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Environmental tracers, groundwater age distributions and vulnerability

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DEFINITIONS AND LIST OF ABBREVIATIONS & ACRONYMS

Definitions
Groundwater vulnerability and intrinsic susceptibility maybe be defined as follows (Focazio et al., 2013)

Vulnerability = "The vulnerability of a groundwater-resource to contamination depends on intrinsic susceptibility as well as the locations and types of sources of naturally occurring and anthropogenic contamination, relative locations of wells, and the fate and transport of the contaminant(s). Water-resource decision makers are often faced with a choice of deciding whether to manage a resource based on knowledge of intrinsic susceptibility or to target more comprehensive and contaminant-specific assessments of vulnerability".

Intrinsic susceptibility = "The intrinsic susceptibility of a ground-water system depends on the aquifer properties (hydraulic conductivity, porosity, hydraulic gradients) and the associated sources of water and stresses for the system (recharge, interactions with surface water, travel through the unsaturated zone, and well discharge). In this way, intrinsic susceptibility assessments do not target specific natural or anthropogenic sources of contamination but instead consider only the physical factors affecting the flow of water to, and through, the ground-water resource".

In this deliverable of HOVER WP6 we consider primarily the intrinsic susceptibility of deep and shallow groundwater wells and aquifers towards non-specified anthropogenic or geogenic substances (contaminants) and we use the terms vulnerability and intrinsic susceptibility as synonyms. The classification of the vulnerability is based on the concentration of environmental tracers in groundwater. The occurrence or non-occurrence of these tracers (e.g. tritium) directly indicate whether the groundwater may be affected by anthropogenic contamination from the surface (e.g. nitrate, pesticides or emerging contaminants) or not, or whether the groundwater may be at risk of elevated concentrations of geogenic elements potentially affecting human health or of over-exploitation (e.g. groundwater without ^{14}C). They may furthermore be used to estimate groundwater age distributions and to calibrate or corroborate groundwater flow models.

The intrinsic susceptibility/vulnerability concepts and definitions used here are closely related to the vulnerability concepts and maps produced in HOVER WP7. However, the vulnerability maps developed in WP7 are for shallow aquifers solely and are based on so-called index methods estimating the vulnerability of large aquifers or volumes of groundwater, based on conditions in the shallow subsurface. Furthermore, they include consideration of the chemical characteristics of the pollutants (primarily nitrate) and may be used for vulnerability mapping at Pan European scale.

Abbreviations and agronyms
GAD = Groundwater age distributions
RTD = Residence time distributions
TTD = Travel time distributions

On the use of the term "groundwater age"
Some authors recommend to abandon the use of "groundwater age" and "mean groundwater age" as it is misleading in many settings (Troldborg et al., 2008; Suckow, 2014). We still believe though that "groundwater age" is a useful term for the general understanding of groundwater aging along flow paths in the subsurface. By using the term groundwater age distribution we imply that groundwater ages vary in time and space and that groundwater collected from even quite small screens is a mixture of groundwater with different age (or travel time) that may vary between a few years in short shallow screens (< 10 cm) and up to thousands of years or more in wells with long screens (>> 10 m), which e.g. short cuts separate aquifers. Here we assume GAD = RTD = TTD and use the terms as synonyms and that "groundwater age" is an "apparent age" covering a range of mixed ages where an average may be misleading.

Based on the contents of environmental tracers this report proposes groundwater age classes suitable for visualization of groundwater age distributions at various scales from shallow and short water supply or monitoring wells to large regional aquifers.

Groundwater flow simulations with groundwater flow models preferably calibrated with tracer concentrations are required for estimation and visualization of groundwater age distributions in large regional aquifers between wells with tracer data. Examples of visualizations of groundwater age distributions in regional aquifers obtained by different modelling techniques are also shown in this report. These visualizations may in some settings be compared directly with and support the vulnerability maps developed in WP7.

The report will be developed further during the GeoERA HOVER project and include examples developed in HOVER in collaboration between the HOVER partners, three of the globally leading environmental tracer and groundwater dating laboratories in Europe, selected water supply companies and European software companies developing software for visualization and interpretation of digital subsurface data, groundwater quality and groundwater age distributions.

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1 INTRODUCTION

Estimation of groundwater age, travel or residence time distributions has become an increasingly important tool for study of groundwater flow and transport in aquifers and aquitards since the concept and potential of using tritium (^3H) and ^{14}C for groundwater dating was introduced e.g. by Kaufman and Libby (1954) and (Ingerson and Pearson, 1964), respectively.

