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Application of groundwater age distributions for design and assessment of monitoring programs and trend assessment

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1 SUMMARY

Water Framework Directive (2000/60/EC) and the daughter directive on Groundwater (2006/118/E) have a main objective of non deterioration of water status and further on, to reach a good status for all waters over Europe.

For groundwater, the GWD implementation led to characterization of the water bodies, using the DPSIR approach. Under this approach, a close link is made between the pressure (P) on a water body and the resulting state (S). This link is the starting point to propose appropriate response (R) and mechanism to evaluate the effect of the responses.

On top of this three building blocks are identified by GWD that one can refers as ‘Good chemical status’, ‘Trend identification and reversal’ and ‘Measures to prevent or limit pollutants input’.

In this context, this study focuses on the use of dating tools to better understand the identified trends and make the link to the groundwater monitoring (State) and management (mitigation measures, Response).

This work is based on literature review. It shows that up to now, the use of the dating tools is mainly carried by researchers, for areas of limited extension.

However, use of dating tools could lead to several insights:

- better knowledge on the processes occurring in the unsaturated zone (USZ) are obtained (mainly the time-lag in the USZ);
- better knowledge of the structure of ages, leading to exhibit the need of appropriate duration for input function (especially for nitrogen) to understand the actual state, and the existing of ‘old waters’ with long term effects;
- more classical knowledge such as origin of recharge and flow path, that could be of interest to focus mitigation measures on certain areas.

The use of a Lumped Parameter Model (LPM) is always needed which could be calibrated also using long time series of both input and output for nitrate. When not available, the need of several tracers is needed (CFC’s, SF6, 3H, 3H/3He, 4He, 85Kr,18O).

A trial to set up a flow chart explaining in which context the use of dating tools could be of interest is made.

As a perspective, a wider use of dating tools to understand actual trends in Nitrates appears to be of great interest. However, it relies on the availability of both data (and thus exhibit the need of national/European databases for tracers) and calculation tools (to operate LPM).

2 INTRODUCTION

Water Framework Directive 2000/60/EC (WFD, European Commission, 2000) and the daughter directive 2006/118/E on Groundwater (GWD, European Commission, 2006) have a main objective of non deterioration of water status and further on, to reach a good status for all waters over Europe.
For groundwater, the GWD implementation led to characterization of the water bodies, using the DPSIR approach. Under this approach, a close link is made between the pressure (P) on a water body and the resulting state (S). This link is the starting point to propose appropriate response (R) and mechanism to evaluate the effect of the responses.

On top of this three building blocks are identified by GWD that one can refers as 'Good chemical status', 'Trend identification and reversal' and 'Measures to prevent or limit pollutants input'.

"Good chemical status" and "Trend identification and reversal" concepts are strongly tight to the monitoring programs as list of parameters, frequency, geographical distribution, choice of sampling sites, etc. will affect the produced dataset and thus the possible computation on this dataset. Design of groundwater monitoring in the context of the implementation of GWD is widely described by Grath J et al., 2008. From this detailed work, one could consider the following items as the most relevant in the context of this work:

- Concepts of 'good status' (that should be initialy reach by 2015) is related to the concept of **groundwater bodies** : « A distinct volume of groundwater within an aquifer or aquifres »;
- The conceptual model of a groundwater body is the **foundation** for the monitoring design ;
- Characteristics of river basins, impacts of human activity should be supported by monitoring in a systematic and comparable way throughout European Union ;
- A Common Implementation Strategy (CIS) was initiate in order to support and hormonise implementation of the GWD. One output of the CIS is the 'Monitoring Guidance for groundwater' ;
- The 'Monitoring Guidance for groundwater' would be the support for implementation of **national** WFD-compliant groundwater **monitoring programmes**.

One last information to keep in mind is the fact that (Grath J et al., 2008) « The results of the monitoring should also be used to i) assist in further characterisation of groundwater bodies, ii) assist in the desgin of programmes of measures, iii) evaluate the effectiveness of programmes of measures. »
It is then clear that the conceptual model of groundwater bodies should be the main driver for definition of the list of parameters to watch out and the sampling frequency,

but also the vertical and/or geographical distribution of the sampling. One should also remarks that as more data are acquired, a more detailed comprehension of the water bodies should arise. This could lead to improve the conceptual model of water bodies, and then to refining the monitoring, and so on (Illustration 1).

