Establishing the European Geological Surveys Research Area to deliver a Geological Service for Europe

# Deliverable 6.2

## Collection of use cases including good practice guidance and age indicator sampling guide

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# 1 INTRODUCTION

Estimation of mean groundwater age, and travel or residence time distributions has become an increasingly important tool in studying groundwater flow and transport. Its application from vulnerability studies of shallow aquifers, to local drinking water supply or large regional and even transboundary resource management has been developed enormously since the middle of the last century. One of the first studies on the concept and the potential of using tritium ($^3H$) and carbon-14 ($^{14}C$) in groundwater dating was introduced e.g. by Kaufman and Libby (1954) and Ingerson and Pearson (1964), respectively.

The creation of the IAEA in 1957 motivated by fears and expectations generated by the discoveries and diverse use of the nuclear technology also contributed to the use of isotopes in groundwater studies. Several case studies have been carried out in Europe. Large basins have been studied over several decades in different parts of the continents, like the London Basin (Smith et al., 1976); the Madrid Basin (Llamas et al., 1982), the Great Hungarian Plain (Deak et al., 1987) and the Paris Basin (Marty et al., 1993, Castro et al. 1998). Studies have also demonstrated that palaeowaters are found in many settings across Europe (Edmunds and Milne, 2001).

Besides improving our understanding of groundwater travel times and groundwater flow and mixing in the subsurface in different types of aquifers (Eberts et al., 2012), groundwater dating is used for several different assessments. These can for example be studies on the advancement of modern, potentially polluted groundwater and the "vulnerability" of water supply wells to pollution from the surface (Hinsby et al., 2001, 2008; Broers, 2004; Manning et al., 2005; Eberts et al., 2012; Jurgens et al., 2016), or assessment of trends of specific contaminants such as nitrate (Bohlke and Denver, 1995; Hansen et al. 2011, Jurgens et al., 2016; Visser et al., 2007), pesticides (Visser et al., 2013, Jakobsen et al., 2019) and veterinary pharmaceuticals (Kivits et al., 2018).

Environmental tracers and model simulations can also be used for the estimation of flow in the unsaturated zone and groundwater recharge (Scanlon et al., 2002, Edmunds and Tyler, 2004).

For the estimation of groundwater ages in short (<< 1m) and shallow screens in relatively homogeneous aquifers a mean groundwater age or travel time to a specific point is a reasonable approximation (Plummer et al., 1993), while for wells with longer screens (which might even connect several different aquifers) or in fractured rocks such an approximation can be misleading. In the latter cases, mean groundwater ages are skewed towards older ages, therefore its application in vulnerability studies for example is not correct. In such cases an estimation of the groundwater age distribution either by groundwater flow and transport models or by the use of a range of environmental tracers suited for dating of groundwater of different age and providing the percentage of modern water is of much more value (Troldborg, 2004; Bethke and Johnson, 2008, Troldborg et al., 2008; Eberts et al., 2012, Jakobsen et al., 2019).

The aim of this report is to identify and describe a number of important European aquifers with a significant amount of age indicators as use cases and develop a good practice protocol on the application of age indicators for estimation of groundwater age distributions in time and space, including a sampling guide.

Therefore, this report briefly introduces a selection of European case studies based on groundwater age distributions in aquifers using environmental tracers for groundwater dating and groundwater age distributions simulated by groundwater flow models. Some studies focus on age distributions in shallow contaminated aquifers with groundwater ages primarily less than 70 years, while other studies focus on large regional aquifers that include paleowaters more than 10.000 years old. Some studies investigate short-screened monitoring well data, while others multiple screened abstraction wells. Studies range from local, through regional to transboundary level.

The distribution of environmental tracers and groundwater age in aquifers indicates the advance of potentially polluted modern or young groundwater (Hinsby et al. 2001b) and they are important tools for assessment of the evolution of groundwater chemical status. The environmental tracers can be used to characterise shallow and deep groundwater recharge zones of the flow systems as well as the occurrence of palaeowaters in deeper or shallower parts of discharge zones. Deep and old groundwater resources may not be sustainable resource in long term, but are still an important strategic resource e.g. in periods of droughts or other negative impacts on the shallow groundwater resources. They can also contribute to renewable energy resources as they can play an important role in the geothermal energy sector, and (especially) if reinjection is applied, then long term sustainable usage can be assured.

# 2 ENVIRONMENTAL TRACERS FOR GROUNDWATER DATING

There is a wide range of environmental tracers applicable for estimation of groundwater age and travel time distributions at small and large spatial, or young and old temporal scales as briefly described in deliverable 6.1 of the HOVER project (Hinsby et al., 2019).

Figure 1 illustrates the tracers used for groundwater dating in different age intervals as well as the analytical methods used for the analysis of the different tracers. The use of multiple tracers for dating of different age intervals is a very powerful tool for identification of the effects of mixing processes and quantification of the amount of different water types with different groundwater age, origin and contents of dissolved contaminants (e.g. Jakobsen et al., 2020; Jurgens et al., 2016).

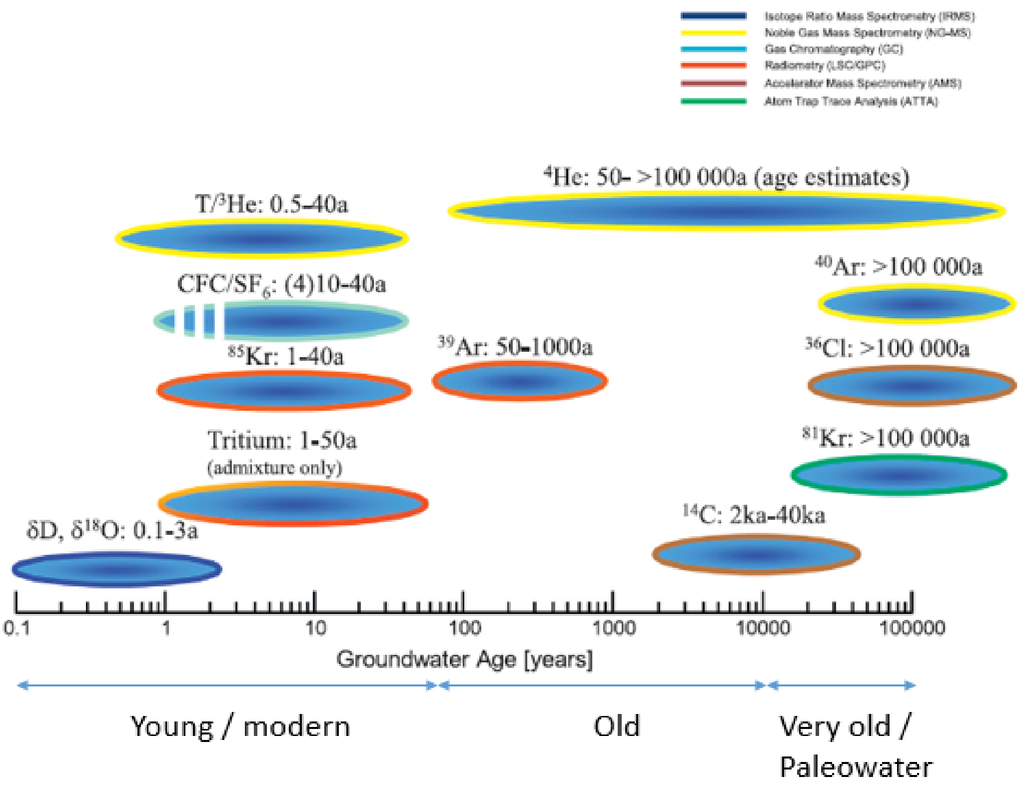



Figure 1. Age intervals and methods for the analysis of environmental tracers used for groundwater dating (modified after Suckow, 2014).

The following chapter provides a range of applications of the groundwater dating tracers collected from more than 20 case studies across Europe demonstrating their value in groundwater management and research not the least when combined with groundwater flow modelling.

For further information on previous studies on the application of groundwater dating tracers, examples and suggestions for using tracers and groundwater dating in general to assess the vulnerability of aquifers and water supply wells towards pollution from the surface please consult deliverable D6.1a of the HOVER project (Hinsby et al., 2019) available from the GeoERA document repository in the European Geological Data Infrastructure (EGDI, 2020).

The case studies presented in the following in combination apply most of the groundwater dating tracers included in Figure 1.

# 3 EUROPEAN CASE STUDIES ON GROUNDWATER AGE DISTRIBUTION

This section presents a selection of 23 European pilot areas, which can serve as case studies on groundwater age distribution. As a result of the good cooperation between the Geological Surveys, not only WP6 partners provided case study results, but studies carried out by BGS and BGR were also shared (latter not part of this report).
Each case study is presented using 1) pilot description form with general information on the background and objectives of the pilot studies and 2) a pilot information template for more specific information on wells and applied tracers.

The description forms provide general background information on the region and the scope of the case studies, on the methods applied and discusses the results of these case studies. The impact of each case study and how it contributes to the overall project aims is addressed.

The information template provides a quick overview of the hydrogeological settings including well and aquifer types in the pilot study areas, the study level (single well(s), local, regional, transboundary), including a study location map, with a cross section. The template also provides information about the main hydrological parameters, information about pumping (if relevant), aquifer-, aquitard- and aquiclude characteristics, applied tracer age and recharge temperature indicators. In order to see if characterization of aquifers is based only on limited or on numerous data, the number of sites (wells/springs) with age indicators is also shown according to 4 groups. Groundwater age ranges (GAR) are presented as percentages according to aquifers/aquitards, and classified as modern (<60 years), old (between 60 and 10 000 years) or as paleowaters (>10 000 years). Aquifer characterizations can vary from extrapolation of data/information of similar hydrogeological settings to complex, calibrated model based surveys, and therefore the template provides information about the base of groundwater age range estimation methods applied. Tracer based estimates, flow and age model simulations, a combination of model and tracer estimates and expert judgement methods are distinguished. Although environmental isotopes can provide excellent and very relevant input for groundwater management, if proper sampling and data interpretation is carried out, they are mainly used in groundwater research and are not widely applied in the management of groundwater resources. This may, however, change in the near future because of new and potentially cheaper analytical methods. The template summaries information on the objective of age dating studies and the types of water usages (drinking water supply, irrigation, industry, other), geo-energy or mining related activities in the investigated areas. References are also provided, and where possible DOI links to journal papers or the EGDI document repository (where documents are open access) is also provided.

Table 1 summarises the provided case studies for each participating country in alphabetical order.

Table 1. Summary table of groundwater dating studies described in more detail in the following pilot description forms and information templates in alphabetical order.

| Country | No. of pilots | Study objectives | Applied tracers | Simulation and Modelling methods |
|---|---|---|---|---|
| **Austria** | 1 | Research /water supply/ vulnerability assessments | $^{3}H$, $^{85}Kr$, $^{14}C$, $^{81}Kr$, $^{4}He$, $^{18}O$, D, noble gases | Tracer based estimates, expert judgement |
| **Croatia** | 3 | Research /water supply/ vulnerability assessments/ pollutant history /transboundary | $^{18}O$, $^{3}H$, $^{3}H/^{3}He$, CFCs, $SF_6$, | LUMPY software, TracerLPM, Visual MODFLOW |
| **Cyprus** | 1 | Research /seawater intrusion / water supply /irrigation/ point source and diffuse pollution | $^{3}H$, CFCs | Tracer based estimates, expert judgement |
| **Denmark** | 6 | Research /water supply / vulnerability assessments/ management* | $^{3}H/^{3}He$; $^{85}Kr$, CFCs, $SF_6$, $^{39}Ar$, $^{14}C$, | TracerLPM, particle tracking, solute transport |
| **Estonia** | 1 | Research /water supply / climate change /management | $\delta^{2}H_{H2O}$, $\delta^{18}O_{H2O}$, $\delta^{13}C_{DIC}$, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, $\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$, $^{3}H$, $^{14}C$, $^{85}Kr$, $^{81}Kr$, $^{40}Ar$, $^{4}He$ | multi-tracer, GWB, PHREEQC,NETPATH |
| **France** | 1 | Research /water supply / vulnerability assessments/ transboundary | $^{34}S/^{32}S$,$^{18}O/^{16}O_{SO4}$, $^{3}H$, $^{13}C$, $^{14}C$, $^{18}O$, D, CFCs (11,12,113), $SF_6$ | Tracer based estimates |
| **Hungary** | 2 | Research /management /transboundary | $^{3}H$, , $^{14}C$-$^{13}C$, $^{18}O$, D, noble gases | Tracer based estimates, Visual MODFLOW |
| **Malta** | 1 | Research/ pollutant history | $^{3}H$, CFCs, $SF_6$ | Tracer based estimates |
| **Netherlands** | 2 | Detection of trends and trend reversal and vulnerability of drinking water well fields | $^{3}H/^{3}He$, $^{4}He$, $^{85}Kr$, $^{39}Ar$, $^{18}O$ | Discrete Travel Time Distribution Model. Piston flow recharge year approach. |
| **Romania** | 1 | Research / surface water groundwater interaction | $^{14}C$, $^{13}C$, $^{18}O$, D, $^{3}H$ | Combination of model (FeFlow) and tracer based estimates |
| **Spain** | 1 | Research / vulnerability assessments | $^{3}H$ (tracer age indicator) + $^{18}O$ | Combination of model (MODFLOW, MODPATH) and tracer based estimates, lumped index |
| **Sweden** | 3 | Research / water supply / vulnerability / nuclear waste disposal | $^{2}H$, $^{3}H$, $^{18}O$, $^{36}Cl$, $^{37}Cl$, $^{13}C$, $^{14}C$, $^{10}B$, $^{11}B$, $^{87}Sr/^{86}Sr$, $^{34}S$, $^{238}U$, $^{234}U$, $^{230}Th$, $^{226}Ra$, $^{222}Rn$, CFCs, $SF_6$, noble gases, $^{3}H$, $^{3}H/^{3}He$, $^{39}Ar$, $^{85}Kr$ | Tracer based estimates, expert judgement |

*Number of studies with water companies on the vulnerability of water supply wells are increasing

## 3.1 Description of the Austrian database of environmental isotopes and noble gases of deep groundwater, Austria

| | |
|---|---|
| Title of Case Study | Database of environmental isotopes and noble gases in Austria's deep groundwaters |
| Location (region, Country) | Austria |
| Other information | |

| Description of Case Study (background information on the region) |
|---|
| In Austria, in the foreland basin and the intermountain basins of the Alps occur productive deep groundwaters (in the "Pilot info template" named "aquifer 1") and even thermal groundwaters ("aquifer 2") of great importance for water management. For instance, an important transboundary thermal groundwater body is situated between Regensburg in Bavaria and Linz in Upper Austria with a length of more than 120 km and a breadth of around 40 km. It is used for spas and district heating. In addition, the thermal springs and deep thermal aquifers of the Vienna and the Styrian basin – the two most important intermountain basins in Austria – also build the basis for several spas and thermal uses. The aquifers of these thermal water occurrences ("aquifer 2") are karstified Mesozoic or Palaeozoic carbonates as well as Cretaceous sandstones and Paleogene and Neogene sands. The foreland basins and the intermountain basins contain also potable deep groundwaters, which are in use for drinking water production ("aquifer 1"). The most important occurrences can be found in Upper Austria, Styria, and Burgenland, but even in Vienna there exist several deep wells that are in use. Layers or channels of sands and gravels within low permeable pelites mostly build the aquifers of these deep groundwaters. Not only in the basins, but also in the mountains thermal waters are present (in the "Pilot info template" named "aquifer 3"). Their recharge areas are situated in higher mountains and the hot springs discharge in valleys – for instance in Bad Kleinkircheim and Bad Gastein. In Bad Kleinkirchheim the aquifer is formed by karstified marbles, in Bad Gastein by fissured orthogneisses.<br>Some of the deep groundwaters are not only used for water supply, spas or district heating, but also for other medical use – and as natural mineral water.<br><br>Isotope and noble gas hydrology is important to understand the genesis and processes in groundwater – especially in such deep groundwater systems as they are given in Austria's foreland basin and deeper intermountain basins. On the one hand, there occurs an exchange between the very deep, but relatively sweet supra regional thermal water systems and the regional and sweet, but moderate deep groundwater circulations. In addition, there happens also mixing of these groundwater systems with more stagnant, highly mineralized formation waters. Isotope hydrology and noble gases plays an important role in the research of such complex groundwater systems, which are – in the case of the foreland basin and the Vienna basin – even in contact with hydrocarbon deposits. Until now there exist only few studies on the noble gases in such basins (*Byrne, D. J., Barry, P. H., Lawson, M. & Ballentine, C. J., 2017, Noble gases in conventional and unconventional petroleum systems, Special Publications, 468, 127-149, Geological Society, London https://doi.org/10.1144/SP468.5*).<br><br>The aim of the Austrian database, which has been compiled in the frame of WP6, is to provide isotope and noble gas data on the Austrian deep groundwaters – basing one existing surveys |

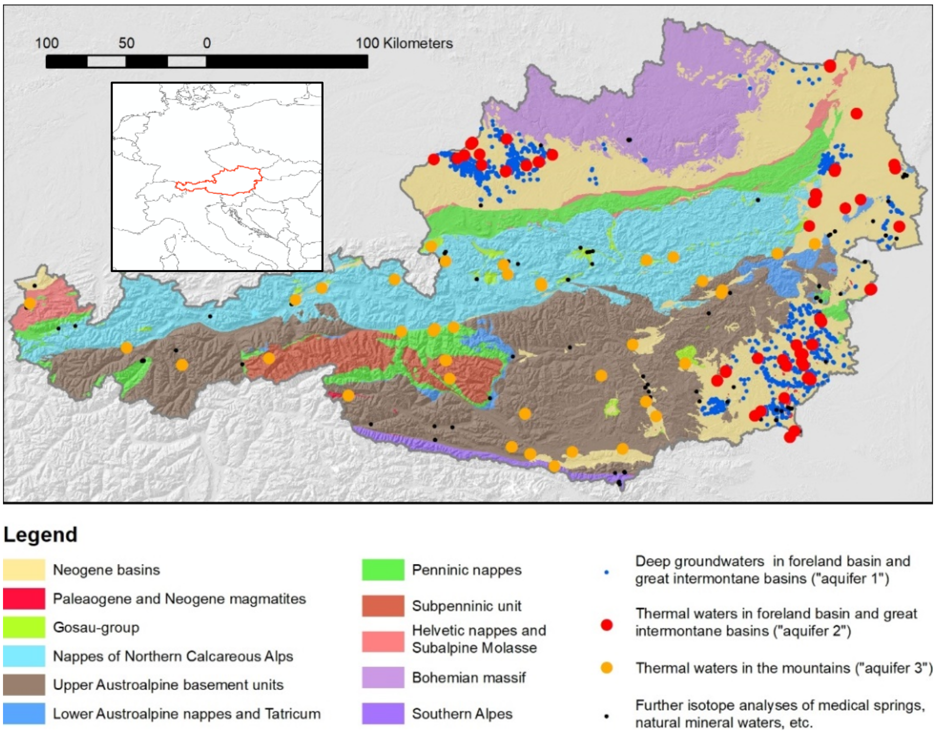
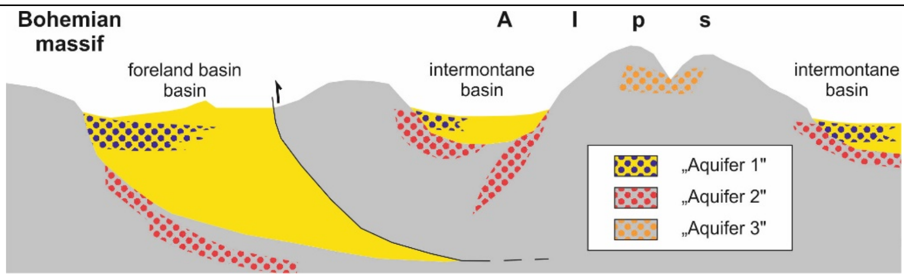
| |
|---|
| over the whole country – as basis for further investigations. The database will be exported into the hydrogeological core database of the Austrian Geological Survey in order to the provide data for further research (see below). |

| Description of problem (why is this location chosen for a Cases Study) |
|---|
| In Austria, deep groundwaters are common in the Alpine foreland basin and the bigger intermontane basins. Isotopes and nobel gases deliver important information on the deep groundwater systems in these regions. In Austria there already exists a public online service concerning isotopes in precipitation and groundwater (*https://secure.umweltbundesamt.at/webgis-portal/isotopen/map.xhtml*), but this database concerns mostly shallow groundwaters and data of deep groundwaters are rare. The actual database should close this gap. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| Within the last years in Austria there were made three surveys on deep and thermal groundwaters across the country. The results were published in monographies by the Geological Survey:<br>*https://www.bmlrt.gv.at/wasser/wasserqualitaet/trinkbare_tiefen_gw.html (Schubert 2015)*<br>*https://www.bmlrt.gv.at/wasser/wasserqualitaet/thermalwaesser.html (Elster et al. 2016)*<br>*https://www.bmlrt.gv.at/wasser/wasserqualitaet/grundwasser/mineral_heilwaesser.html (Elster et al. 2018)*<br>In the frame of WP6 the data of these publications have been compiled in a database which will be integrated into the hydrogeological core database of the Geological Survey in order to provide this data for further investigations. In the future also data of further projects will be maintained in this database. |

| Results from this Case Study |
|---|
| In the moment, the database contains analyses of the following parameters: deuterium, tritium, carbon-13, carbon-14, oxygen-18, sulphur-34, krypton-85, krypton-81, radon-222 and radium-226. The process of maintaining new data in the database is still going on. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| The database will give an overview on the isotope and noble gas data of Austria’s deep groundwaters. |

| **Name of pilot area / aquifers / type:** Austria / basement, Palaeozoic and Mesozoic carbonates and sandstones, Paleogene and Neogene sediments /porous and fissured | **Country:** Austria<br>**Region:** foreland basin and intermountain basin, Alps |
|---|---|
| **Study level** | Transboundary : ☐ Regional: x 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)<br>☐ Long screened observation wells (not pumped)<br>x Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>x Springs<br>x Other (eg. research wells; indicate type and information on pumping): artesian wells |
| **Approximate location of pilot:** |  |
| **Geological cross section / conceptual model of the pilot area:** |  |

| | | | | |
|---|---|---|---|---|
| **Name of Shape- / Geopackage file defining the area:** | | **Projection to be used:**<br>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)** |
| | 400–3800, in average 1100 (*BMLRT 2007*) | | 0–11, in average 6 (*BMLRT 2007*) | 0–1000 (in the karst of the Northern Calcareous Alps groundwater table can be very deep) |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):** 864–6912 (artesian overflow 2–691) | | **Typical pump discharge of complete well field ($m^3$/day):**<br>*If relevant* |
| **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<br>**Aquitard no. (aqt):** 2<br>**Aquiclude no. (aqc):** 1 | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Paleogene and Neogene sands confined by pelite aquitards | fine sand to gravel | 10–500 | 60–> 10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt-1: | Paleogene and Neogene marine and limnic-fluvial pelites | clay-silt, marl | | |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: X |
| Aqf-2: | Jurassic carbonates, Cretaceous sandstones, Paleogene sands | dolomite, limestone, sandstone | 0–> 6000 | > 10,000–565,000 |
| **Porosity type** | Porous: X | Fissured: X | Karst: X | Fissured and porous / dual porosity: X |

| | | | | |
|---|---|---|---|---|
| Aqt-2: | Palaeozoic and Mesozoic shales, Paleogene and Neogene pelites | shales, clay-silt, marl | | |
| **Porosity type** | Porous: □ | Fissured: □ | Fissured and porous / dual porosity: □ | No hydraulically active porosity: X |
| Aqf-3: | Crystalline basement in mountain regions | marl, orthogneiss | 0–2000 | 0–> 60 |
| **Porosity type** | Porous: □ | Fissured: X | Karst: X | Fissured and porous / dual porosity: □ |
| Aqc-3: | Crystalline basement in mountain regions | phyllites, mica schists, phyllonites | | |
| **Porosity type** | Porous: □ | Fissured: X | Fissured and porous / dual porosity: □ | No hydraulically active porosity: X |

| | |
|---|---|
| **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.)<br>**Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | **Aquifer-1**<br>$^{3}H$, $^{14}C$, $^{4}He$, $^{18}O$, D, noble gases<br>**Aquifer-2**<br>$^{3}H$, $^{85}Kr$, $^{14}C$, $^{81}Kr$, $^{4}He$, $^{18}O$, D, noble gases<br>**Aquifer-3**<br>$^{3}H$, $^{14}C$, $^{18}O$, D |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-1**<br>**1-5:** □ **5-10:** □ **10-25:** □ **>25:** X<br>**Aquifer-2**<br>**1-5:** □ **5-10:** □ **10-25:** □ **>25:** X<br>**Aquifer-3**<br>**1-5:** □ **5-10:** □ **10-25:** □ **>25:** X |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-1**<br>**GAR-1: 1-10%:** □ **10-25%:** X **25-50%:** □ **>50%:** □<br>**GAR-2: 1-10%:** □ **10-25%:** □ **25-50%:** X **>50%:** □<br>**GAR-3: 1-10%:** □ **10-25%:** □ **25-50%:** X **>50%:** □<br>**Aquifer-2**<br>**GAR-1: 1-10%:** X **10-25%:** □ **25-50%:** □ **>50%:** □<br>**GAR-2: 1-10%:** X **10-25%:** □ **25-50%:** □ **>50%:** □<br>**GAR-3: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** X<br>**Aquifer-3**<br>**GAR-1: 1-10%:** □ **10-25%:** □ **25-50%:** X **>50%:** □<br>**GAR-2: 1-10%:** □ **10-25%:** □ **25-50%:** X **>50%:** □<br>**GAR-3: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** □ |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates** X<br>**Flow and age model simulations** □<br>**Combination of model and tracer estimates** □ |

<table>
<tr><td colspan="3"></td><td colspan="4">Expert judgement: X</td></tr>
<tr><td colspan="7">Objective of age dating studies:</td></tr>
<tr><td>Basic research or General groundwater management</td><td colspan="2">Assessment of pollutant history</td><td colspan="2">Assessment of the efficiency of remediation and mitigation measures</td><td colspan="2">Indication of vulnerability of aquifers and water supply wells</td></tr>
<tr><td>X</td><td colspan="2"></td><td colspan="2"></td><td colspan="2">X</td></tr>
<tr><td rowspan="2">Water Usage<br>(not relevant for observation wells)</td><td colspan="2">Water supply</td><td>Irrigation</td><td>Industry</td><td colspan="2">Other</td></tr>
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<tr><td rowspan="2">Geoenergy related activities<br>(not relevant for observation wells)</td><td>Shallow Geo-T</td><td>Deep Geo-T</td><td colspan="2">Hydrocarbons</td><td>Nuclear waste disp.</td><td>$CO_2$ storage</td></tr>
<tr><td>X</td><td>X</td><td colspan="2">X</td><td></td><td></td></tr>
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<tr><td colspan="7">REFERENCES<br>Elster, D., Goldbrunner, J., Wessely, G., Niederbacher, P., Schubert, G., Berka, R., Philippitsch, R. & Hörhan, T., 2016, Erläuterungen zur geologischen Themenkarte Thermalwässer in Österreich 1:500.000, 296 p., Geological Survey of Austria, Vienna, ISBN: 978-3-85316-086-2<br>Elster, D., Fischer, L., Hann, S., Goldbrunner, J., Schubert, G., Berka, R., Hobiger, G., Legerer, P. & Philippitsch, R., 2018, Österreichs Mineral- und Heilwässer, 448 p., Geological Survey of Austria, Vienna, ISBN: 978-3-85316-097-8<br>Schubert, G. (Ed.), Trinkbare Tiefengrundwässer in Österreich, Abhandlungen der Geologischen Bundesanstalt, 64, 179 p., Geological Survey of Austria, Vienna, ISSN 0378-0864, ISBN 978-3-85316-085-5<br>Heidinger, M., Eichinger, F., Purtschert, R., Mueller, P., Wirsing, G., Geyer, T., Fritzer, T., Groß, D., 2019, Altersbestimmung an thermalen Tiefenwässern im Oberjura des Molassebeckens mittels Krypton-Isotopen, 81Kr/85Kr-Dating of thermal groundwaters in the Upper Jurassic (Molasse Basin), Grundwasser, 24, 287-294 p., Springer, doi.org/10.1007/s00767-019-00431-0<br>BMLRT (Ed.), 2007, Hydrologischer Atlas Österreichs, Österreichischer Kunst- und Kulturverlag, ISBN 3-85437-250-7</td></tr>
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<tr><td colspan="7">Remarks / other relevant information:</td></tr>
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## 3.2 Description of the Rječina and Zvir springs catchment area case study, Croatia

| | |
|---|---|
| Title of Case Study | Catchment area of the Rječina and Zvir springs |
| Location (region, Country) | Western Croatia |
| Other information | Transboundary (SI-HR border) karst aquifer |

| Description of Case Study (background information on the region) |
|---|
| The case study is located in western Croatia and stretches from the Adriatic coast to the mountainous area to the north that encompasses parts of eastern Ćićarija, the peaks of the V. Snežnik (1796 m) in Slovenia and the mountainous area of west Gorski Kotar, including parts of Risnjak (1528 m) and Snježnik (1505 m). It has dominant karst features. The primary part of the catchment consists of shallow-water carbonates, mostly limestones and dolomites with subordinate carbonate breccias, deposited from the Lower Jurassic to the Eocene. The Rječina spring is a speleological object with known horizontal spreading in the subsurface of approximately 300 m and a depth of over 50 m below the spring level. The majority of the cave system is filled with groundwater, however, during the dry season the underground channels have no direct connection with the retention areas and the spring water present consists only of the last remaining outflow in the cave channels. Groundwater at the Zvir spring discharges from the sunken cave channel that was developed along the expressed tectonic fissures in the Upper Cretaceous limestone on the west bank of the Rječina River. The spring is permanent and is the major water supply resource when the Rječina spring discharge is reduced or the spring dries up. The maximum measured discharge of the Rječina spring is 45 $m^3/s$, and the minimum value is zero. The minimum discharge of the Zvir spring is 0.9 $m^3/s$, and the maximum discharge is 18 $m^3/s$. |

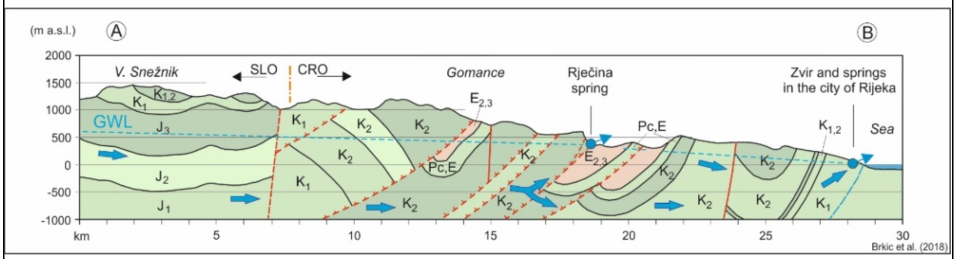
| Description of problem (why is this location chosen for a Cases Study) |
|---|
| Karst aquifers in the Croatia have a fundamental importance to water supply. Due to their specific hydrogeologic properties, these aquifers are sometimes difficult to use because of the high discharge variations of the karst springs and are almost always sensitive to pollution. With an aim to better understand karst aquifers, different research methods are used to study the karst groundwater system in Croatia. The spring hydrograph and the stable isotope ($\delta^{18}O$, $\delta^2H$) compositions in the water samples collected from the Rječina and Zvir springs and precipitation were analysed and used to characterize the karst aquifer. These springs are the major source for the water supply of the Kvarner Bay area. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| A mean residence time (MRT) of groundwater was calculated for stable isotope $\delta^{18}O$ using lumped parameter approach by applying the exponential model, combined exponential-piston and dispersion models to isotopic input (rainfall) and output (spring) data sets during 2011–2013. The LUMPY software was used. |

| Results from this Case Study |
|---|
| The recession coefficient obtained from the hydrograph analysis indicates only a fast-flow spring component at the Rječina spring. The lack of the base-flow spring component is the primary reason for the spring drying out during the dry periods. The low recession coefficient of |

| |
|---|
| the Zvir spring indicates a base-flow and discharge from well-drained fissures and fractures in the spring catchment area during the low water stage.<br>The MRTs of 3.24 and 3.6 months for the Rječina spring and 7.2 months for the Zvir spring suggest the presence of recent groundwater recharge from precipitation, as well as fast groundwater flow. The cumulative age distributions show that the proportion of water younger than 1xMRT at both springs was more than 50% and that the proportion of water younger than 2xMRT was more than almost 90%.<br>Knowledge of the pollutant travel times through a groundwater body is necessary for the early warning of deterioration and the efficient protection of groundwater quality. For the investigated springs, it is fortunate that the largest part of their hinterland is not burdened by potential pollutants. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| This Case Study describes an important transboundary karst aquifer between Croatia and Slovenia. It demonstrates the use of groundwater age for assessment of groundwater vulnerability. |

| | |
|---|---|
| **Name of pilot area / aquifers / type:** Catchment of the Rječina and Zvir springs / karst aquifer | **Country:** Croatia<br><br>**Region:** western Croatia (HR-SI border aquifer) |
| **Study level** | Transboundary : X 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)<br>☐ Long screened observation wells (not pumped)<br>☐ Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>X Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot:** |  |
| **Geological cross section / conceptual model of the pilot area:** |  |
| **Name of Shape- / Geopackage file defining the area:** HoverHRPilotSub.shp | **Projection to be used:** HTRS96/TM |

| 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) |
|---|---|---|---|---|
| | 1500-3500 | 750-1750 | 3-13 | 0-800 |

| | | |
|---|---|---|
| **Pumped wells only** | **Typical pump discharge of sampled individual well ($m^3$/day):** | **Typical pump discharge of complete well field ($m^3$/day):** *If relevant* |
| **List of aquifers and aquitards in pilot area** | **No. of confined or semiconfined aquifers in pilot area:** | **No. of unconfined aquifers in pilot area: 1** |

| **Aquifer no. (aqf):** 1 **Aquitard no. (aqt): Aquiclude no. (aqc):** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
|---|---|---|---|---|
| Aqf-1: | Rijeka springs aquifer | Karstic limestone | > 1000 | < 1 |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: X | Fissured and porous / dual porosity: ☐ |

| | |
|---|---|
| **Applied tracer age indicators** ($^3H$, $^3H/^3He$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $^{36}Cl$, $^{81}Kr$, $^4He$, CFCs, $SF_6$, etc.) **Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | **Aquifer-1** $^{18}O$ |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-1** **1-5: X 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)** | **Aquifer-1** **GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X** **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 X** **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** | **Indication of vulnerability of aquifers and water supply wells** |
| X | | | X |

<table>
<tr><td rowspan="2">Water Usage<br>(not relevant for observation wells)</td><td colspan="2">Water supply</td><td>Irrigation</td><td colspan="2">Industry</td><td colspan="2">Other</td></tr>
<tr><td colspan="2">X</td><td></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td rowspan="2">Geoenergy related activities<br>(not relevant for observation wells)</td><td>Shallow Geo-T</td><td>Deep Geo-T</td><td colspan="3">Hydrocarbons</td><td>Nuclear waste disp.</td><td>$CO_2$ storage</td></tr>
<tr><td></td><td></td><td colspan="3"></td><td></td><td></td></tr>
<tr><td rowspan="2">Mining activities<br>(not relevant for observation wells)</td><td colspan="2">Construction materials</td><td>Minerals / metals</td><td colspan="2">Coal</td><td colspan="2">Other</td></tr>
<tr><td colspan="2"></td><td></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td colspan="8">REFERENCES</td></tr>
<tr><td colspan="3">OPEN Access reports and papers (PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches):</td><td colspan="5">Reports and papers with restricted access:<br><br>Brkić, Ž., Kuhta, M. & Hunjak, T. (2018): Groundwater flow mechanism in the well-developed karst aquifer system in the western Croatia: Insights from spring discharge and water isotopes. Catena (Cremlingen), 161, 14-26.</td></tr>
<tr><td colspan="8">Remarks / other relevant information:</td></tr>
</table>

## 3.3 Description of the Zagreb aquifer case study, Croatia

| | |
|---|---|
| Title of Case Study | Zagreb aquifer |
| Location (region, Country) | Zagreb area, Croatia |
| Other information | Transboundary (SI-HR border) alluvial aquifer |