Since the introduction of the concept of groundwater dating several classical regional studies were conducted in Europe e.g. in the East Midlands aquifer (Andrews and Lee, 1979) and the studies in large European basins such as 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). Previous European studies demonstrated that Palaeowaters are found in many coastal settings around 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 assessment of the advance of modern potentially polluted groundwater and the susceptibility / "vulnerability" of water supply wells towards pollution from the surface (Hinsby et al., 2001, 2008; Broers, 2004; Manning et al., 2005; Eberts et al., 2012; Jurgens et al., 2016), and the assessment of trends and history of specific contaminants such as nitrate (Bohlke and Denver, 1995; Broers et al.,?, Hansen et al. 2011, Jurgens et al., 2016), pesticides (Visser et al., 2013, Jakobsen et al., 2019) and veterinary pharmaceuticals (Kivits et al., 2018).

Environmental tracers and model simulations may 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 age or travel time to a specific point is a reasonable approximation (Plummer et al., 1993), while for wells screened or open in several different aquifers or in fractured rocks such an approximation does not make sense. In such cases an estimation of the groundwater age distributions 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 is of much more value (Troldborg, 2004; Bethke and Johnson, 2008, Troldborg et al., 2008; Eberts et al., 2012, Jakobsen et al., 2019).

This report briefly introduces environmental tracers for groundwater dating and groundwater age intervals useful for visualisation of groundwater age distributions and assessment of groundwater vulnerability. The distribution of environmental tracers and groundwater age in aquifers indicate 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 may be used to characterise shallow and main groundwater recharge zones of the systems as well as the occurrence of palaeowaters in deep or shallow parts of discharge zones. Deep and old groundwater resources may not be a long-term sustainable groundwater resource, but still an important strategic resource e.g. in periods of droughts or other negative impacts on the shallow groundwater resources.

2 ENVIRONMENTAL TRACERS FOR GROUNDWATER DATING

There is a wide range of environmental tracers, which are applied for estimation of groundwater age and travel time distributions at small and large spatially scales or young and old temporal scales. General descriptions of the methods may be found in e.g. Cook and Herczeg (2000) and Kazemi et al. (2006), while research needs on the methods can be found in Newman et al. (2010). The concept and terminology of groundwater dating and groundwater age is a matter of debate (e.g. Bethke and Johnson, 2008, Suckow 2014), but the value of understanding groundwater travel time distributions in the subsurface both for groundwater research and management is widely accepted.

Figure 1 shows the most common environmental tracers used for estimation of groundwater age or travel time distributions for groundwater recharged to the aquifers less than 10 years to more than 1.000.000 of years ago.

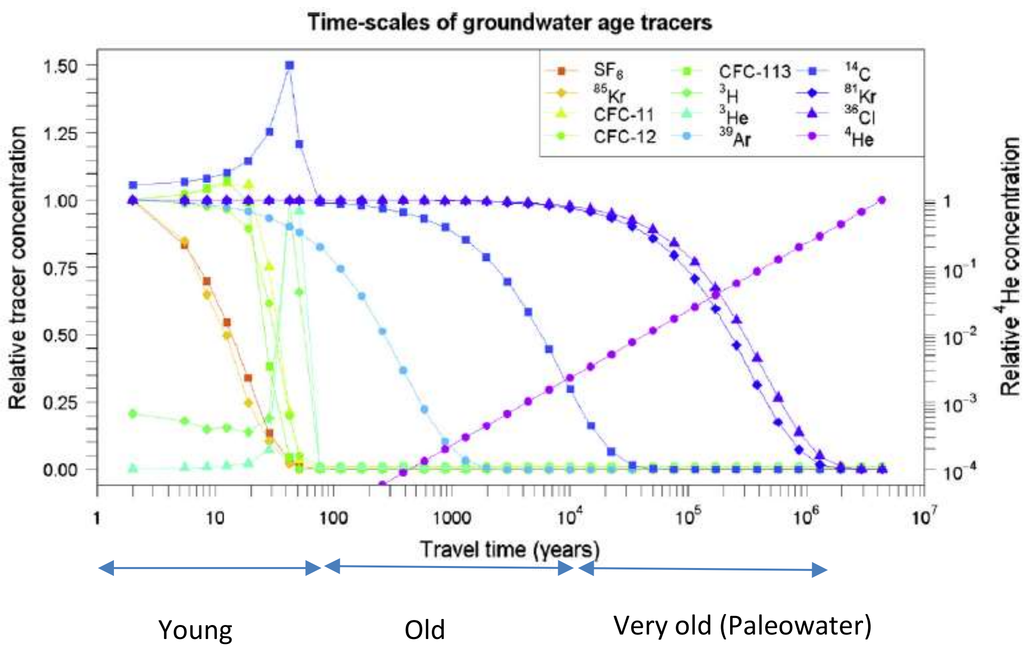

Figure 1 Diagram showing the relative tracer concentrations in groundwater of tracers used for groundwater dating in the different groundwater age intervals defined here for young, old and very old (palaeo) groundwater (Modified from Massoudieh et al., 2014).