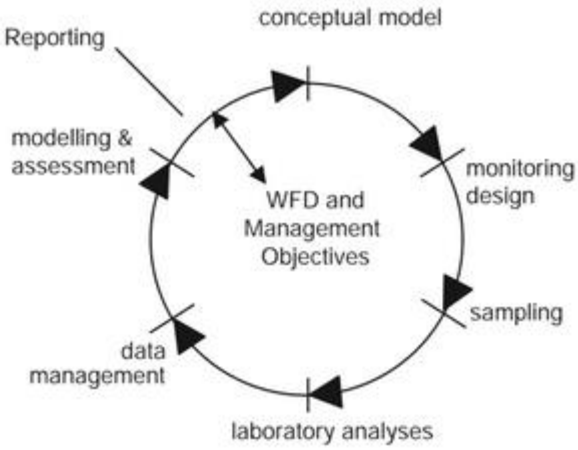

Illustration 1

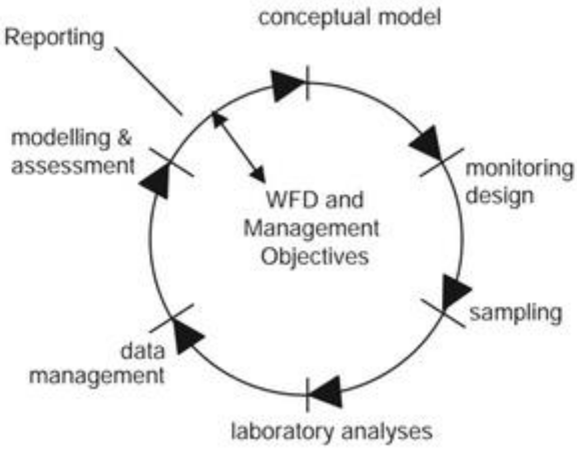

Illustration 1 Monitoring : cyclic procedue according to the Water Framework Directive, from Grath J et al., 2008.

What is behind the word of conceptual model then ? Illustration 2 gives an overview of the concept, in the context of the WFD. It should be understood as the synthesis of information on i) natural characteristics on both structure (geology, overlying strata) and functioning (hydraulic properties, precipitation, link to other hydrosystems) and ii) pressures, in the perspective of the understanding of the **effects of pressures**.