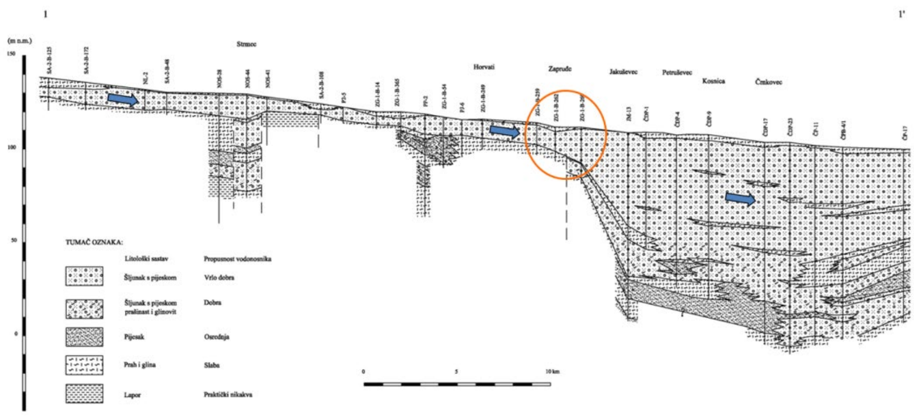
| Description of Case Study (background information on the region) |
|---|
| The Zagreb alluvial aquifer system is located in the southwestern part of the Pannonian Basin, in the Sava Valley in Croatia. It is composed of Quaternary unconsolidated deposits. In the western part of the investigated area the aquifer thickness reaches only 10-15 m. At the East, the aquifer thickness is much higher and reaches up to 100 m. Permeable and semi permeable layers alternate in the vertical profile of the aquifer system. However, semi permeable layers pinchout in many places, and, consequently, the aquifer acts as a single hydrogeologic unit. The covering aquitard is composed of silt, sand and clay. Its thickness reaches only 2-3 m. The aquifer is unconfined. The hydraulic conductivity values of the aquifer reach up to 0.02 m/s. |

| Description of problem (why is this location chosen for a Cases Study) |
|---|
| The Zagreb aquifer is highly utilised, mainly as a water supply for more than the one million inhabitants of the wider area of the capital city of Croatia. It is burdened with a number of potential pollutants. Due to the absence of covering deposits, the vulnerability of high permeable aquifer is very pronounced. In the study area (the catchment area of the Mala Mlaka pumping site), groundwater contains increased concentrations of nitrates and the nitrate origin is associated with the impact of agricultural activity. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| A mean residence time (MRT) of groundwater was calculated using tracer based estimates as well as lumped parameter approach by applying the exponential mixing model and dispersion model. The TracerLPM software was used. |

| Results from this Case Study |
|---|
| According to the conducted analyses, the groundwater age up to a depth of 30 m was generally estimated at less than 10 years. An association of the reduction of nitrate concentrations in groundwater with regard to the load from agriculture and the mean age of groundwater was found. Further research is ongoing. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| This Case Study describes an important Zagreb alluvial aquifer in Croatia. It demonstrates the use of groundwater age for assessment an impact agricultural activity on groundwater. |

| Name of pilot area / aquifers / type: | Country: Croatia |
|---|---|
| Zagreb area / Quaternary alluvial aquifer / porous | **Region:** Zagreb area (HR-SI border aquifer) |
| **Study level** | Transboundary : X 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)* | X Short screened observation wells (not pumped)<br>X Long screened observation wells (not pumped)<br>☐ Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot:** |   |
| **Geological cross section / conceptual model of the pilot area:** |   |

<table>
<tr><td colspan="2">Name of Shape- / Geopackage file defining the area: HoverHRPilotSub.shp</td><td colspan="4">Projection to be used:<br>HTRS96/TM</td></tr>
<tr><td rowspan="2">Hydrological parameters:</td><td>Mean annual precipitation (mm or range in mm)</td><td>Mean annual groundwater recharge (mm or range in mm)</td><td colspan="2">Mean annual groundwater recharge temperature (°C)</td><td>Thickness of unsaturated zone (range in m)</td></tr>
<tr><td>850</td><td>260-300</td><td colspan="2">10-11</td><td>4-10</td></tr>
<tr><td colspan="2">Pumped wells only</td><td colspan="2">Typical pump discharge of sampled individual well (m$^3$/day):</td><td colspan="2">Typical pump discharge of complete well field (m$^3$/day):<br>If relevant</td></tr>
<tr><td colspan="2">List of aquifers and aquitards in pilot area</td><td colspan="2">No. of confined or semiconfined aquifers in pilot area:</td><td colspan="2">No. of unconfined aquifers in pilot area:1</td></tr>
<tr><td>Aquifer no. (aqf): 1<br>Aquitard no. (aqt):<br>Aquiclude no. (aqc):</td><td>Aquifer/aquitard type and/or name</td><td>Lithology (Resource WP6 terminology)</td><td>Depth range (m)</td><td colspan="2">GW age range (yr)</td></tr>
<tr><td>Aqf-1:</td><td>Zagreb aquifer</td><td>Gravel</td><td>< 30</td><td colspan="2">< 20</td></tr>
<tr><td>Porosity type</td><td>Porous: X</td><td>Fissured: ☐</td><td>Karst: ☐</td><td colspan="2">Fissured and porous / dual porosity: ☐</td></tr>
<tr><td colspan="2">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.)<br>Applied recharge temperature indicators ($^{18}O$, D, noble gases)</td><td colspan="4">Aquifer-1<br>$^{3}H$, $^{3}H/^{3}He$, CFCs, $SF_6$</td></tr>
<tr><td colspan="2">Number of sites (wells/springs) with age indicators</td><td colspan="4">Aquifer-1<br>1-5: ☐ 5-10: X 10-25: ☐ >25: ☐</td></tr>
<tr><td colspan="2">GW age range (GAR)<br>GAR-1: Modern (< 60 yr)<br>GAR-2: Old (> 60 yr and 10 kyr)<br>GAR-3: Paleowaters (> 10 kyr)</td><td colspan="4">Aquifer-1<br>GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X<br>GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐<br>GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐</td></tr>
<tr><td colspan="2">Groundwater age ranges (GAR) estimated by:</td><td colspan="4">Tracer based estimates X<br>Flow and age model simulations ☐<br>Combination of model and tracer estimates X<br>Expert judgement: ☐</td></tr>
<tr><td colspan="6">Objective of age dating studies:</td></tr>
</table>

| 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** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** | |
| | | | | | |
| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** / **Deep Geo-T** | **Hydrocarbons** | | **Nuclear waste disp.** | **$CO_2$ storage** |
| | | | | | |
| **Mining activities** *(not relevant for observation wells)* | **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:** |
|---|---|
| | Brkić, Ž., Kuhta, M., Larva, O. & Marković, T. (2019): Groundwater age dating as a tool for nitrogen pollution risk assessment in Croatia. Abstract book, 6th Croatian Geological Congress, 41-42.<br>Brkić, Ž., Kuhta, M. (2020): Monitoring the groundwater age for the purpose of defining the effectiveness of protection measures. Technical report for Hrvatske vode (a legal entity for water management in Croatia) (in Croatian). Croatian Geological Survey, Zagreb. |

**Remarks / other relevant information:**

## 3.4 Description of the Drava aquifer case study, Croatia

| | |
|---|---|
| Title of Case Study | Drava aquifer |
| Location (region, Country) | Varaždin-Koprivnica area, NW Croatia |
| Other information | Transboundary (SI-HR border) alluvial aquifer system |

| Description of Case Study (background information on the region) |
|---|
| Drava alluvial aquifer is composed of sediments of the Quaternary age. It consists primarily of gravel and sand. The thickness of the aquifer varies from less than 5 m in the western to more than 100 m in the eastern. In the study area, the aquifer system is divided into two aquifers separated by a relatively thin semipermeable interlayer. The covering semipermeable layer of the aquifer is not continuously developed, which makes the aquifer vulnerable to contamination. The aquifer is unconfined. |

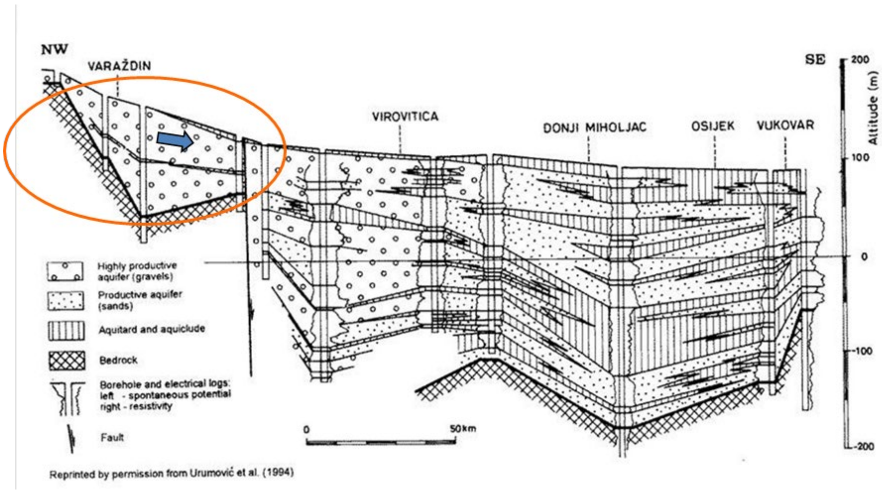
| Description of problem (why is this location chosen for a Cases Study) |
|---|
| The aquifer system represents the main source of potable water for this part of Croatia. It is burdened with different potential pollutants of which the largest is agricultural activity. Due to the absence of covering deposits the aquifer vulnerability is very pronounced. In the study area, groundwater contains increased concentrations of nitrates. The nitrate origin is associated with the impact of agricultural activity. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| A mean residence time (MRT) of groundwater was calculated using tracer based estimates as well as lumped parameter approach by applying the exponential piston-flow model, the exponential mixing model, the partial exponential model and dispersion model. The TracerLPM software was used. MRT was also analyzed by groundwater simulation model (Visual MODFLOW). |

| Results from this Case Study |
|---|
| The groundwater age by the conducted analyzes was estimated for the first and second layers separated by aquitard. The decrease in the concentration of nitrate in the first aquifer west of the city of Koprivnica as well as the increase in the concentration of nitrate in the second aquifer southeast of the city is related to the historical load of agriculture in relation to the mean groundwater age. Further research is ongoing. |

| Impact - how this Case Study contributes to the overall project aims (see objectives WP6) |
|---|
| This Case Study describes an important Drava alluvial aquifer in Croatia. It demonstrates the use of groundwater age for assessment an impact agricultural activity on groundwater. |

<table>
<tr><td>Name of pilot area / aquifers / type: Varaždin-Koprivnica area / Quaternary alluvial aquifer / porous</td><td colspan="2">Country: Croatia<br><br>Region: NW Croatia (HR-SI border aquifer)</td></tr>
<tr><td>Study level</td><td colspan="2">Transboundary : X Regional: ☐ Local: ☐ Single well(s): ☐</td></tr>
<tr><td>Type of observations<br>(choose one of the options, create separate template if needed for each type if each type need specific information)</td><td colspan="2">X Short screened observation wells (not pumped)<br>X Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping):</td></tr>
<tr><td>Approximate location of pilot:</td><td colspan="2">


</td></tr>
<tr><td>Geological cross section / conceptual model of the pilot area:</td><td colspan="2">


</td></tr>
</table>

| | | | | |
|---|---|---|---|---|
| **Name of Shape- / Geopackage file defining the area:** HoverHRPilotSub.shp | | **Projection to be used:** HTRS96/TM | | |
| **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)** |
| | 820-850 | 150-300 | 10-11 | 2-13 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):** | | **Typical pump discharge of complete well field ($m^3$/day):**<br>*If relevant* |
| **List of aquifers and aquitards in pilot area** | | **No. of confined or semiconfined aquifers in pilot area: 1** | | **No. of unconfined aquifers in pilot area: 1** |
| **Aquifer no. (aqf): 2**<br>**Aquitard no. (aqt):**<br>**Aquiclude no. (aqc):** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Drava aquifer I | Gravel | < 35 | < 30 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-2: | Drava aquifer II | Gravel | 40 - 120 | 20 - < 60 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| **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.)<br>**Applied recharge temperature indicators** ($^{18}$O, D, noble gases) | | **Aquifer-1**<br>$^3$H, $^3$H/$^3$He, CFCs, $SF_6$<br><br>**Aquifer-2**<br>$^3$H, $^3$H/$^3$He, CFCs, $SF_6$ | | |
| **Number of sites (wells/springs) with age indicators** | | **Aquifer-1**<br>**1-5: ☐ 5-10: X 10-25: ☐ >25: ☐**<br><br>**Aquifer-2**<br>**1-5: X 5-10: ☐ 10-25: ☐ >25: ☐** | | |
| **GW age range (GAR)** | | **Aquifer-1**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** | | |

| | |
|---|---|
| **GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-2**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: ☐ 10-25%: X 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates X**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates X**<br>**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** | **Indication of vulnerability of aquifers and water supply wells** |
|---|---|---|---|
| | X | | |

| **Water Usage** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
|---|---|---|---|---|
| | | | | |

| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
|---|---|---|---|---|---|
| | | | | | |

| **Mining activities** *(not relevant for observation wells)* | **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:**<br>Brkić, Ž., Kuhta, M., Larva, O. & Marković, T. (2019): Groundwater age dating as a tool for nitrogen pollution risk assessment in Croatia. Abstract book, 6th Croatian Geological Congress, 41-42.<br>Brkić, Ž., Kuhta, M. (2020): Monitoring the groundwater age for the purpose of defining the effectiveness of protection measures. Technical report for Hrvatske vode (a legal entity for water management in Croatia) (in Croatian). Croatian Geological Survey, Zagreb. |

**Remarks / other relevant information:**

Only one pumping well was sampled for groundwater age estimation. Since a pumping well is not a well from which groundwater is constantly pumped (usually only at night), it could be considered an observation well. Sampling was performed in a low-flow regime (approximately 1 L/min) in all wells, so it can practically be considered to have been performed in a short-screened observation well (mixing is negligible).

## 3.5 Description of the Kiti - pervolia aquifer case study, Cyprus

| | |
|---|---|
| Title of Case Study | Tritium (and (CFCs) concentration analysis of groundwater samples |
| Location (region, Country) | Kiti – pervolia aquifer, Cyprus |
| Other information | — |

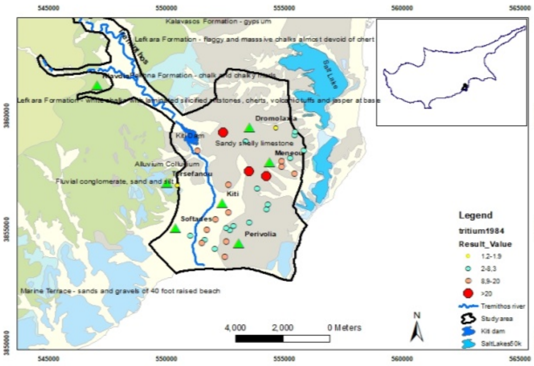
| Description of Case Study (background information on the region) |
|---|
| The kiti – pervolia aquifer is situated in the southern part of Cyprus and covers an area of 40Km$^2$. It's a small phreatic aquifer and it extends from the Kiti dam to the north to the Larnaka Salt Lake(s) to east and up to the chalks and marls outcrops of the Lefkara formation to the west (near Tersefanou village). The southern boundary of the aquifer is in hydraulic contact with the sea. Tremithos River runs from north to south and discharges to the sea, along the western half of the aquifer. In 1964, however, the Kiti recharge dam was constructed on Tremithos River, at the northwestern part of the aquifer. The two dominant land use types are agriculture and urbanization. The area's surficial geology is dominated by Pleistocene marine terraces and Holocene alluvial sediments. Underlying the abovementioned sediments are the chalks and marls of the Lefkara (Paleocene-Oligocene) and Pachna (Miocene). The aquifer is phreatic and it develops in alluvial sediments and marine terraces with the Paleogene chalks and marls acting as the impervious base of the aquifer. Groundwater is recharged through the dam, Tremithos river bed infiltration, from precipitation and return irrigation.<br>The whole area is characterized by semi-arid conditions, with a mean annual precipitation of 330,6 mm and a mean annual temperature of 19.9°C. Precipitation is not distributed evenly throughout the year, though. The months of December followed by January are the wettest with an average annual rainfall of 84mm and 76mm, respectively. Winter and spring seasons are usually followed by dry summers with little or no precipitation. |

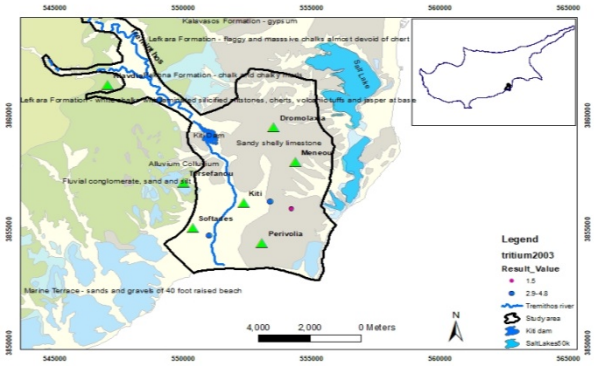
| Description of problem (why is this location chosen for a Cases Study) |
|---|
| Kiti – pervolia aquifer is a small, coastal aquifer of vital importance to local economy, agriculture and environment. Intense agriculture is practice along these typical coastal aquifers where major irrigation projects have been implemented. Decreasing precipitation during the last decades has caused a dramatic decrease of water inflow to the recharge dam and artificial recharge activities have been put on hold due to the general water deficit in the country. Overpumping and decreased recharge have led to negative water balance of the aquifers. The area is affected by both point and diffuse pollution sources thus deteriorating groundwater quality. Sea water intrusion and nitrate pollution are the main pressures on kiti-pervollia groundwater quality status. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| Two tritium sampling campaigns were carried out in 1984 and in 2003. In 1984, 31 groundwater samples were collected and in 2003 four (4). Furthermore groundwater samples from two boreholes were collected for CFCs (CFC-11 and CFC-12, and CFC-113) analysis, in 2003.<br>Concentrations of CFCs and tritium in 2003 were determined at the Hydroisotop GmbH, in Munich. All samples were collected from the alluvial part of the aquifer. |

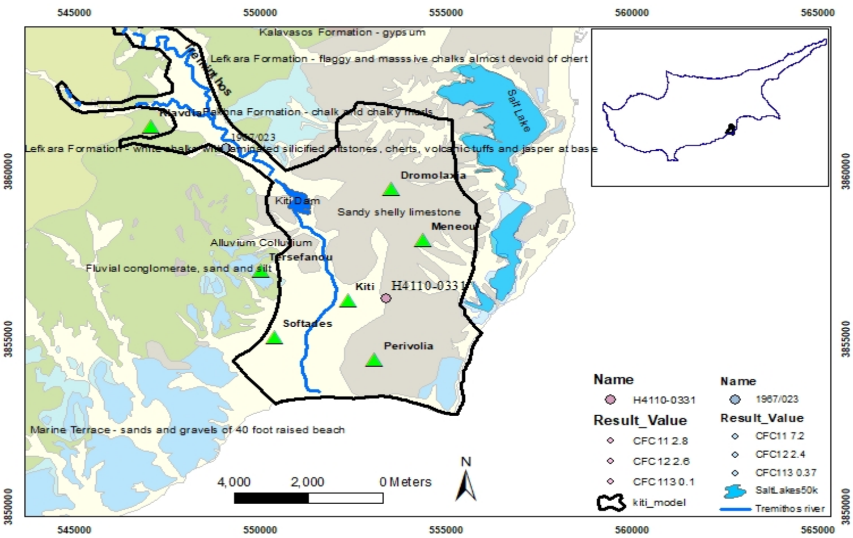
## Results from this Case Study

Tritium activity concentration in groundwater wells in both sampling campaigns varied from 1.2 TU to 23 TU. All groundwater samples were found to be younger than 50 years old (the limit of tritium dating). Tritium results indicate a mixture of very young water and water 20-30-year old. However, mixing with older water (0.8–2 TU) is also observed. This can be attributed to i) lateral flow of old groundwater from the chalks, in its western part aquifer (Tersefanou area) and ii) groundwater upwelling from well that have intersected the confined lower chalk aquifer.



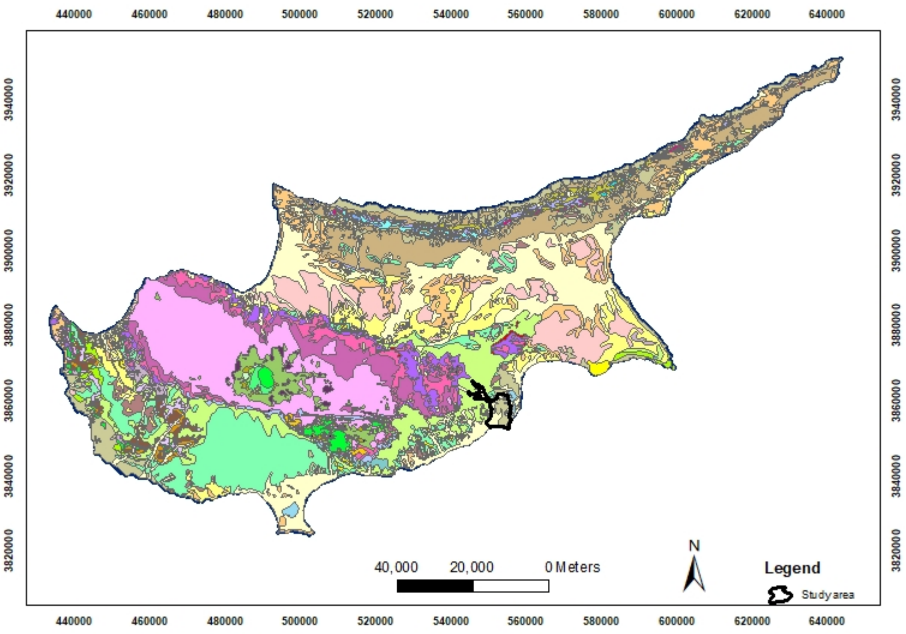



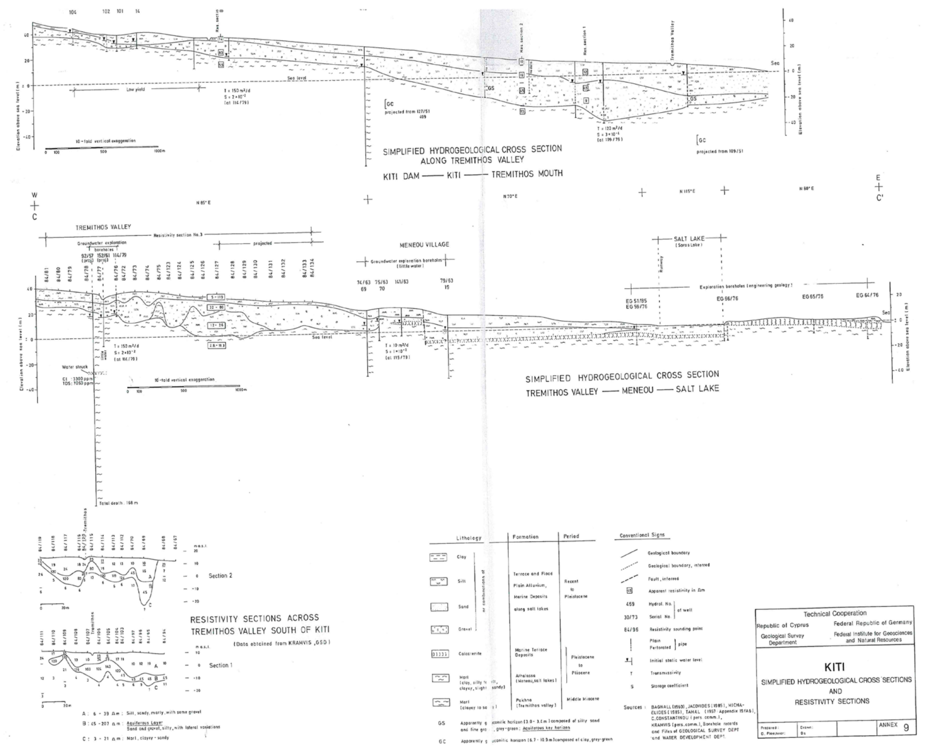

The highest concentration in CFCs was recorded in the groundwater sample from borehole 1967/023, which is located in the alluvium of Tremithos River. Substantial surface flow occurred during the wet period of 2002–2004 in the Tremithos River, which has contributed to the recharge of the aquifer with young and CFCs rich water.




## Impact - how this Case Study contributes to the overall project aims

Kiti – pervolia aquifer is a small, coastal aquifer of vital importance to local economy, agriculture and environment of Cyprus and can serve as a case study for other similar aquifers on the Island. Tritium and CFC dating on such typical aquifer can contribute to establish a harmonized database on groundwater age tracers, thus contributing in improving groundwater management and protection.

| | |
|---|---|
| **Name of pilot area / aquifers / type:** Kiti-pervolia-aquifer / Multi-layer aquifer | **Country:** Cyprus<br>**Region:** Kiti - pervolia |
| **Study level** | Transboundary: ☐ Regional: ☐ Local: **x** 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)<br>☐ Long screened observation wells (not pumped)<br>**x** Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot:** |  |
| **Geological cross section / conceptual model of the pilot area:** | |

<table>
<tr><td></td><td colspan="5">
</td></tr>
<tr><td colspan="2">Name of Shape- / Geopackage file defining the area:</td><td colspan="4">Projection to be used:<br>WGS84 (Epsg4326)</td></tr>
<tr><td rowspan="2">Hydrological parameters:</td><td>Mean annual precipitation (mm or range in mm)</td><td>Mean annual groundwater recharge (mm or range in mm)</td><td colspan="2">Mean annual groundwater recharge temperature (°C)</td><td>Thickness of unsaturated zone (range in m)</td></tr>
<tr><td>330</td><td>40-50</td><td colspan="2"></td><td>10</td></tr>
<tr><td colspan="2">Pumped wells only</td><td colspan="2">Typical pump discharge of sampled individual well ($m^3$/day): 50</td><td colspan="2">Typical pump discharge of complete well field ($m^3$/day):<br>If relevant</td></tr>
<tr><td colspan="2">List of aquifers and aquitards in pilot area</td><td colspan="2">No. of confined or semiconfined aquifers in pilot area: /</td><td colspan="2">No. of unconfined aquifers in pilot area: 1</td></tr>
<tr><td>Aquifer no. (aqf): 1<br>Aquitard no. (aqt): 1<br>Aquiclude no. (aqc):</td><td>Aquifer/aquitard type and/or name</td><td>Lithology (Resource WP6 terminology)</td><td>Depth range (m)</td><td colspan="2">GW age range (yr)</td></tr>
<tr><td>Aqf-1:</td><td>Mainly unconfined</td><td>sand to gravel</td><td>20-45</td><td colspan="2">Less than 20 year</td></tr>
</table>

| Porosity type | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
|---|---|---|---|---|
| Aqt-1: | | marl | | |

| | |
|---|---|
| **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.)<br>**Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | **Aquifer-1**<br>$^{3}H$, CFCs |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-1**<br>**1-5: ☐ 5-10: ☐ 10-25: ☐ >25: X** |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-1**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates: X**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates ☐**<br>**Expert judgement: X** |

**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** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
|---|---|---|---|---|
| | x | x | | |

| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
|---|---|---|---|---|---|
| | | | | | |

| **Mining activities** *(not relevant for observation wells)* | **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:<br><br>Groundwater Quality Investigations in Cyprus. Main Results of a Project of Technical Cooperation in Applied Sciences, by S.L. Zomenis, W. Wagner and D. Ploethner, 1988 (Project report hydrochemistry 7 and 14)<br><br>Udluft, P., Külls, C., 2003. Re-evaluation of Groundwater Resources of Cyprus for the Republic of Cyprus. Task4: New Investigations. Ministry of Agriculture, Natural Resources and Environment Geological Survey Department Nicosia. |
|---|---|
| **Remarks / other relevant information:** | |

## 3.6 Description of the Southern Jutland case study, Denmark

| | |
|---|---|
| Title of Case Study | Southern Jutland |
| Location (region, Country) | The Jutland part of the Region of Southern Denmark |
| Other information | The included area corresponds to model four of the National Danish Water Resources model (the DK-model) that comprises seven regional models: http://dk.vandmodel.dk/in-english/. The regional models are all physically distributed and integrated groundwater – surface water models. |

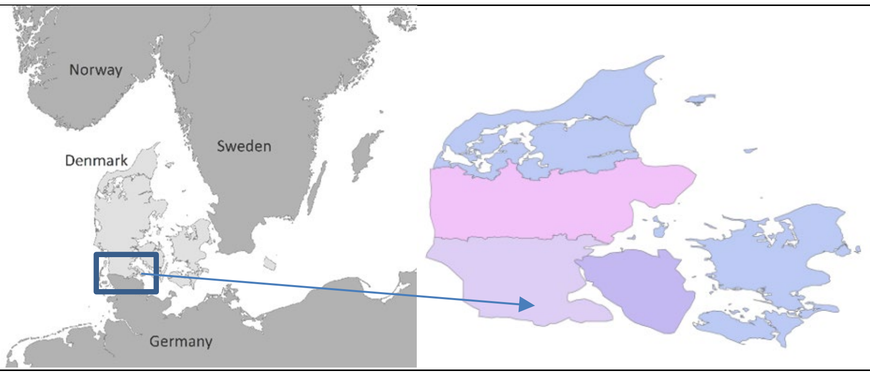
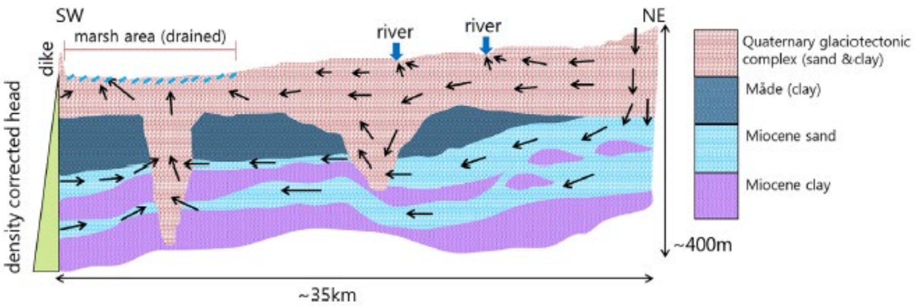
| Description of Case Study (background information on the region) |
|---|
| The region is a border region between Southern Denmark and Northern Germany, which has been studied in several EU (Framework 5 and 6, Interreg North Sea) projects and national studies that included groundwater dating and groundwater flow modelling studies of the regional Quaternary and Miocene sand aquifers in the region. Depending on the location three or more confined or semi-confined sandy Quaternary or Miocene aquifers are located from 0 – 400 m below surface where shallow aquifers are frequently contaminated with nitrate and pesticides and deep aquifers or shallow local discharge areas contain groundwater recharged at lower temperature during the late Pleistocene based on primarily $^{14}C$, $\delta^{13}C$, heavy noble gases, $\delta^{18}O$ and $\delta D$ measurements in samples collected from monitoring wells in the aquifers. Locally, the aquifers are affected by saltwater intrusion primarily in the western part of the region (Meyer et al., 2019). |

| Description of problem (why is this location chosen for a Case Study) |
|---|
| The investigated regional aquifers were included as the region were part of the PALEAUX project on evolution of coastal aquifers in Europe (Edmunds and Milne, 2001) in the EU Framework five program and BASELINE of the EU Framework six programme (Edmunds and Shand, 2008). The region was selected as it has several important Quaternary (e.g. buried valleys) and Miocene aquifers exploited by drinking water and irrigation wells, which are very important for the region. Several previous studies conducted during the past 25 years provide insights about groundwater travel times, paleoclimate indicators, saltwater intrusion, Pleistocene and Holocene evolution of groundwater quantity and quality. Paleoclimate indicators (heavy noble gases and stable isotopes) combined with isotope data from primarily $^{14}C$ and $^{39}Ar$ indicate local presence of Pleistocene and Little Ice Age groundwater with ages of more than 10.000 and 300 years, respectively. The data is important for assessment of the vulnerability to pollution from the surface and natural groundwater quality (natural background values) of the aquifers. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| The case study include the application of a wide range of groundwater age and paleoclimate indicators including: $^{3}H/^{3}He$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $d^{13}C$, $^{18}O$, $^{2}H$, $^{4}He$, heavy noble gases (Xe, Rn) as well as groundwater flow modelling by MODFLOW and the National Danish Water Resources Model, demonstrating the distribution of young potentially contaminated waters, Holocene and Pleistocene (Paleowater) groundwaters in regional aquifers. |

| Results from this Case Study |
| --- |
| The tracer and groundwater flow modelling studies conducted in the investigated area demonstrate that the groundwater evolved in the regional aquifers from modern/young polluted groundwater in the eastern part of the area to late Pleistocene groundwater in the deepest and/or most westerly parts of the aquifer. Pleistocene groundwaters have been found in aquifers at depths more than 300 meters below surface in east, central and western parts of the aquifer as well as in some shallow wells in the discharge areas close to the North / Wadden Sea at depths less than 50 meter. Groundwater flow modelling studies e.g. partly based on the distribution of groundwater dating tracers and paleoclimate indicators also provided insights to salt water intrusion during the Holocene as the level rise induced salt water intrusion to aquifers and occasionally flooding as the sea level increased from more than 120 meter below the surface at the last glacial maximum to the present day level (Hinsby et al., 2001; Meyer et al., ). They furthermore provide insights to the general assessment of the vulnerability of the aquifers and drinking water wells in the area (Hansen et al.). |

| Impact - how this Case Study contributes to the overall project aims |
| --- |
| The case study was part of and contributes with information on the evolution of coastal aquifers in Europe since the late Pleistocene (Edmunds and Milne, 2001, Edmunds et al., 2001) – here exemplified for aquifers located in a border region between Denmark and Germany. The case study area is located between the South-Eastern part of the North Sea and South Western part of the Baltic Sea demonstrating the wide application of groundwater dating and the estimation of travel times and groundwater age distributions in regional coastal aquifers in different geological settings.<br>The Studies include investigations of the natural groundwater quality and the natural background levels of groundwater in the Miocene sand aquifers of the region (Hinsby and Rasmussen, 2008) related to activities in HOVER WP3 on natural background levels, groundwater vulnerability to pollution from the surface related to HOVER WP7 (Hansen et al., 2016) and saltwater intrusion (Meyer et al. 2018, 2019) related to WP5 of the TACTIC (Tools for assessment of climate change impacts on groundwater and adaptation strategies) project. |

| | |
|---|---|
| **Name of pilot area / aquifers / type:** Southern Jutland / Quaternary and Miocene sand aquifers / porous | **Country:** Denmark<br><br>**Region:** Southern Jutland (DK-DE border aquifers) |
| **Study level** | Transboundary : ☐ Regional: x 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)* | x Short screened observation wells (not pumped)<br>x Long screened observation wells (not pumped)<br>☐ Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot (WGS84):**<br>**minX: 8.456955**<br>**maxX: 9.671778**<br>**minY: 54.916425**<br>**maxY: 55.246433** |  |
| **Geological cross section / conceptual model of the pilot area:** |  |
| **Name of Shape- / Geopackage file defining the area:**<br>HoverDKPilotsSub.shp | **Projection to be used:**<br>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)** |
| | 800-1000 | 300-400 | 9 | 5-50 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):** | | **Typical pump discharge of complete well field ($m^3$/day):** *If relevant* |
| **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 Aquitard no. (aqt): 2 Aquiclude no. (aqc): 1** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Quaternary sands locally confined by clay till aquitards | Fine sand to gravel | 0 – 100 (400) | 5 - > 10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt-1: | Miocene marine clay | Silty clays | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: ☐ |
| Aqf-2: | Miocene sands | Fine sand to gravel | 100 - > 250 | 100 - > 10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt-2: | Miocene marine clay | Clay | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: ☐ |
| Aqf-3: | Miocene sands | Fine sand to gravel | 250 - 400 | 1000 - > 10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqc-1: | Oligocene clay | clay | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: ☐ |

| | |
|---|---|
| **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.)<br>**Applied recharge temperature indicators** ($^{18}$O, D, noble gases) | **Aquifer-1**<br>$^3$H, $^3$H/$^3$He, $^{14}$C, $^4$He, $^{18}$O, D noble gases |
| | **Aquifer-2**<br>$^3$H, $^3$H/$^3$He, $^{14}$C, $^4$He, $^{18}$O, D noble gases |
| | **Aquifer-3**<br>$^3$H, $^3$H/$^3$He, $^{14}$C, $^4$He, $^{18}$O, D noble gases |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-1**<br>**1-5: ☐ 5-10: ☐ 10-25: X >25: ☐** |
| | **Aquifer-2**<br>**1-5: X 5-10: ☐ 10-25: ☐ >25: ☐** |
| | **Aquifer-3**<br>**1-5: X 5-10: ☐ 10-25: ☐ >25: ☐** |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-1**<br>**GAR-1: 1-10%: ☐ 10-25%: X 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-3: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| | **Aquifer-2**<br>**GAR-1: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-3: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| | **Aquifer-3**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-3: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates ☐**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates X**<br>**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 | Indication of vulnerability of aquifers and water supply wells |
|---|---|---|---|
| x | | | |

| **Water Usage** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
|---|---|---|---|---|
| | x | x | x | ? |

| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
|---|---|---|---|---|---|
| | x | | | | |

| **Mining activities** *(not relevant for observation wells)* | **Construction materials** | **Minerals / metals** | **Coal** | **Other** |
|---|---|---|---|---|
| | x | | | |

| 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:** |
| **Remarks / other relevant information:** | |

## 3.7 Description of the Central Jutland case study, Denmark

| | |
|---|---|
| Title of Case Study | Central Jutland |
| Location (region, Country) | Part of Central Jutland, Denmark |
| Other information | The included area covers part of the National Danish Water Resources model (the DK-model) http://dk.vandmodel.dk/in-english/ for the Central Jutland region. |

| Description of Case Study (background information on the region) |
|---|
| Groundwater in the investigated Miocene (Burdigalian) aquifer flow from the eastern part of the area towards the North Sea at the western coastline of Jutland. The area is primarily located to the west of the Main Stationary Line of the last glaciation, which e.g. has resulted in clay tills at the surface and confined or semi-confined aquifers in the eastern part of the area, and mainly outwash sands a the surface and unconfined aquifers in the western part of the area.<br>The project included a PhD study (Scharling, 2009, 2011) funded by GeoCenter Denmark (https://www.geocenter.dk/ to investigate the distribution and extent of Miocene sand aquifers in Central Jutland (Rasmussen, 2007) including the vulnerability towards pollution from the surface and the general distribution of groundwater age and transit times (Sonnenborg et al., 2016). Depending on the location three or more confined, semi-confined or unconfined sandy Quaternary or Miocene aquifers occur at different depths between 0 – 200 m below surface (or <20 - < -200 meter above sea level). Applied tracers include $^{39}Ar$, $^{85}Kr$, $^{14}C$, $\delta^{13}C$, $\delta^{18}O$, and δD measurements in samples collected from monitoring and irrigation wells in the aquifers. The groundwater flow, age and $^{39}Ar$ distributions were simulated by the use of various techniques (Sonnenborg et al., 2016). |