Figure 2 illustrate the tracers used for dating groundwater in different age intervals as well as the analytical methods used for the analysis of the different tracers. The use of different tracers for dating of different age intervals provides additional valuable information e.g. for identification of mixing of different water types with different groundwater age.

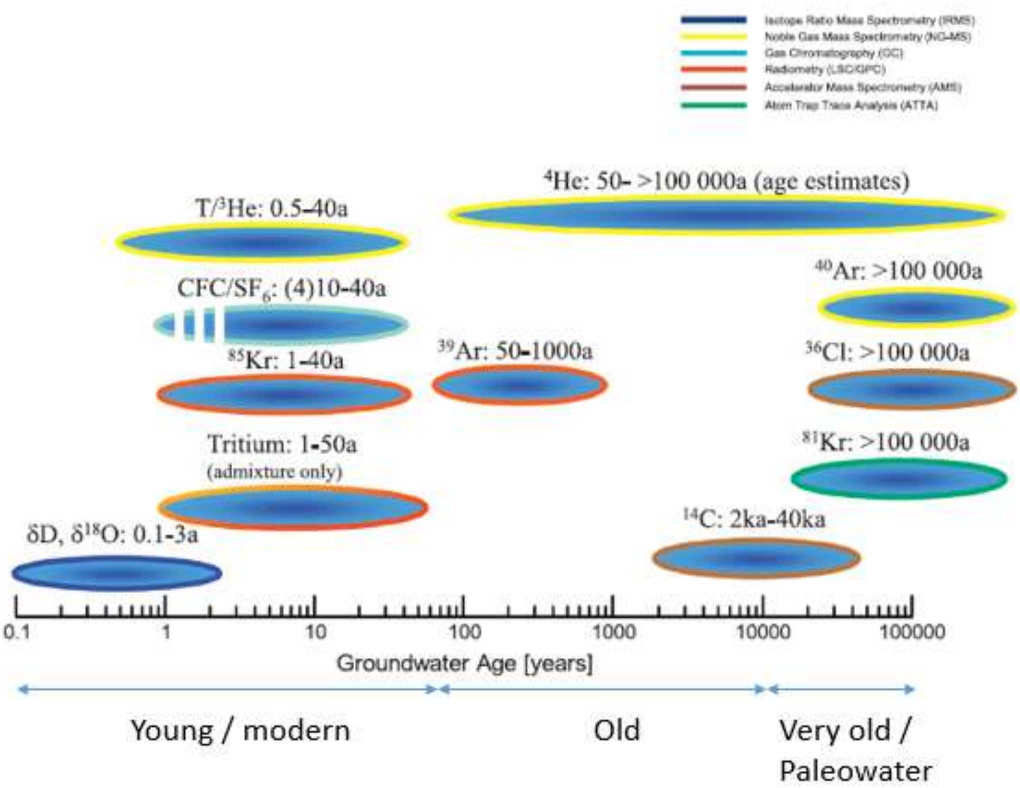

Figure 2. Age intervals and methods for the analysis of environmental tracers used for groundwater dating (modified after Suckow, 2014).

An introduction and more information about the theoretical background for, strength and weaknesses and application of the different environmental tracers can be found in articles and book chapters listed in Table 1. Examples of the application and analysis of tracers for dating of different age intervals can be found in:

young groundwater: Bohlke and Denver (1995); Schlosser et al., Solomon et al., Hinsby et al. (2001a, 2007); Broers (2004); Troldborg et al. (2008); Gourcy et al. (2009); Hansen et al. (2011)

Old groundwater: Sonnenborg et al. (2016)

Very old / palaeowater: Edmunds and Milne (2001), Castro et al., 1998, Hinsby et al. (2001b), Pärn et al. 2019,

Table 1 List of environmental tracers and dating ranges

Environmental tracer(s)	Approximate age range (yr)	References	Source of tracer etc.
$^{3}H/^{3}He$	Post 1950 (< 70)	Solomon (2000)	Radionuclide (naturally and anthropogenic) - decays to 3He with half life of 12.32 years
^{85}Kr	Post 1970 (< 50)	Loosli et al. (2000)	Radionuclide (occuring in atmosphere due to contamination from nuclear power plants) decays with half-life of 10.76 yr
CFCs	Post 1960	Plummer and Busenberg (2000)	Industrial gas occurring in the atmosphere due to contamination
SF_6	Post 1970 (< 50)	Busenberg and Plummer (2000)	Industrial gas occurring in the atmosphere due to contamination
^{39}Ar	50 < - < 1000	Loosli et al. (2000)	Naturally occurring in the atmosphere
^{14}C	1000 < - < 30.000	Kalin (2000)	14C (Natural and anthropogenic) decays with half life of 5730
^{4}He	>100 -	Solomon (2000)	Stable isotope produced by decay of radionuclides in the subsurface in contrast to the radionuclides in the list it increases with the age of groundwater (see Fig. 1)
^{81}Kr	>100.000	Loosli et al. (2000)	Radionuclide with half-life of 2.29E+05 used for dating of very old groundwater
^{36}Cl	>100.000	Philips (2000)	Radionuclide with half-life of 3.01E+05 used for dating of very old groundwater

