water companies responsible for water supply to the second and third largest cities in Denmark, Aarhus and Odense, respectively, and an important urbanized region of Eastern Jutland. About 30 wells were sampled and analysed for a wide range of dating tracers in order to investigate the age and vulnerability of the wells towards pollution. The screens of the wells are between 3 and 40 meters long, but most are between 10 and 15 meters and installed at depths between 20 and 150 m below surface. The pilot study is made possible through funding from Innovation Fund Denmark (IFD) supporting the Danish part of all the GeoERA groundwater projects, Minerals4EU and the information platform project (GIP) of the GeoERA programme. IFD funds about half of the tracer analyses, while the other half is funded by the involved water companies. The well selection and sampling were done in collaboration with the water companies, the environmental radionuclides research group at the Physics Institute of University of Bern, and the "Helis – Helium isotope studies Bremen" lab. at university of Bremen and TNO. The dating tracers $^{3}H/^{3}He$ were analysed by the Helis lab. at University of Bremen, the ^{39}Ar and ^{85}Kr tracers were analysed by University of Bern. A few wells were selected for the analysis of veterinary antibiotics found in some Dutch aquifers in collaboration with TNO.

Description of problem (why is this location chosen for a Case Study)
The wells were selected in well fields experiencing impacts of pesticide pollution to improve the understanding of travel times from potential pollutant source areas at the surface and the vulnerability of the wells and well fields towards pollution from the surface. Observed pollutants in the investigated wells include pesticides and their degradation products e.g. Disphenyl Chloridazon (DPC), Dimethylsulfide (DMS), 4-Chlorophenoxy-propionic acid (4-CPP), a degradation product of dichlorprop (DPCC), mechlorprop, dichlorobenzamide. Most of the observed pesticides have either been completely banned or regulated.

Methods used or to be used in the Case Study (analytical and isotope techniques, modelling)
The case study include the application of the groundwater age indicators ^{85}Kr, ^{39}Ar, $^{3}H/^{3}He$, ^{4}He, ^{14}C, $\delta^{13}C$, CFCs and SF_6 the lumped parameter modelling tool "TracerLPM" (https://www.usgs.gov/software/tracerlpm, Jurgens et al. 2012) and particle tracking by groundwater models. ^{85}Kr and ^{39}Ar sampling and analyses were conducted by the research group on environmental radionuclides at Climate and Environmental Physics, University of Bern (https://www.climate.unibe.ch/research/research_groups/environmental_radionuclides/index_eng.html), - 3H/3He and ^{4}He were analysed by the Helis lab. At University of Bremen https://www.noblegas.uni-bremen.de/eng/

Results from this Case Study
The Study is on-going, and some analyses have been delayed due to the Covid-19 pandemic, which temporarily closed the laboratories. This delays the deliverables of HOVER WP6 and many other activities in the GeoERA program. Preliminary results were presented at the virtual General Assembly of the European Geosciences Union (EGU2020) in April (Hinsby et al., 2020). The EGU abstract and a pdf of the presentation will be uploaded to the document repository of the GeoERA information platform (EGDI, the European Geological Data Infrastructure).

Impact - how this Case Study contributes to the overall project aims (see objectives WP6)
The case study investigate the vulnerability, groundwater age and travel time distributions of a long-screened water supply wells of the major Danish water companies by new tracer techniques and hence it contributes to the objectives of WP6 task 6.4 on groundwater age and travel time distributions of long-screened wells, as well as related studies in HOVER WP5 and 7 on travel times for nitrate and pesticides and the vulnerability of aquifers towards pollution from the surface, respectively. We hope that the studies will inspire to other similar studies and make the application of the dating tracers for vulnerability assessments of water supply wells and the history and fate of contaminants in these (Jakobsen et al., 2020) much more common. Information on groundwater ages and travel times to water supply wells in well fields will enable much better management and protection of the well fields e.g. by optimizing groundwater abstraction from the different wells and better regulation on the use of pesticides etc. The cited references and access information are listed at the end of the following information template.

Name of pilot area / aquifers / type: Eastern Jutland and Funen – complex Pleistocene confined, semi-confined and unconfined aquifer systems	
Study level	Transboundary : ☐ Regional: ☐ Local: ☐ Single well(s): ☒
Type of observations *(choose one of the options, create separate template if needed for each type if each type need specific information)*	☒ Short screened observation wells (not pumped) ☐ Long screened observation wells (not pumped) ☒ Pumped wells, long screens in one aquifer ☒ Pumped wells, long screens over multiple aquifers ☐ Springs ☐ Other (eg. research wells; indicate type and information on pumping):
Approximate location of pilot:	
Geological cross section / conceptual model of the pilot area:	The example below shows a cross section of the complex aquifer systems, which are typical for the case study area. The shown example is from the Odense region in the lower right corner of the blue rectangle on the map above. 
Name of Shape- / Geopackage file defining the area: HoverDKPilotsSub.shp	**Projection to be used:** WGS84 (Epsg4326)