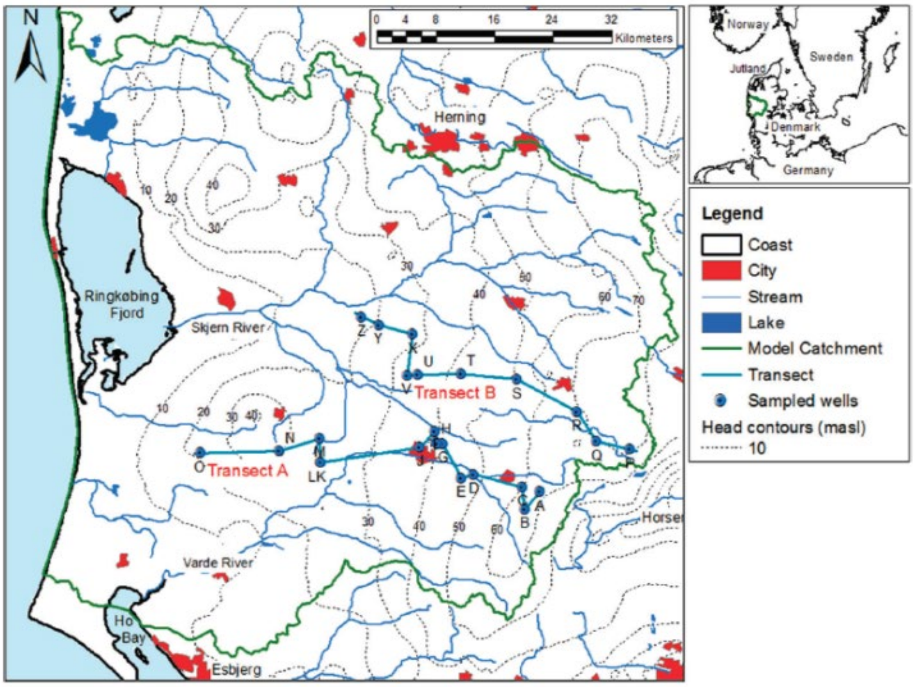
| Description of problem (why is this location chosen for a Case Study) |
|---|
| The relatively deep lying Miocene sand aquifers in central and southern Jutland (see also specific pilot description for Southern Jutland) have attracted special attention during the past couple of decades due to increasing pollution of the shallow Quaternary aquifers in the area. The Miocene aquifers may be well protected against pollution and constitute an additional important strategic reserve. The data obtained in this study are important for assessment of the vulnerability of the Miocene aquifers to pollution from the surface and natural groundwater quality (natural background values) of the aquifers. The results demonstrate that the investigated Burdigalian aquifer is more vulnerable to pollution from the surface than previously thought, but that it is an important water resource primarily for water supply and irrigation. |

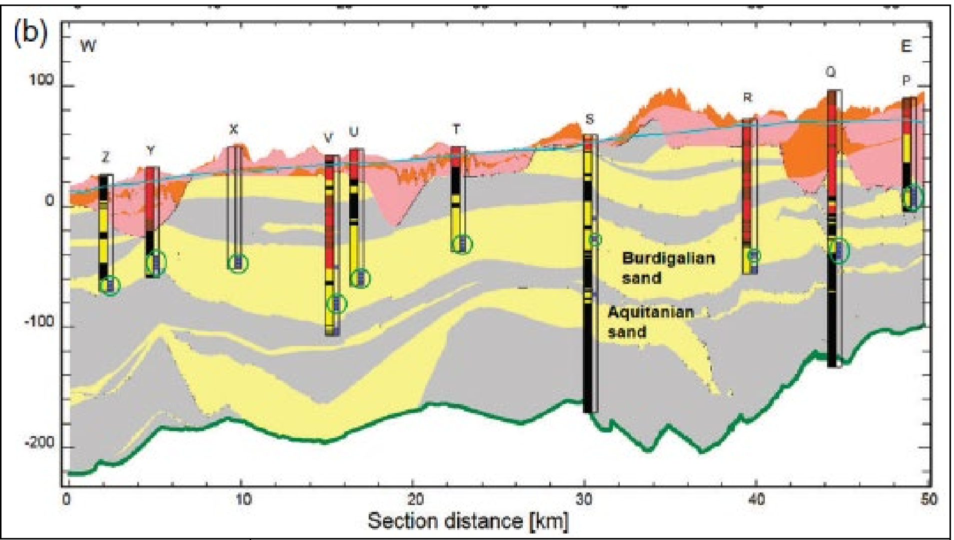
| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| The case study includes the application of the following groundwater age and paleoclimate indicators $^{85}Kr$, $^{39}Ar$, $^{14}C$, $d^{13}C$, $^{18}O$and δD. Model codes and techniques applied include MODFLOW, MTD3MS, RTD3 and PEST (Sonnenborg et al., 2016). The $^{85}Kr$ 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)

| Results from this Case Study |
|---|
| The tracer and groundwater flow modelling studies conducted in the investigated area demonstrate that the groundwater evolved in the regional aquifers from modern/young polluted groundwater less than 60 years old to groundwater older than 300 years without human impact. Both tracers and groundwater flow models demonstrate that young potentially polluted groundwater is more widespread than anticipated and hence that the groundwater resources in the Miocene (Burdigalian) sand aquifer typically at a depth of 50 - 100 meter is more vulnerable to pollution from the surface than expected. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| The case study investigate the vulnerability, groundwater age and travel time distributions of important aquifers in the Central part of Jutland, Denmark, and hence it contributes to the objectives of WP6 on groundwater age and travel time distributions as well as related studies in HOVER WP5 and 7 on travel times for nitrate and pesticides and the vulnerability of aquifers, respectively.<br>The location of the study site and the references cited in the text above can be found in the following information template. The PhD thesis, Scharling et al. (2011), and the open-access paper by Rasmussen et al. (2007) can be downloaded from the EGDI repository. |

| | |
|---|---|
| **Name of pilot area / aquifers / type:** Central Jutland / Miocene (Burdigalian) delta and marine sand aquifer / porous | **Country:** Denmark<br><br>**Region:** Central Jutland |
| **Study level** | Transboundary : ☐ Regional: x Local: ☐ Single well(s): ☐ |
| **Type of observations**<br>*(choose one of the options, create separate template if needed for each type if each type need specific information)* | X Short screened observation wells (not pumped)<br>X Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot:** |  |
| **Geological cross section / conceptual model of the pilot area:** | A geological cross-section at Transect B on map above is shown below with indication of sampled sceens (green circles) |

<table>
<tr><td></td><td colspan="4">
</td></tr>
<tr><td colspan="2">Name of Shape- / Geopackage file defining the area:<br>HoverDKPilotsSub.shp</td><td colspan="3">Projection to be used:<br>WGS84 (Epsg4326)</td></tr>
<tr><td rowspan="2">Hydrological parameters:</td><td>Mean annual precipitation (mm or range in mm)</td><td>Mean annual groundwater recharge (mm or range in mm)</td><td>Mean annual groundwater recharge temperature (°C)</td><td>Thickness of unsaturated zone (range in m)</td></tr>
<tr><td>700-1100</td><td>300-500</td><td>9</td><td>1-30</td></tr>
<tr><td colspan="2">Pumped wells only</td><td colspan="2">Typical pump discharge of sampled individual well (m³/day):</td><td>Typical pump discharge of complete well field (m³/day):<br>If relevant</td></tr>
<tr><td colspan="2">List of aquifers and aquitards in pilot area</td><td colspan="2">No. of confined or semiconfined aquifers in pilot area: 3</td><td>No. of unconfined aquifers in pilot area: 1</td></tr>
<tr><td>Aquifer no. (aqf): 3<br>Aquitard no. (aqt): 2<br>Aquiclude no. (aqc): 1</td><td>Aquifer/aquitard type and/or name</td><td>Lithology (Resource WP6 terminology)</td><td>Depth range (m)</td><td>GW age range (yr)</td></tr>
<tr><td>Aqf-1:</td><td>Quaternary sands locally confined by clay till aquitards</td><td>Fine sand to gravel</td><td>0 – 100 (400)</td><td>< 5 - > 300 (expert Judgement)</td></tr>
<tr><td>Porosity type</td><td>Porous: X</td><td>Fissured: □</td><td>Karst: □</td><td>Fissured and porous / dual porosity: □</td></tr>
<tr><td>Aqt-1:</td><td>Miocene marine clay</td><td>Silty clays</td><td></td><td></td></tr>
<tr><td>Porosity type</td><td>Porous: X</td><td>Fissured: □</td><td>Fissured and porous / dual</td><td>No hydraulically active porosity: □</td></tr>
</table>

| | | | | |
|---|---|---|---|---|
| | | | porosity: ☐ | |
| Aqf-2: | Miocene sands | Fine sand to gravel | < 20 - 100 | < 60 - > 300 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt-2: | Miocene marine clay | Clay | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: ☐ |
| Aqf-3: | Miocene (Burdigalian) deltaic and marine sands | Fine sand to gravel | 30 - 180 | < 50 - 500 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqc-1: | Oligocene clay | clay | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: ☐ |
| **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.)<br>**Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | | **Aquifer-1** | | |
| | | **Aquifer-2** | | |
| | | **Aquifer-3**<br>$^{39}Ar$, $^{14}C$ | | |
| **Number of sites (wells/springs) with age indicators** | | **Aquifer-1**<br>**1-5: ☐ 5-10: ☐ 10-25: ☐ >25: ☐** | | |
| | | **Aquifer-2**<br>**1-5: ☐ 5-10: ☐ 10-25: ☐ >25: ☐** | | |
| | | **Aquifer-3**<br>**1-5: ☐ 5-10: ☐ 10-25: X >25: ☐** | | |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | | **Aquifer-1**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** | | |
| | | **Aquifer-2**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** | | |
| | | **Aquifer-3**<br>**GAR-1: 1-10%: ☐ 10-25%: X 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** | | |

| | |
|---|---|
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates ☐**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates X**<br>**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** | **Indication of vulnerability of aquifers and water supply wells** |
|---|---|---|---|
| x | | | x |

| **Water Usage** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
|---|---|---|---|---|
| | x | x | x | ? |

| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
|---|---|---|---|---|---|
| | | | | | |

| **Mining activities** *(not relevant for observation wells)* | **Construction materials** | **Minerals / metals** | **Coal** | **Other** |
|---|---|---|---|---|
| | x | | | |

**REFERENCES**


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

Rasmussen, Erik S., Thomas Vangkilde-Pedersen, and Peter Scharling. 2007. "Prediction of Reservoir Sand in Miocene Deltaic Deposits in Denmark Based on High-Resolution Seismic Data." Geological Survey of Denmark and Greenland Bulletin, no. 13: 17–20. https://doi.org/10.34194/geusb.v13.4966 .

Scharling, P.B. 2011. Hydrogeological modeling of Miocene aquifers in western Denmark. PhD thesis, University of Copenhagen, Copenhagen, Denmark.

PB Scharlings PhD thesis mentioned above has been uploaded to the EGDI document repository

**Reports and papers with restricted access:**

Scharling, Peter B., Erik S. Rasmussen, Torben O. Sonnenborg, Peter Engesgaard, and Klaus Hinsby. 2009. "Three-Dimensional Regional-Scale Hydrostratigraphic Modeling Based on Sequence Stratigraphic Methods: A Case Study of the Miocene Succession in Denmark." *Hydrogeology Journal* 17 (8): 1913–33. https://doi.org/10.1007/s10040-009-0475-6

Sonnenborg, T.O., P.B. Scharling, K. Hinsby, E.S. Rasmussen, and P. Engesgaard. 2016. "Aquifer Vulnerability Assessment Based on Sequence Stratigraphic and39Ar Transport Modeling." Groundwater 54 (2). https://doi.org/10.1111/gwat.12345.


**Remarks / other relevant information:**

## 3.8 Description of the Northern Jutland – Loekken – case study, Denmark

| Title of Case Study | Loekken water supply well |
|---|---|
| Location (region, Country) | Loekken, Northern Jutland, Denmark |
| Other information | Water supply well located close to and between a golf course and corn fields applying pesticides regulated in 1995, which are still found in the well |

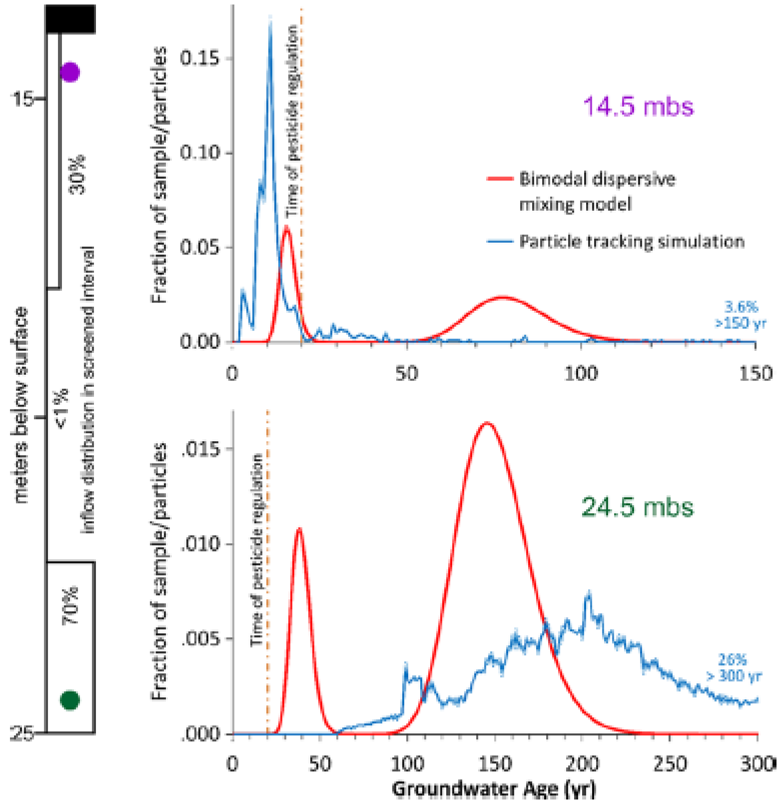
| Description of Case Study (background information on the region) |
|---|
| Pilot study in a 25 m deep water supply well with a 12 m screen, 13-25 m below surface, in a Holocene marine and aeolian sand aquifer used for water supply. The well is in a holiday area with significant seasonal variation in abstractions.<br>The project was conducted by GEUS for the Danish Environmental Protection Agency (Jakobsen et al., 2020) to investigate the history and fate of pesticides observed in the well. The water supply well was sampled at different specific levels (top, center and bottom of the screen) by separation pumping (Nilsson et al., 1995) to identify, which parts of the aquifer were contaminated by the pesticides. The samples were collected in collaboration with 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. The dating tracers $^{3}H/^{3}He$ were analysed by the Helis laboratory at University of Bremen, the $^{39}Ar$ and $^{85}Kr$ tracers were analysed by University of Bern. The tracer and age distribution at different levels in the water supply well were then simulated by a lumped parameter model (TracerLPM) developed by the USGS (Jurgens et al., 2012) and particle tracking. |

| Description of problem (why is this location chosen for a Case Study) |
|---|
| The two pesticides, bentazon and dichlorprop, have been found at the top and bottom of the 25 m deep water supply well, respectively. The pesticides are still found in the well although they were regulated in 1995, and the Danish EPA wanted to understand, why they are still found in the well. |

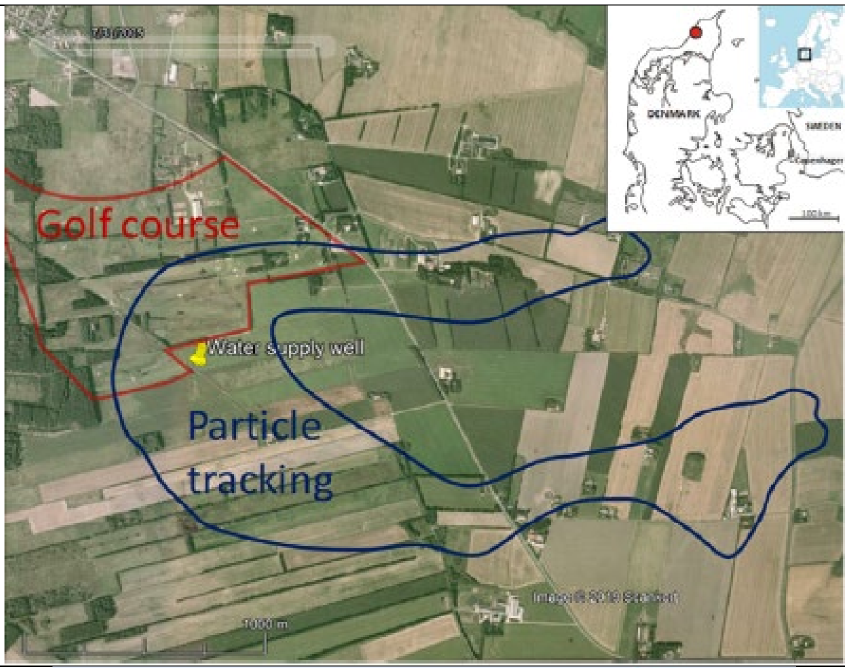
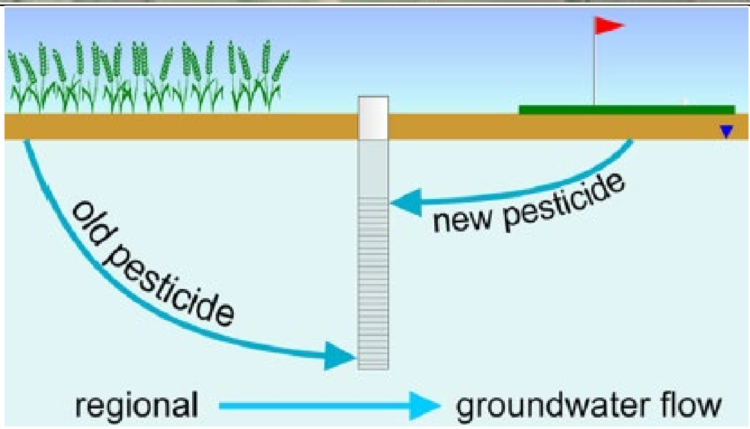
| Methods used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| The case study include the application of the groundwater age indicators $^{85}Kr$, $^{39}Ar$, $^{3}H/^{3}He$, the lumped parameter modelling tool "TracerLPM" (https://www.usgs.gov/software/tracerlpm) and particle tracking by MODFLOW and MODPATH modules in GMS. $^{85}Kr$ 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), - $^{3}H/^{3}He$ were analysed by the Helis lab. At University of Bremen https://www.noblegas.uni-bremen.de/eng/. |

| Results from this Case Study |
|---|
| The assessment show that the upper part of the screen, which is contaminated by bentazon has a bimodal age distribution of which a significant part is less than 10 years and another significant part is older than 60 years (65%), see figure below. The lower part, which is contaminated by dichlorprop also has a bimodal distribution with a significant part (about 15%) with an age of less than 60 years and another part (85%) with an age of more than 100 years. |

Hence, the investigations show that the bentazon pollution in the top of the well occurred after the regulation in 1995, and the dichlorprop found at the bottom of the well occurred long before the regulation (in the 1970's). The bentazon contamination in the top of the well indicates that the regulation in 1995 is either not followed or not strict enough.




| Impact - how this Case Study contributes to the overall project aims |
|---|
| The case study investigate the vulnerability, groundwater age and travel time distributions of a long-screened water supply well in Northern Jutland, Denmark, 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.<br>The cited references and access information are listed at the end of the following information template. |

<table>
<tr><td colspan="2">Name of pilot area / aquifers / type:<br>North Jutland / Holocene marine and aeolian sand semi-confined aquifer / porous</td><td>Country: Denmark<br><br>Region: Northern Jutland</td></tr>
<tr><td>Study level</td><td colspan="2">Transboundary : ☐ Regional: ☐ Local: ☐ Single well(s): X</td></tr>
<tr><td>Type of observations<br>(choose one of the options, create separate template if needed for each type if each type need specific information)</td><td colspan="2">☐ Short screened observation wells (not pumped)<br>☐ Long screened observation wells (not pumped)<br>☐ Pumped wells, long screens in one aquifer<br>X Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping):</td></tr>
<tr><td>Approximate location of pilot:</td><td colspan="2"><br></td></tr>
<tr><td>Geological cross section / conceptual model of the pilot area:</td><td colspan="2"><br><br>Conceptual model of groundwater flow with dissolved pesticides to water supply well</td></tr>
</table>

| | | | | |
|---|---|---|---|---|
| **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)** | **Mean annual groundwater recharge temperature (°C)** | **Thickness of unsaturated zone (range in m)** |
| | 1000 | 400 | 8 | 2 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day): 50 – 100 $m^3$** | | **Typical pump discharge of complete well field ($m^3$/day):** *If relevant* |
| **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: 0** |
| **Aquifer no. (aqf): 2 Aquitard no. (aqt): 1 Aquiclude no. (aqc):** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Holocene sands locally confined by clay/silt | Fine to medium sand to gravel | 13 - 18 | < 5 - 100 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt-1: | Holocene marine silty clay | Silty clays | 18-22 | |
| **Porosity type** | Porous: X | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: ☐ |
| Aqf-2: | Holocene sands | Medium sand | 22 -25 | 25 - 250 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| **Applied tracer age indicators** ($^3H$, $^3H/^3He$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $^{36}Cl$, $^{81}Kr$, $^4He$, CFCs, $SF_6$, etc.) **Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | | **Aquifer-1** $^3H/^3He$, $^{39}Ar$ , $^{85}Kr$, | | |
| | | **Aquifer-2** $^3H/^3He$, $^{39}Ar$ , $^{85}Kr$, | | |
| **Number of sites (wells/springs) with age indicators** | | **Aquifer-1** **1-5: X 5-10: ☐ 10-25: ☐ >25: ☐** | | |
| | | **Aquifer-2** **1-5: X 5-10: ☐ 10-25: ☐ >25: ☐** | | |

<table>
<tr><td colspan="2" rowspan="2">GW age range (GAR)<br>GAR-1: Modern (< 60 yr)<br>GAR-2: Old (> 60 yr and <10 kyr)<br>GAR-3: Paleowaters (> 10 kyr)</td><td colspan="4">Aquifer-1<br>GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: X >50%: ☐<br>GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X<br>GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐</td></tr>
<tr><td colspan="4">Aquifer-2<br>GAR-1: 1-10%: ☐ 10-25%: X 25-50%: ☐ >50%: ☐<br>GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X<br>GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐</td></tr>
<tr><td colspan="2">Groundwater age ranges (GAR) estimated by:</td><td colspan="4">Tracer based estimates ☐<br>Flow and age model simulations ☐<br>Combination of model and tracer estimates X<br>Expert judgement: ☐</td></tr>
<tr><td colspan="6">Objective of age dating studies:</td></tr>
<tr><td>Basic research or General groundwater management</td><td>Assessment of pollutant history</td><td colspan="2">Assessment of the efficiency of remediation and mitigation measures</td><td colspan="2">Indication of vulnerability of aquifers and water supply wells</td></tr>
<tr><td>x</td><td>x</td><td colspan="2">x</td><td colspan="2">x</td></tr>
<tr><td rowspan="2">Water Usage<br>(not relevant for observation wells)</td><td>Water supply</td><td>Irrigation</td><td>Industry</td><td colspan="2">Other</td></tr>
<tr><td>x</td><td></td><td></td><td colspan="2"></td></tr>
<tr><td rowspan="2">Geoenergy related activities<br>(not relevant for observation wells)</td><td>Shallow Geo-T | Deep Geo-T</td><td colspan="2">Hydrocarbons</td><td>Nuclear waste disp.</td><td>$CO_2$ storage</td></tr>
<tr><td></td><td colspan="2"></td><td></td><td></td></tr>
<tr><td rowspan="2">Mining activities<br>(not relevant for observation wells)</td><td>Construction materials</td><td>Minerals / metals</td><td>Coal</td><td colspan="2">Other</td></tr>
<tr><td></td><td></td><td></td><td colspan="2"></td></tr>
<tr><td colspan="6">REFERENCES</td></tr>
<tr><td colspan="2">OPEN Access reports and papers (PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches):<br><br>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.</td><td colspan="4">Reports and papers with restricted access:<br><br>Jakobsen, Rasmus, Klaus Hinsby, Jens Aamand, Peter van der Keur, Jacob Kidmose, Roland Purtschert, Bryant Jurgens, Jürgen Sültenfuss, and Christian N. Albers. 2019. “History and Sources of Co-Occurring Pesticides in an Abstraction Well Unraveled by Age Distributions of Depth-Specific Groundwater Samples.” Environmental Science & Technology. https://doi.org/10.1021/acs.est.9b03996 .</td></tr>
<tr><td colspan="6">Remarks / other relevant information:</td></tr>
</table>

## 3.9 Description of the Eastern Jutland and Funen area, water supply wells case study, Denmark

| | |
|---|---|
| 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.<br>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” laboratory at university of Bremen and TNO. The dating tracers $^{3}H/^{3}He$ were analysed by the Helis laboratory 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 |

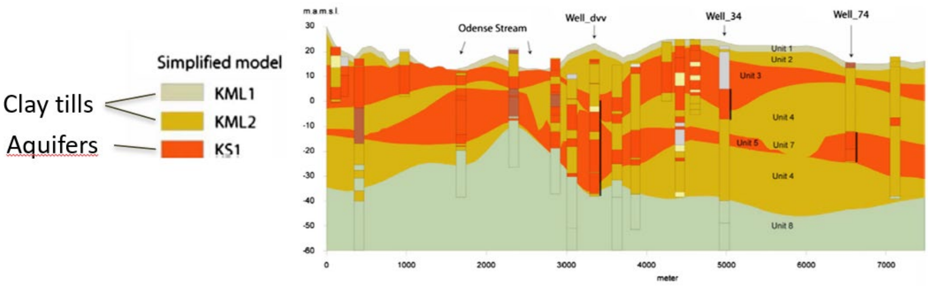
| |
|---|
| groundwater models. $^{85}Kr$ and $^{39}Ar$ sampling and analyses were conducted by the research group on environmental radionuclides at Climate and Environmental Physics, University of Bern (https://www.climate.unibe.ch/research/ research_groups/environmental_radionuclides/index_eng.html), - 3H/3He and $^{4}He$ were analysed by the Helis laboratory 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 |
|---|
| 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.<br>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.<br>The cited references and access information are listed at the end of the following information template. |

<table>
<tr><td>Name of pilot area / aquifers / type: Eastern Jutland and Funen – complex Pleistocene confined, semi-confined and unconfined aquifer systems</td><td>Country: Denmark<br><br>Region: Eastern Jutland and Funen</td></tr>
<tr><td>Study level</td><td>Transboundary : ☐ Regional: ☐ Local: ☐ Single well(s): X</td></tr>
<tr><td>Type of observations<br>(choose one of the options, create separate template if needed for each type if each type need specific information)</td><td>X Short screened observation wells (not pumped)<br>☐ Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>X Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping):</td></tr>
<tr><td>Approximate location of pilot:</td><td>


</td></tr>
<tr><td>Geological cross section / conceptual model of the pilot area:</td><td>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.




</td></tr>
<tr><td>Name of Shape- / Geopackage file defining the area:<br>HoverDKPilotsSub.shp</td><td>Projection to be used:<br>WGS84 (Epsg4326)</td></tr>
</table>

| **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 - 1000 | 150 - 500 | 9 | 1 - 50 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):** 50 – 100 $m^3$ | | **Typical pump discharge of complete well field ($m^3$/day):** *If relevant* |
| **List of aquifers and aquitards in pilot area** | | **No. of confined or semiconfined aquifers in pilot areas:** 2-3 | | **No. of unconfined aquifers in pilot areas:** 0-1 |
| **Aquifer no. (aqf): 2 Aquitard no. (aqt): 3 Aquiclude no. (aqc):** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Pleistocene sands locally confined by clay/silt | Fine to medium sand and gravel | Varying (0 – ~60) | Not yet estimated |
| **Porosity type** | Porous: X | Fissured: □ | Karst: □ | Fissured and porous / dual porosity: □ |
| Aqt-1: | Clay tills | | | |
| **Porosity type** | Porous: X | Fissured: □ | Fissured and porous / dual porosity: □ | No hydraulically active porosity: □ |
| Aqf-2: | Pleistocene sands | Fine to medium sand and gravel | Varying (40 - ~150) | Not yet estimated |
| **Porosity type** | Porous: X | Fissured: □ | Karst: □ | Fissured and porous / dual porosity: □ |
| **Applied tracer age indicators** ($^3H$, $^3H/^3He$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $^{36}Cl$, $^{81}Kr$, $^4He$, CFCs, $SF_6$, etc.) **Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | | **Aquifer-1** $^3H/^3He$, $^4He$, $^{39}Ar$ , $^{85}Kr$, $^{14}C$, (CFCs and SF6 – only on Funen) | | |
| | | **Aquifer-2** $^3H/^3He$, $^4He$, $^{39}Ar$ , $^{85}Kr$, $^{14}C$, (CFCs and SF6 – only on Funen) | | |
| **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: □** | | |
| **GW age range (GAR)** | | **Aquifer-1 – (preliminary assessment)** **GAR-1: 1-10%: □ 10-25%: □ 25-50%: □ >50%: X** | | |

| | |
|---|---|
| **GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and <10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: X >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br><br>**Aquifer-2 – (preliminary assessment)**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: X >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates X**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates (X)**<br>**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** | **Indication of vulnerability of aquifers and water supply wells** |
|---|---|---|---|
| x | x | x | x |

| **Water Usage** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
|---|---|---|---|---|
| | x | | | X (monitoring) |

| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
|---|---|---|---|---|---|
| | | | | | |

| **Mining activities** *(not relevant for observation wells)* | **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:** |
|---|---|
| Presentation of preliminary results at EGU2020 by:<br><br>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 | The investigations conducted in this study are expected to provide results similar to what was presented in the study below, which is also described in the Loekken – NJutland information tables of the previous study<br>Jakobsen, Rasmus, Klaus Hinsby, Jens Aamand, Peter van der Keur, Jacob Kidmose, Roland Purtschert, Bryant Jurgens, Jürgen Sültenfuss, and Christian N. Albers. 2020. "History and Sources of Co-Occurring Pesticides in an Abstraction Well Unraveled by Age Distributions of Depth-Specific Groundwater Samples." Environmental Science & Technology. https://doi.org/10.1021/acs.est.9b03996 . |

| | |
|---|---|
| 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<br><br>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 investigations conducted in this study are expected to provide results similar to what was presented in the study by Jakobsen et al. above, which is also described in the Loekken – NJutland information tables of the previous pilot study. However, the studies conducted in the pilot area presented here collected only one mixed sample per well except for one well, which had three samples taken (top, bottom and mixed). The study is on-going and part of WP6 task 6.4 on new techniques for the investigation of groundwater age distributions in long-screened wells with groundwater ages in the range of 10 – 1000 years. The majority of the 30 wells investigated in this study is a mixture of young contaminated or potentially contaminated groundwater and old and pristine groundwater. A research paper is expected to be submitted at the end of GeoERA illustrating the mixing ratios etc. The information template will be updated as soon as all tracer results and simulations are ready and the paper has been published.

## 3.10 Falster Island case study, Denmark

| | |
|---|---|
| Title of Case Study | Falster Island, Denmark |
| Location (region, Country) | Marielyst, Southern Falster, Denmark |
| Other information | Eleven mainly open water supply wells abstracting water from a confined fractured chalk aquifer partly affected by glaciotectonics and land reclamation in the 18$^{th}$ century were investigated due to increasing salinity in some of the water supply wells. A study on climate change impacts on the aquifer were furthermore conducted (Rasmussen et al. 2013). |

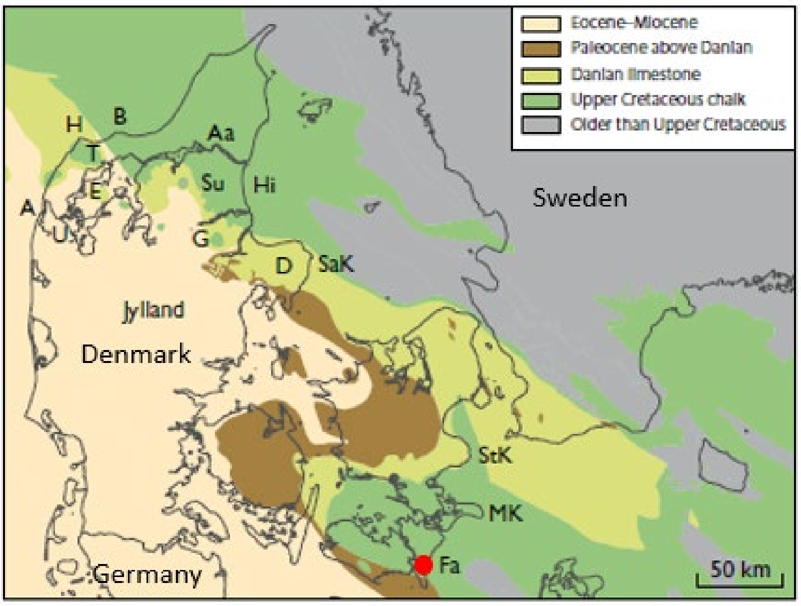
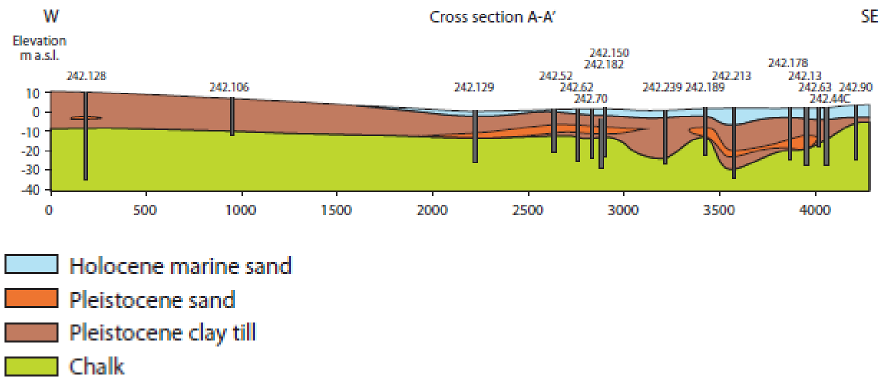
| Description of Case Study (background information on the region) |
|---|
| Pilot study in collaboration with a small Danish water company supplying water to a holiday summer housing area primarily during summer time. Eleven wells were sampled and analysed for $^3H/^3HE$, $^4He$ and $^{14}C$. The wells typically abstract water from the upper 10 meter of a confined chalk aquifer highly affected by the last glaciation. On average about 2000 m$^3$/day is abstracted during the summer while only about 300 m$^3$/day is abstracted during winter time.<br>Salt water intrusion processes were investigated in several national and EU projects made possible through funding from Danish ministries and EU (Horizon 2020) to assess potential impacts of climate change and sea level rise and explore possible adaptation strategies by the use of integrated groundwater and surface water modelling (Rasmussen et al., 2013). The dating tracers $^3H/^3He$ were analysed by the Helis lab. at University of Bremen to assess groundwater age and recharge since the land reclamation activities were initiated in 1861. |

| Description of problem (why is this location chosen for a Case Study) |
|---|
| Several water abstraction wells of the Marielyst waterworks experience increasing salinity. The pilot study site was selected to assess climate change impacts and potential remediation options for protecting the freshwater resources in the area. |

| Methods used or to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| Integrated groundwater-surface water modelling, airborne geophysical measurements (SkyTEM), use of groundwater dating tracers for assessment of groundwater recharge. The case study include the application of the groundwater age indicators $^3H/^3He$, $^4He$, $^{14}C$, $\delta^{13}C$, as well as stable isotopes of strontium, oxygen and hydrogen. |

| Results from this Case Study |
|---|
| The results of the $^3H/^3He$ analyses showed no or very low tritium and tritiogenic helium in the collected samples demonstrating rather old groundwater and little groundwater recharge at the shallow depth from where water supply wells abstracts water (approx.. 10-20 below surface). This indicates that the land reclamation activities (drainage pipes, canals and pumping station) have reduced groundwater recharge in the area significantly and that water abstraction by the water works is mining the existing groundwater resources at least locally. This increases the risk of continuous salinization and calls for remediation measures such as desalinization, managed aquifer recharge and water banking e.g. storage from winter to summer to protect and ensure continuous water supply from the area. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| The case study investigate groundwater recharge and salinization processes in a coastal area affected by salt water intrusion and contributes to demonstrating how groundwater dating tracers can be used to understand groundwater recharge and vulnerability to saltwater intrusion. Hence, it contributes to both the objectives of especially HOVER WP6 and TACTIC WP5 and 6 objectives i.e. understanding groundwater recharge, flow and saltwater intrusion issues and to provide advice on groundwater management and adaptation strategies in a changing climate.<br>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 towards saltwater intrusion (Rasmussen et al., 2013) much more common. Information on groundwater flow dynamics based on tracer analyses and groundwater flow modelling will enable much better management and protection of the well fields e.g. by distributing and optimizing groundwater abstraction from water supply wells to avoid increasing salinity and/or to design remediation measures e.g. applying carefully designed managed aquifer recharge of desalinized brackish waters from deeper part of the local aquifer during winter time for abstraction in the upper parts again during summer time where peak abstraction is required.<br>The cited references and access information are listed at the end of the following information template. |

| | |
|---|---|
| **Name of pilot area / aquifers / type:** Marielyst, Falster / fractured chalk glacitectonite / confined | **Country:** Denmark<br><br>**Region:** Island of Falster |
| **Study level** | Transboundary : ☐ Regional: ☐ Local: ☐ Single well(s): X |
| **Type of observations**<br>*(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)<br>☐ Long screened observation wells (not pumped)<br>X Pumped wells, long screens and open wells in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot: (red circle)** | <br>Pre-Quaternary aquifers & aquitards in Denmark |
| **Geological cross section / conceptual model of the pilot area:** |  |
| **Name of Shape- / Geopackage file defining the area:** | **Projection to be used:** |

| **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)** |
|---|---|---|---|---|
| | 700 | 80 - 400 | 9 | 1 - 2 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well (m$^3$/day):** Winter (0), summer (50) | | **Typical pump discharge of complete well field (m$^3$/day):** N/A<br>*If relevant* |
| **List of aquifers and aquitards in pilot area** | | **No. of confined or semiconfined aquifers in pilot areas:** 1 | | **No. of unconfined aquifers in pilot areas:** 0 |
| **Aquifer no. (aqf): 1**<br>**Aquitard no. (aqt): 1**<br>**Aquiclude no. (aqc):** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqt-1: | Clay tills | Clayey till | 5-10 | |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Fissured and porous / dual porosity: X | No hydraulically active porosity: ☐ |
| Aqf-1: | Cretaceous chalk | chalk | ~10 – ~25 | >70 |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: X |
| **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.)<br>**Applied recharge temperature indicators** ($^{18}$O, D, noble gases) | | **Aquifer-1**<br>$^3$H/$^3$He, $^4$He, $^{14}$C,<br>$^{18}$O, D<br>Other applied isotope tracers: $^{87}$Sr/$^{86}$Sr | | |
| **Number of sites (wells/springs) with age indicators** | | **Aquifer-1**<br>**1-5: ☐ 5-10: ☐ 10-25: X >25: ☐** | | |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and <10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | | **Aquifer-1**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** | | |
| **Groundwater age ranges (GAR) estimated by:** | | **Tracer based estimates X**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates (☐)**<br>**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 | Indication of vulnerability of aquifers and water supply wells |
|---|---|---|---|
| X | | | X (towards salt water intrusion) |

| Water Usage *(not relevant for observation wells)* | Water supply | Irrigation | Industry | Other |
|---|---|---|---|---|
| | x | X | | |

| Geoenergy related activities *(not relevant for observation wells)* | Shallow Geo-T | Deep Geo-T | Hydrocarbons | Nuclear waste disp. | $CO_2$ storage |
|---|---|---|---|---|---|
| | | | | | |

| Mining activities *(not relevant for observation wells)* | 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:** |
|---|---|
| Rasmussen, P., T. O. Sonnenborg, G. Goncear, and K. Hinsby. 2013. "Assessing Impacts of Climate Change, Sea Level Rise, and Drainage Canals on Saltwater Intrusion to Coastal Aquifer." Hydrology and Earth System Sciences 17 (1): 421–43. | |