3 GROUNDWATER AGE CLASSES FOR APPLICATION AND VISUALISATION OF TRAVEL TIME DISTRIBUTIONS AT DIFFERENT SPATIAL SCALES

3.1 Introduction

Important examples of the application of estimated groundwater age and travel time distributions include:

1) Assessment of the vulnerability and susceptibility of shallow aquifers and water supply wells towards pollution from the surface
2) Evaluation of the history, fate and sources of contaminants in shallow aquifers
3) Timescales for geochemical reactions and contaminant degradation processes in aquifers
4) Assessment of the efficiency of regulations, mitigation and remediation measures
5) Understanding the effect of varying paleoclimatic conditions on paleowaters in large regional aquifers and basins
6) Estimation of groundwater recharge
7) Assessment of the risk of over-exploitation
8) Assessment of the risk of salt water intrusion and elevated contents of trace elements and total dissolved solids in general

The relevant and appropriate visualisation of travel time distributions depends on the purpose of the visualisations and the age distributions in the investigated aquifer or well field. In the following we propose age interval classes, which may be applied to visualize age distributions from small to large spatial and temporal scales. Generally, we propose the use of 2-5 different classes with different resolution depending on the application and the scale of the visualizations. However, in some cases the use of up to ten age intervals may be appropriate as shown in the next section. In the following we show examples of different relevant scales and applications. Other age classes may be applied, but we believe the suggested classes will be appropriate for most applications similar to the ones described.

3.2 Examples of the assessment of groundwater age distributions and susceptibility of water supply wells and well fields

For the visualization of age distributions in shallow water supply wells with or without contamination we suggest to use a relatively fin resolution of the groundwater age intervals to indicate the intrinsic vulnerability and susceptibility of the water supply wells towards contamination from the surface. Generally, we suggest illustrating different age intervals and hence susceptibility by using red and orange colours to indicate high and medium susceptibility to pollution, while yellow and green indicate low susceptibility to pollution.

Table 2 Example of age intervals suitable for visualization of groundwater age distributions and vulnerability of shallow water supply wells and well fields.

Suggested age intervals (yr)	Vulnerability to pollution	Suggested colour
< 70 (post 1950)	high	red
>70 (pre 1950)	low	green

Figure 3 shows a schematic illustration of groundwater flow lines and ages/travel times (isochrones) to a water supply well screened at a depth of 30-40 meters below surface. The groundwater age distribution and vulnerability of the well could e.g. be demonstrated for easy overviews by a screened section with a red colour in the upper five meters and a green colour in the lower five meters. Indicating that the upper five meter has a high risk of contamination and the lower five meters a low risk of contamination. If a contaminant is observed in the well or e.g. the water company wants to reduce the risk for contamination it may want to consider closing the upper section of the screen.

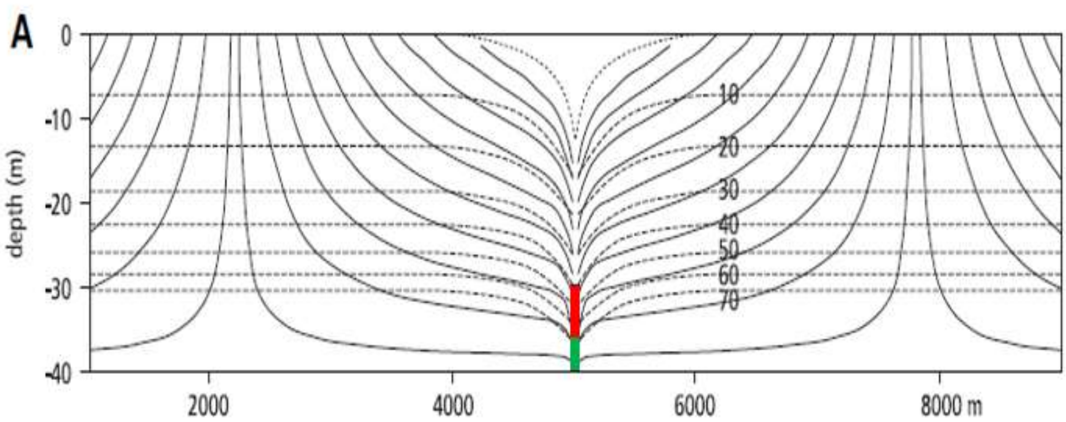

Figure 3. Simulated streamlines and isochrones showing the travel time from the water table to a shallow water supply well in a homogeneous aquifer. Dashed lines indicate drawdown at pumping well solid lines streamlines and isochrones (modified after Broers and van Geer, 2005).