Hydrological parameters:	**Mean annual precipitation (mm or range in mm)**	**Mean annual groundwater recharge (mm or range in mm)**
	750 - 1000	150 - 500
Pumped wells only		**Typical pump discharge of sampled individual well (m^3/day):** 50 – 100 m^3
List of aquifers and aquitards in pilot area		**No. of confined or semiconfined aquifers in pilot areas:** 2-3
Aquifer no. (aqf): 3 Aquitard no. (aqt): 2 Aquiclude no. (aqc):	**Aquifer/aquitard type and/or name**	**Lithology *(Resource WP6 terminology)***
Aqf-1:	Pleistocene sands locally confined by clay/silt	Fine to medium sand and gravel
Porosity type	Porous: X	Fissured: ☐
Aqt-1:	Clay tills	
Porosity type	Porous: X	Fissured: ☐
Aqf-2:	Pleistocene sands	Fine to medium sand and gravel
Porosity type	Porous: X	Fissured: ☐
Applied tracer age indicators (^{3}H, ^{3}H/^{3}He, ^{85}Kr, ^{39}Ar, ^{14}C, ^{36}Cl, ^{81}Kr, ^{4}He, CFCs, SF_6, etc.) **Applied recharge temperature indicators** (^{18}O, D, noble gases) ***List according to aquifers/aquitards if relevant***		**Aquifer-1** ^{3}H/^{3}He, ^{4}He, ^{39}Ar , ^{85}Kr, ^{14}C, (CFCs and SF6 – only on Funen) **Aquifer-2** ^{3}H/^{3}He, ^{4}He, ^{39}Ar , ^{85}Kr, ^{14}C, (CFCs and SF6 – only on Funen)
Number of sites (wells/springs) with age indicators ***List according to aquifers/aquitards if relevant***		**Aquifer-1** **1-5:** ☐ **5-10:** ☐ **10-25:** ☒ **>25:** ☐ **Aquifer-2** **1-5:** ☐ **5-10:** ☐ **10-25:** ☒ **>25:** ☐

GW age range (GAR) **GAR-1: Modern (< 60 yr)** **GAR-2: Old (> 60 yr and <10 kyr)** **GAR-3: Paleowaters (> 10 kyr)** ***List according to aquifers/aquitards if relevant***	**Aquifer-1 – Not yet estimated** **GAR-1: 1-10%: ☐ 10-25%: ☐** **25-50%: ☐ >50%: ☐** **GAR-2: 1-10%: ☐ 10-25%: ☐** **25-50%: ☐ >50%: ☐** **GAR-3: 1-10%: ☐ 10-25%: ☐** **25-50%: ☐ >50%: ☐** **Aquifer-2 – Not yet estimated** **GAR-1: 1-10%: ☐ 10-25%: ☐** **25-50%: ☐ >50%: ☐** **GAR-2: 1-10%: ☐ 10-25%: ☐** **25-50%: ☐ >50%: ☐** **GAR-3: 1-10%: ☐ 10-25%: ☐** **25-50%: ☐ >50%: ☐**
Groundwater age ranges (GAR) estimated by:	**Tracer based estimates ☒** **Flow and age model simulations ☐** **Combination of model and tracer estimates (☒)** **Expert judgement: ☐**

Objective of age dating studies:			
Basic research or General groundwater management	**Assessment of pollutant history**		**Assessment of the efficiency of remediation and mitigation measures**
x	x		x
Water Usage *(not relevant for observation wells)*	**Water supply**		**Irrigation**
	x		
Geoenergy related activities *(not relevant for observation wells)*	**Shallow Geo-T**	**Deep Geo-T**	**Hydrocarbons**
Mining activities *(not relevant for observation wells)*	**Construction materials**		**Minerals / metals**
REFERENCES			

OPEN Access reports and papers (PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches):

Presentation of preliminary results at EGU2020 by:

Hinsby, K., Purtschert, R., Musy, S., Sültenfuss, J., Wachs, D., Aescbach-Hertig, W., Kidmose, J., Troldborg, L. and Guldrandsen. 2020. Use of multiple tracers and groundwater flow modelling for the estimation of groundwater travel times to water supply wells, vulnerability assessments and improved management of well fields. https://doi.org/10.5194/egusphere-egu2020-20340

Jurgens, B. C.; Bohlke, J. K.; Eberts, S. M. TracerLPM (Version 1): An Excel Workbook for Interpreting Groundwater Age Distributions from Environmental Tracer Data. U.S. Geological Survey Techniques and Methods Report, 4-F3, 60; 2012. https://pubs.er.usgs.gov/publication/tm4F3
https://doi.org/10.3133/tm4F3

The TracerLPM Workbook described in the report above will be used for simulation of tracer and groundwater age distributions in the investigated water supply wells

Remarks / other relevant information:
The study is on-going and part of WP6 task 6.4 on new techniques for the investigation of groundwater age distributions in long-screeened wells with groundwater ages in the range of 10 – 1000 years. The information template will be updated as soon as all tracer results and simulations are ready.