The pilot site was part of the SubSol project on Subsurface Water Solutions: http://www.subsol.org/ (2015-2018), and presented with investigations of climate change impacts on other coastal aquifers primarily in the North Sea region in a HESS Open Access special issue (Hinsby et al., 2011, Assessing the impact of climate change for adaptive water management in coastal regions, special issue 149, Hydrological and Earth System Sciences: https://hess.copernicus.org/articles/special_issue149.html

## 3.11 Tools for quantification of duration and effect of sources of pesticides to the groundwater resource case study, Denmark

| | |
|---|---|
| Title of Case Study | Industrial PhD project: Tools for quantification of duration and effect of sources of pesticides to the groundwater resource |
| Location (region, Country) | Marbaek, Northern Zealand, Denmark |
| Other information | The abstraction wells are affected by the fungicide/biocide metabolite DMS. The monitoring wells are located at an upgradient site which is believed to be the source of contamination. The land use of this site was formerly storage and rental of agricultural machinery and cultivation of strawberries. |

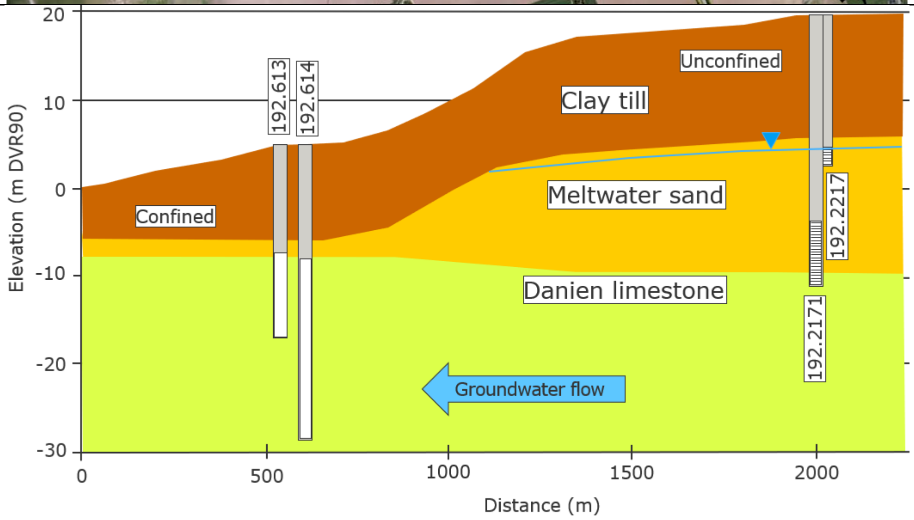
| Description of Case Study (background information on the region) |
|---|
| This case study is one of two in an industrial PhD project conducted by the Environmental Institute at Technical University of Denmark and the consultancy company Ramboll. The regional authority The Capital Region of Denmark and the water utilities Novafos and HOFOR are partners in the project, and GEUS supervises on the use of groundwater dating tracers for assessment of the history and fate of the investigated contaminants. The focus is on the metabolite DMS, which derives from the fungcides/biocides tolylfluanid and dichlofluanid.<br>The limestone aquifer is the main source of drinking water in this region. All six wells in the well field are affected by DMS, four more severely (frequently >0.1 µg/L). The abstraction wells are open in the limestone, from about 14 m bgs. One well is 22 m deep (192.613), the other is 33 m deep (192.614). They are sampled at depth specific levels by separation pumping at the main inflow zones at respectively 14 and 19 m bgs (192.613) and 15 and 20 m bgs (192.614).<br>The believed origin of the pesticide contamination is situated 1.4 km upgradient of the abstraction wells. The two monitoring wells are screened in the meltwater sand aquifer at respectively 12-14 m bgs (192.2217) and 17-24 m bgs (192.2171). The highest DMS concentrations measured are 9,5 µg/L (192.2217) and 5,9 µg/L (192.2171). A range of other pesticides are found in substantial concentrations, most notably benazolin at 48 µg/L.<br>The source is currently thought to be a combination of a DMS point source from the agricultural machinery rental and a more diffuse effect of DMS from the cultivation of strawberries. Investigation of the source site and the catchment area of the well field is in progress.<br>The samples were collected in collaboration with GEUS, The Geological Survey of Denmark and Greenland. The dating tracers $^3H/^3He$ will be analysed at the Helis lab. at University of Bremen, Germany, while $SF_6$ is analysed at Spurenstofflabor in Wachenheim, Germany. The tracer and age distribution will be simulated by a lumped parameter model (TracerLPM) developed by the USGS (Jurgens et al., 2012) and particle tracking. |

| Description of problem (why is this location chosen for a Case Study) |
|---|
| The abstraction wells are contaminated with the pesticide metabolite DMS in levels exceeding the national drinking water criterion as well as the groundwater criterion specified by the Danish EPA. This site is chosen because the pesticide levels are high, the site is quite well-studied and the geology is believed to be relevant to other sites nationally. |

| Methods used in the Case Study (analytical and isotope techniques, modelling) |
| --- |
| The case study includes the application of the groundwater age indicators $SF_6$ and $^3H/^3He$, the lumped parameter modelling tool "TracerLPM" (https://www.usgs.gov/software/tracerlpm) and particle tracking by numerical modelling. $^3H/^3He$ is analysed by the Helis lab. at University of Bremen https://www.noblegas.uni-bremen.de/eng/ . $SF_6$ is analysed by the Spurenstofflabor in Wachenheim (no web site). |

| Results from this Case Study |
| --- |
| The results from the laboratories will be received ultimo 2020 and primo 2021. |

| Impact - how this Case Study contributes to the overall project aims |
| --- |
| The case study investigates the groundwater age and travel time distributions of two long-screened abstraction wells in Northern Zealand, Denmark, 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.<br>The cited references and access information are listed at the end of the following information template. |

<table>
<tr><td>Name of pilot area / aquifers / type:<br>Marbæk – glacial deposits and limestone, confined and unconfined aquifer systems</td><td colspan="2">Country: Denmark<br><br>Region: The Capital Region of Denmark (Northern Zealand)</td></tr>
<tr><td>Study level</td><td colspan="2">Transboundary : ☐ Regional: ☐ Local: ☐ Single well(s): X</td></tr>
<tr><td>Type of observations<br>(choose one of the options, create separate template if needed for each type if each type need specific information)</td><td colspan="2">X Short screened observation wells (not pumped)<br>X Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping):</td></tr>
<tr><td>Approximate location of pilot:</td><td colspan="2"><br></td></tr>
<tr><td>Geological cross section / conceptual model of the pilot area:</td><td colspan="2"><br><br>Conceptual model of geology with sampled wells and regional groundwater flow.</td></tr>
</table>

| | | | | |
|---|---|---|---|---|
| **Name of Shape- / Geopackage file defining the area:** IOL_Marbaek_200aar.shp | **Projection to be used:** UTM32N (ETRS89) | | | |
| **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 | 240 | 10 | 0-1 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day): 100 – 200 $m^3$** | | **Typical pump discharge of complete well field ($m^3$/day): 450 $m^3$** |
| **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 Aquitard no. (aqt): 1 Aquiclude no. (aqc): 0** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqt-1: | Glacial clay till | Sandy, contains ochre and limestone | 0-10 | |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: X |
| Aqf-1: | Glacial meltwater sand overlain by clay till | Fine to medium sand, some gravel | 10-24 | < 5 – 100 ? |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-2: | Danien limestone | Limestone | 24 - ? | 25 - ? |
| **Porosity type** | Porous: ☐ | Fissured: X | Karst: (X) | Fissured and porous / dual porosity: (X) |
| **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) | | **Aquifer-1** $^3$H/$^3$He, $SF_6$ | | |
| | | **Aquifer-2** $^3$H/$^3$He, $SF_6$ | | |
| **Number of sites (wells/springs) with age indicators** | | **Aquifer-1** **1-5: X 5-10: ☐ 10-25: ☐ >25: ☐** | | |
| | | **Aquifer-2** **1-5: X 5-10: ☐ 10-25: ☐ >25: ☐** | | |

| | |
|---|---|
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and <10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-1**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br><br>**Aquifer-2**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: ☐ 10-25%: X 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates ☐**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates X**<br>**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** | **Indication of vulnerability of aquifers and water supply wells** |
|---|---|---|---|
| x | x | | |

| **Water Usage** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
|---|---|---|---|---|
| | x | | | |

| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
|---|---|---|---|---|---|
| | | | | | |

| **Mining activities** *(not relevant for observation wells)* | **Construction materials** | **Minerals / metals** | **Coal** | **Other** |
|---|---|---|---|---|
| | | | | |

| | |
|---|---|
| **References:**<br>**OPEN Access reports and papers:**<br>(PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches):<br><br>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. | **References:**<br>**Reports and papers with restricted access:** |

**Remarks / other relevant information:**
Groundwater age dating results are yet to be received.

## 3.12 Description of a glacial paleowater case study, Estonia

| | |
|---|---|
| Title of Case Study | Dating of Glacial Palaeogroundwater and its Implications on Groundwater Management in Estonia, North-Eastern Europe. |
| Location (region, Country) | north-eastern Europe, Estonia |
| Other information | |

| Description of Case Study (background information on the region) |
|---|
| Estonian territory is located in the northern part of the Baltic Artesian Basin (BAB), which is a groundwater reservoir in north-eastern Europe. Here, groundwater recharged prior to the beginning of the Holocene has been observed in various depths and locations. In northern Estonia, groundwater originating from subglacial recharge during the Pleistocene glaciations has been preserved in the deep sandstone aquifers of Cambrian-Vendian (Ediacaran) and Ordovician-Cambrian aquifers (Vaikmäe et al., 2001; Raidla et al., 2009, 2012; Pärn et al., 2016, 2019). Their presence is revealed mainly by very light isotopic composition ($\delta^{18}O$ values from −16‰ to −23‰) that differs markedly from values found in modern precipitation and shallow groundwater in the study area (about −10‰ to −12‰; Raidla et al., 2016). More recently this groundwater has also been dated using $^{3}H$, $^{14}C$, $^{85}Kr$, $^{81}Kr$, $^{40}Ar$ and radiogenic $^{4}He$ as tracers (Raidla et al., 2012; Gerber et al., 2017; Pärn et al., 2019). |

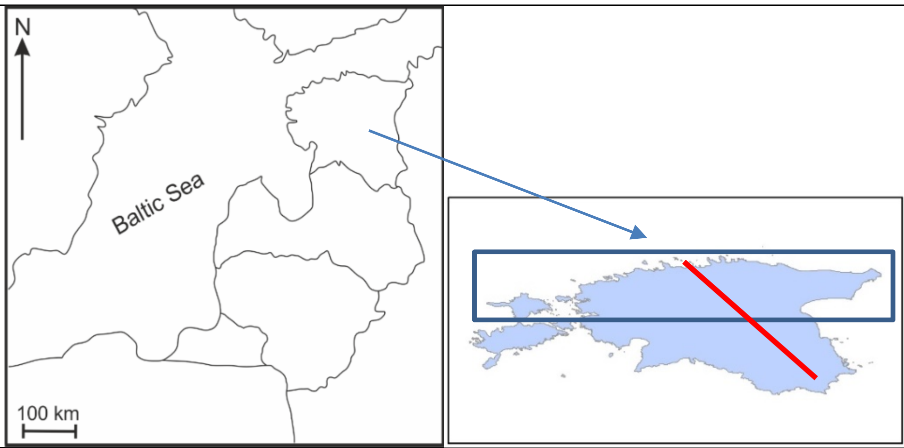
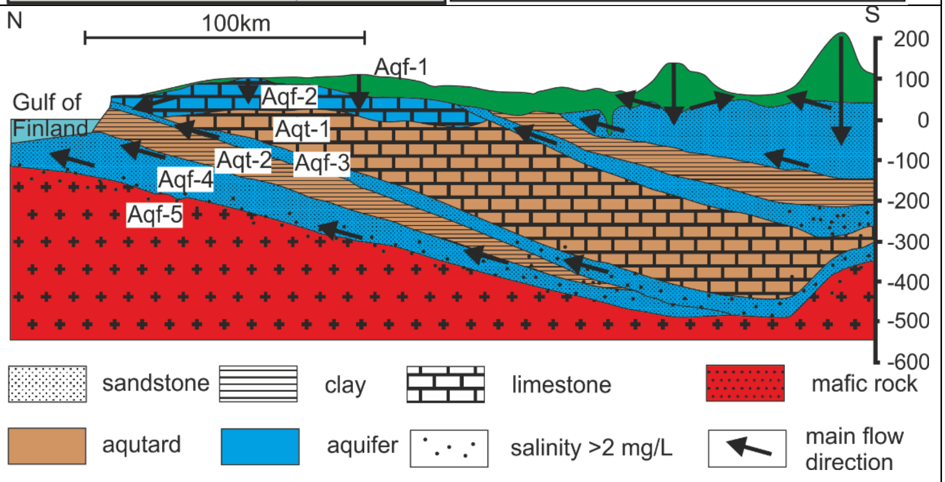
| Description of problem (why is this location chosen for a Cases Study) |
|---|
| Groundwater in the Cambrian-Vendian and Ordovician-Cambrian aquifer system is a unique groundwater resource in Europe, where a large portion of water originating from the Pleistocene Ice Sheets has been preserved. The first step towards a responsible and sustainable management of such a resource would be the determination of its origin, age and renewal rates. Groundwater is the most important source of public water supply in Estonia making up ~60% of all consumed water from public water supply networks. Understanding the processes influencing recharge and geochemical evolution of groundwater is crucial for predicting the effects of groundwater abstraction on its composition and availability. Also, glacial palaeogroundwater offers possibilities to study the multi-faceted nature of information about pre-Holocene environmental conditions recorded in palaeogroundwater reservoirs. More specifically, they provide an example on how groundwater can serve as an important paleoenvironmental archive enabling the study of variations in climatic and environmental conditions during glacial-interglacial cycles in the Pleistocene (Raidla et al., 2019). Finally, the study of palaeogroundwater occurrence enables one to establish the depth of the zone where active exchange with modern infiltration takes place and renewable groundwater is formed. A weak connection of glacial palaeogroundwater reservoirs with modern groundwater recharge and isolation from potential anthropogenic contamination makes it a high-quality resource, which should be treated as a strategic reserve and used for specific purposes (e.g. for potable water). |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| Glacial palaeogroundwater in Estonia has been studied using a multi-tracer approach involving the hydrochemical composition of groundwater, a suite of stable ($\delta^{2}H_{H2O}$, $\delta^{18}O_{H2O}$, $\delta^{13}C_{DIC}$, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, $\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$) and radioactive isotope tracers ($^{3}H$, $^{14}C$, $^{85}Kr$, $^{81}Kr$, $^{40}Ar$ and radiogenic $^{4}He$) and the study of dissolved gas compositions in groundwater ($CH_4$, $CO_2$, noble |

gases). In addition, the geochemical evolution and groundwater age has been studied with geochemical modelling using the software programs GWB, PHREEQC and NETPATH.

| Results from this Case Study |
|---|
| The spatial and vertical distribution of glacial palaeogroundwater in the northern part of the BAB is shown to be wider than previously thought (e.g. Pärn et al., 2016; Pärn, 2018). The corrected radiocarbon age of the Cambrian–Vendian groundwater suggests that infiltration occurred not earlier than 14,000–27,000 radiocarbon years ago, which is coeval with the advance and maximum extent of Scandinavian Ice Sheet during the LGM (Raidla et al., 2012). The dating of glacial palaeogroundwater in the O-Cm aquifer system allowed to identify groundwater originating from three different climatic periods: (1) the Holocene (0–10 ka BP); (2) the LGM (~10–22 ka BP) and (3) the pre-LGM period (>22 ka BP; Pärn et al., 2019). To the south the salinity and residence time of groundwater increases with brines found in the central parts of the BAB (Latvia and Lithuania) having ages >1.3 Ma years based on noble gas age tracers $^{81}Kr$, $^{4}He$ and $^{40}Ar$ (Gerber et al., 2017). Glacial palaeogroundwater in the northern BAB has gone through a significant geochemical evolution after its infiltration. Its chemical composition has been altered through the dissolution of carbonate minerals, cation exchange reactions, oxidation of organic matter and mixing with groundwater originating from modern precipitation, saline formation water and the Baltic Sea. These processes have sometimes led to an increase in concentrations of $F^-$, $NH_4^+$, $Ba^{2+}$, $^{226}Ra$ and $CH_4$ which can affect the drinking water quality, but overall the glacial palaeogroundwater complies well with the drinking water quality standards (Marandi, 2007; Suursoo et al., 2017; Pärn et al., 2018; Raidla et al., 2019a, b). The results also suggest that the zone where active exchange with modern infiltration takes place and renewable groundwater is formed, does not reach as deep as previously thought (down to 250 m), but glacial palaeogroundwater weakly connected to the modern hydrologic cycle can already be found locally at shallow depths of 50 m, b.g.s. Finally, the study of the isotopic composition of $CH_4$ suggests that during the advance of continental ice sheets in Pleistocene, large volumes of this organic matter accumulated beneath it. Subsequently, both the organic matter and its oxidation products were carried into the subsurface by infiltrating glacial meltwater (Raidla et al., 2019). |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| The results of the Case Study contribute to the enhancement of understanding of natural variability of groundwater quality and the risk of transfer of anthropogenic dissolved compounds to aquifers. More specifically the results contribute to quantifying groundwater age distributions and evaluating the efficiency of programme of measures, the design and assessment of monitoring programmes and the creation of EU-wide aquifer vulnerability maps. |

<table>
<tr><td>Name of pilot area / aquifers / type: North Estonia / Quaternary, Ordovician, Cambrian and Ediacaran sand- and limestone aquifers / dual porosity</td><td colspan="4">Country: Estonia<br><br>Region: North-Estonia</td></tr>
<tr><td>Study level</td><td>Transboundary : ☐</td><td>Regional: x</td><td>Local: ☐</td><td>Single well(s): ☐</td></tr>
<tr><td>Type of observations<br>(choose one of the options, create separate template if needed for each type if each type need specific information)</td><td colspan="4">☐ Short screened observation wells (not pumped)<br>☐ Long screened observation wells (not pumped)<br>x Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping):</td></tr>
<tr><td>Approximate location of pilot:</td><td colspan="4">
</td></tr>
<tr><td>Geological cross section / conceptual model of the pilot area:</td><td colspan="4">
</td></tr>
<tr><td>Name of Shape- / Geopackage file defining the area: Eesti_wgs84.shp</td><td colspan="4">Projection to be used:<br>WGS84 (Epsg4326)</td></tr>
</table>

| **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)** |
|---|---|---|---|---|
| | 600-800 | 30-270 | unknown | 0-30 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):** | | **Typical pump discharge of complete well field ($m^3$/day):** *If relevant* |
| **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): 5**<br>**Aquitard no. (aqt): 2**<br>**Aquiclude no. (aqc): 0** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: Q | Quaternary deposits | Fine sand to gravel | Mainly 0 – 50 (locally up to 100 m) | unknown |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-2: S-O | Silur-Ordovician | Limestones | 0 – 200 | unknown ($\delta^{18}O$=-11 to -16‰) |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: X |
| Aqt-1: O | | Clay, argillite | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: ☐ |
| Aqf-3: O-Cm | Ordovician-Cambrian | Sandstones | 0 – 250 | modern – >30,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt-2: Cm | | Clay | | |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: X |
| Aqf-4: Cm-V | Cambrian-Vendian | Sandstone | 60 – 300 | 14,000 – at least 180,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-5: $PR_2$ | Crystalline | Mafic rocks | unknown | unknown |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: ☐ | Fissured and porous / |

| | |
|---|---|
| | dual porosity: X |
| **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.)<br>**Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | **Aquifer-1**<br>$^{18}O$, D<br>**Aquifer-2**<br>$^{14}C$, $^{18}O$, D<br>**Aquifer-3**<br>$^{3}H$, $^{3}H/^{3}He$, $^{14}C$, $^{4}He$, $^{18}O$, D noble gases<br>**Aquifer-4**<br>$^{14}C$, $^{18}O$, D noble gases<br>**Aquifer-5**<br>$^{14}C$, $^{18}O$, D |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-1**<br>**1-5:** □ **5-10:** X **10-25:** □ **>25:** □<br>**Aquifer-2**<br>**1-5:** □ **5-10:** □ **10-25:** □ **>25:** X<br>**Aquifer-3**<br>**1-5:** □ **5-10:** □ **10-25:** □ **>25:** X<br>**Aquifer-4**<br>**1-5:** □ **5-10:** □ **10-25:** □ **>25:** X<br>**Aquifer-5**<br>**1-5:** X **5-10:** □ **10-25:** □ **>25:** □ |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-1**<br>**GAR-1: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** X<br>**GAR-2: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** □<br>**GAR-3: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** □<br>**Aquifer-2**<br>**GAR-1: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** X<br>**GAR-2: 1-10%:** □ **10-25%:** □ **25-50%:** X **>50%:** □<br>**GAR-3: 1-10%:** X **10-25%:** □ **25-50%:** □ **>50%:** □<br>**Aquifer-3**<br>**GAR-1: 1-10%:** X **10-25%:** □ **25-50%:** □ **>50%:** □<br>**GAR-2: 1-10%:** □ **10-25%:** □ **25-50%:** X **>50%:** □<br>**GAR-3: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** X<br>**Aquifer-4**<br>**GAR-1: 1-10%:** X **10-25%:** □ **25-50%:** □ **>50%:** □<br>**GAR-2: 1-10%:** □ **10-25%:** X **25-50%:** □ **>50%:** □<br>**GAR-3: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** X<br>**Aquifer-5**<br>**GAR-1: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** □<br>**GAR-2: 1-10%:** □ **10-25%:** □ **25-50%:** X **>50%:** □<br>**GAR-3: 1-10%:** □ **10-25%:** □ **25-50%:** □ **>50%:** X |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates** X<br>**Flow and age model simulations** X<br>**Combination of model and tracer estimates** X<br>**Expert judgement:** X |

| **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** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
|---|---|---|---|---|
| | x | x | x | |

| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
|---|---|---|---|---|---|
| | x | | | | |

| **Mining activities** *(not relevant for observation wells)* | **Construction materials** | **Minerals / metals** | **Coal** | **Other** |
|---|---|---|---|---|
| | x | | x | |

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


Marandi, A., 2007. Natural Chemical Composition of Groundwater as a Basis for Groundwater Management in the Cambrian-Vendian Aquifer System in Estonia. Dissertationes Geologicae Universitatis Tartuensis 21. Tartu: Tartu University Press. https://dspace.ut.ee/handle/10062/3460

Raidla, V., Pärn, J., Aeschbach, W., Czuppon, G., Ivask, J., Kiisk, M., Mokrik, R., Samalavičius, V., Suursoo, S., Tarros, S., Weissbach, T., 2019. Intrusion of Saline Water into a Coastal Aquifer Containing Palaeogroundwater in the Viimsi Peninsula in Estonia. Geosciences 9, 47. https://www.mdpi.com/2076-3263/9/1/47

Pärn J. (2018). Origin and Geochemical Evolution of Palaeogroundwater in the Northern Part of the Baltic Artesian Basin. Tallinn University of Technology. Doctoral thesis. p. 226. https://digi.lib.ttu.ee/i/?10917

Vaikmäe, R., Martma, T., Ivask, J., Kaup, E., Raidla, V., Rajamäe, R., Vallner, L., Mokrik, R., Samalavičius, V., Kalvāns, A., Babre, A., Marandi, A., Hints, O., Pärn, J. 2020. Baltic


Reports and papers with restricted access


Gerber, C., Vaikmäe, R., Aeschbach, W., Babre, A., Jiang, W., Leuenberger, M., Lu, Z.T., Mokrik, R., Müller, P., Raidla, V., Saks, T., Waber, H.N., Weissbach, T., Zappala, J.C., Purtschert, R. (2017). Using $^{81}Kr$ and noble gases to characterize and date groundwater and brines in the Baltic Artesian Basin on the one-million-year timescale. Geochim. Cosmochim. Acta, 205, 187–210. https://doi.org/10.1016/j.gca.2017.01.033

Pärn, J., Raidla, V., Vaikmäe, R., Martma, T., Ivask, J., Mokrik, R., Erg, K., 2016. The recharge of glacial meltwater and its influence on the geochemical evolution of groundwater in the Ordovician-Cambrian aquifer system, northern part of the Baltic Artesian Basin. Appl. Geochem. 72, 125–135. https://doi.org/10.1016/j.apgeochem.2016.07.007.

Pärn, J., Walraevens, K., van Camp, M., Raidla, V., Aeschbach, W., Friedrich, R., et al. 2019. Dating of glacial palaeogroundwater in theOrdovician-Cambrian aquifer system, northern Baltic Artesian Basin.Applied Geochemistry, 102, 64–76. https://doi.org/10.1016/j.apgeochem.2019.01.004

Raidla, V., Kirsimäe, K., Vaikmäe, R., Jõeleht, A., Karro, E., Marandi, A., Savitskaja, L., 2009. Geochemical evolution of groundwater in the Cambrian-Vendian aquifer system of the Baltic Basin. Chemical Geology 258, 219-231. https://doi:10.1016/j.chemgeo.2008.10.007

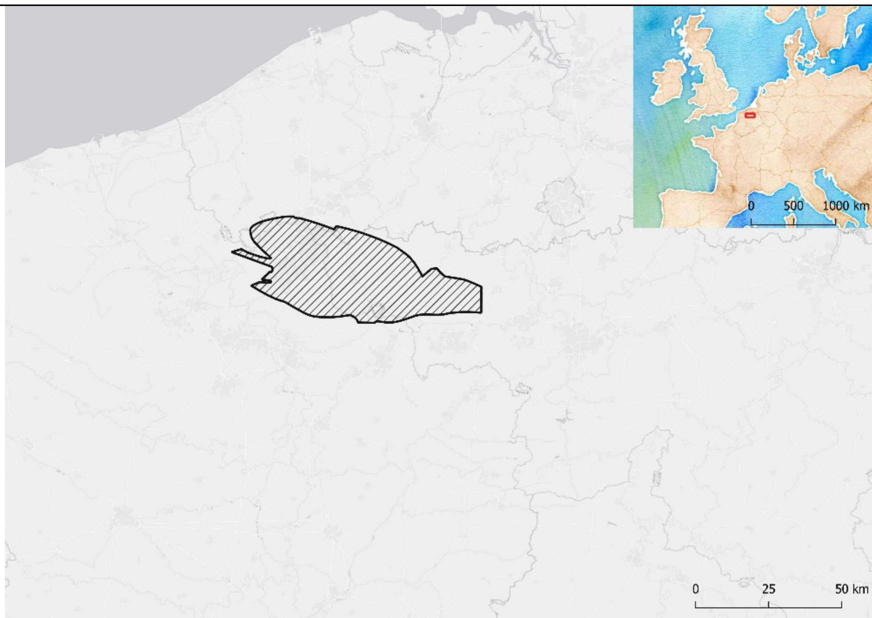
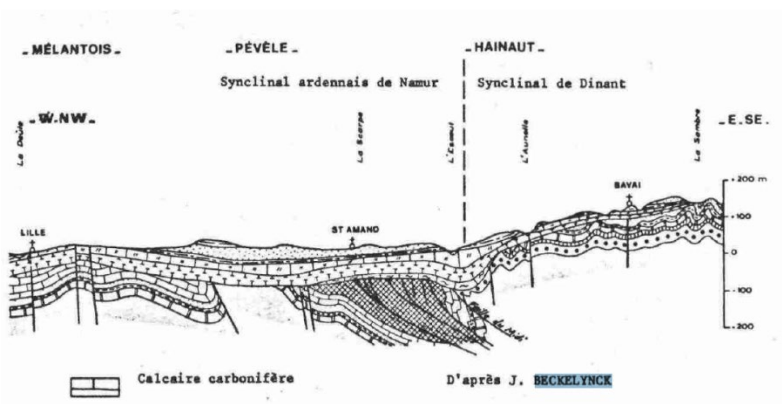
Raidla V., Kirsimäe K., Vaikmäe R., Kaup E., Martma T., 2012. Carbon isotope systematics of the Cambrian-Vendian aquifer system in the northern Baltic Basin: implications to the age and evolution of groundwater. Appl. Geochem. 27, 2042–2052. https://doi.org/10.1016/j.apgeochem.2012.06.005.

Raidla, V., Kern, Z., Pärn, J., Babre, A., Erg, K., Ivask, J., et al., 2016. A$\delta^{18}O$ isoscape for the shallow groundwater in the Baltic ArtesianBasin.Journal of Hydrology, 542, 254–267.

| | |
|---|---|
| groundwater isotope-geochemistry database. Department of Geology, Tallinn University of Technology. https://doi.org/10.15152/GEO.488. | https://doi.org/10.1016/j.jhydrol.2016.09.004<br>Raidla, V., Pärn, J., Schloemer, S., Aeschbach, V., Czuppon, G., Ivask, J., Marandi, A., Sepp, H., Vaikmäe, R., Kirsimäe, K. (2019). Origin and formation of methane in groundwater of glacial origin from the Cambrian-Vendian aquifer system in Estonia. Geochimica et Cosmochimica Acta, 251, 247−264.<br>10.1016/j.gca.2019.02.029<br>Vaikmäe, R., Vallner, L., Loosli, H.H., Blaser, P.C., Juillard-Tardent, M., 2001. Palaeogroundwater of glacial origin in the Cambrian–Vendian aquifer of northern Estonia. In: Edmunds, W.M., Milne, C.J. (Eds.), Palaeowaters of Coastal Europe: Evolution of Groundwater since the late Pleistocene. Geological Society, London, Special Publications, vol. 189, pp. 17–27. |

**Remarks / other relevant information:** The serious consequence of intensive groundwater use in Soviet era (1950 to 1990) include the formation of regional depressions of potentiometric level, which has caused cardinal changes in the direction and velocity of filtration flows in the lower aquifers (O-Cm and Cm-V). Nowadays use of groundwater could be little or missing in these urban (eg Tallinn) or former industrial areas, but the groundwater potentiometric level is still more than 10 m lower than the natural potentiometric level. Lateral flows conduce the transport of brackish water from the deeper Crystalline aquifer. Seawater intrusion into the groundwater intakes has not noted yet. In this light, the pumping rate of individual well ($m^3$/day) doesn't reflect the real situation and we don't give any number because they can be very misleading.