The example shown in Figure 3 may be considered the simplest way to illustrate intrinsic groundwater vulnerability or susceptibility of a screened section in a water supply well. In the example shown in Figure 3 we assume thin saturated zones with travel times to the water table of less than one year. If thick unsaturated zones with large travel times to the water table (>> 1 yr) occur in the groundwater recharge zone then these travel times have to be added. For example, if the travel time through the unsatured zone is 10 years then 10 years have to be added to the shown isochrones (the 70 yr isochrone becomes an 80 yr isochrones etc.), and hence the green colour in the screen needs to be moved upwards to the next isochrone in the screen.

More detailed groundwater age and vulnerability classes is often required in order to describe the flow system and travel time distributions in more detail. This could e.g. be the case if a water company, authority or research institute need to investigate and understand the sources and history of a contamination in more detail (Bohlke and Denver, 1995, Troldborg et al., 2008, Hansen et al., 2011, Visser et al., 2013). Including assessing the efficiency of a regulation of a specific contaminant e.g. a pesticide in more detail (Jakobsen et al., 2019).

The groundwater age distributions in a Danish water supply well estimated by particle tracking and multiple tracer simulations for water flowing to the top of the well screen both indicate that the observed bentazone contamination occurred after regulation of bentazone by the Danish Environment Protection Agency in 1995. This implies that the regulation may not be strict enough or that bentazone users do not follow the regulations.

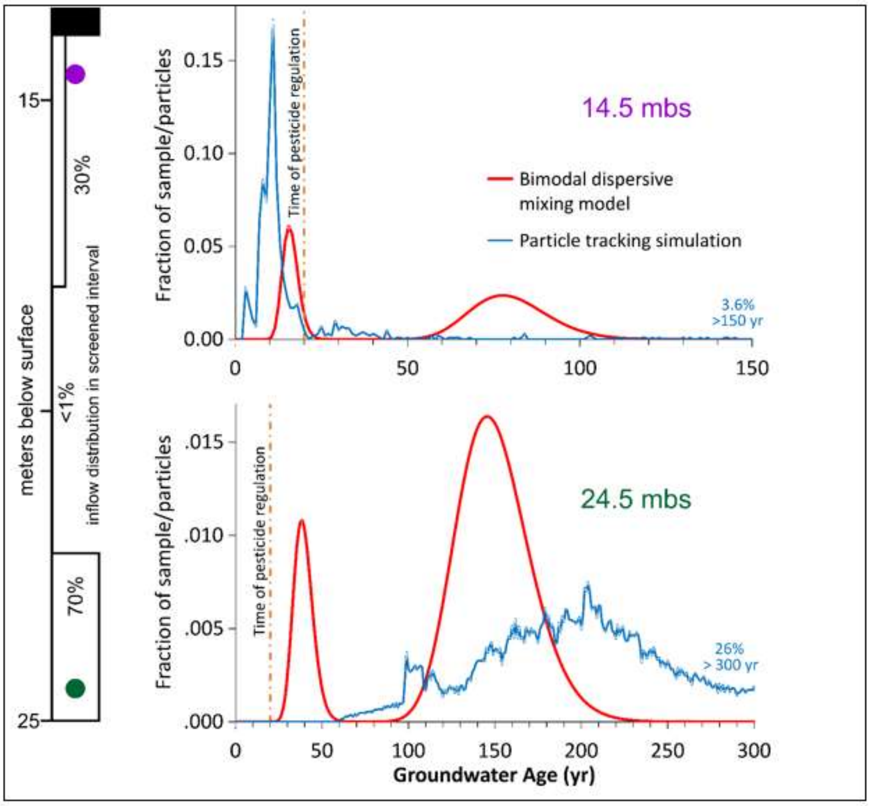

Figure 4. Age and travel time distributions of groundwater flowing to the top and bottom of a water supply well screened at a depth between 14 and 25 m below surface in a sandy aquifer. The middle section of the screen do not produce or produce very little water due to high contents of silt and clay. The blue curves show age distributions simulated by particle tracking in a groundwater model developed by a consulting company. The red curves show age distributions simulated by TracerLPM (Jurgens et al., 2012) based on the measurements of multiple tracers ($^{3}H/^{3}He$, ^{85}Kr, ^{39}Ar and ^{14}C) (After Jakobsen et al., 2019).

The amount of data needed for developing Figure 4 are not available in most studies and visualisations of groundwater age distributions in well fields and water supply wells typically rely on less data and a combination of age estimates by a few environmental tracers and/or groundwater flow models. A few selected examples are shown below in Figure 5 and 6.

Table 3 Example of age intervals suitable for visualization of groundwater age distributions and vulnerability of shallow water supply wells and well fields where more details are required for a better understanding of contaminant sources and history.

Suggested age intervals (yr)	Vulnerability to pollution	Suggested colour
< 10	very high	Dark red
>10 - 25	high	Bright red
>25 - 50	medium-high	Orange
>50 - 70	medium	Yellow
>70	low	Green

An example of the use of groundwater age classes similar to the classes shown in Table 2 is illustrated in Figure 4. Note however, that the colour scale is different. As mentioned previously we suggest to use red colours to indicate young (modern) and potentially contaminated groundwater.

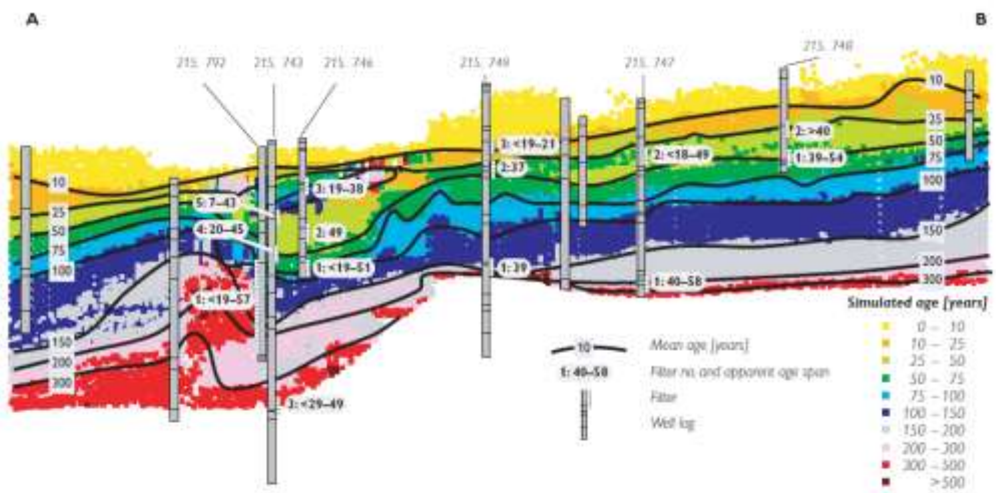

Figure 5. Example of age distributions simulated by particle tracking applying detailed age intervals in a shallow aquifer system (Troldborg et al, 2007).

Figure 5 shows an alternative way of illustrating groundwater age distributions supplementing the visualizations of groundwater age distributions shown in Figure 3 and 4. Figure 6 illustrate groundwater age distribution in relation to the location of aquifers and aquitards i.e. in relation to the distribution of hydraulic parameters and general physical characteristics representing the layers in one of many possible geological models of a specific aquifer system (Troldborg, 2004, Troldborg et al., 2007, 2008).

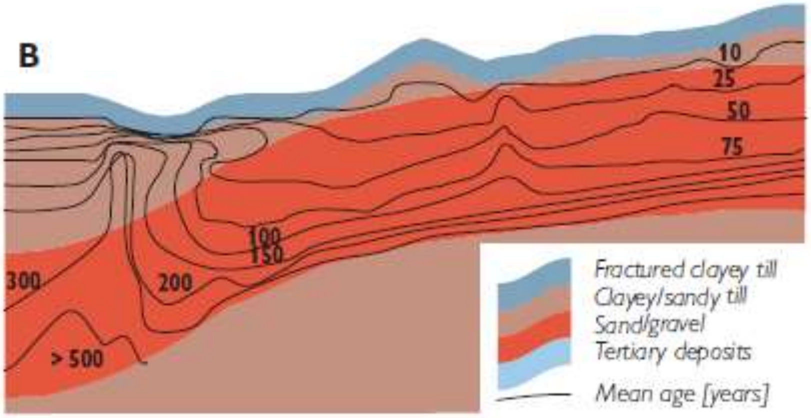

Figure 6. Example of age distributions (isochrones) simulated by particle tracking applying detailed age intervals in a shallow aquifer system and indicating aquifer and aquitard lithology (Troldborg et al., 2007).

Table 4. Age intervals for visualization of groundwater age distributions in water supply wells and well fields with wells at shallow to intermiate depths .

Suggested Age intervals (yr)	Suggested colour
< 10	Dark red
>10 - 50	Bright red
>50 - 100	Orange
>100 - 200	Yellow
>200	Green

3.3 Examples of groundwater age classes for visualisation of groundwater age distributions in 2D cross sections and areal maps of regional aquifers

The most simple definition of groundwater age classes used for visualization of age distributions in large regional aquifers corresponds to the scale shown in figure 1 defining young, old and very old (paleowaters) groundwater as shown in Table 4 below.