## 3.13 Description of the Nord-Pas-De-Calais French-Belgian transboundary aquifer case study

| | |
|---|---|
| **Name of pilot area / aquifers / type:** Carboniferous/ Early Carboniferous Limestones and dolomite/ porous and karstified | **Country:** FRANCE/BELGIUM<br><br>**Region:** Nord-Pas-De-Calais (Northern part of France) (FR-BE border aquifers) |
| **Study level** | Transboundary : x 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)<br>☐ Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot:** |  |
| **Geological cross section / conceptual model of the pilot area:** |  |

| | | | | |
|---|---|---|---|---|
| **Name of Shape- / Geopackage file defining the area:** carboniferous_limestones_surface_extent.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)** | **Mean annual groundwater recharge temperature (°C)** | **Thickness of unsaturated zone (range in m)** |
| | 600 | 200 | | |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well (m³/day):** | | **Typical pump discharge of complete well field (m³/day):** *16.10⁶ m3/year = 43800 m3/day* |
| **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):5 Aquitard no. (aqt): 4 Aquiclude no. (aqc): -** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Quaternary alluvial deposits + Miocene sands | Sand, gravel, pebbles + sands | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt-1: | Upper Eocene clay | Clay | | |
| Aqf-2: | Eocene aquifer | sand | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt-2: | Ypresian | Sandy clay | | |
| Aqf-3 | Thanetian aquifer | Sand and gravel | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt 3 | Gault Clay | clay | | |
| Aqf-4 | Upper cretaceous | Chalk | | |
| **Porosity type** | Porous: X | Fissured: X | Karst: ☐ | Fissured and porous / dual porosity: X |
| Aqt-5 | Low cretaceous clay | | | |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: X | Fissured and porous / |

| | | | | |
|---|---|---|---|---|
| | | | | dual porosity: ☐ |

| | |
|---|---|
| **Applied tracer age indicators** ($^3H$, $^3H/^3He$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $^{36}Cl$, $^{81}Kr$, $^4He$, CFCs, $SF_6$, etc.)<br>**Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | **Aquifer-1**<br>– |
| | **Aquifer-2**<br>– |
| | **Aquifer-3**<br>– |
| | **Aquifer-4**<br>$^{34}S/^{32}S$, $^{18}O/^{16}O$ on sulphates, $^3H$, $^{13}C$, $^{14}C$, $^{18}O$, D, CFC's (11,12,113), SF6 |
| | **Aquifer-5**<br>$^{34}S/^{32}S$, $^{18}O/^{16}O$ on sulphates, $^3H$, $^{13}C$, $^{14}C$, $^{18}O$, D, CFC's (11,12,113), SF6 |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-1**<br>**1-5: ☐ 5-10: ☐ 10-25: ☐ >25: ☐** |
| | **Aquifer-2**<br>**1-5: ☐ 5-10: ☐ 10-25: ☐ >25: ☐** |
| | **Aquifer-3**<br>**1-5: ☐ 5-10: ☐ 10-25: ☐ >25: ☐** |
| | **Aquifer-4**<br>**1-5: X 5-10: ☐ 10-25: ☐ >25: ☐** |
| | **Aquifer-5**<br>**1-5: ☐ 5-10: ☐ 10-25: X >25: ☐** |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-1**<br>– |
| | **Aquifer-2**<br>– |
| | **Aquifer-3**<br>– |
| | **Aquifer-4**<br>**GAR-1: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| | **Aquifer-5**<br>**GAR-1: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates X**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates ☐**<br>**Expert judgement: ☐** |

<table>
<tr><td colspan="7">Objective of age dating studies:</td></tr>
<tr><td>Basic research or General groundwater management</td><td colspan="2">Assessment of pollutant history</td><td colspan="2">Assessment of the efficiency of remediation and mitigation measures</td><td colspan="2">Indication of vulnerability of aquifers and water supply wells</td></tr>
<tr><td>x</td><td colspan="2"></td><td colspan="2"></td><td colspan="2">X</td></tr>
<tr><td rowspan="2">Water Usage<br>(not relevant for observation wells)</td><td colspan="2">Water supply</td><td>Irrigation</td><td>Industry</td><td colspan="2">Other</td></tr>
<tr><td colspan="2">x</td><td>x</td><td>x</td><td colspan="2"></td></tr>
<tr><td rowspan="2">Geoenergy related activities<br>(not relevant for observation wells)</td><td>Shallow Geo-T</td><td>Deep Geo-T</td><td colspan="2">Hydrocarbons</td><td>Nuclear waste disp.</td><td>$CO_2$ storage</td></tr>
<tr><td>x</td><td></td><td colspan="2"></td><td></td><td></td></tr>
<tr><td rowspan="2">Mining activities<br>(not relevant for observation wells)</td><td colspan="2">Construction materials</td><td>Minerals / metals</td><td>Coal</td><td colspan="2">Other</td></tr>
<tr><td colspan="2"></td><td></td><td></td><td colspan="2"></td></tr>
<tr><td colspan="7">REFERENCES</td></tr>
<tr><td colspan="3">OPEN Access reports and papers (PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches):<br><br>https://www.sciencedirect.com/science/article/pii/S1878522013001215</td><td colspan="4">Reports and papers with restricted access:</td></tr>
<tr><td colspan="7">Remarks / other relevant information:</td></tr>
</table>

## 3.14 Description of the Great Hungarian Plain case study, Hungary

| | |
|---|---|
| Title of Case Study | Great Hungarian Plain |
| Location (region, Country) | Great Hungarian Plain, Hungary |
| Other information | The data and results of this study form part of a general national hydrogeochemical project of the Mining and Geological Survey of Hungary, where hydrogeological-hydrogeochemical characterization of aquifers is supported by multiple isotope and noble gas surveys. |

| Description of Case Study (background information on the region) |
|---|
| The Great Hungarian Plain (GHP) located East of the Danube River, in the Eastern – South-Eastern part of Hungary is the largest sub-basin of the Pannonian Basin, covering about 52,000 $km^2$, and has been extensively studied. This sub-basin developed in the Early-Middle Miocene as a result of a back-arc style extension (Horváth and Royden, 1981; Fodor et al., 2002) and is up to about 7000 meters thick, averaging 2-3000 m. The basin is built up of Upper Miocene sediment successions which form large, regional aquifers. The Nagyalföld and Zagyva Formations (referred as Aquifer 3 in the GHP pilot template) form the upper part of the aquifer, while below them the Újfalu Formation (referred as Aquifer 4) represents the bottom of the lower regional flow system. While the upper part is mainly used in the drinking water supply, the lower part is the main thermal water aquifer. Quaternary sediments, above the Miocene sediment sequence, with various thicknesses form the main drinking water aquifer (Aquifer 2) which is characterised by a large regional flow system. The uppermost, near surface Quaternary sediments host local flow systems (Aquifer 1).<br>Large scale hydrogeological studies have been carried out since the first part of the 20th century, eg. Erdélyi (1975), however, Stute and Deák (1989) performed the first integrated evaluation applying environmental isotopes, noble gases and hydraulics to regional flow systems. Detailed studies for example by Varsányi et al. (2009, 2011) and Szocs et al. (2015, 2017) have been carried out on the different parts of the GHP. |

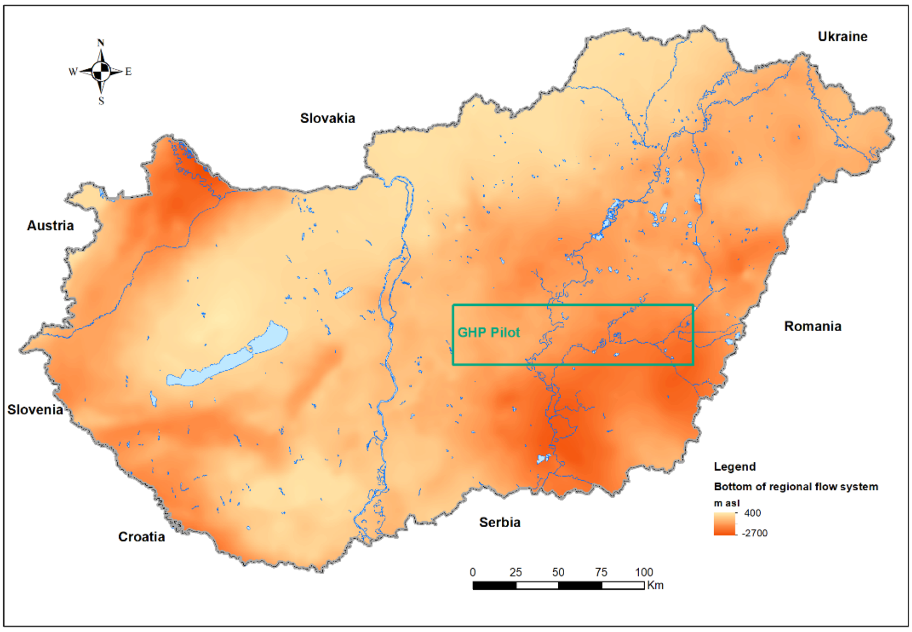
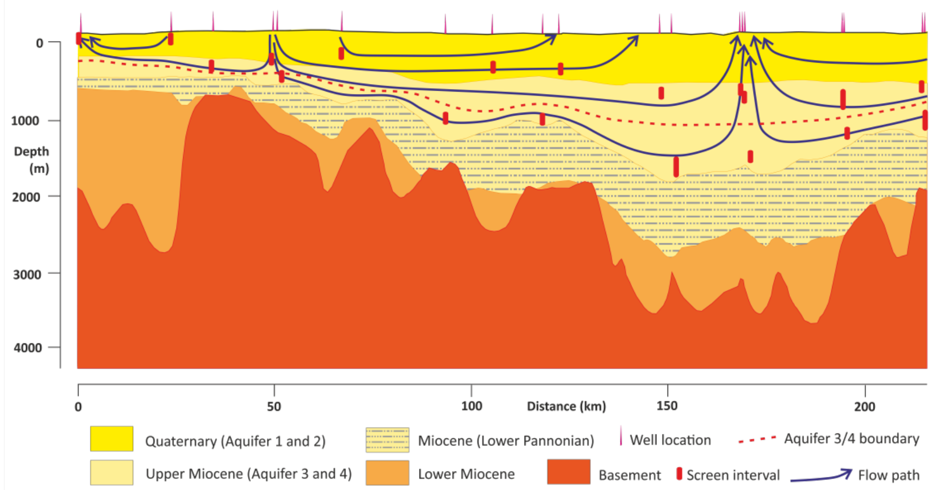
| Description of problem (why is this location chosen for a Cases Study) |
|---|
| The GHP is an important groundwater reservoir. Its aquifers are used from the near surface for domestic or agricultural use to drinking water and industrial supply in the deeper horizons, while the thermal properties of its deep regional aquifer are used amongst other things in balneology, in green houses or for district heating. Several aquifers are transboundary, with recharge areas outside of Hungary. In some regions oil and gas reservoirs can be found at the same depths as the thermal aquifer. These groundwater abstractions, done for different purposes can affect each other's long term abstraction, both related to groundwater pressure and chemistry. As reinjection is not compulsory, pressure drop is already a problem in some areas, and reinjecting in shallower aquifer horizons can cause chemical pollution. While drinking water protection areas and protection zones are defined, as well as geothermal protection zones below 2500 meters, in other cases protection zones are not required by law. As there is an ongoing economic development in Central Europe, with a pronounced agricultural sector development in Hungary and renewable energy share increase, it is important to be able to provide sound information, supported by scientific data to decision makers and potential investors. Hydrogeochemical and isotope data provide independent parameters for numerical modelling and can help to better evaluate the mean residence time |

in the different aquifers and their potential vulnerability to pollution. As the GHP is expected to be negatively affected by climate change, an increase in the use of groundwater instead of surface can also be expected.

| Methods used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| The GHP case study includes the application of groundwater age indicators $\delta^{18}O$-$\delta D$, $^{14}C$-$\delta^{13}C$ and limited $^{87}Sr/^{86}Sr$, chlorine stable isotope and helium isotope data in addition to the previously applied chemical data. $\delta^{18}O$ and $\delta D$ were determined using a GasBench-II preparation system and a Thermo Finnigan delta plus XP spectrometer (Institute for Geochemical Research of the Hungarian Academy of Sciences). $^{14}C$ measurements were carried out from the DIC content of groundwater precipitated with barium-chloride during sampling after adding saturated NaOH to ensure a pH above 11. The $CO_2$ gas from the $BaCO_3$ was converted to lithium carbide, then to acetylene which was then cyclotrimerised to benzene. The radiocarbon activity of benzene was counted by ultra-low level liquid scintillation analyser (PerkinElmer Quantulus 1220; Hydrosys Laboratory Ltd). Stable carbon isotope ratios were determined by conventional stable isotope ratio mass spectrometry using a Thermo Finnigan delta plus XP. Water samples for noble gas analyses were collected in copper tubes and measured by a VG5400 noble gas mass spectrometer. Carbon-13 and noble gases were analysed in the Hertelendi Laboratory of Environmental Studies in the Institute of Nuclear Research of the Hungarian Academy of Sciences. Strontium and chlorine stable isotopes were measured by the University of Waterloo. |

| Results from this Case Study |
|---|
| Results show groundwater is of meteoric origin even in the deep regional flow systems, with isotopic signatures indicative of the hydrocarbon producing units in the deeper part of the GHP. Based on the carbon isotopes, the groundwater residence times vary from a few thousand to tens of thousands of years. The aquifer is recharged, and abstractions are feasible based on careful studies and where needed, in combination with reinjection.<br>Based on the $^{3}He/^{4}He$ ratios, not only crustal, but also mantle helium origin were detected not just in the deeper aquifer, but even in the Quaternary sediments. Strontium isotope ratios show enrichment where higher bicarbonate values indicate carbonate dissolution in the Upper Miocene aquifers. Depletion of the heavier $^{37}Cl$ isotope could be observed along the flow paths. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| This case study contributes to the establishment of a harmonized database on groundwater age indicators with data on paleo waters. It helps to define residence time categories for large basins and regional groundwater flow systems. It can contribute to the objectives of the GeoERA RESOURCE project for the characterization of important aquifer types and to produce a map of the fresh groundwater resources of Europe. It shows that isotope hydrogeology can be a useful tool to help subsurface management and quality assessment. |

<table>
<tr><td>Name of pilot area / aquifers / type:<br>Great Hungarian Plain / Quaternary and upper Miocene sedimentary aquifers / porous</td><td colspan="4">Country: Hungary<br><br>Region: Great Hungarian Plain</td></tr>
<tr><td>Study level</td><td>Transboundary : ☐</td><td>Regional: X</td><td>Local: ☐</td><td>Single well(s): ☐</td></tr>
<tr><td>Type of observations<br>(choose one of the options, create separate template if needed for each type if each type need specific information)</td><td colspan="4">☐ Short screened observation wells (not pumped)<br>☐ Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping):</td></tr>
<tr><td>Approximate location of pilot:</td><td colspan="4">
</td></tr>
<tr><td>Geological cross section / conceptual model of the pilot area:</td><td colspan="4">
</td></tr>
</table>

| Name of Shape- / Geopackage file defining the area: HOVER_WP6_HU_GHP_polygon_ETRS.shp | **Projection to be used:** ETRS 1989 LEAE | | | |
|---|---|---|---|---|
| **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)** |
| | 500-550 | 15-30 mm/year | 10.5 | 1 –-3.8 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well (m³/day):** NA | | **Typical pump discharge of complete well field (m³/day):** – *If relevant* |
| **List of aquifers and aquitards in pilot area** | | **No. of confined or semiconfined aquifers in pilot area: 3** | | **No. of unconfined aquifers in pilot area: 1** |
| **Aquifer no. (aqf): 4**<br>**Aquitard no. (aqt): 0**<br>**Aquiclude no. (aqc): 1** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Quaternary fluvial-limnic alternating sedimentary sequence, locally aeolean | alternation of unconsolidated sedimentary hydrogeofacies/ Loess | 1 – 55<br>(thickness 34–51) | No data |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-2: | Quaternary fluvial-limnic alternating sedimentary sequence | alternation of unconsolidated sedimentary hydrogeofacies | cold:<br>35 – 550<br>(thickness 85–515)<br>thermal:<br>550 – 695<br>(thickness 0–142) | 5,000 – >10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-3: | Pliocene - upper Miocene fluvial-limnic alternating sedimentary sequence | alternation of unconsolidated sedimentary hydrogeofacies | 125 – 695<br>(thickness 0–350) | >10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-4: | upper Miocene deltafront and deltaplain sediments | Sandstone | 385 – 2370<br>(thickness 0–1960) | >10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |

| | | | | |
|---|---|---|---|---|
| Aqc-1: | upper Miocene basin fill | Siltstone, marlstone | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: ☐ |

| | |
|---|---|
| **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.)<br>**Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | **Aquifer-2**<br>$^{3}H$, $^{3}H/^{3}He$, $^{14}C$-$^{13}C$, $^{4}He$, $^{18}O$, D, noble gases |
| | **Aquifer-3**<br>$^{3}H$, $^{3}H/^{3}He$, $^{14}C$-$^{13}C$ $^{4}He$, $^{18}O$, D, noble gases |
| | **Aquifer-4**<br>$^{3}H$, $^{3}H/^{3}He$, $^{14}C$-$^{13}C$, $^{4}He$, $^{18}O$, D, noble gases |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-2**<br>**1-5: ☐ 5-10: ☐ 10-25: X >25: ☐** |
| | **Aquifer-3**<br>**1-5: ☐ 5-10: X 10-25: ☐ >25: ☐** |
| | **Aquifer-4**<br>**1-5: ☐ 5-10: ☐ 10-25: X >25: ☐** |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-2**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X** |
| | **Aquifer-3**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X** |
| | **Aquifer-4**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X** |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates X**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates ☐**<br>**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** | **Indication of vulnerability of aquifers and water supply wells** |
| **X** | | | |

| | | | | |
|---|---|---|---|---|
| **Water Usage**<br>*(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
| | X | | X | **Balneology** |

| | | | | | |
|---|---|---|---|---|---|
| **Geoenergy related activities**<br>*(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
| | | **X** | | | |

| **Mining activities**<br>*(not relevant for observation wells)* | **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):<br>Szocs, T., Frape, S., Gwynne, R. Integrating hydrogeochemical and isotope data in studying regional groundwater flow systems in the Great Hungarian Plain. Procedia Earth and Planetary Science 2015; 13, 177–180. DOI: 10.1016/j.proeps.2015.07.041<br>Szocs, T., Frape, S., Gwynne, R., Palcsu, L. Chlorine stable isotope and helium isotope studies contributing to the understanding of the hydrogeochemical characteristics of old groundwater. Procedia Earth and Planetary Science 2017; 17, 877-880 DOI information: 10.1016/j.proeps.2017.01.004 | **Reports and papers with restricted access:** |
| **Remarks / other relevant information:** | |

## 3.15 Description of the Mura-Zala transboundary aquifer case study, Hungary-Slovenia

| | |
|---|---|
| Title of Case Study | Hungarian-Slovenian Transboundary Thermal Aquifer |
| Location (region, Country) | Mura-Zala basin, Hungary, Slovenia |
| Other information | This study was carried out within the framework of the T-JAM project (Thermal Joint Aquifer Management: Screening of geothermal utilization, evaluation of thermal groundwater bodies and preparation of joint aquifer management plan in the Mura-Zala basin) between 2009 and 2011 as part of the Slovenia-Hungary Operational Programme 2007-2013, and was co-financed by ERFA. It was performed by the geological surveys of Hungary and Slovenia. A monitoring and management plan was developed in cooperation with the West-Transdanubian Water Directorate of Hungary. |

| Description of Case Study (background information on the region) |
|---|
| The Mura-Zala basin mainly covers NE Slovenia and SW Hungary, with minor parts in Croatia and Austria. It is located in the southwestern part of the Pannonian basin and is one of the deepest Pannonian sub-basins. Its thickness varies between 4,000-6,000 m in the deepest parts with 2,500-3,000 m thick Pannonian (Miocene) sediments. The thermal groundwater flow direction is from Slovenia to Hungary. Although the existence of transboundary geothermal aquifers was “common knowledge”, little bilateral scientific hydrogeological cooperation was established before 2009.<br><br>The shallow groundwater flow system is in unconfined Quaternary aquifers (referred to as Aquifer 1), while the confined part of the Quaternary is referred to as Aquifer 2. The underlying Pliocene delta- and alluvial plain aquifers (Ptuj-Grad Formation in Slovenia, Zagyva and Somló-Tihany Formations in Hungary; Aquifer 3) are part of the intermediate flow system and contain thermal water in their deeper parts. The deep regional thermal groundwater flow system is developed in the Mura/Újfalu aquifers (Aquifer 4). |

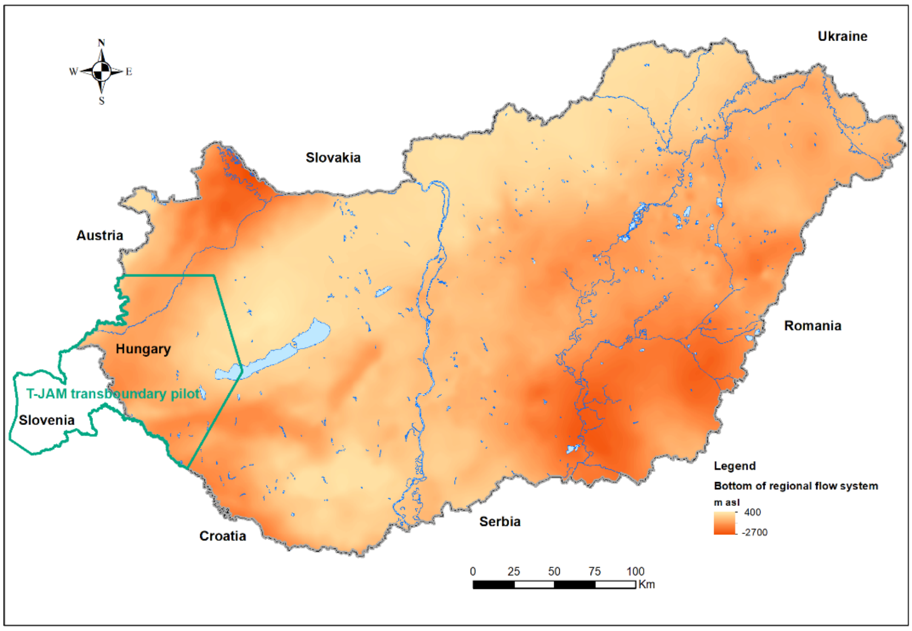
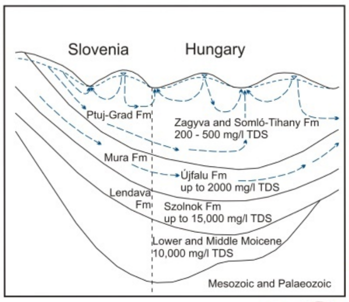
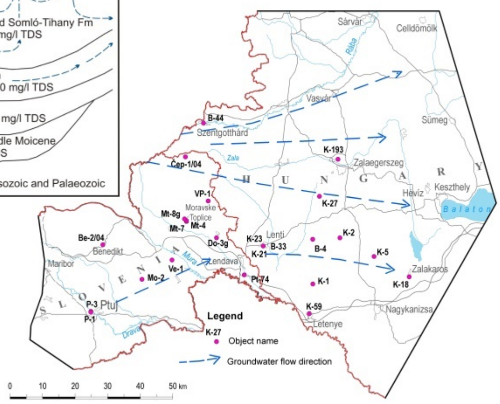
| Description of problem (why is this location chosen for a Cases Study) |
|---|
| The foreseen socio-economic development of the transboundary Mura – Zala region predicted a large increase in thermal water demand (Rman et al., 2011; Rman and Fuks, 2012) in line with the renewable energy goals set out in the Directive of the European Commission on the promotion of the use of energy from renewable sources (2009/28/EC). This had to be done by respecting the environmental objectives and the goals of the Water Framework Directive.<br><br>Although a successful transboundary surface water management scheme has been in operation between Hungary and Slovenia for several decades, the Slovenian-Hungarian Water Management Commission started discussions about transboundary groundwater resources only in 2011. The aims of this study were to understand and identify the groundwater flow paths, and to delineate transboundary aquifers based on thermal and cold groundwater geochemical and isotope properties in the Mura-Zala basin. The results were presented to the |

| |
|---|
| Permanent Bilateral Slovenian-Hungarian Water Management Commission and the transboundary thermal aquifer delineated in the study was proposed to be acknowledged by the ICPDR as a Danube basin level important transboundary groundwater body. It has to be mentioned, that the transboundary groundwater bodies between Slovenia and Hungary are not yet officially delineated, and there is no common management of thermal groundwater. |

| Methods used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| $\delta^{18}O$ and $\delta D$ were determined using a GasBench-II preparation system and a Thermo Finnigan delta plus XP spectrometer (Institute for Geochemical Research of the Hungarian Academy of Sciences). $^{14}C$ measurements were carried out from the DIC content of groundwater precipitated with barium-chloride in the field during sampling after adding saturated NaOH. The radiocarbon activity of benzene was counted by ultra-low level liquid scintillation analyser (PerkinElmer Quantulus 1220; Hydrosys Lab. Ltd). Stable carbon isotope ratios were determined by conventional stable isotope ratio mass spectrometry (Thermo Finnigan delta plus XP). Water samples for noble gas analyses were collected in copper tubes and measured by a VG5400 noble gas mass spectrometer. Carbon-13 and noble gases were analysed in the Hertelendi Laboratory of Environmental Studies in the Institute of Nuclear Research of the Hungarian Academy of Sciences Strontium and chlorine stable isotopes were measured by the University of Waterloo. A 3D steady-state hydrogeological numerical modelling was performed in VisualModflow with a grid size of 500 × 500 m and a vertical extension of 2 km. |

| Results from this Case Study |
|---|
| The hydrogeochemical-isotope survey (Rman et al., 2011d; Szőcs et al., 2012) contributed to the characterization of different transboundary aquifers. Most of the $\delta D$ and $\delta^{18}O$ data of the groundwater from the Mura/Újfalu aquifers are positioned on the meteoric water line, showing precipitation origin. The $^{14}C$ values indicate older than 20,000 years residence times. The $\delta^{18}O$ and $\delta D$ values are more positive than the "typical ice-age" groundwater values which suggests a recharge during a warmer period of the Pleistocene. Based on the numerically modelled travel times of water particles, the majority of thermal groundwater in the Mura/Újfalu aquifer might have been recharged into the flow-system before the last ice age, most probably in the Riss-Würm interglacial period (between 93,000-132,000 years BP). Based on this case study the thermal groundwater of the Mura/Újfalu aquifer could be clearly distinguished from the deeper groundwaters which show no (or only limited) connection to the regional thermal groundwater flow system. Based on the scientific results a transboundary thermal groundwater body was outlined and a guide to its sustainable use was prepared. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| This case study contributes to the establishment of a harmonized database on groundwater age indicators with data on paleo waters. It is a good example how harmonized, common data interpretation and numerical modelling of two geological surveys could confirm the existence of a transboundary aquifer. The study helps to define residence time categories for large basins and regional groundwater flow systems. |

| | |
|---|---|
| **Name of pilot area / aquifers / type:** T-JAM transboundary pilot/ Quaternary and upper Miocene sedimentary aquifers / porous | **Country:** Hungary, Slovenia<br>**Region:** Zala-Mura Basin |
| **Study level** | Transboundary : X    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)<br>☐ Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>X Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot:** | <br> |
| **Geological cross section / conceptual model of the pilot area:** | <br><br><br><br>Szocs et al., 2013. |

| | | | | |
|---|---|---|---|---|
| **Name of Shape- / Geopackage file defining the area:** | | **Projection to be used:**<br>ETRS 1989 LEAE | | |
| **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)** |
| | 750-900 | 40-90 | 11 | 1-80 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):**<br>6 – 115 (4-80 l/min) at sampling | | **Typical pump discharge of complete well field ($m^3$/day):**<br>*Not relevant* |
| **List of aquifers and aquitards in pilot area** | | **No. of confined or semiconfined aquifers in pilot area: 3** | | **No. of unconfined aquifers in pilot area: 1** |
| **Aquifer no. (aqf): 4**<br>**Aquitard no. (aqt): 0**<br>**Aquiclude no. (aqc):1** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Quaternary fluvial-limnic alternating sedimentary sequence locally aeolean | alternation of unconsolidated sedimentary hydrogeofacies/ Loess | 1 – 160<br>(thickness 15–135) | >60 – 1,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-2: | Quaternary fluvial-limnic alternating sedimentary sequence | alternation of unconsolidated sedimentary hydrogeofacies | 35 – 260<br>(thickness 85–100) | > 10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-3: | Pliocene - upper Miocene fluvial-limnic alternating sedimentary sequence | alternation of unconsolidated sedimentary hydrogeofacies | 125 – 1080<br>(thickness 30–950) | > 10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-4: | upper Miocene deltafront and deltaplain sediment sequence | Sandstone | 200 – 1550<br>(thickness 0-1046) | > 10,000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |

| | | | | |
|---|---|---|---|---|
| Aqc-1: | upper Miocene basin fill | Siltstone, marlstone | | |
| **Porosity type** | Porous: X | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: ☐ |
| **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.)<br>**Applied recharge temperature indicators** ($^{18}$O, D, noble gases) | **Aquifer-1**<br>$^{3}$H, $^{14}$C-δ$^{13}$C, δ$^{18}$O, δD, noble gases<br>**Aquifer-2**<br>$^{14}$C-δ$^{13}$C, δ$^{18}$O, δD, noble gases<br>**Aquifer-3**<br>$^{3}$H, $^{14}$C-δ$^{13}$C, δ$^{18}$O, δD, noble gases<br>**Aquifer-4**<br>$^{14}$C-δ$^{13}$C, δ$^{18}$O, δD, noble gases | | | |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-1**<br>**1-5: X 5-10: ☐ 10-25: ☐ >25: ☐**<br>**Aquifer-2**<br>**1-5: X 5-10: ☐ 10-25: ☐ >25: ☐**<br>**Aquifer-3**<br>**1-5: X 5-10: ☐ 10-25: ☐ >25: ☐**<br>**Aquifer-4**<br>**1-5: ☐ 5-10: X 10-25: ☐ >25: ☐** | | | |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-1**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: X >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**Aquifer-2**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**Aquifer-3**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**Aquifer-4**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X** | | | |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates ☐**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates X**<br>**Expert judgement: ☐** | | | |
| **Objective of age dating studies:** | | | | |
| **Basic research or General** | **Assessment of pollutant history** | **Assessment of the efficiency of remediation and mitigation** | **Indication of vulnerability of aquifers and water** | |

| | | | | | | |
|---|---|---|---|---|---|---|
| **groundwater management** | | | **measures** | | **supply wells** | |
| X | | | | | | |
| **Water Usage** *(not relevant for observation wells)* | **Water supply** | | **Irrigation** | **Industry** | **Other** | |
| | X | | | | Balneology, Orchid farm | |
| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | | **Nuclear waste disp.** | **$CO_2$ storage** |
| | | X | | | | |
| **Mining activities** *(not relevant for observation wells)* | **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:** |
| Nádor, A., Lapanje, A., Tóth,Gy., Rman, N., Szőcs, T., Prestor, J., Uhrin, A., Rajver, D., Fodor, L., Muráti, J., Székely, E., 2012: Transboundary geothermal resources of the Mura-Zala basin: a need for joint thermal aquifer management of Slovenia and Hungary. GEOLOGIJA 55/2, pp. 209–224, Ljubljana 2012. doi:10.5474/geologija.2012.013 | Szocs, T., Rman, N., Suveges, M., Palcsu, L., Toth, Gy., Lapanje, A., 2013: The application of isotope and chemical analyses in managing transboundary groundwater resources. Applied Geochemistry 32 (2013) 95–107 doi:10.1016/j.apgeochem.2012.10.006. |

**Remarks / other relevant information:**

## 3.16 Description of the Malta Mean Sea Level Aquifer System case study, Malta

| | |
|---|---|
| Title of Case Study | Malta Mean Sea Level Aquifer System (MSLA) |
| Location (region, Country) | Malta |
| Other information | |

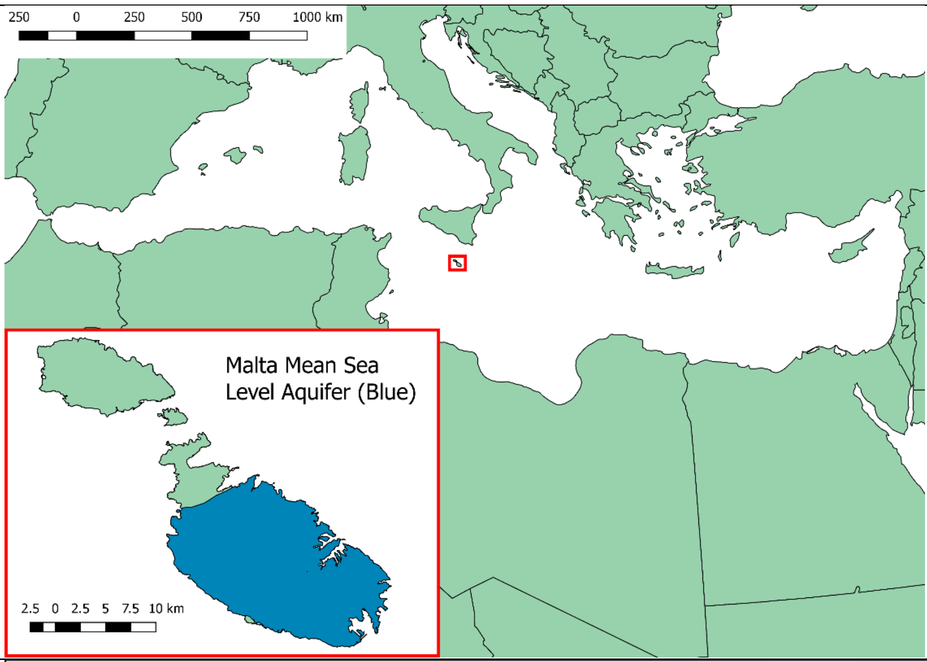
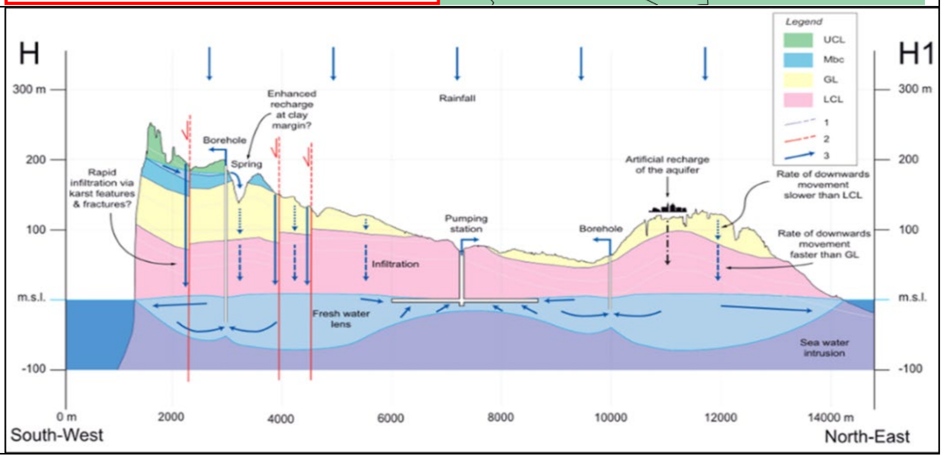
| Description of Case Study (background information on the region) |
|---|
| The Malta Mean Sea Level Aquifer system extends over an area of 216.6km$^2$, underlying almost the whole land-area of the island of Malta. Over this area, a freshwater lens is developed in the Lower Coralline Limestone, a permeable carbonate formation which extends to depth beneath the island. The groundwater body essentially takes the form of a freshwater lens floating on the denser sea-water and hence is in lateral vertical and horizontal contact with the bounding sea-water in the bedrock. It is therefore highly vulnerable to sea-water intrusion in response to abstraction activities, and therefore groundwater abstraction needs to be carefully managed to protect the quality of the abstracted water from the direct intrusion of sea-water under the abstraction point (sea-water upconing). |

| Description of problem (why is this location chosen for a Cases Study) |
|---|
| The Malta mean sea-level aquifer (MSLA) system is by far the most important groundwater body in the Maltese islands, providing around 65% of the total mean annual groundwater yield. The strategic importance of this groundwater body for the water supply of the Maltese islands warrants an increased understanding of the aquifer system in order to increasingly ensure its sustainable use.<br><br>The conceptual models of this aquifer system project a slow responding groundwater body as a result of its high storage capacity to annual recharge ratio. The aim of this case study was focused on the assessment of the groundwater residence time in the saturated zone, and therefore confirming the understanding of the conceptual model of the aquifer system. A slow responding groundwater body offers more resilience to the quantitative impacts of prolonged droughts and therefore offers broader management possibilities. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| The case study involves the application of $^3H$ as an isotopic tracer reflecting the expected age-range derived from the conceptual model of the groundwater body, supported by CFCs and $SF_6$ as additional tracers. |

| Results from this Case Study |
|---|
| A key finding of this case-study is the confirmation of the long saturated zone residence times in the Malta mean sea-level aquifer system. This result has important implications from a water management perspective. The long residence times confirm:<br>(i) the high recharge to storage ratio characteristics of the groundwater body, thereby increasing its resilience to short-term over-abstraction; and<br>(ii) the long expected response times of the groundwater body to the implementation of measures in its surface catchment area. |

| Impact - how this Case Study contributes to the overall project aims (see objectives WP6) |
| --- |
| This case study focuses on groundwater residence times and the response function of the aquifer system to groundwater management actions. It therefore contributes to the objectives of WP6 related to the assessment of groundwater age. Other aspects of the case study which focused on the source tracing of nitrate contamination, support further assessments under HOVER WP5 related to the determination of travel times for nitrate to groundwater. |

| | |
|---|---|
| **Name of pilot area / aquifers / type:**<br>Malta Mean Sea Level Aquifer | **Country:** Malta<br>**Region:** Malta |
| **Study level** | Transboundary : ☐ Regional: x Local: ☐ Single well(s): ☐ |
| **Type of observations**<br>*(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)<br>☐ Long screened observation wells (not pumped)<br>☐ Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>x Other (unscreened observation and pumping wells, drilled in a consolidated carbonate formation): |
| **Approximate location of pilot:** | <br> |
| **Geological cross section / conceptual model of the pilot area:** | <br> |

| | | | | |
|---|---|---|---|---|
| **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)** |
| | 550mm | 135 | 19 | 50 - 100 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):** 200 | | **Typical pump discharge of complete well field ($m^3$/day):** Not Relevant |
| **List of aquifers and aquitards in pilot area** | | **No. of confined or semiconfined aquifers in pilot area:** | | **No. of unconfined aquifers in pilot area: 1** |
| **Aquifer no. (aqf): 1**<br>**Aquitard no. (aqt):**<br>**Aquiclude no. (aqc):** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Lower Coralline Limestone | Limestone | +150 - -160 | 15 – 40 (residence time) |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: x |
| **Applied tracer age indicators** ($^3H$, $^3H/^3He$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $^{36}Cl$, $^{81}Kr$, $^4He$, CFCs, $SF_6$, etc.)<br>**Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | | **Aquifer-1**<br>$^3H$, CFCs, $SF_6$ | | |
| **Number of sites (wells/springs) with age indicators** | | **Aquifer-1**<br>**1-5: ☐ 5-10: ☐ 10-25: x >25: x** | | |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | | **Aquifer-1**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** | | |
| **Groundwater age ranges (GAR) estimated by:** | | **Tracer based estimates x**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates ☐**<br>**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** | | **Indication of vulnerability of aquifers and water supply wells** |

<table>
<tr><td>x</td><td colspan="2">x</td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td rowspan="2">Water Usage<br>(not relevant for observation wells)</td><td colspan="2">Water supply</td><td>Irrigation</td><td>Industry</td><td colspan="2">Other</td></tr>
<tr><td colspan="2">x</td><td>x</td><td>x</td><td colspan="2"></td></tr>
<tr><td rowspan="2">Geoenergy related activities<br>(not relevant for observation wells)</td><td>Shallow Geo-T</td><td>Deep Geo-T</td><td colspan="2">Hydrocarbons</td><td>Nuclear waste disp.</td><td>$CO_2$ storage</td></tr>
<tr><td></td><td></td><td colspan="2"></td><td></td><td></td></tr>
<tr><td rowspan="2">Mining activities<br>(not relevant for observation wells)</td><td colspan="2">Construction materials</td><td>Minerals / metals</td><td>Coal</td><td colspan="2">Other</td></tr>
<tr><td colspan="2">x</td><td></td><td></td><td colspan="2"></td></tr>
<tr><td colspan="7">REFERENCES</td></tr>
<tr><td colspan="3">OPEN Access reports and papers (PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches):<br><br>BGS (2008) A Preliminary Study on the Identification of the Sources of Nitrate Contamination in Groundwater in Malta Results and Interpretation. British Geological Survey, UK.<br><br>EWA (2015) Second Water Catchment Management Plan for the Malta Water Catchment District 2015 2021. Energy and Water Agency, Malta.</td><td colspan="4">Reports and papers with restricted access:</td></tr>
<tr><td colspan="7">Remarks / other relevant information:</td></tr>
</table>

## 3.17 Description of the Noord-Brabant & Limburg case study, The Netherlands

| | |
|---|---|
| Title of Case Study | Noord-Brabant and Limburg |
| Location | Provinces of Noord-Brabant and Limburg, Netherlands |
| Other information | The case study summarizes 3 studies that were published in peer-reviewed journals which focus on the applications of age dating of shallow groundwater for trend detection and process understanding in one of the most intensive farming areas of Europe. The case study is focusing on the consequences of excessive use of manure and fertilizer on agricultural lands and leaching of veterinary antibiotics from manure towards groundwater. |

| Description of Case Study |
|---|
| The provinces of Noord-Brabant and the Northern part of the province of Limburg present one of the areas in Europe which is most affected by agricultural pollution, because intensive livestock farming in the area produces a large surplus of manure. Agricultural land covers > 60% in the sandy regions of Noord-Brabant and Limburg. The agricultural area of these provinces is vulnerable to diffuse groundwater pollution with nitrate because groundwater and contaminants can easily reach deeper parts of the aquifer due to the permeable sandy subsoil. The subsurface consists of fluvial unconsolidated sand and gravel deposits from the Meuse River, locally overlain by an approximately 30 m thick cover of Middle- and Upper-Pleistocene fluvio-periglacial and aeolian deposits consisting of fine sands and loam. In large parts of the pilot region, pyrite occurs in the subsurface. Zhang et al. (2009) describe nitrate reduction by pyrite oxidation as a process determining the fate of nitrate. The pilot region is a relatively flat area with altitudes ranging from 0 m above mean sea level (MSL) in the north and west to about 40 m above MSL in the southeast. Groundwater tables are generally shallow, usually within 5 m below the surface. |