Table 5 Age intervals for visualization of groundwater age distributions in large regional aquifers

Suggested Age intervals	Age	Suggested colour
< 100	Young	red
<10.000	Old	green
>10.000	Very Old (paleowater)	purple

Depending on the characteristics of the investigated aquifer and the purpose of the visualizations of the classes listed in the table above table may be too rough. In such a case propose using the more detailed groundwater age classification shown in Table 5 equivalent to the scale shown in Figure 1.

Table 6. Alternative more detailed groundwater age scale used for visualisation of groundwater age distribution in large regional aquifers.

Suggested Age intervals	Suggested colour
< 100	red
100	dark green
>500	light green
>1000	Yellow
>10.000	purple

Appropriate age intervals for visualisation of groundwater age distributions will vary and depend on the hydro(geo)logical setting. Table 6 and Figure 3 show the use of age intervals for a regional aquifer at shallow to intermediate depths (0-300 m) in a humide temperate climate, which may be used in large parts of Europe.

Table 7. Alternative detailed groundwater age scale used for visualisation of groundwater age distribution in regional aquifers at intermediate depth in a humid climate (Figure 3).

Suggested Age intervals	Suggested colour
< 100	red
100 - 200	orange
200 - 300	yellow
300 - 400	green
➢ 400	blue

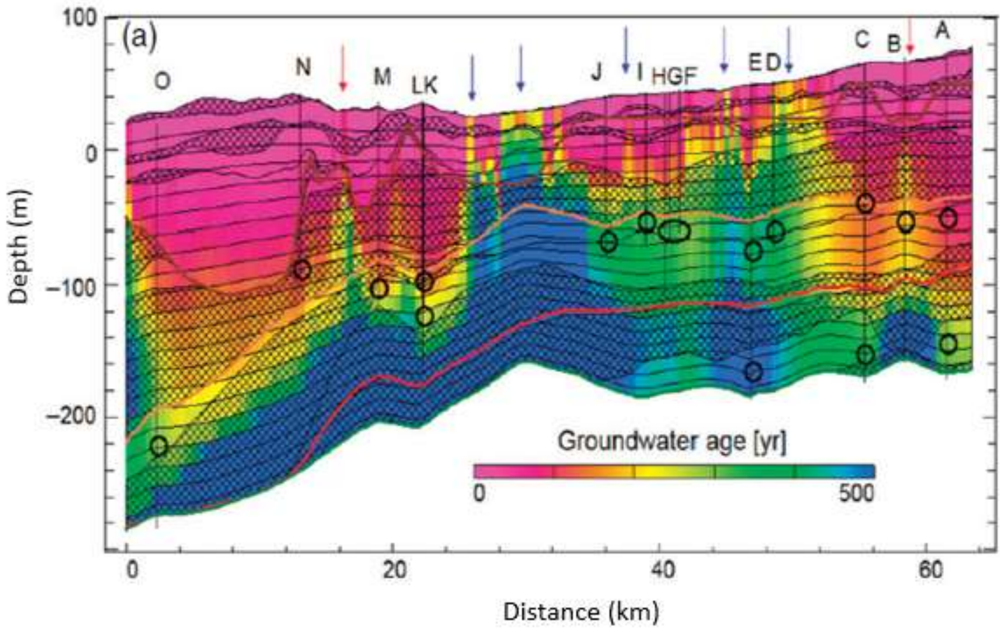

Figure 7. Visualisation of the groundwater age distribution in aquifers at shallow to intermediate depths in a temperate humid climate (Sonnenborg et al., 2016).

In deeper regional aquifers age intervals with a larger resolution is required to illustrate the groundwater age distributions. An example is shown in Figure 4.

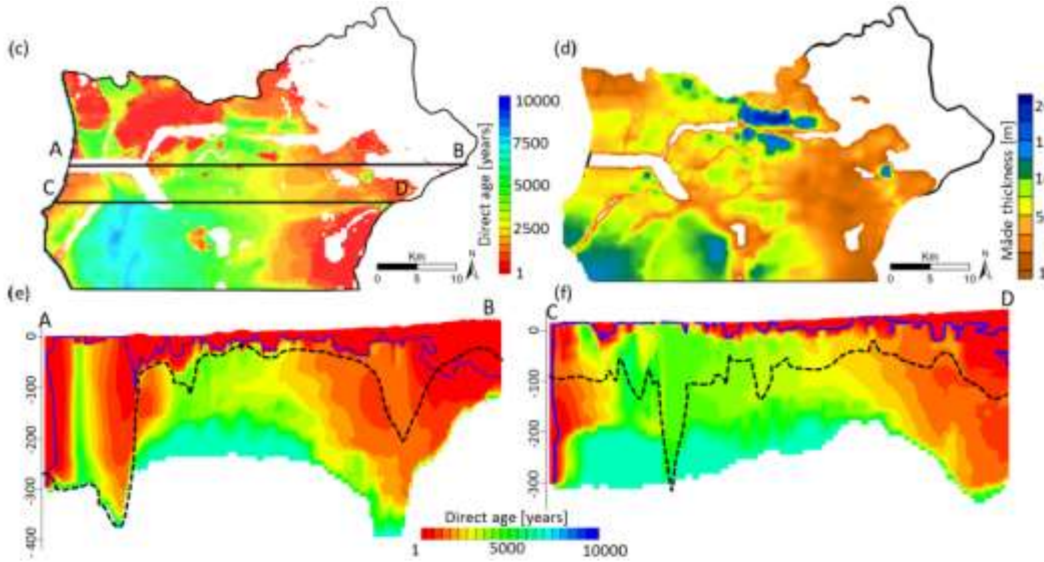

Figure 8. Example of groundwater age distribution in a regional aquifer systems with depths up to 400 m (Meyer et al., 2018).

3.4 Groundwater age classes for easy overview of groundwater age distributions and vulnerability to pollution in 2D areal views at large e.g. Pan European scale

Table 8 Age intervals for visualization and easy overview of groundwater age distributions and groundwater vulnerability in shallow aquifers in areal maps.

Suggested Age intervals	Vulnerability class	Suggested colour
post 1950	Young / Modern - high	red
>50 – 100 (mixed)	Mixed / orange	yellow
Pre 1950	Old low	green

The classification shown in Table XX is well suited for an overview of the ratio between young groundwater with a high risk of contamination and old groundwater with a low risk of contamination on large areal maps, e.g. where tritium is the only age indicator for groundwater. An example from the USA is shown in Figure XX.

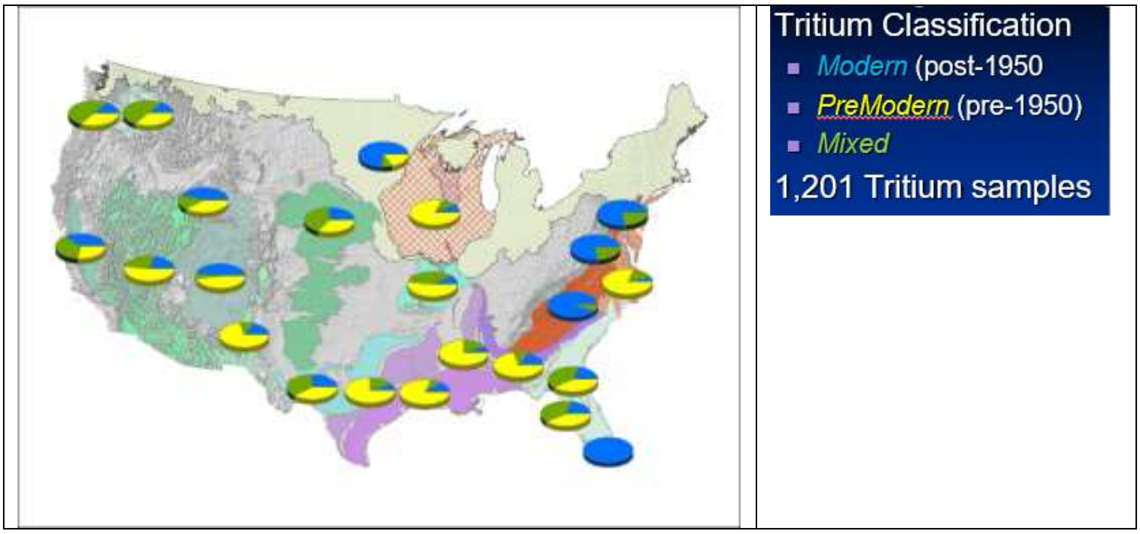

Figure 9. Illustration of age distributions in aquifers at large scales (pers.comm B. Jurgens, USGS, 2019)

4 PERSPECTIVES AND FUTURE ACTIVITIES

This report does not intend to be exhaustive in any way, but just to serve as inspiration for managers and scientists working on the evolution of groundwater quantity and quality. It is a working document that will be extended and improved during the GeoERA programme with examples developed in the HOVER project. An important goal 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/). In a longer perspective, this will include 3D and even 4D visualisations of groundwater age distributions and vulnerability of wells fields e.g. demonstrating the impact of climate change and the efficiency of different adaptation measures and abstraction schemes developed for adaptation to climate change.

It is our hope that the European Geological Surveys in collaboration with other research institutes and authorities will be able to continue providing sound and valuable digital information about groundwater age distributions and vulnerability for EGDI beyond GeoERA. The provided information indicate the vulnerability towards pollution from the surface in shallow aquifers and elevated concentrations of harmful geogenic trace elements in deep aquifers as well as 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, Accesible, 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 before the GeoERA programme obtained funding, and this collaboration continues within GeoERA. European water companies collaborating with the partners of WP6 may be the first companies in the world systematically using 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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