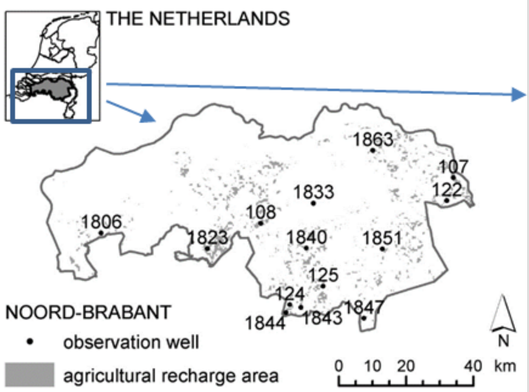
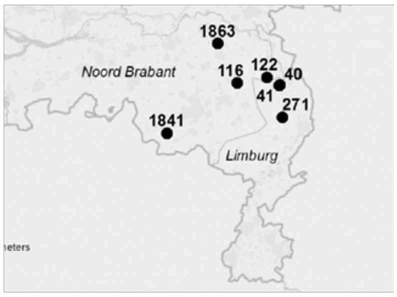
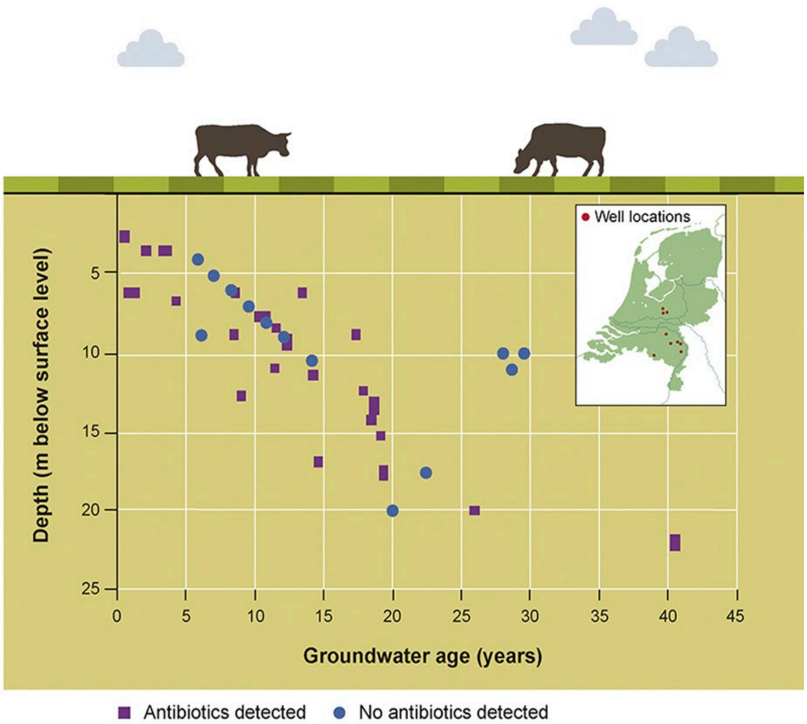
| Description of problem |
|---|
| Since around 1985 a set of measures was introduced to reduce the impacts of farming on the environment including groundwater resources. The legislation started with the Dutch Manure Law from (1985) and was followed by the EU Nitrate Directive (2000), the Directive on veterinary medicinal products (2001/82/EC) and the Dutch regulation on veterinary medication (nr. WJZ/12375453, 2012). Groundwater age dating has been applied in order to evaluate the effectiveness of these measures with respect to the contamination of groundwater. Because our pilot area is one of the most affected and known for exceedance of nitrate concentrations in shallow groundwater, the monitoring networks of the two provinces were used as a starting point for surveillance monitoring. Initial work has focuses on the fate and transport of nitrate (Visser et al. 2007, 2009a,b,c) and reaction products of nitrate reduction (Zhang et al. 2009, 2013). Recent work focuses on the fate and transport of veterinary antibiotics (Kivits et al. 2018). |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| The studies make use of an existing set of multi-level observation wells which are part of the |

| |
|---|
| provincial monitoring networks of the provinces of Noord-Brabant and Limburg and dedicated multi-level wells at an abandoned drinking water well field in Oostrum (Limburg). The wells consist of purpose-built nested piezometers with a diameter of 2 inch and a screen length of 2 m between depth of 2 and 40 m below surface. The wells were sampled for $^{3}H/^{3}He$ which was used to quantify the apparent groundwater age, correcting for degassing where necessary. A correction for degassing appeared to be necessary, as the reduction of excessive nitrate sometimes led to the of a $N_2$ gas phase. The use of CFC's and SF6 as age tracers has been explored, but appeared to be ineffective due to the degradation of the CFC's and degassing of SF6 in our hydrogeological situation (Visser et al. 2009c). PHT3D modelling of ages and geochemical processes was applied in the Zhang et al. 2013 study. Measured $^{3}H/^{3}He$ profiles were used to support the calibration of flow and conservative transport processes, while the comparison of simulated and measured sulfur isotope signatures acted as additional calibration constraint for the reactive processes affecting sulfur cycling. |

| Results from this Case Study |
|---|
| Using the results of the $^{3}H/^{3}He$ age dating, we could clearly demonstrate the trend reversal of groundwater nitrate, showing that concentrations increased in groundwater recharged before the enaction of the Manure Law in 1985 and decreased subsequently after 1990. Age dating also helped to unravel the hydrogeochemical processes, such as nitrate reduction coupled to pyrite oxidation. The calibrated age model of Zhang et al. 2013 was used to understand the lag times of nitrate and sulfate in receiving surface waters. The model illustrated that denitrification largely prevented an elevated discharge of nitrate to surface waters, while sulfate discharges were significantly<br>increased, peaking around 15 years after the maximum nitrogen inputs. The Kivits (2018) study clearly links the presence of veterinary antibiotics to the application history of the medicinal products in farming. Antibiotics were found in water of 25 years age and in deeper mixed waters with an apparent age of ~ 40 years. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| The case study is beneficial for the aim of establishing a good practice protocol on the application of age indicators and for demonstrating the use of groundwater age information for the evaluation of the effectiveness of monitoring programs. The study gives practical guidance for the assessment of pollution trends and trend reversal in relation with the application history of contaminants introduced under farmlands and yields better understanding of the fate and transport of contaminants in a reactive subsoil which has major implications for the assessment and understanding of groundwater chemical status. |

| | |
|---|---|
| **Name of pilot area / aquifers / type:**<br>Noord-Brabant | **Country:** Netherlands<br><br>**Region:** Noord-Brabant province, Netherlands |
| **Study level** | Transboundary : ☐ Regional: X Local: ☐ Single well(s): ☐ |
| **Type of observations** | X Short screened observation wells (not pumped)<br>☐ Long screened observation wells (not pumped)<br>☐ Pumped wells, long screens and open wells in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot (WGS84):**<br>**minX: 4.193000**<br>**maxX: 6.247500**<br>**minY: 51.130000**<br>**maxY: 51.845000** |  |
| **Geological cross section / conceptual model of the pilot area:** |  |

| | | | | |
|---|---|---|---|---|
| **Name of Shape- / Geopackage file defining the area: Netherlands pilot HOVER shape** | | **Projection to be used:**<br>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 |
| **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): 2**<br>**Aquitard no. (aqt):**<br>**Aquiclude no. (aqc):** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Eolian and fluvio-periglacial fine sands and loam (Quaternary) | Mostly fine sands | 0 – 15 | < 60 year in recharge areas |
| **Porosity type** | Porous: X | | | |
| Aqf-2: | Fluvial sands and gravel (Quarternary) | Fine sand to gravel | 0-50 | < 60 year in recharge areas |
| **Porosity type** | Porous: X | | | |
| **Applied tracer age indicators** ($^3H$, $^3H/^3He$)<br><br>**Applied recharge temperature indicators**<br>none | | **Aquifer-1**<br>$^3H$, $^3H/^3He$<br><br>**Aquifer-2**<br>$^3H$, $^3H/^3He$ | | |
| **Number of sites (wells/springs) with age indicators** | | **Aquifer-1**<br>**1-5: □ 5-10: □ 10-25: X >25: □**<br>**Aquifer-2**<br>**1-5: □ 5-10: □ 10-25: X >25: □** | | |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | | **Aquifer-1**<br>**GAR-1: 1-10%: □ 10-25%: □ 25-50%: □ >50%: X**<br>**GAR-2: 1-10%: □ 10-25%: X 25-50%: □ >50%: □**<br>**GAR-3: 1-10%: 0 10-25%: □ 25-50%: □ >50%: □** | | |

<table>
<tr><td colspan="3"></td><td colspan="4">Aquifer-2<br>GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X<br>GAR-2: 1-10%: ☐ 10-25%: X 25-50%: ☐ >50%: ☐<br>GAR-3: 1-10%: 0 10-25%: ☐ 25-50%: ☐ >50%: ☐</td></tr>
<tr><td colspan="3">Groundwater age ranges (GAR) estimated by:</td><td colspan="4">Tracer based estimates X<br>Flow and age model simulations X<br>Combination of model and tracer estimates X</td></tr>
<tr><td colspan="7">Objective of age dating studies:</td></tr>
<tr><td>Basic research or General groundwater management</td><td colspan="2">Assessment of pollutant history</td><td colspan="2">Assessment of the efficiency of remediation and mitigation measures</td><td colspan="2">Indication of vulnerability of aquifers and water supply wells</td></tr>
<tr><td></td><td colspan="2">x</td><td colspan="2">x</td><td colspan="2">x</td></tr>
<tr><td rowspan="2">Water Usage</td><td colspan="2">Water supply</td><td>Irrigation</td><td>Industry</td><td colspan="2">Other</td></tr>
<tr><td colspan="2"></td><td></td><td></td><td colspan="2"></td></tr>
<tr><td rowspan="2">Geoenergy related activities</td><td>Shallow Geo-T</td><td>Deep Geo-T</td><td colspan="2">Hydrocarbons</td><td>Nuclear waste disp.</td><td>$CO_2$ storage</td></tr>
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<tr><td rowspan="2">Mining activities</td><td colspan="2">Construction materials</td><td>Minerals / metals</td><td>Coal</td><td colspan="2">Other</td></tr>
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<tr><td colspan="7">REFERENCES</td></tr>
<tr><td colspan="3">OPEN Access reports and papers<br><br>Kivits, T., Broers, H., Beeltje, H., Vliet, M., Griffioen, J., 2018. Presence and fate of veterinary antibiotics in age-dated groundwater in areas with intensive livestock farming. Environ Pollut 241, 988–998.</td><td colspan="4">Reports and papers with restricted access:<br><br>Visser, Broers, H.P., van der Grift, Bierkens, M.F.P., 2007. Demonstrating trend reversal of groundwater quality in relation to time of recharge determined by 3H/3He. Environmental Pollution 148, 797–807.<br><br>Visser, A. H.P. Broers, R. Heerdink and M.F.P. Bierkens (2009a) Trends in pollutant concentrations in relation to time of recharge and reactive transport at the groundwater body scale. Journal of Hydrology, 369:427-439.<br><br>Visser, A., Dubus, I., Broers, H., Brouyère, S., Korcz, M., Orban, P., Goderniaux, P., Batlle-Aguilar, J., Surdyk, N., Amraoui, N., Job, H., Pinault, J., Bierkens, M. (2009b). Comparison of methods for the detection and extrapolation of trends in groundwater quality. J Environ Monitor 11, 2030–2043.<br><br>Visser, A. J.D. Schaap, H.P. Broers and M.F.P. Bierkens (2009c). Degassing of 3H/3He, CFCs and SF6 by denitrification: measurements and two-phase transport simulations. Journal of</td></tr>
</table>

| | |
|---|---|
| | Contaminant Hydrology (103)3-4:206-218.<br><br>Zhang, Y.C., Prommer, H., Slomp, C.P., H.P. Broers, B. van der Grift, Passier, H.F., Greskowiak J., Boettcher M.E. and van Cappellen, Ph. (2013). Model based analysis of the biogeochemical and isotope dynamics in a nitrate-polluted pyritic aquifer. Environmental Science and Technology 47:10415-10422.<br><br>Zhang Y.C., C.P. Slomp, H.P. Broers, H.F. Passier and Ph. Van Cappellen (2009) Denitrification coupled to pyrite oxidation and changes in groundwater quality in a shallow sandy aquifer. Geochemica et Cosmochimica Acta 73:6716-6726. |
| **Remarks / other relevant information:** | |

## 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.<br>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 |

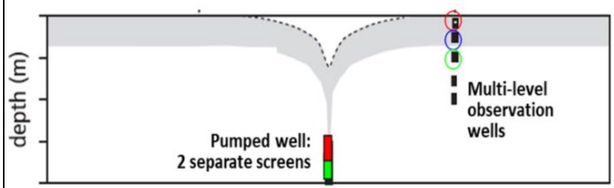
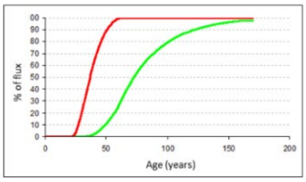
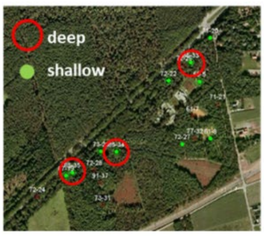
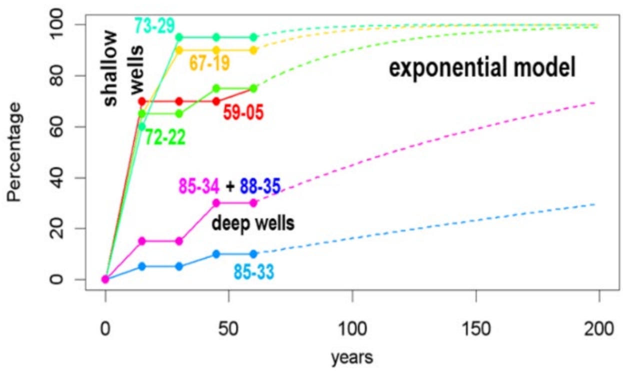
| Description of problem |
|---|
| The evolution of water quality in the well field was difficult to understand and especially fluctuations in concentrations of agriculturally derived contaminants including nitrate and sulfate made it uncertain which management options would be preferable for sustainable 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.<br>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.<br>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: | |
|---|---|
| **Name of pilot area / aquifers / type:**<br>Holten well field | **Country:** Netherlands<br><br>**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)<br>☐ Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot (WGS84):**<br>**minX: 6.327500**<br>**maxX: 6.500000**<br>**minY: 52.250000**<br>**maxY: 52.310000** |    |
| **Geological cross section / conceptual model of the pilot area:** |         |
| **Name of Shape- / Geopackage file defining the area:** | **Projection to be used:**<br>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** ($^{3}$H, $^{3}$H/$^{3}$He, $^{85}$Kr, $^{39}$Ar) **Applied recharge temperature indicators** ($^{18}$O) | | **Aquifer-1** $^{3}$H/$^{3}$He | | |
| | | **Aquifer-2** $^{3}$H, $^{3}$H/$^{3}$He, $^{39}$Ar, $^{85}$Kr, $^{4}$He, $^{18}$O | | |
| | | **Aquifer-3** $^{3}$H, $^{3}$H/$^{3}$He, $^{39}$Ar, $^{85}$Kr, $^{4}$He, $^{18}$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%: □** | | |

| | |
|---|---|
| **GAR-3: Paleowaters (> 10 kyr)** | **GAR-3: 1-10%: 0 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| | **Aquifer-2**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: X 10-25%: X 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: 0 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| | **Aquifer-3**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: X >50%: X**<br>**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** |
|---|---|---|---|---|
| | | | | |

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|---|---|
| | 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.<br><br>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:**

## 3.19 Description of the South Dobrogea aquifers case study, Romania

| | |
|---|---|
| Title of Case Study | Dating of Sarmatian and Upper Jurassic – Lower Cretaceous aquifers from South Dobrogea and the Implications on Groundwater Management in Romania, South-Eastern Europe. |
| Location (region, Country) | South-Eastern Europe, Romania |
| Other information | |

| Description of Case Study (background information on the region) |
|---|
| Romanian territory is located in the eastern part of the Black Sea Basin, and the case study area is situated near the Black Sea coast, at the border with Bulgaria. The Sarmatian aquifer and the Upper Jurassic – Lower Cretaceous aquifer are cross–border aquifers, and they are important water reservoirs for the South Dobrogea region. These two aquifers provide water supply for two Municipalities, Constanța and Mangalia, and for 58 communes of the Constanța County, as well as for several resorts situated on the seashore of the Black Sea.<br>The upper aquifer, which is the Sarmatian (Middle Miocene - Volhynian, Bessarabian, Kersonian) aquifer, has a surface of 2192 km$^2$, and is an unconfined aquifer hosted in limestones and covered by Pleistocene loess. The lower aquifer (having a surface of almost 4000 km$^2$) which is the Upper Jurassic - Lower Cretaceous Aquifer is a confined aquifer on almost 60% of the surface of the South Dobrogea. |

| Description of problem (why is this location chosen for a Cases Study) |
|---|
| For the last 25 years, for Dobrogea de Sud region, isotopic monitoring ($^3$H, $^{14}$C, $^{13}$C, D, $^{18}$O) has been performed by integrated research of all-natural types of waters in order to improve the knowledge of the hydrogeological parameters and of the regional flow pattern. The origin and the age of groundwater have been determined, for both aquifers. The major objectives that have been constantly considered are:<br>- delimiting the recharge areas of the Sarmatian and the Barremian-Jurassic aquifers;<br>- determining certain regional hydrodynamics parameters of the two aquifers;<br>- assessing the changes over time in regional isotopic distribution as a consequence of interaction with surface waters.<br>Together with the conclusions for the regional studies of the two main aquifers, the acquired isotopic data have also been used to emphasize some local aspects, such as the interrelations between the surface waters (Lake Siutghiol) and the groundwater extractions, by using tritium based isotopic method for the quantitative assessment of the water mixture. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| A study conducted in 1986 (Tenu at al., 1986) was mainly based on the determination of environmental isotopes ($^3$H, $^{14}$C, $^{13}$C, D, $^{18}$O) along with thermal and physic-chemical parameters which were determined both in situ and in the laboratory. This association of parameters was very useful in certain interpretations and also in correcting radiocarbon ages. Except for the $^{14}$C and $^{13}$C analyses, which were carried out at a single stage, starting from 1983, all determinations were resumed annually using the samples taken in May from a network of water points maintained unchanged. Based on this network, a synthesis study has been conducted in 1986 by Tenu et al. This database has been updated and new assessments have |

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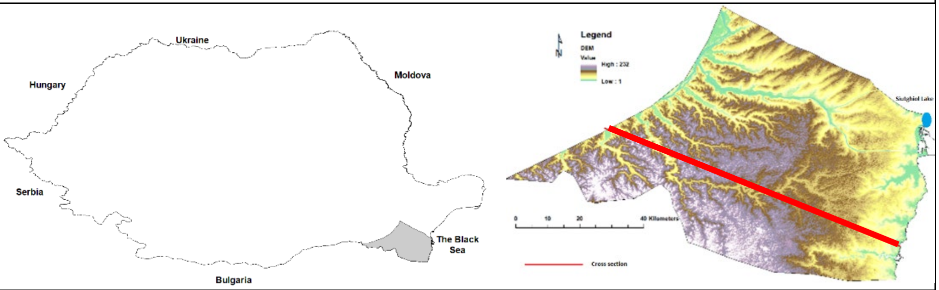
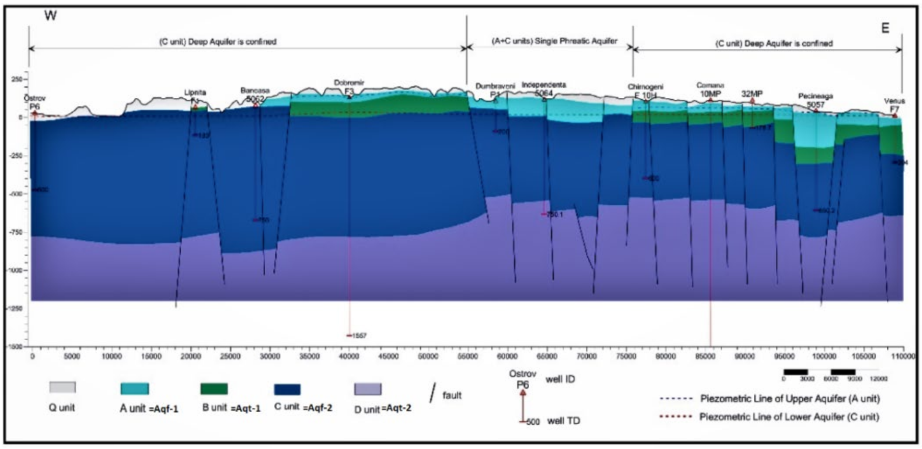
| been published in 1993, 1994, 1995, 2004, and 2014 by Tenu et al. Radiocarbon and tritium measurements were carried out using liquid scintillation counting. Deuterium and oxygen-18 isotopic composition was determined by mass spectrometry. Research by means of artificial tracers has been conducted since 1971 (Gâstescu & Hîncu, 1971; Gaspar & Orãşeanu, 1987). The software that has been mainly used is FeFlow. |

| Results from this Case Study |
|---|
| By means of isotopic research correlated with other methods, a conceptual model of the aquifers of South Dobrogea has been realized by Tenu et al in 1986 and reassessed in 2004. Thus, regarding aquifer types, there have delineated: 1. the shallow groundwater ($^{14}C$ = 20 to 50 pMC, $^{3}H$ = 0.8 to 14.3 TU); 2. the partial confined aquifer (local covered by the Lower Cretaceous aquitard: $^{14}C$ = 5.0 to 10 pMC, $^{3}H$ = < 0,8 to 1,1 TU); 3. the confined aquifer covered by the intermediate complex aquitard: $^{14}C$ = 1.0 to 10 pMC, $^{3}H$ = < 0.8 TU). The recharge area is located mainly in the Pre-Balkan Platform (Bulgaria); the main groundwater flow direction is east-northeast, towards the Siutghiol Lake, and the flow velocities, at the regional scale, vary from 100 m/year on a secondary groundwater flow and 500-1,800 m/year on the main mentioned one. The adventive recharge (by surface water) area is located in the northern area of the region. Regarding drainage: there is a natural drainage area (Np below + 17 m) near Lake Siutghiol, and a major (natural and anthropic conditioned) discharge area (Np below + 2m). Regarding hydraulic of groundwater: there is a flow direction of groundwater, confirmed by isotopic means and the value of hydraulic gradient is between 0.0001 to 0.0024, and there is a flow direction of groundwater, suggested by underground hydraulic information but non-confirmed by radiocarbon, having the direction from SV to NE. Also, there is a zero line of the area having the piezometric head with up to 15 m above the upper aquifer. Based on $^{14}C$ and $^{13}C$ analyses the age of the upper aquifer (Sarmatian) is estimated for between 1 (in the western area) to 12.3 thousand years (in the eastern part of the region). The values of $^{14}C$ isochrones for the lower aquifer vary from 5.7 to 21 thousand years. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| The isotopic research brings an essential contribution to creating a detailed groundwater flow model that leads to a proper management of the aquifers from South Dobrogea. Thus, based on this model, it was possible to dimension the water supply systems, delimit the areas of vulnerability of the aquifers and take the necessary measures to protect them. |

<table>
<tr><td colspan="2">Name of pilot area / aquifers / type:<br>South Dobrogea / Sarmatian, Upper Jurassic – Lower Cretaceous/ limestone aquifers / karst</td><td colspan="3">Country: Romania<br><br>Region: South – East Romania</td></tr>
<tr><td>Study level</td><td colspan="4">Transboundary : ☐ Regional: X Local: ☐ Single well(s): ☐</td></tr>
<tr><td>Type of observations<br>(choose one of the options, create separate template if needed for each type if each type need specific information)</td><td colspan="4">☐ Short screened observation wells (not pumped)<br>X Long screened observation wells (not pumped)<br>☐ Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping):</td></tr>
<tr><td>Approximate location of pilot:</td><td colspan="4">
</td></tr>
<tr><td>Geological cross section / conceptual model of the pilot area:</td><td colspan="4">

Reproduced after Popa el al, 2019. A unit is Sarmatian aquifer; C unit is Barremian – Jurassic aquifer.</td></tr>
<tr><td colspan="2">Name of Shape- / Geopackage file defining the area: Eesti_wgs84.shp</td><td colspan="3">Projection to be used:<br>WGS84 (Epsg4326)</td></tr>
<tr><td rowspan="2">Hydrological parameters:</td><td>Mean annual precipitation (mm or range in mm)</td><td>Mean annual groundwater recharge (mm or range in mm)</td><td>Mean annual groundwater recharge temperature (°C)</td><td>Thickness of unsaturated zone (range in m)</td></tr>
<tr><td>500 - 550</td><td>unknown</td><td>unknown</td><td>0-60</td></tr>
</table>

| | | | | |
|---|---|---|---|---|
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):** | | **Typical pump discharge of complete well field ($m^3$/day):**<br>*If relevant* |
| **List of aquifers and aquitards in pilot area** | | **No. of confined or semiconfined aquifers in pilot area: 1** | | **No. of unconfined aquifers in pilot area: 1** |
| **Aquifer no. (aqf): 2**<br>**Aquitard no. (aqt): 1**<br>**Aquiclude no. (aqc): 1** | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: Sarmatian | **Sarmatian** | Limestones | Mainly 0 – 60 (locally up to 100 m) | 1000 - 12500 |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: X |
| Aqf-2: Upper Jurassic – Lower Cretaceous | **Upper Jurassic – Lower Cretaceous** | Limestones and dolomites | 60 – 800 | 5000 - 25000 |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: X | Fissured and porous / dual porosity: |
| Aqt-1: Senonian | **Senonian** | Chalk | | |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: X |
| Aqc-1: Devonian | **Devonian** | Clay shales, quartz sandstone | 800 - 1500 | |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Fissured and porous / dual porosity: ☐ | No hydraulically active porosity: X |
| **Applied tracer age indicators** ($^3H$, $^3H/^3He$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $^{36}Cl$, $^{81}Kr$, $^4He$, CFCs, $SF_6$, etc.)<br>**Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | | **Aquifer-1**<br>$^{14}C$, $^{13}C$, $^{18}O$, D, $^3H$<br>**Aquifer-2**<br>$^{14}C$, $^{13}C$, $^{18}O$, D, $^3H$ | | |
| **Number of sites (wells/springs) with age indicators** | | **Aquifer-1**<br>**1-5:** ☐ **5-10:** X **10-25:** ☐ **>25:** ☐<br>**Aquifer-2**<br>**1-5:** ☐ **5-10:** ☐ **10-25:** X **>25:** ☐ | | |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)** | | **Aquifer-1**<br>**GAR-1: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** ☐<br>**GAR-2: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** X | | |

| | |
|---|---|
| **GAR-3: Paleowaters (> 10 kyr)** | **GAR-3: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** X **>50%:** ☐<br><br>**Aquifer-2**<br>**GAR-1: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** ☐<br>**GAR-2: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** X **>50%:** ☐<br>**GAR-3: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** X |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates** ☐<br>**Flow and age model simulations** X<br>**Combination of model and tracer estimates** ☐<br>**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** | **Indication of vulnerability of aquifers and water supply wells** |
|---|---|---|---|
| X | | | |

| **Water Usage** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
|---|---|---|---|---|
| | X | X | X | |

| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
|---|---|---|---|---|---|
| | | | | | |

| **Mining activities** *(not relevant for observation wells)* | **Construction materials** | **Minerals / metals** | **Coal** | **Other** |
|---|---|---|---|---|
| | X | | | |

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| | |
|---|---|
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| **Remarks / other relevant information:** | |

## 3.20 Description of the Campo de Montiel aquifer case study, Spain

| | |
|---|---|
| Title of Case Study | Campo de Montiel aquifer |
| Location (region, Country) | Ciudad Real and Albacete, Castilla la Mancha, España |
| Other information | |

| Description of Case Study (background information on the region) |
|---|
| Campo de Montiel aquifer covers an area of near 2200 $km^2$ located between Ciudad Real and Albacete provinces in the Mediterranean region of EU. This aquifer is part of the Upper Guadiana Basin. It is mainly composed by limestones and Jurassic carbonated formations. Its altitude varies between 800 and 1000 m.a.s.l. The mean annual temperature is about 14 °C. The annual precipitation varies between 400 and 500 mm. It is a semiarid region where groundwater use has helped to transform a largely poor rural region into a prosperous agricultural area. In Campo de Montiel aquifer strong natural interactions between groundwater and surface water are observed, which gives rise to some of the one hundred wetlands that make up UNESCO's Mancha Húmeda Biosphere Reserve. |

| Description of problem (why is this location chosen for a Cases Study) |
|---|
| This pilot area highlights the strong conflict between groundwater-dependent ecosystems and groundwater pumping to supply demands (mainly irrigation demands). Also the pumping volumes are not so high (about 9 $hm^3$/year), the wetlands are very sensible to groundwater levels. Moreover, the intense agricultural activity has produced a clear qualitative deterioration of the aquifer. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| Some studies based on isotopes ($^3H$ and $^{18}O$) have been conducted in this area in order to improve the knowledge of the hydrogeological system and to determine groundwater age and the origin of the high nitrate concentration in the aquifer.<br>Moreover, the River Basin Authority developed a groundwater flow model (MODFLOW) covering eight groundwater bodies in the Upper Guadiana Basin to simulate groundwater levels. This model can be used to determine the groundwater volume and to perform a first assessment of the residence time of the aquifer. |

| Results from this Case Study |
|---|
| We have performed a preliminary assessment of a distributed map of mean groundwater age distribution from the $^3H$ by applying interpolation techniques. |

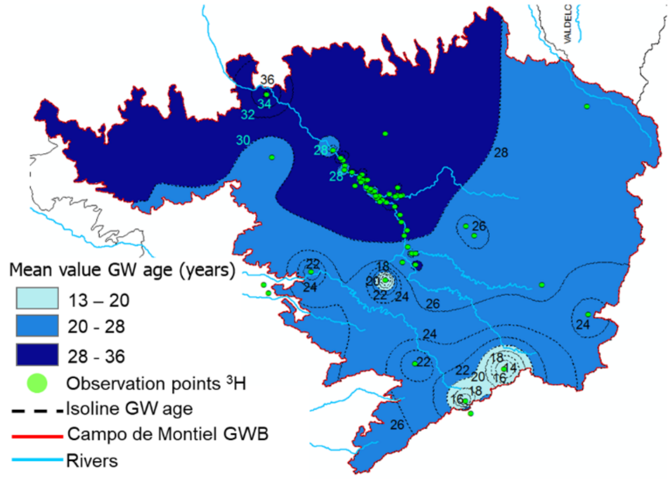
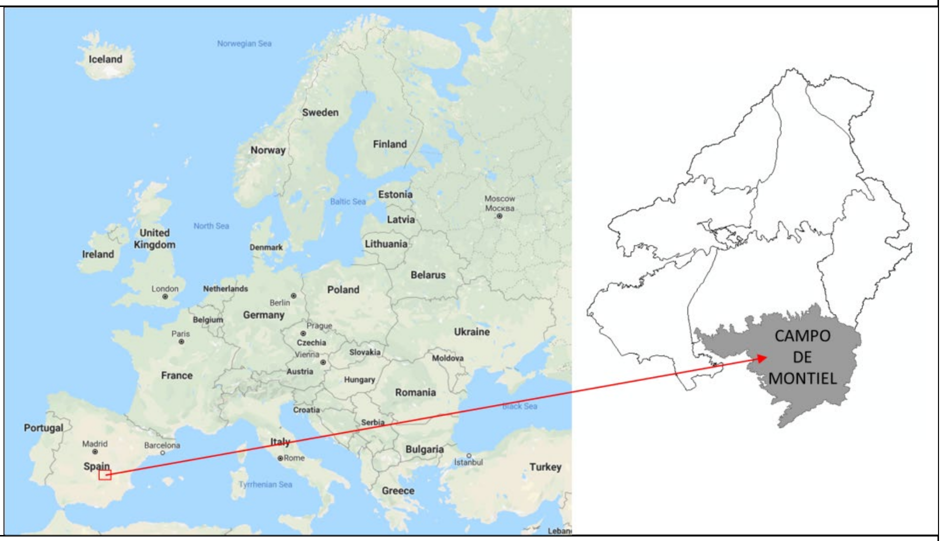
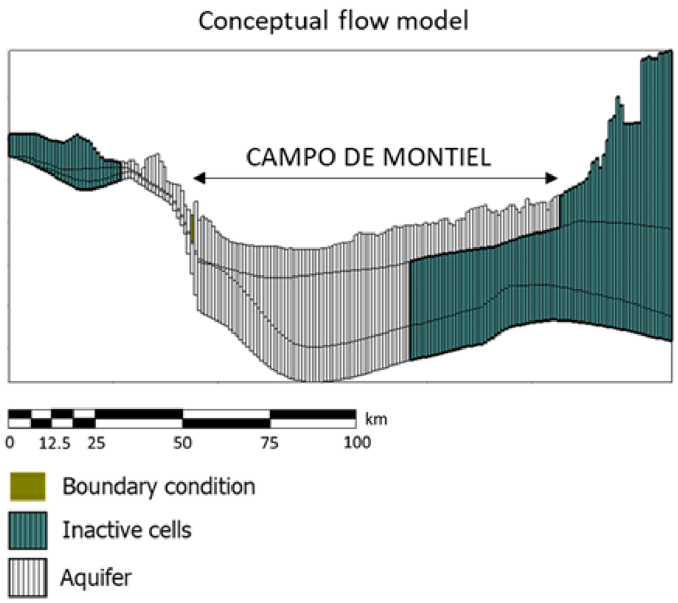


Fig. 1 Distributed groundwater age in Campo de Montiel aquifer.

We intend to produce the same map based from the calibrated MODFLOW model by using MODPATH and to compare results.
The lumped mean groundwater age obtained from the map (Figure 1) is 27.8 years. The groundwater age obtained by applying the turn over time index approach (obtained by dividing the aquifer groundwater storage by the mean net aquifer recharge) is 17 years, which is in the range of the values in Figure 1 (13 - 36 years).
We are also studying the correlation between the turn over time index and the lumped vulnerability value to surface pollutant in the eight aquifer bodies located within Alto Guadiana Basin.

| Impact - how this Case Study contributes to the overall project aims |
|---|
| It intends to contribute to test different techniques for estimating groundwater age with residence times mainly in the age range of 10 to 1000 years. In our demonstration pilot we will compare mean spatial distribution obtained from a numerical model with those obtained from a numerical model. We also analysed lumped mean values, comparing those obtained from the cited maps with values estimated by applying the simple turn over time index. |

| | |
|---|---|
| **Name of pilot area / aquifers / type:** Campo de Montiel / Jurassic limestones / carbonated | **Country:** Spain<br><br>**Region:** Campo de Montiel aquifer (Upper Guadiana Basin) |
| **Study level** | Transboundary : ☐ Regional: x 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)<br>☐ Long screened observation wells (not pumped)<br>**X** Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot:** |  |
| **Geological cross section / conceptual model of the pilot area:** |  |

<table>
<tr><td colspan="2">Name of Shape- / Geopackage file defining the area: HoverSPPilots.shp</td><td colspan="4">Projection to be used:<br>WGS84 (Epsg4326)</td></tr>
<tr><td rowspan="2">Hydrological parameters:</td><td>Mean annual precipitation (mm or range in mm)</td><td>Mean annual groundwater recharge (mm or range in mm)</td><td colspan="2">Mean annual groundwater recharge temperature (°C)</td><td>Thickness of unsaturated zone (range in m)</td></tr>
<tr><td>450-500</td><td>50-90</td><td colspan="2"></td><td>0-180</td></tr>
<tr><td colspan="2">Pumped wells only</td><td colspan="2">Typical pump discharge of sampled individual well ($m^3$/day): 115</td><td colspan="2">Typical pump discharge of complete well field ($m^3$/day): 30796</td></tr>
<tr><td colspan="2">List of aquifers and aquitards in pilot area</td><td colspan="2">No. of confined or semiconfined aquifers in pilot area: 2</td><td colspan="2">No. of unconfined aquifers in pilot area: 1</td></tr>
<tr><td>Aquifer no. (aqf): 1</td><td>Aquifer/aquitard type and/or name</td><td>Lithology (Resource WP6 terminology)</td><td>Depth range (m)</td><td colspan="2">GW age range (yr)</td></tr>
<tr><td>Aqf-1: Campo de Montiel aquifer</td><td>Campo de Montiel aquifer</td><td>Jurasic carbonated aquifer + Limestones</td><td>50 - 200</td><td colspan="2">5 - 100</td></tr>
<tr><td>Porosity type</td><td>Porous: X</td><td>Fissured: ☐</td><td>Karst: ☐</td><td colspan="2">Fissured and porous / dual porosity: X</td></tr>
<tr><td colspan="2">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.)<br>Applied recharge temperature indicators ($^{18}O$, D, noble gases)</td><td colspan="4">Aquifer-1:<br>(A) $^{3}H$ (tracer age indicator) + $^{18}O$ (recharge temperature indicator).<br>(B) Applied groundwater distributed model (MODFLOW + MODPATH)<br>(C) Lumped index (turn over time index = total storage/mean recharge)</td></tr>
<tr><td colspan="2">Number of sites (wells/springs) with age indicators</td><td colspan="4">Aquifer-1<br>1-5: ☐ 5-10: ☐ 10-25: ☐ >25: X</td></tr>
<tr><td colspan="2">GW age range (GAR)<br>GAR-1: Modern (< 60 yr)<br>GAR-2: Old (> 60 yr and 10 kyr)<br>GAR-3: Paleowaters (> 10 kyr)</td><td colspan="4">Aquifer-1<br>GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X<br>GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐<br>GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐</td></tr>
</table>

<table>
<tr><td colspan="2">Groundwater age ranges (GAR) estimated by:</td><td colspan="4">Tracer based estimates ☐<br>Flow and age model simulations ☐<br>Combination of model and tracer estimates X<br>Expert judgement: ☐</td></tr>
<tr><td colspan="6">Objective of age dating studies:</td></tr>
<tr><td>Basic research or General groundwater management</td><td>Assessment of pollutant history</td><td colspan="2">Assessment of the efficiency of remediation and mitigation measures</td><td colspan="2">Indication of vulnerability of aquifers and water supply wells</td></tr>
<tr><td>X</td><td></td><td colspan="2"></td><td colspan="2">X</td></tr>
<tr><td rowspan="2">Water Usage<br>(not relevant for observation wells)</td><td>Water supply</td><td>Irrigation</td><td>Industry</td><td colspan="2">Other</td></tr>
<tr><td>x</td><td>x</td><td></td><td colspan="2"></td></tr>
<tr><td rowspan="2">Geoenergy related activities<br>(not relevant for observation wells)</td><td>Shallow Geo-T / Deep Geo-T</td><td colspan="2">Hydrocarbons</td><td>Nuclear waste disp.</td><td>$CO_2$ storage</td></tr>
<tr><td></td><td colspan="2"></td><td></td><td></td></tr>
<tr><td rowspan="2">Mining activities<br>(not relevant for observation wells)</td><td>Construction materials</td><td>Minerals / metals</td><td>Coal</td><td colspan="2">Other</td></tr>
<tr><td></td><td></td><td></td><td colspan="2"></td></tr>
<tr><td colspan="6">REFERENCES</td></tr>
<tr><td colspan="2">OPEN Access reports and papers (PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches):</td><td colspan="4">Reports and papers with restricted access:<br><br>MINISTERIO DE MEDIO AMBIENTE Y MEDIO RURAL Y MARINO and CONFEDERACIÓN HIDROGRÁFICA DEL GUADIANA (2009). MEJORA DEL CONOCIMIENTO HIDROLÓGICO E HIDROGEOLÓGICO DEL ALTO GUADIANA.<br>Clave: 04.803-246/0411.<br>MINISTERIO DE MEDIO AMBIENTE Y MEDIO RURAL Y MARINO and CEDEX (2008). ESTUDIO HIDROGEOLÓGICO E ISOTÓPICO EN LA MASA DE AGUA SUBTERRÁNEA CAMPO DE MONTIEL (041.010).</td></tr>
<tr><td colspan="6">Remarks / other relevant information:</td></tr>
</table>

## 3.21 Description of the Forsmark site case study, Sweden

| | |
|---|---|
| Title of Case Study | The Forsmark site |
| Location (region, Country) | Northeastern Uppland, Sweden |
| Other information | The evaluation of ground water age is restricted to groundwaters in the bedrock. |

| Description of Case Study (background information on the region) |
|---|
| The Forsmark site is located north-east of Forsmark village (approx. 100 km north-east of Stockholm) along the Baltic Sea coast. In the area (ten square kilometres in size), where a final repository for spent nuclear fuel is proposed to be located, extensive site investigations have been conducted since 2002. These investigations include, among others, hydrogeochemical characterisation of groundwaters (e.g. groundwater age assessments) down to 1,000 metres depth in the bedrock. The ground surface is characterised by low relief with small-scale topography and is almost entirely located below 20 metres above sea level. The Quaternary till deposits that characterise the surface are less than 20 m thick and cover around 90 percent of the ground surface; rock outcrops are common. The bedrock is dominated by different types of Precambrian crystalline rock types (mainly granite and granodiorite), formed between 1.89 and 1.85 billion years ago (1.89-1.85 Ga). The annual precipitation and runoff are 560 mm and 160 mm, respectively. Simulated annual groundwater recharge in bedrock ranges from 29 to 53 mm, depending on depth and methodologies used. The groundwater level in the soil layers is located less than a metre below the ground surface for most of the year. Groundwater levels in rock are very equalized and lie just below sea level. The equalized and low levels can be assumed to be due to the highly penetrative horizontal and sub-horizontal fractures present in the uppermost parts of the rock. Several groundwater types which are now present in the bedrock can be associated with past climatic events in the late Pleistocene and Holocene. Among these, the last glaciation and post glacial period is the most important for the groundwater development. |

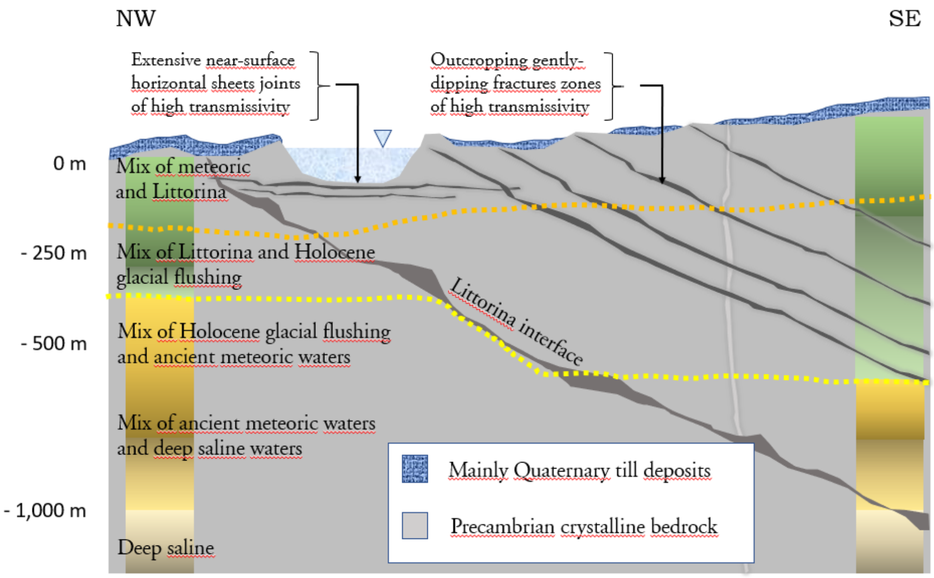
| Description of problem (why is this location chosen for a Cases Study) |
|---|
| The site investigations for a possible final repository for spent nuclear fuel have generated a good hydrogeochemical understanding of the site, both of present and past conditions. Numerous reports have been produced, approximately 800 dealing with the site investigations, and can be downloaded from SKBs (the Swedish Nuclear Fuel and Waste Management Company) website: www.skb.se. The Case Study reveals the groundwater development in the area over a very long time period (1.5 Ma – present) and groundwater age assessments are carried out for groundwaters down to great depth (~ 1.000 m) in the bedrock. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| Explorative analyses and modelling of groundwater chemistry data have been used to evaluate the hydrogeochemical conditions at the site in terms of origin of the groundwater and the processes that control the groundwater composition. The occurrence of old groundwater is evident from analyses of the isotopes carbon-14 and chlorine-36 ($^{36}Cl$), as well as the presence of $^{4}He$, which is formed in the Earth's crust and mantle and is transported upward. Low oxygen-18 values ($\delta^{18}O$) indicate admixture of water originating from a very cold climate, which is interpreted as being meltwater from the continental ice sheet. Admixture of very young surface |

| |
|---|
| water – from the 1950s and younger – is revealed by detectable quantities of the hydrogen isotope tritium ($^{3}H$). The following stable and radioactive isotopes have been analysed in the water: $^{2}H$, $^{3}H$, $^{18}O$, $^{36}Cl$, $^{37}Cl$, $^{13}C$, $^{14}C$ (pmC), $^{10}B$, $^{11}B$, $^{87}Sr/^{86}Sr$, $^{34}S$, $^{238}U$, $^{234}U$, $^{230}Th$, $^{226}Ra$, $^{222}Rn$. |

| Results from this Case Study |
|---|
| The groundwater in the bedrock consists of different mixtures of 1) modern or old surface water, 2) meltwater from the continental ice sheet, 3) water from the Littorina Sea (7,500 BC-present) and 4) extremely old and saline “deep water” from the deep bedrock.<br>• **Recent to young fresh groundwaters**, some showing signs of mixing with Littorina-type groundwaters, characterise the upper approximately 100-150 m of the bedrock. At these depths, because the hydraulic system is more dynamic, climatic changes have resulted in the cyclic introduction and flushing out of different groundwater types over tens of thousands of years such that residence times for individual groundwater types seem relatively short (i.e. probably some hundreds to a few thousand years). This is shown by tritium ($^{3}H$) and $^{14}C$ which indicate that near-surface groundwaters have short residence times in the order of only a few decades to a few hundred years.<br>• **Older groundwaters** with a heavy contribution from the Littorina Sea occur from approximately 150 m to depths of around 300-600 m (depending on the location and fracture transmissivity). The radiocarbon analyses ($^{14}C$) support a postglacial origin of brackish marine groundwater. This is in accordance with palaeohydrogeological estimations, which suggests an age of approximately 5,000 to 6,000 years, covering the period of maximum salinity during the Littorina stage (4,500-3,000 BC).<br>• **Significantly older groundwaters**, found at depths greater than around 300-600 m (depending on the location and the fracture transmissivity) to around 1,000 m, are characterised initially by brackish non-marine groundwaters which become successively more mineralised with increasing depth (to saline in type) by water-rock interaction, mixing with deep saline groundwater, and exchange with the rock matrix porewater. Hydraulic conditions at these depths indicate low groundwater flow to stagnant conditions and suggest residence times that appear to be considerable. From $^{36}Cl$ the residence time of the brackish to saline non-marine groundwaters can be shown to extend back to at least 1,5 Ma, which is in accordance with the $^{4}He$ systematics. |

| Impact - how this Case Study contributes to the overall project aims |
|---|
| The Case Study depicts extensive site investigations, described in numerous reports (in English) that are readily available for the public. A significant amount of age tracers has been used to describe the groundwater development over a long time period and to great depth in the bedrock. |

<table>
<tr><td>Name of pilot area / aquifers / type:<br>The Forsmark site / Precambrian crystalline bedrock aquifers / fissured</td><td colspan="2">Country: Sweden<br><br>Region: Uppland, 100 km north-east of Stockholm</td></tr>
<tr><td>Study level</td><td colspan="2">Transboundary: ☐ Regional: ☐ Local: X Single well(s): ☐</td></tr>
<tr><td>Type of observations<br>(choose one of the options, create separate template if needed for each type if each type need specific information)</td><td colspan="2">☐ Short screened observation wells (not pumped)<br>☐ Long screened observation wells (not pumped)<br>☐ Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>X Other (research wells; not pumped)</td></tr>
<tr><td>Approximate location of pilot:</td><td colspan="2">
</td></tr>
<tr><td>Geological cross section / conceptual model of the pilot area:</td><td colspan="2">
<br>Conceptual model for Forsmark illustrating present hydraulic conditions and distribution of the different groundwater types. Modified from Follin et al. 2007.</td></tr>
</table>

| | | | | |
|---|---|---|---|---|
| **Name of Shape- / Geopackage file defining the area:** | | **Projection to be used:**<br>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)** |
| | 560 | ≤ 50 *<br>* simulated groundwater recharge in bedrock | 6-7 | 0-10 |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):** | | **Typical pump discharge of complete well field ($m^3$/day):**<br>*If relevant* |
| **List of aquifers and aquitards in pilot area** | | **No. of confined or semiconfined aquifers in pilot area:** 1*<br>* Aqf-1a, Aqf-1b and Aqf-1c | | **No. of unconfined aquifers in pilot area:** 0 |
| **Aquifer no. (aqf):** 1 (aqf-1a, aqf-1b & aqf-1c)<br>**Aquitard no. (aqt):** 0<br>**Aquiclude no. (aqc):** 0 | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1a: | Precambrian crystalline rocks (recent to young fresh groundwaters) | Crystalline rocks | 0 – 150 | <60 – 5,000 |
| **Porosity type** | Porous: ☐ | Fissured: X | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-1b: | Precambrian crystalline rocks (old groundwaters) | Crystalline rocks | 150 – 300/600 (depending on location) | 5000 – 10,000 |
| **Porosity type** | Porous: ☐ | Fissured: X | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-1c: | Precambrian crystalline rocks (significantly older groundwaters) | Crystalline rocks | 300/600 – 1.000 | > 10,000 – $1.5 \times 10^6$ |
| **Porosity type** | Porous: ☐ | Fissured: X | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| **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.) | | **Aquifer-1a**<br>$^{3}H$, $^{14}C$, $^{36}Cl$, $^{4}He$, $^{18}O$, noble gases | | |
| | | **Aquifer-1b** | | |

| | |
|---|---|
| **Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | $^{3}H$, $^{14}C$, $^{36}Cl$, $^{4}He$, $^{18}O$, noble gases |
| | **Aquifer-1c**<br>$^{3}H$, $^{14}C$, $^{36}Cl$, $^{4}He$, $^{18}O$, noble gases |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-1a**<br>**1-5: □ 5-10: □ 10-25: X >25: □** |
| | **Aquifer-1b**<br>**1-5: □ 5-10: □ 10-25: X >25: □** |
| | **Aquifer-1c**<br>**1-5: □ 5-10: □ 10-25: X >25: □** |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-1a**<br>**GAR-1: 1-10%: □ 10-25%: □ 25-50%: X >50%: □**<br>**GAR-2: 1-10%: □ 10-25%: □ 25-50%: X >50%: □**<br>**GAR-3: 1-10%: □ 10-25%: □ 25-50%: □ >50%: □** |
| | **Aquifer-1b**<br>**GAR-1: 1-10%: □ 10-25%: □ 25-50%: □ >50%: □**<br>**GAR-2: 1-10%: □ 10-25%: □ 25-50%: □ >50%: X**<br>**GAR-3: 1-10%: □ 10-25%: □ 25-50%: □ >50%: □** |
| | **Aquifer-1c**<br>**GAR-1: 1-10%: □ 10-25%: □ 25-50%: □ >50%: □**<br>**GAR-2: 1-10%: □ 10-25%: □ 25-50%: X >50%: □**<br>**GAR-3: 1-10%: □ 10-25%: □ 25-50%: □ >50%: X** |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates X**<br>**Flow and age model simulations □**<br>**Combination of model and tracer estimates □**<br>**Expert judgement: X** |

**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** *(not relevant for observation wells)* | **Water supply** | **Irrigation** | **Industry** | **Other** |
|---|---|---|---|---|
| | | | | |

| **Geoenergy related activities** *(not relevant for observation wells)* | **Shallow Geo-T** | **Deep Geo-T** | **Hydrocarbons** | **Nuclear waste disp.** | **$CO_2$ storage** |
|---|---|---|---|---|---|
| | | | | X | |

| **Mining activities** *(not relevant for observation wells)* | **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:** |
|---|---|
| **Follin S., 2008.** Bedrock hydrology Forsmark. Site descriptive modelling, SDM-Site Forsmark. SKB R-08-95, Svensk Kärnbränslehantering AB.<br>**Laaksoharju M., Smellie J., Tullborg E-L., Gimeno M., Hallbek L., Molinero J. & Waber N., 2008.** Bedrock hydrogeochemistry Forsmark. Site descriptive modelling SDM-Site Forsmark. SKB R-08-47, Svensk Kärnbränslehantering AB.<br>**Lundin L., Lode E., Stendahl J., Melkerud P-A. Björkvald L. & Thorstensson A., 2004.** Soils and site types in the Forsmark area. SKB R-04-08, Svensk Kärnbränslehantering AB.<br>**Nilsson A-C., Tullborg, E-L., Smellie J., Gimeno, M.J., Gomez J.B., Auqué L.F., Sandström B. & Pedersen K., 2011.** SRF site investigation Bedrock Hydrogeochemistry. SKB R-11-06. Svensk Kärnbränslehantering AB.<br>**SKB, 2012.** Site Investigation, Forsmark, Annual Report 2002-2007. Second edition April 2012. Svensk Kärnbränslehantering AB.<br>**Smellie J. Tullborg E-L., Nilsson A-C., Sandström B., Waber N., Gimeno M. & Gascoyne M., 2008.** Explorative analysis of major components and isotopes. SDM-Site Forsmark. SKB R-08-84. Svensk Kärnbränslehantering AB.<br>**Söderbäck B. (ed), 2008.** Geological evolution, paleoclimate and historical development of the Forsmark and Laxemar-Simpevarp areas. Site descriptive modelling, SDM-Site. SKB R-08-19, Svensk Kärnbränslehantering AB. | **Follin S., Stephens M.B., Laaksoharju M., Nilsson A-C., Smellie J.A.T. & Tullborg, E-L. 2008.** Modelling the evolution of hydochemical conditions in the Fennoscandian Shield during Holocene time using multidisciplinary information. Applied Geochemistry 23, 2004-2020. |

**Remarks / other relevant information:**

The evaluation of ground water age is restricted to groundwaters in the bedrock. The aquifer in the bedrock has been subdivided into three sections (Aqf-1a, Aqf-1b and Aqf-1c), depending on differences in estimated groundwater age with depth.

## 3.22 Description of the Skåne (SW and NE) case study, Sweden

| | |
|---|---|
| Title of Case Study | Skåne (SW, NE) |
| Location (region, Country) | Skåne |
| Other information | |

| Description of Case Study (background information on the region) |
|---|
| The southernmost part of Sweden, known as Scania, is one of the country's most densely populated regions. Scania relies on groundwater for 50% of its water supply, and groundwater is also extracted for agricultural and industrial purposes. Groundwater pressure is substantial, both in quantitative and qualitative terms. Groundwater contamination is a prevalent concern throughout the region and during more recent years, certain areas have repeatedly suffered from seasonal groundwater shortages. With predicted effects of climate change, negative water balances are likely to become more prevalent in both time and space.<br>Geologically and hydrogeologically, Scania is a heterogeneous and thus inherently complex though interesting region to study. The geological record is extensive, and the stratigraphy varies substantially within the region, often over relatively short distances. This is due to Scania's location, on a previously glaciated and once tectonically much active border region between Precambrian crystalline rocks of the Fennoscandian shield, and a range of sedimentary rocks typical to Phanerozoic Europe. Types of aquifers span fractured gneisses and sandstones, dual-porosity lime- and sandstones and a wealth of superficial to more or less buried glacifluvial deposits. The total amount of delineated groundwater bodies within the region is just over 200, most of which equals porous sand-gravel aquifers. |

| Description of problem (why is this location chosen for a Cases Study) |
|---|
| Scania is one of few regions in Sweden where groundwater age assessments have been performed. This is likely due to the relatively high regional groundwater pressure and thus vulnerability, as well as the Geological Survey of Sweden's local presence. The hydrogeological heterogeneity has also spurred a general interest for tracer methodology testing in the area in general. |

| Methods to be used in the Case Study (analytical and isotope techniques, modelling) |
|---|
| The Skåne-pilot relies solely on previous studies and has not involved any novel sampling or analysis. The pilot, however, is the first compilation and joint assessment of existing data, albeit on a relatively simplified and general, conceptual scale.<br>Available data mainly involves sporadic, single, isolated tracer analyses in individual long-screened pumping wells. Tritium is the overall most common tracer applied though later work has also included CFCs, $SF_6$, noble gases, $^{3}H$-$^{3}He$, $^{39}Ar$ and $^{85}Kr$. $^{14}C$-analyses are known from some areas. |

| Results from this Case Study |
|---|
| The amount of available tracer data from Skåne is relatively substantial. However, thorough analyses of age ranges and hydraulics within individual aquifers are scarce. Limitations include a lack of longer time-series, multi-tracer analyses and analyses from observation-wells. Regional groundwater management would benefit from more holistic and systematic analyses of existing and supplementary tracer data, including coupled tracer-modelling assessments of age ranges |

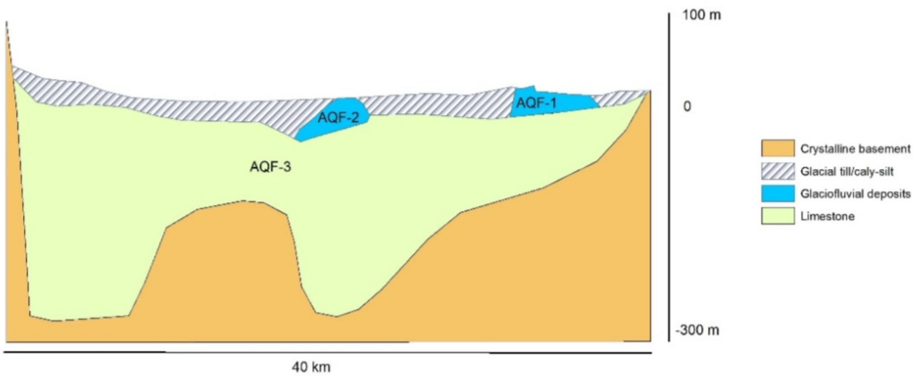
and hydraulics, with the aid of (in places already existing) numerical hydrogeological models.
Groundwater ages in aquifers in the region vary from <1 yr to >10 kyrs. At specific locations within Skåne, one may observe general trends and patterns in terms of groundwater age with e.g. depth. However, due to the general hydrogeological heterogeneity, patterns are oftentimes inherently difficult to deduce over some distance, both vertically and horizontally. Rather, on a regional scale and with regards to existing tracer data, it appears more suitable to discuss and infer GAR at a given location depending on the specific aquifer type in question, specifically with regards to porosity type (possibility for fissure flow or not) and level of confinement. E.g., surficial, unconfined porous aquifers are likely to exhibit relatively narrow groundwater age ranges spanning mainly recent decades, with a relatively young mean groundwater age. Deep, semi-confined aquifers with possibility for fissure flow may, at the other end of the scale, exhibit relatively wide groundwater age ranges spanning hundreds to thousands of years. While the mean groundwater age ought to be somewhat older, the most recent contributions might still be significantly young, i.e. <1 yr.
Overall, modern waters (< 60 yrs) appear considerably present down to standard depths for drinking water wells in most aquifer types throughout the region, indicating a large degree of regional vulnerability in terms of e.g. pollution risk. The only apparent exception in this regard - based on available data - appears to be narrow portions of deep, confined aquifers.
In terms of specific tracers, previous studies have shown that:

- $SF_6$-concentrations throughout the region are among the highest ever reported and are interpreted to stem from natural sources. Accordingly, $SF_6$ does not appear a suitable groundwater tracer in the area. However, the region ought to be considered an interesting site for studies into natural $SF_6$-sourcing.
- He-concentrations are generally high, suggesting Skåne is an interesting area for studies into the mechanisms and rates of radiogenic $^4He$ release in mixed young groundwater.
- Local contamination sources of CFC's appear regionally considerable.

| Impact - how this Case Study contributes to the overall project aims |
| --- |

This case study contributes to:

- Establishing a European-wide harmonized database on groundwater age tracers and indicators.
- Identifying and describing important European aquifers with a significant amount of age indicators.
- Demonstrating the use (and limitations) of groundwater age tracer analyses with regards to characterisation and management of important European aquifers.

| | |
|---|---|
| **Name of pilot area / aquifers / type:** Skåne NE / Quaternary sand aquifers, Cretaceous limestone and sandstone aquifer / porous, dual-porosity | **Country:** Sweden<br>**Region:** Skåne |
| **Study level** | Transboundary: ☐ Regional: x Local: ☐ Single well(s): ☐ |
| **Type of observations**<br>*(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)<br>☐ Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping): |
| **Approximate location of pilot:** |  |
| **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)** |
| | 600-800 | <200-300 | 8-9 | 0-5 m |
| **Pumped wells only** | | **Typical pump discharge of sampled individual well ($m^3$/day):** 1-1000 | | **Typical pump discharge of complete well field ($m^3$/day): -** *If relevant* |
| **List of aquifers and aquitards in pilot area*** **Given no:s = along cross section < within full pilot area* | | **No. of confined or semiconfined aquifers in pilot area:** 2 | | **No. of unconfined aquifers in pilot area:** 1 |
| **Aquifer no. (aqf):** 3 **Aquitard no. (aqt):** 1 | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Glaciofluvial deposits, locally confined | Fine sand to gravel | 0-30 | <5 - >60 |
| **Porosity type** | Porous: X | Fissured: □ | Karst: □ | Fissured and porous / dual porosity: □ |
| Aqt-1: | Glacial till/clay-silt | Clay-silt, clayey-clay till | | |
| **Porosity type** | Porous: □ | Fissured: □ | Fissured and porous / dual porosity: X | No hydraulically active porosity: □ |
| Aqf-2: | Glaciofluvial deposits | Fine sand to gravel | 0-50 | <5 - >60 |
| **Porosity type** | Porous: X | Fissured: □ | Karst: □ | Fissured and porous / dual porosity: □ |
| Aqf-3: | Cretaceous limestone and glauconitic sandstone | Limestone, sandstone | 20-300 | <5 - >5 000 |
| **Porosity type** | Porous: □ | Fissured: □ | Karst: □ | Fissured and porous / dual porosity: X |
| **Applied tracer age indicators** ($^3H$, $^3H/^3He$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $^{36}Cl$, $^{81}Kr$, $^4He$, CFCs, $SF_6$, etc.) **Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | | **Aquifer-1** $^3H$, $^3H/^3He$, $^4He$, CFC, $SF_6$, noble gases | | |
| | | **Aquifer-2** $^3H$, $^3H/^3He$, $^4He$, CFC, $SF_6$, noble gases | | |
| | | **Aquifer-3** $^3H$, $^3H/^3He$, $^4He$, CFC, $SF_6$, noble gases, $^{14}C$ | | |

<table>
<tr><td rowspan="3">Number of sites (wells/springs) with age indicators</td><td colspan="5">Aquifer-1<br>1-5: X* 5-10: ☐ 10-25: ☐ >25: ☐<br>*Total no. of samples from similar type-aquifers within the greater pilot area</td></tr>
<tr><td colspan="5">Aquifer-2<br>1-5: X* 5-10: ☐ 10-25: ☐ >25: ☐<br>*Total no. of samples from similar type-aquifers within the greater pilot area</td></tr>
<tr><td colspan="5">Aquifer-3<br>1-5: ☐ 5-10: ☐ 10-25: X >25: ☐</td></tr>
<tr><td rowspan="3">GW age range (GAR)<br>GAR-1: Modern (< 60 yr)<br>GAR-2: Old (> 60 yr and 10 kyr)<br>GAR-3: Paleowaters (> 10 kyr)</td><td colspan="5">Aquifer-1*<br>GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X<br>GAR-2: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐<br>GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐<br>*GAR extrapolated from similar aquifer-type in greater pilot area</td></tr>
<tr><td colspan="5">Aquifer-2*<br>GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X<br>GAR-2: 1-10%: ☐ 10-25%: X 25-50%: ☐ >50%: ☐<br>GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐<br>*GAR extrapolated from similar aquifer-type in NW Skåne</td></tr>
<tr><td colspan="5">Aquifer-3<br>GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: X >50%: ☐<br>GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: X >50%: ☐<br>GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐</td></tr>
<tr><td>Groundwater age ranges (GAR) estimated by:</td><td colspan="5">Tracer based estimates X<br>Flow and age model simulations ☐<br>Combination of model and tracer estimates ☐<br>Expert judgement: X</td></tr>
<tr><td colspan="6">Objective of age dating studies:</td></tr>
<tr><td>Basic research or General groundwater management</td><td colspan="2">Assessment of pollutant history</td><td colspan="2">Assessment of the efficiency of remediation and mitigation measures</td><td>Indication of vulnerability of aquifers and water supply wells</td></tr>
<tr><td>x</td><td colspan="2"></td><td colspan="2"></td><td>x</td></tr>
<tr><td rowspan="2">Water Usage<br>(not relevant for observation wells)</td><td colspan="2">Water supply</td><td>Irrigation</td><td>Industry</td><td>Other</td></tr>
<tr><td colspan="2">x</td><td>x</td><td>x</td><td></td></tr>
<tr><td rowspan="2">Geoenergy related activities<br>(not relevant for observation wells)</td><td>Shallow Geo-T</td><td>Deep Geo-T</td><td colspan="2">Hydrocarbons</td><td>Nuclear waste disp. | $CO_2$ storage</td></tr>
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<tr><td rowspan="2">Mining activities<br>(not relevant for observation wells)</td><td colspan="2">Construction materials</td><td>Minerals / metals</td><td>Coal</td><td>Other</td></tr>
<tr><td colspan="2">x</td><td></td><td></td><td></td></tr>
<tr><td colspan="6">REFERENCES</td></tr>
</table>

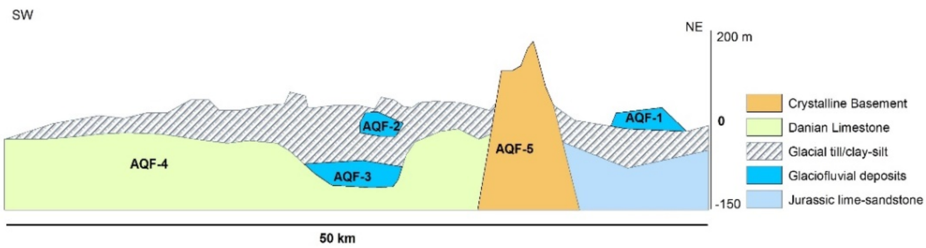
| **OPEN Access reports and papers** (PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches): | **Reports and papers with restricted access:** |
|---|---|
| **Gustafsson O., Andersson J-E. and De Geer J., 1979.** Sammanställning av hydrogeologiska data från Kristianstadslätten. SGU-Ser. Rapporter och meddelanden 12. Sveriges geologiska undersökning/Geological Survey of Sweden.<br>**Gustafsson O., Jonasson S.A., Magnusson E. and Andersson C., 1988.** Grundvattenundersökningar på Kristianstadslätten 1976–1987. SGU-Ser. Rapporter och meddelanden 52. Sveriges geologiska undersökning/Geological Survey of Sweden.<br>**Persson G.N., 1974.** Tritium data from groundwater in the Kristianstad plain, southern Sweden. Conference abstract. IAEA-SM-182/3.<br>**Åkesson M., 2014.** On the scope and assessment of pesticides in groundwater in Skåne, Sweden. LUNDQUA Thesis 74. Quaternary Sciences, Department of Geology, Lund University. | **Possnert G. 2008.** Ålder – en väsentlig kvalitet. Single analysis report to Malmberg Borrning AB from Ångströmslaboratoriet, Uppsala University 2008-07-07.<br>**Åkesson M., Suckow A., Visser A., Sültenfuss J., Laier T., Purtschert R. and Sparrenbom C.J., 2015**. Constraining age distributions of groundwater from public supply wells in diverse hydrogeological settings in Scania, Sweden. Journal of Hydrology 582: 217-229. |

**Remarks / other relevant information:**

The conceptual model is, obviously, a simplification but meant to visualise general stratigraphy and aquifer types within the region, and the general GAR-pattern. Please note that AQF-1, AQF-2 and AQT-1 are not spatially continuous units and that within the entire region, there are really several AQF-1's, AQT-1's and AQF-2's. Also, AQF-3 is sometimes regarded as two separate hydraulic units: an upper dual-porosity limestone aquifer, and a lower porous glauconitic sandstone aquifer.

The provided information on age range for AQF-1 and -2 is based on information from similar aquifer types in the region, although not from the specific aquifers along the given section.

Note that tracer data and thus GAR-estimates ought to be regarded as maximally representative down to standard depths of drinking water wells (here max c. 100-150 m).

<table>
<tr><td colspan="3">Name of pilot area / aquifers / type:<br>Skåne SW / Quaternary sand aquifers, Cretaceous limestone and crystalline bedrock aquifers / porous, dual-porosity and fissured</td><td colspan="2">Country: Sweden<br><br>Region: Skåne</td></tr>
<tr><td>Study level</td><td colspan="4">Transboundary : ☐ Regional: x Local: ☐ Single well(s): ☐</td></tr>
<tr><td>Type of observations<br>(choose one of the options, create separate template if needed for each type if each type need specific information)</td><td colspan="4">☐ Short screened observation wells (not pumped)<br>☐ Long screened observation wells (not pumped)<br>X Pumped wells, long screens in one aquifer<br>☐ Pumped wells, long screens over multiple aquifers<br>☐ Springs<br>☐ Other (eg. research wells; indicate type and information on pumping):</td></tr>
<tr><td>Approximate location of pilot:</td><td colspan="4">
</td></tr>
<tr><td>Geological cross section / conceptual model of the pilot area:</td><td colspan="4">
</td></tr>
<tr><td colspan="2">Name of Shape- / Geopackage file defining the area:</td><td colspan="3">Projection to be used:<br>WGS84 (Epsg4326)</td></tr>
<tr><td rowspan="2">Hydrological parameters:</td><td>Mean annual precipitation (mm or range in mm)</td><td>Mean annual groundwater recharge (mm or range in mm)</td><td>Mean annual groundwater recharge temperature (°C)</td><td>Thickness of unsaturated zone (range in m)</td></tr>
<tr><td>600-800</td><td>200-350</td><td>8-9</td><td>0-5 m</td></tr>
<tr><td colspan="2">Pumped wells only</td><td colspan="2">Typical pump discharge of</td><td>Typical pump</td></tr>
</table>

| | | | | |
|---|---|---|---|---|
| | | **sampled individual well ($m^3$/day):** 1-1000 | | **discharge of complete well field ($m^3$/day): -**<br>*If relevant* |
| **List of aquifers and aquitards in pilot area***<br>**Given no:s = along cross section < within full pilot area* | | **No. of confined or semiconfined aquifers in pilot area:** 3 | | **No. of unconfined aquifers in pilot area:** 2 |
| **Aquifer no. (aqf):** 5<br>**Aquitard no. (aqt/acl):** 2 | **Aquifer/aquitard type and/or name** | **Lithology *(Resource WP6 terminology)*** | **Depth range (m)** | **GW age range (yr)** |
| Aqf-1: | Glaciofluvial deposits | Fine sand to gravel | 0-30 | <5 - >60 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt/acl -1: | Glacial till/clay-silt | Clay-silt, clayey-clay till | | |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Fissured and porous / dual porosity: X | No hydraulically active porosity: X |
| Aqf-2: | Glaciofluvial deposits | Fine sand to gravel | 10-40 | <5 - >60 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqt/acl -2: | Glacial till/clay-silt | Clay-silt, clayey-clay till | | |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Fissured and porous / dual porosity: X | No hydraulically active porosity: X |
| Aqf-3: | Glaciofluvial deposits | Coarse sand to gravel | 40-80 | >50 - >2 000 |
| **Porosity type** | Porous: X | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| Aqf-4: | Danian limestone | Limestone | 5->80 | <60 - >10 000 |
| **Porosity type** | Porous: ☐ | Fissured: ☐ | Karst: ☐ | Fissured and porous / dual porosity: X |
| Aqf-5 | Crystalline basement | Granite, gneiss | 0- | <1 - >100 |
| **Porosity type** | Porous: ☐ | Fissured: X | Karst: ☐ | Fissured and porous / dual porosity: ☐ |
| **Applied tracer age indicators** ($^3H$, $^3H/^3He$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $^{36}Cl$, $^{81}Kr$, $^4He$, CFCs, $SF_6$, etc.)<br>**Applied recharge temperature indicators** ($^{18}O$, D, noble gases) | | **Aquifer-1**<br>$^3H$, $^3H/^3He$, $^4He$, CFC, $SF_6$, noble gases | | |
| | | **Aquifer-2**<br>$^3H$, $^3H/^3He$, $^4He$, CFC, $SF_6$, noble gases | | |
| | | **Aquifer-3**<br>$^3H$, $^3H/^3He$, $^4He$, CFC, $SF_6$, noble gases, $^{14}C$, $^{39}Ar$, $^{85}Kr$, $^{18}O$, D | | |

| | |
|---|---|
| | **Aquifer-4**<br>$^{3}H$, $^{14}C$, $^{18}O$, D |
| | **Aquifer-5**<br>$^{3}H$, $^{3}H/^{3}He$, $^{4}He$, CFC, $SF_6$, noble gases |
| **Number of sites (wells/springs) with age indicators** | **Aquifer-1**<br>**1-5: ☐ 5-10: X* 10-25: ☐ >25: ☐**<br>**Total no. of samples from similar type-aquifers within the greater pilot area* |
| | **Aquifer-2**<br>**1-5: X* 5-10: ☐ 10-25: ☐ >25: ☐**<br>**Total no. of samples from similar type-aquifers within the greater pilot area* |
| | **Aquifer-3**<br>**1-5: ☐ 5-10: ☐ 10-25: X >25: ☐** |
| | **Aquifer-4**<br>**1-5: ☐ 5-10: ☐ 10-25: ☐ >25: X** |
| | **Aquifer-5**<br>**1-5: X* 5-10: ☐ 10-25: ☐ >25: ☐- None**<br>**Samples from similar type-aquifer in NW Skåne* |
| **GW age range (GAR)**<br>**GAR-1: Modern (< 60 yr)**<br>**GAR-2: Old (> 60 yr and 10 kyr)**<br>**GAR-3: Paleowaters (> 10 kyr)** | **Aquifer-1***<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR extrapolated from similar aquifer-type in NE Skåne* |
| | **Aquifer-2***<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: ☐ 10-25%: X 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR extrapolated from similar aquifer-type in NW Skåne* |
| | **Aquifer-3**<br>**GAR-1: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| | **Aquifer-4**<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: X >50%: ☐**<br>**GAR-2: 1-10%: ☐ 10-25%: ☐ 25-50%: X >50%: ☐**<br>**GAR-3: 1-10%: X 10-25%: ☐ 25-50%: ☐ >50%: ☐** |
| | **Aquifer-5***<br>**GAR-1: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: X**<br>**GAR-2: 1-10%: ☐ 10-25%: X 25-50%: ☐ >50%: ☐**<br>**GAR-3: 1-10%: ☐ 10-25%: ☐ 25-50%: ☐ >50%: ☐**<br>**Extrapolated from similar aquifer-type in NW Skåne* |
| **Groundwater age ranges (GAR) estimated by:** | **Tracer based estimates X**<br>**Flow and age model simulations ☐**<br>**Combination of model and tracer estimates ☐**<br>**Expert judgement: X** |
| **Objective of age dating studies:** | |

<table>
<tr><td>Basic research or General groundwater management</td><td colspan="2">Assessment of pollutant history</td><td colspan="2">Assessment of the efficiency of remediation and mitigation measures</td><td colspan="2">Indication of vulnerability of aquifers and water supply wells</td></tr>
<tr><td>x</td><td colspan="2"></td><td colspan="2"></td><td colspan="2">x</td></tr>
<tr><td rowspan="2">Water Usage<br>(not relevant for observation wells)</td><td colspan="2">Water supply</td><td>Irrigation</td><td>Industry</td><td colspan="2">Other</td></tr>
<tr><td colspan="2">x</td><td>x</td><td>x</td><td colspan="2"></td></tr>
<tr><td rowspan="2">Geoenergy related activities<br>(not relevant for observation wells)</td><td>Shallow Geo-T</td><td>Deep Geo-T</td><td colspan="2">Hydrocarbons</td><td>Nuclear waste disp.</td><td>$CO_2$ storage</td></tr>
<tr><td>x</td><td></td><td colspan="2"></td><td></td><td></td></tr>
<tr><td rowspan="2">Mining activities<br>(not relevant for observation wells)</td><td colspan="2">Construction materials</td><td>Minerals / metals</td><td>Coal</td><td colspan="2">Other</td></tr>
<tr><td colspan="2">x</td><td></td><td></td><td colspan="2"></td></tr>
</table>

**REFERENCES**

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

**Barmen G., 1992.** On the combination of isotope hydrogeology with regional flow and transport modelling. PhD-thesis. Department of Engineering Geology, Lund Institute of Technology, Lund University.

**Gustafsson O., 1972.** Beskrivning till hydrogeologiska kartbladet Trelleborg NV och Malmö SV. SGU-Ser. Ag 4. Sveriges geologiska undersökning/Geological Survey of Sweden.

**Gustafsson O., 1978.** Beskrivning till hydrogeologiska kartbladet Trelleborg NO/Malmö SO. SGU-Ser. Ag 6.
Sveriges geologiska undersökning/Geological Survey of Sweden.

**Gustafsson O., 1981.** Beskrivning till hydrogeologiska kartbladet Malmö NV. SGU-Ser. Ag 14. Sveriges geologiska undersökning/Geological Survey of Sweden.

**Åkesson M., 2014.** On the scope and assessment of pesticides in groundwater in Skåne, Sweden. LUNDQUA Thesis 74. Quaternary Sciences, Department of Geology, Lund University.

**Reports and papers with restricted access:**

**Åkesson M., Suckow A., Visser A., Sültenfuss J., Laier T., Purtschert R. and Sparrenbom C.J., 2015**. Constraining age distributions of groundwater from public supply wells in diverse hydrogeological settings in Scania, Sweden. Journal of Hydrology 582: 217-229.

**Remarks / other relevant information:**

This case study is meant to exemplify the geological and hydrogeological heterogeneity of SW Skåne, and the resulting GAR diversity. The conceptual model is, obviously, a simplification but meant to visualise general stratigraphy and aquifer types within the region. Please note that no hydrogeological unit is spatially continuous along the profile/over the region, which is also the reason for why aquitards/aquicludes are not specified as either or – the exact lithology and hydraulic function varies depending on location. Also, within the entire region, there are really several AQF-1's and AQF-2's. AQF-3 and -4 are likely hydraulically connected.

The provided information on age range is partly based on site-specific data (AQF-3, AQF-4) and partly on data from other parts of Skåne, from similar aquifer types (AQF-1, AQF-2, AQF-6).

Note that tracer data and thus GAR-estimates ought to be regarded as maximally representative down to standard depths of drinking water wells (here max c. 100 m).

# 4 PERSPECTIVES AND FUTURE ACTIVITIES

This report does not intend to provide a complete description of all groundwater dating studies in Europe. The intention is to provide selected good examples, which hopefully will inspire groundwater managers and scientists to conduct additional work and research on determination, application and visualization of groundwater age and travel time distributions in the assessment of groundwater quantitative and chemical status at local and regional scales. To help its further and wider application, a guide for age indicator sampling is provided based on existing sampling protocols.

The presented case studies presented here serve to reinforce the general principle that multiple sampling points with multiple environmental tracers (stable and radioactive isotopes, noble gases, groundwater temperature, and water chemistry) are needed to provide the information necessary for an adequate characterization of mean groundwater ages along flow paths together with available resources or vulnerability of aquifers. This information and the ages can then be combined with numerical hydrodynamic modelling where these data are applied as independent constraints allowing optimization of the hydraulic models to best fit age indicator data.An important goal of HOVER WP6 is to present the information of groundwater age distributions and vulnerability in new innovative ways on the digital GeoERA Information Platform / EGDI (the European Geological Data Infrastructure). Results will be shown on the GeoERA HOVER website (http://geoera.eu/projects/hover8/) and the EGDI platform (www.europe-geology.eu/). The information compiled in the WP6 templates of the pilot areas makes it possible to directly feed the EGDI platform with groundwater age indicator data.

The ongoing discussions and cooperation of the European Geological Surveys with other research institutes and authorities provide a good basis for a sound and valuable digital information about groundwater age distributions and vulnerability for EGDI beyond GeoERA. The information provided indicates the vulnerability to pollution from the surface in shallow aquifers, together with elevated concentrations of harmful geogenic trace elements in deep aquifers. This is combined with the risk of over-exploitation in an ever-increasing number of European groundwater bodies.

The goal is to develop the European Geological Data Infrastructure as one of the leading groundwater information platforms, globally, providing “FAIR” (Findable, Accessible, Interoperable and Reusable) access to highly relevant and sound groundwater information and data for Europe and potentially interested partners abroad that want to develop similar services.

Besides the European geological surveys, this will benefit authorities, consultants and software companies e.g. developing add on services to the digital information platform tailored for specific end users. The partners involved in HOVER WP6 established collaboration with and between globally leading groundwater dating laboratories and the US Geological Survey for the analysis of environmental tracers in groundwater long before the GeoERA programme obtained funding, and this collaboration still continues within GeoERA. European water companies collaborating with some of the partners of WP6 may be the first companies in the world to systematically use a wide range of tracers suitable for dating of groundwater in defined age intervals of less than 10 to more than 100.000 years for vulnerability assessments and advanced groundwater management of well fields.

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# 6 APPENDIX I: SAMPLING GUIDELINES

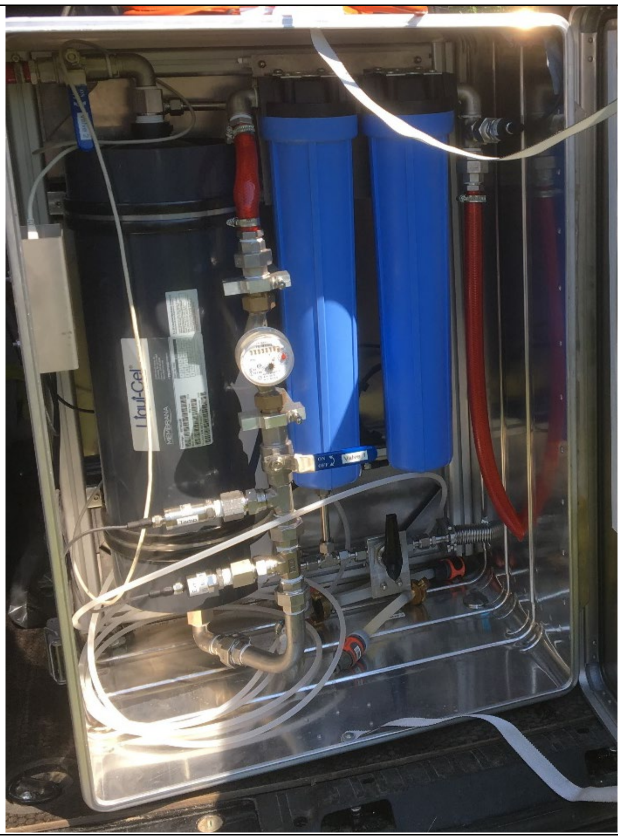
As groundwater age - unless it is modelled - is estimated based on environmental tracer data, it is crucial that the analyses are carried out on reliable groundwater samples. Sampling is often considered a scientifically less important part of a survey, and non-professional technician staff carries out sampling, but inappropriately collected samples can result in wrong data, leading to incorrect interpretations. Hence, it is extremely important that the samples are collected correctly. This appendix provides some guidelines describing procedures for the sampling of the most important groundwater dating tracers used by some of the leading laboratories in an outside Europe.

**Groundwater sampling guidance for the most common groundwater dating tracers ($^{3}H/^{3}He$, CFCs, $SF_6$, $^{85}Kr$, $^{39}Ar$, $^{14}C$, $\delta^{13}C$) for dating of young and old groundwater.**

In the following we provide information on selected groundwater dating laboratories and selected sampling guidance described by some of these laboratories in and outside Europe. Typically, the different laboratories use variations of the same techniques for groundwater sampling, however, it is recommended to always consult the laboratories to which the samples will be send before the sampling campaigns are performed. The sampling procedures described on the following pages provide a basic understanding of what issues the scientists and technicians collecting the samples need to be aware of and offer special attention to during sampling.

Additional information can be found at the websites of the dating laboratories some of the most well known in Europe and abroad are listed at the end of the appendix.

Equipment for $^{85}Kr$ & $^{39}Ar$ analyses on groundwater developed by Climate and Environmental Physics at University of Bern, Switzerland



Equipment for $^{85}Kr$ & $^{39}Ar$ analyses on groundwater developed in collaboration between the Noble Gas Laboratory at University of Heidelberg, Germany and the Geological Survey of the Netherlands (TNO)

The equipment shown above were used for the collection of samples for groundwater dating in HOVER WP6 by $^{39}Ar$ and $^{85}Kr$ used in water supply wells of VCS Denmark in June 2019. The samples were collected by GEUS (the Geological Survey of Denmark and Greenland) in collaboration with University of Bern, University of Heidelberg, TNO, University of Bremen and VCS Denmark. The results of the analyses will be presented in the HOVER deliverable D6.4 report and uploaded to the EGDI document repository in 2021.

**EXAMPLES OF SAMPLING PROCEDURES FOR ISOTOPE HYDROLOGY AND GROUNDWATER DATING DEVELOPED BY THE INTERNATIONAL ATOMIC ENERGY AGENCY (IAEA) AND OTHER LEADING GROUNDWATER DATING LABORATORIES.**

Sampling for groundwater dating with $SF_6$ at University of Heidelberg. The sampling is conducted during a thunderstorm by the master students David Wachs and Francesco Pineider from University of Heidelberg and University Sapienza in Rome, respectively, in water supply wells of VCS Denmark around the city of Odense, Denmark, June 2019.

# Sampling Procedures for Isotope Hydrology

Proper sampling and field measurements of both physicochemical and isotopic parameters are critical to ensure high quality analysis, reliable interpretation of data and consistency for incorporation of results in global hydrological databases. This booklet is a companion to the IAEA video "Introduction to Water Sampling and Analysis for Isotope Hydrology". It can be easily taken on-site, and serves as a guide during sampling to ensure that all procedures are performed correctly.

Before embarking on a sampling campaign, ensure that all materials and equipment needed for field work have been properly checked and packed.

IAEA

Water Resources Programme

## 1. LOCATION OF SAMPLING POINT (COORDINATES)

Once on-site, the location of a sampling point must be recorded as accurately as possible either by using the global positioning system (GPS), or a high resolution topographic map. Record the **coordinates**, i.e. latitude, longitude and altitude, and nearby landmarks, if any. It is preferable that coordinates are given in decimal degrees (with at least four decimal places and preferably using the WGS-84 datum). Also, note the date and time of sampling.

## 2. WATER DEPTH MEASUREMENT

The static water level of a well should be measured below a reference point. This measurement should be made before the well is purged to remove stagnant water. Measure the water level using either a measuring tape or commercially available electrical sounders and record the readings (this may be complemented with information on total depth, screen depth, etc.).

## 3. PURGING OF WELL

After recording the water level, purge the well with a pump. In general, three well volumes should be pumped out before samples are collected.

## 4. ON-SITE PHYSICOCHEMICAL MEASUREMENTS

After purging is complete, the well is ready for field measurements of **conductivity**, **temperature**, **pH**, **dissolved oxygen** and **alkalinity**.

### Conductivity

The conductivity meter must be calibrated following the manufacturer's instructions. Normally, a calibration standard with a conductivity of 1413 μS/cm at 25°C is used. The conductivity meter should be calibrated before use.

Make sure that the electrode is rinsed with distilled or well water before measurements are made. To measure sample conductivity, the sample is poured into a beaker or into a flow through cell and the conductivity electrode is inserted. Once the readings have stabilized, record the temperature and conductivity of the water sample.

### pH

Operate the pH meter according to the manufacturer's instructions and calibrate the meter accordingly. Two or three standard solutions or pH buffers are used for this calibration. Commercially available pH buffers may be found in different forms, including tablets, colour-coded solutions, or disposable packs.

Set the pH meter to calibration mode. Insert the electrode into the first buffer of higher pH, for example pH7. When the correct pH display is seen, store the reading in the unit by pressing the appropriate key. Remove and rinse the electrode. Place the electrode into the second buffer solution of lower pH, e.g. pH4. When the reading stabilizes and the correct pH display is seen, the pH meter is calibrated and ready for measuring.

Switch to measurement mode. To measure the pH of a sample, insert the electrode into the sample (beaker or flow though cell), press the appropriate key, and wait for the reading to stabilize.

Do not stir the electrode as vigorous stirring may change the sample pH through degassing of carbon dioxide. After measurements have been made, clean the electrode and store in the storage solution.

### Dissolved oxygen

Dissolved oxygen is measured either by using a meter with a dedicated submersible probe, or with the spectrophotometric method described below, using vacu-vials and a field spectrophotometer.

Using this second method, insert the sealed zero-oxygen blank ampoule into the sample slot aligning the marks on the meter and the ampoule. This calibrates the spectrophotometer.

Fill the sample container (beaker) with well water. Insert the vacu-vial filled with the necessary reagents into the water and break the tip of the vial. Water is sucked into the vial and a blue colour develops depending on the concentration of dissolved oxygen. Clean the vial using tissue paper and depress into the sample slot, aligning the marks on the spectrophotometer. Record the dissolved oxygen value of the sample, usually expressed in milligrams per litre or parts per million.

### Alkalinity

Alkalinity is usually measured through chemical titration using commercially available field kits. Instructions for use are generally included with these kits.

Fill the vial up to the mark with the water sample. Add a drop or two of phenolphthalein solution. The sample will turn from colourless to pink. Titrate with the acid supplied in the kit. For best results, add one drop of the acid, shake the beaker, and note the colour. If there is no change in colour, repeat the procedure until the solution becomes colourless. Record the amount of acid used to reach this point.

Next, add a drop or two of total alkalinity indicator solution to the sample. Titrate further to the end point as indicated in the kit, in this case from green to brown. Record once again the amount of acid used and calculate the alkalinity value according to instructions, usually expressed in mg/L $HCO_3$.

## 5. FILTRATION, ACIDIFICATION AND LABELLING OF SAMPLES FOR CHEMISTRY

Filtration of samples in the field is required for laboratory measurement of cations and anions.

After disassembling the two-chamber filtering unit, remove the filter cover, which is usually bluish in colour. Lift, using forceps, the white 0.45 μm membrane filter and place onto the filter holder. Place the filter holder on the lower chamber of the filtration unit and screw on the upper chamber.

Unscrew the lid of the upper chamber and pour about 500 mL of the sample into the chamber. Screw on the lid of the upper chamber and apply a vacuum with a hand pump.

When the sample is filtered, unscrew the upper chamber and pour the filtered sample into the sampling bottles.

For **cations, acidify** the filtered water sample using a few drops of **concentrated nitric acid**. Close the lid and shake the bottle (collect about 125 mL).

For **anions, do not acidify**; there is no need to add any chemicals (collect about 125 mL).

Label the bottles carefully with the relevant information about the sample.

## 6. STABLE ISOTOPE SAMPLING

Sampling for oxygen-18 and deuterium is simple. No sample filtration or preservation is required. Fill a 50 mL, double capped, glass or polyethylene bottle directly from the source or from a secondary container. Clearly label the sample with all details. Make sure the bottles are tightly capped. During sampling, storage and transportation to the laboratory, take care to avoid evaporation of the sample.

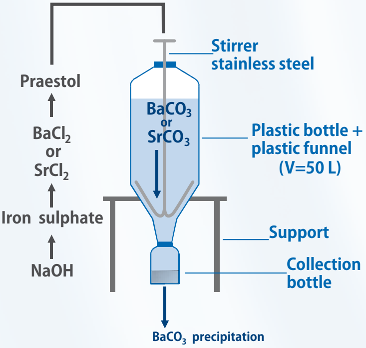
## 7. TRITIUM SAMPLING

Sampling for tritium is also simple. Normally, a 500 mL sample is sufficient. Depending upon the tritium content and measurement technique, a larger, 1 L sample may be necessary. Polyethylene or glass bottles are suitable for tritium sampling. No filtration or preservation is necessary for tritium samples. Label bottles properly and carefully with waterproof markers. Ensure that no writing is smeared due to water. If necessary write sample numbers at different places on a bottle or on labels.

## 8. CARBON-13 AND RADIOCARBON SAMPLING

### CONVENTIONAL METHOD

For carbon-13 and carbon-14 analyses, about 2.5 g of carbon are required. This amount of carbon may be obtained from a 40–60 L sample volume, depending upon the alkalinity of the water. Therefore, sample processing in the field is essential to avoid shipment of large volumes of water to the laboratory. With this method, all inorganic carbonate species are precipitated from the water at high pH and the wet precipitate is shipped to the laboratory.




The field apparatus consists of a 60 L specially fabricated plastic container to which a wide mouthed plastic bottle of 1 L capacity can be screwed. The amount of water to be processed is calculated using the alkalinity measurement from the field. Generally, a minimum amount of 50 L is processed.

Fill the container up to the top with groundwater. Insert the stirrer and close the lid.

Add about 50 mL of carbonate-free concentrated sodium hydroxide to raise the pH of the sample to about 11. If necessary, confirm the raised pH of the sample by using pH testing paper or a pH meter. Cabonate-free sodium hydroxide solution should be prepared and aliquots bottled in a laboratory prior to the sampling campaign.

After adding sodium hydroxide, minimize exposure to the atmosphere so that atmospheric carbon dioxide does not contaminate the sample.

Stir the sample using the stirrer. Add about 5 g of iron sulphate to the sample. This will facilitate formation of carbonate precipitate.

Add about 150 g of strontium chloride or barium chloride powder to form a fine cloud of carbonates. Close the lid and stir the sample.

Check for complete precipitation by adding a small amount (25–30 g) of chloride powder to the top of the tank without stirring. If any cloudiness appears, indicating further precipitation, more chloride powder and possibly sodium hydroxide solution must be stirred in to ensure complete precipitation.

Add 40 mL of Praestol solution to the sample. It is a polyacrylamide and is used as a coagulant to speed up this process.

After addition of all these reagents, the precipitate quickly starts to settle to the bottom of the apparatus, filling the 1 L bottle attached to the bottom of the container. When all the precipitate settles at the bottom of the funnel portion of the container filling the attached bottle, a rubber stopper fitted at the end of a steel rod is inserted and the container is closed at the bottom, so the filled 1 L bottle can be removed. If necessary, more bottles should be attached and precipitate collected. Tightly cap and properly label the bottles, indicating the sample number, date, and other relevant details.

### ALTERNATIVE METHOD

#### Accelerator mass spectrometer (AMS) method for carbon-14

For AMS analysis, to extract 2 mg of carbon required, about 200 mL of water is needed. To prevent contamination, bottles should be made of glass and must be fully filled and perfectly closed. The samples should be sterilized for conservation by adding 5 drops of $I_2$–KI solution per 100 mL sample. This $I_2$–KI solution can be prepared by dissolving 1.5 g $I_2$ and 3 g KI in 100 mL of demineralized water. Another possibility is to add 2 to 3 drops of $HgCl_2$ solution.

#### Carbon-13 sampling

Collect about 250 mL to 1 L of water in a high density plastic or a dark glass bottle with a tight seal. If the sample is to be stored for more than a week, sodium azide ($NaN_2$) or mercury (II) chloride ($HgCl_2$) should be added to avoid alteration due to biological activity. Generally, 5–10 mg of carbonate is sufficient for mass spectrometric measurement.

## 9. TRITIUM–HELIUM SAMPLING

Samples for tritium–helium are collected in copper tubes with specially designed clamps. It is important to ensure that water samples are collected without any entrapped air bubbles.


Tritium


$^{13}C$ filtered
sodium azide ($NaNH_3$)
mercury (II) chloride ($HgCl_2$)


Cations filtered and acidified


Anions filtered


$^{18}O$ and $^{2}H$

It is recommended that water be pumped from the well or spring using a transparent plastic tube. Connect the plastic tube to the copper tube. Allow the water to flow through the copper tube. It is important to tap the frame lightly with the spanner to remove any air bubbles that may be trapped inside the copper tube. When ready to collect the sample, close the outflow end of the copper tube first by tightening the clamp while water is still flowing through the tube. Repeat the process to close the clamp at the inflow end of the tube, thus stopping the water supply.

Label the sample using a waterproof marker on adhesive tape or on the metallic frame. Record sample number, date, time and temperature.

### Chlorofluorocarbons sampling (CFC)

Samples are usually collected in duplicate or triplicate using amber glass bottles with special aluminium lined caps.

Connect the plastic tube to the smaller metal tube, which fits inside the glass bottle. Ensure that no air bubbles are present in the plastic tube. Label bottles prior to sampling. Fill a metal container and allow it to overflow. Submerge the bottles and aluminium lined caps into the overflowing metallic container and allow flushing to take place for 10–15 minutes. Cap filled sample bottles under water to ensure that no air bubbles enter the samples.

For the above two parameters, it is advisable to contact the respective laboratories for specific and more detailed instructions, or refer to the IAEA CFC guidebook or tritium–helium procedure.

## 10. SUMMARY

To summarize, a normal set of groundwater samples, for commonly analysed isotopes and chemical analysis, at a sampling point consists of:

- Two bottles for hydrochemistry, both filtered and one acidified;
- One 500 mL (or 1 L) bottle for tritium;
- One 50 mL bottle for oxygen-18 and deuterium;
- One or two 1 L bottles of wet carbonate precipitate or water for carbon-14 and associated carbon-13 measurements. Or, if using the alternative method, a 250 mL glass bottle for AMS.

Field measurements and analyses to be done on collected samples and other details should be filled in the field sheets shown in the templates. These are available at www.iaea.org/water or upon request.

More detailed procedures on sampling can be provided by:

Isotope Hydrology Section
International Atomic Energy Agency
ihs@iaea.org, www.iaea.org/water

## LIST OF SAMPLES FOR ISOTOPE OR CHEMICAL ANALYSIS

COUNTRY AND PROJECT CODE: ______________________________ DATE: ___/___/______

INSTITUTE: ______________________________ RESPONSIBLE OFFICER: ______________________

| No. | Sample code [a] (local) | Sampling date YY/MM/D | Type [b] | No. of bottles shipped | Other information | Required analysis [c] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | O-18 | H-2 | H-3 | C-13 | C-14 | Chemistry | Other |
| 1 | | | | | | | | | | | | |
| 2 | | | | | | | | | | | | |
| 3 | | | | | | | | | | | | |
| 4 | | | | | | | | | | | | |
| 5 | | | | | | | | | | | | |
| 6 | | | | | | | | | | | | |
| 7 | | | | | | | | | | | | |
| 8 | | | | | | | | | | | | |

[a] It is essential that codes placed on labels coincide with sample codes listed in this table.

[b] GWB-groundwater (borehole); GWD-groundwater (dug, shallow well); GWS-spring; SLA-lake ; SRE-reservoir; SRI-river; SPR-precipitation.

[c] For chemical analysis, major ions are assumed. Please indicate if other parameters are required.

Recommended amount of sample for analysis:

- Oxygen-18 and hydrogen-2: 50 mL.
- Tritium: 500–1000 mL.
- For carbon-14 + carbon-13; follow the instructions for precipitating $SrCO_3$ in the field, if to be analysed using conventional methods. For analyses by AMS, collect 200 mL for carbon-14 and 250–1000 mL for carbon-13.
- Chemistry: Send two bottles (one with125 mL for cations, acidified with 3 drops of conc. $HNO_3$, and one with 125 mL left untreated for other analyses). If samples contain sediment, appropriate filters should be used.

## ADDITIONAL INFORMATION COLLECTED IN THE FIELD

COUNTRY AND PROJECT CODE: ______________________________ DATE: ___/___/______

INSTITUTE: ______________________________ RESPONSIBLE OFFICER:__________________

| No. | Sample code (local name) | Sample site name | Aquifer name | Sample depth [a] | Coordinates (specify units) [b] | | Altitude (m) | Field data | | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Latitude (N/S DDMMSS.DD) | Longitude (W/E DDDMMSS.DD) | | Cond. µS/cm | Temp. °C | pH | Alk mg/L | |
| 1 | | | | | | | | | | | | |
| 2 | | | | | | | | | | | | |
| 3 | | | | | | | | | | | | |
| 4 | | | | | | | | | | | | |
| 5 | | | | | | | | | | | | |
| 6 | | | | | | | | | | | | |
| 7 | | | | | | | | | | | | |
| 8 | | | | | | | | | | | | |
| 9 | | | | | | | | | | | | |
| 10 | | | | | | | | | | | | |
| 11 | | | | | | | | | | | | |
| 12 | | | | | | | | | | | | |

[a] For samples collected from aquifers, lakes and reservoirs, the sampling depth field (specific depth, range of depths or screen ranges) should always be completed.

[b] Coordinates can be taken with a GPS, or from a 1:50 000 topographic map, and are preferably stated in decimal degrees, or in deg-min-sec (WGS-84 datum). If relevant, please provide a short description of aquifer lithologies in the study area.

**Groundwater sampling guidance for 3H/3He analyses and dating:**

Keep the outlet upwards!!

# Notes for sampling:

## most important in brief

**Sampling of groundwater for noble gas analysis:**

- use transparent hose to connect Copper tube with pumping line
- connect a short transparent hose with the other end of the tube and narrow it to increase the water pressure in the tube or connect a valve and a manometer
- raise the outlet of the tube by approx. 45°
- flush the tube (40 cc) at least 10 times
- meanwhile hit the aluminium rack with a stiff tool (ratchet wrench), to release air bubbles from the inner walls of the tube. IMPORTANT!!
- screw down real tight **first outlet, then inlet**
  Planar surfaces of the clamps must rest on back-to-back
- don´t bend, squeeze, or do the like to the ends of the tube
- don´t forget to label the tube!!

The wall thickness of the tube is 1mm. The clamps are made in a manner, so that the copper will be squeezed down to 0.7mm. By that the Cu-tube is absolutely helium tight and can stand a high inner pressure and the sample can be stored for years.

**Sampling of groundwater for tritium analysis:**

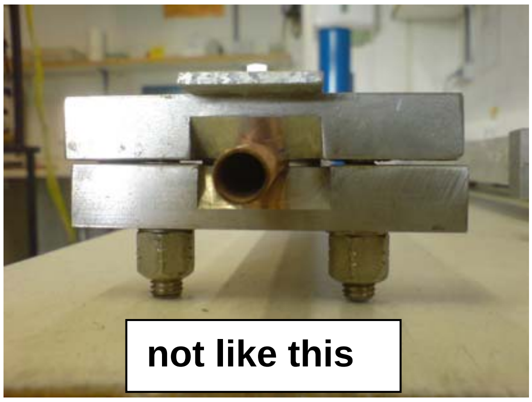
- the sampling container (plastic or glass bottle) muss be dry.
- flush the bottle with low water pressure. Try to reduce foaming and bubbling.
- avoid contact of the hose with the ambient matter.
- amply spill the bottle gently
- pour out some water (1-5cc) and seal the bottle with a dry closing.

Contact of the sampled water with the ambient water should be reduced to a minimum. The tritium concentration of the ambient water might be 1000times higher that in your sample.

Luminescint watches can contain extremely high amounts of tritium. Wearing such watches should be strictly avoided.

any questions?
mail to suelten@uni-bremen.de
or call ++49 421 218 62152

# Samples for Helium-Isotope-Analysis




**<u>sampling</u>**

**IMPORTANT: close clamps completely!**

**There should be no gap visible!**

**<u>Important: labeling</u>**

**Name of institute resp. company /**

**sequential number of well in this campaign /**

**name of well /**

**sequential number of sample (each sample gets its own number!)**

| |
|---|
| Inst.of Water **/** 3 **/** toad spring 3a , 70m **/** 7 |

wooden sticks in boxes need to be placed like they were found, i.e. to the outer end of the upright bars. So, tubes can not slide.

<u>Send digital sample list when shipping the samples.</u>

## Samples for Tritium Analyses:

**<u>Sampling:</u>**

**fill 1000ml water in dry bottles: plastic or glass is ok**

**leave some ml for volume change**

**<u>Important: labeling</u>**

**Name of institute resp. company /**

**sequential number of well in this campaign /**

**name of well /**

**sequential number of sample (each sample gets its own number!)**

| |
|---|
| Inst.of Water **/** 3 **/** toad spring 3a , 70m **/** 7 |

<u>Send digital sample list when shipping the samples.</u>

Contact:
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## background of the procedure for Helium-Sampling

(absolutely to read !)

Groundwater should be analysed for Helium- and Neon-Isotopes ($^3He$, $^4He$, $^{20}Ne$, $^{22}Ne$).
These lightweight noble gases move very fast in water. Also most materials can not be used for sample-containers because of the mobility of the gases. Copper (Cu) tubes have been proved to be a good choice. Cu-tubes will be squeezed at their ends and also can be stored for years. It is important that the ends remain undamaged!

The quality of the analysis depends very much on the contamination of atmospheric air during the sampling. The concentration of the isotopes can be measured better than 0.5%. An air bubble of $2mm^3$ contains such quantities of gases. The Cu-tube are degreased on the inner walls, so water can establish a good contact to the copper and air bubbles will lose their adhesive strength. During filling of the tube one should take care that no air bubbles will be released from the pumping line. To monitor that a transparent hose should be use to connect the pumping line with the tube. However we strongly recommend to hit the aluminium rack with a stiff object during flushing to remove possible air bubbles from the tube.

Groundwater from large depths can contain large amounts of gases according to the hydrostatic pressure. For example, water from a water column of 10m can contain twice as much gas (e.g. $CO_2$, $CH_4$, $H_2S$) as at surface conditions (altitude = 0m). If the water is transferred to the surface the hydrostatic pressure is reduces and the oversaturated gas escapes in form of bubbles. Other dissolved gases, like the noble gases, will diffuse into these bubbles, where the partial pressure is low at first. The time interval of this process is short. This means the degassed proportion of the faster helium is larger as the degassed proportion of the slower neon.
Because of possible degassing, one should try to obtain a high water pressure in the Cu-Tube (> hydrostatic pressure of sampling depth). This can be achieved if a valve and a manometer is connected to the outlet of the tube. Is this not available one can put a hose clip onto the hose to increase the pressure and increase the flux.

Samples for noble gas analysis should be taken with submerged pumps. The pump MP1 made by Grundfos has been proven to be suitable.

Perfect for sampling are closed boreholes. Open wells may have equilibrated their gases with the atmosphere to a large extent. Boreholes should be flushed quite amply. Also the tube and all hoses should be flushed broadminded. If various hoses are connected the diameter should decrease in flow direction. Otherwise there might be cavities, where water can degas. Bubbles may form which move individually with the flow and therefore the gas concentration in the tube will fluctuate.

For the evaluation some sample parameters are needed:
- the temperature of the sampled water
- the salinity, if significant (> 1g/L)
- the altitude of the sampling location
- the altitude of the assumed infiltration area
- the assumed temperature of the infiltration temperature

necessary tools:
- ratchet wrench with 13mm-nut
- 2 transparent hoses with inner diameter of 10mm
- 1 valve and a manometer or a hose clip
- various other connecting pieces

At least 2 Cu-tubes should be fill for each sample.
Also if sampling conditions do not seem to be perfect (large gas build up in the aquifer) there is still a good chance to come to robust interpretation of the sample data.

Cu-tubes with aluminium rack will be provided by us in wooden boxes. One box can contain 24 racks and has the size of 43*107*27cm and a weight of 45kg.

**Put the wooden stickes exactly like on the photo**

Some photos:

fig. 1: flush the hose and attach it to the Cu tube. Fix the hose on the Cu with a clip

fig. 2: hit the aluminium rack with (most convenient here with the rachet)

## Keep the outlet upwards!!

fig: 3: close outlet first.  fig. 4: keep hose on the Cu tube until also inlet is closed.

If water is salty please flush end to prevent corrosion like on the photo

Contact:
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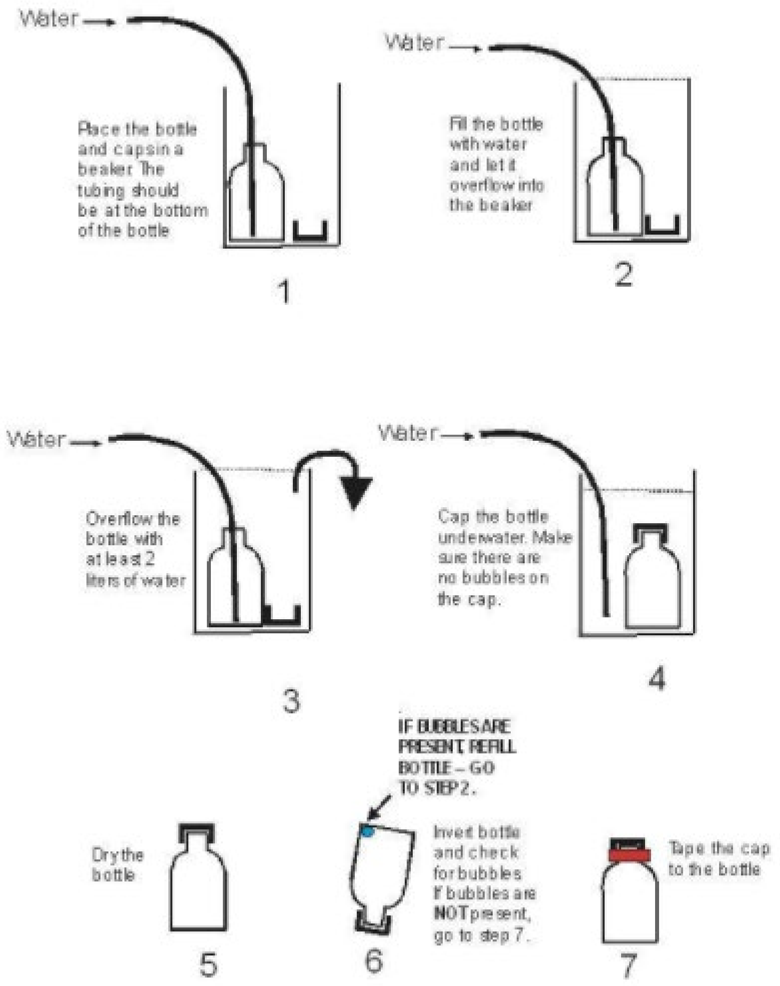
email: suelten@uni-bremen.de

**USGS SAMPLING PROCEDURES FOR GROUNDWATER DATING WITH CFCs and $SF_6$**




For more detailed description please consult the USGS website:

https://water.usgs.gov/lab/chlorofluorocarbons/sampling/bottles/

For a detailed description of sampling for archiving samples over a longer period please consult:

https://water.usgs.gov/lab/chlorofluorocarbons/sampling/ampoules/

For sampling for $SF_6$ dating – please consult:

https://water.usgs.gov/lab/sf6/sampling/

Selected laboratories in and outside Europe performing analyses of groundwater dating tracers. More information about their services can be found at the provided links or via the contact email addresses.

| Laboratory | Tracers | Contact | Link |
|---|---|---|---|
| IAEA | $^{3}H/^{3}He$, $^{14}C$, $\delta^{13}C$, CFCs, etc. | ihl@iaea.org | http://www-naweb.iaea.org/napc/ih/IHS_programme_ihl.html |
| Helis / Univ. Bremen | $^{3}H/^{3}He$, CFCs, $SF_6$ | suelten@uni-bremen.de | https://www.noblegas.uni-bremen.de/eng/ |
| CEP/Univ. Bern | $^{85}Kr$, $^{39}Ar$, etc. | purtschert@climate.unibe.ch | https://www.climate.unibe.ch/services/ services_of_cep/index_eng.html |
| Univ. Heidelberg | $^{3}H/^{3}He$, Noble gases, CFCs, $SF_6$ | aeschbach@iup.uni-heidelberg.de | https://www.hce.uni-heidelberg.de/analytics_en/lab_nobelgas.html |
| BGS | CFCs, $SF_6$, $^{3}H$, $^{14}C$ | https://www.bgs.ac.uk/people/gooddy-daren/ | https://www2.bgs.ac.uk/groundwater/dating/home.html |
| USGS | $^{3}H/^{3}He$, CFCs, SF6 | cfc@usgs.gov | https://water.usgs.gov/lab/ |

Note! The list above is not in anyway comprehensive but it is beyond the scope of this appendix to provide an exhaustive list of groundwater dating laboratories in and outside Europe