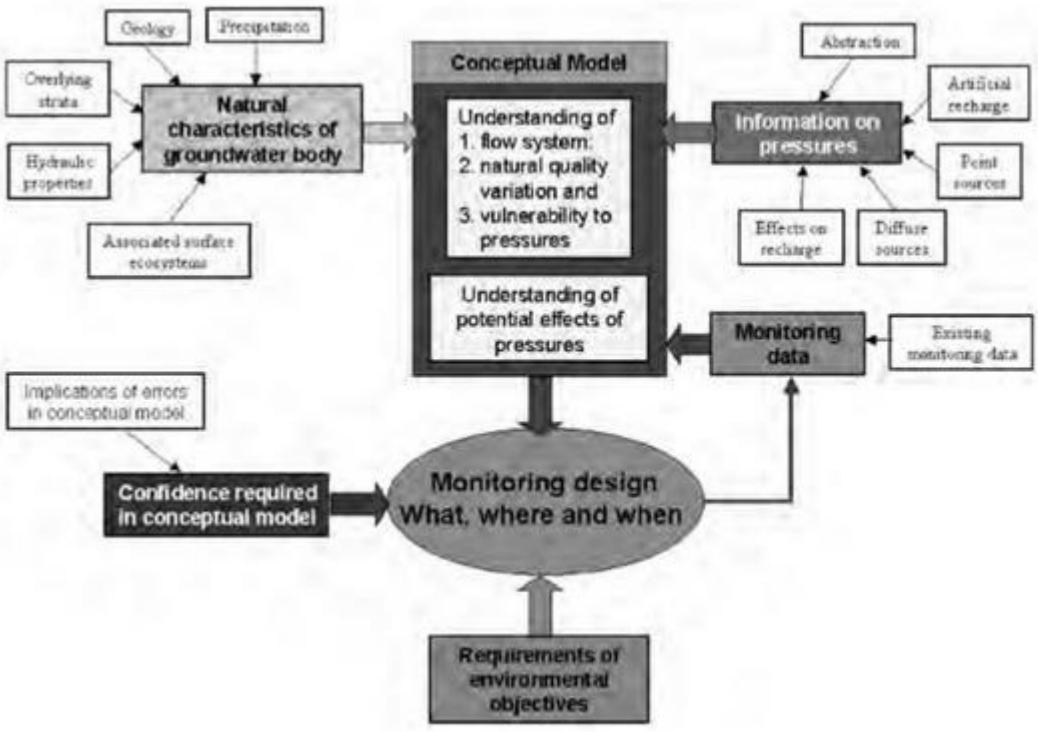

Illustration 2 Link between the conceptual model/understanding and monitoring, from Grath J et al., 2008

Make the link between the pressures and their (potential) effects is then one objective of the conceptual model and the monitoring program should help to reach this goal.
The link between pressure and their effects on the aquifer is often very little discuss on the perspective of the **time** needed by a certain pressure to have a measurable effect on the aquifer. Even when dealing with concentrations of pollutant measured in grouwdater emphasis is made, for exemple, on the type of soil (for exemple in Hansen et al., 2019), land use and position is the catchment (Rajanayaka et al., 2020). Nevertheless, some authors (for exemple Gerber et al., 2018; Kim et al., 2020; Koh et al., 2020) highlight the concept of 'time lag', which is basically the time needed for a particule of water to flow from soil surface to the sampling point in groundwater[1].
This amount of time needed for a water particle to flow form subsurface/soil to the sampling point in groundwater depends of large amount of factors (Hinsby et al., 2008), for example the recharge rate, the type of velocity of flows, interaction with matric (soil, sediments and rocks). A detailed knowledge and computation of these factors is hard to reach, mainly because of the lack of geological information on the subsurface.

[1] One should note here that if certain amount of time is needed for a pressure to have measurable effect, a longer time is needed between the mitigation measure and the measurable effect.

In this case, environmental tracers are very usefull tools to estimate the travel time. And this could be achieve using the so called 'dating techniques', relaying in various 'tracers' (natural of anthropogenic).
Aim of this work is to give some clues to understand the benefit of using the dating techniques and tools in the comprehension of trends in ground water, and make suggestion on a better integration of this information in perspective of the monitoring of groundwater quality.
Quick review of the environmental tracers is made, followed by a review of the informations provided by the dating tools.

3 ENVIRONMENTAL TRACERS AND DATING TOOLS

Environmental tracers are usually presented in two categories: the water molecule tight (which means they can only be dependant of the H (hydrogen) or O (oxygene) of the H_2O water molecule) and the dissolved one (gas or solute). The first have the great advantage of travelling with the water particles in soils and rocks with no to little possibility of contamination or depletion (sorption, oxidation, gasification, etc…). But they represents a rather small amount of possibility as only two atoms are in the game: oxygen and hydrogen. In that case, their isotopes are considered: ^{16}O and ^{18}O for oxygen, ^{2}H and ^{3}H for hydrogen. Interest for theses tracers has emerged in the 50's (Dansgaard, 1954, 1953; Libby, 1953) and there is still a strong interest for it.
Alternatives have been rapidly search (Busenberg and Plummer, 2000, 1992; Lehmann et al., 1993; Rozanski and Florkowski, 1978; Wilson and Mackay, 1996), and a wide set of tracers are now considered in hydrogeology. They can be naturally produced (^{14}C, ^{4}He, Noble Gases, ^{39}Ar), anthropogenic (CFC's, SF6) or both (^{3}H, ^{85}Kr).

A detailed explanation of each of this tools is not is the scope of this work, and only the key features of each of this tracers are reminded here. The main concept to keep in mind is the fact that "*environmental tracers provide an ability to assess the internal dynamics of a groundwater system and to qualify timescales associated with groundwater flow"* (Turnadge and Smerdon, 2014). In other words, environmental tracers provide an integrated overview of the processes occurring inside an aquifer. The aquifer could be seen as a "transfer function" that could transport with or without any modification an input signal (the tracer) down to a sampling site.

3.1.1 Need for selecting the appropriate tracers

Due to their own properties, each tracers is available in a certain range of age, i.e. given a certain question, the more relevant tracers should be selected to fall into their range of definition.

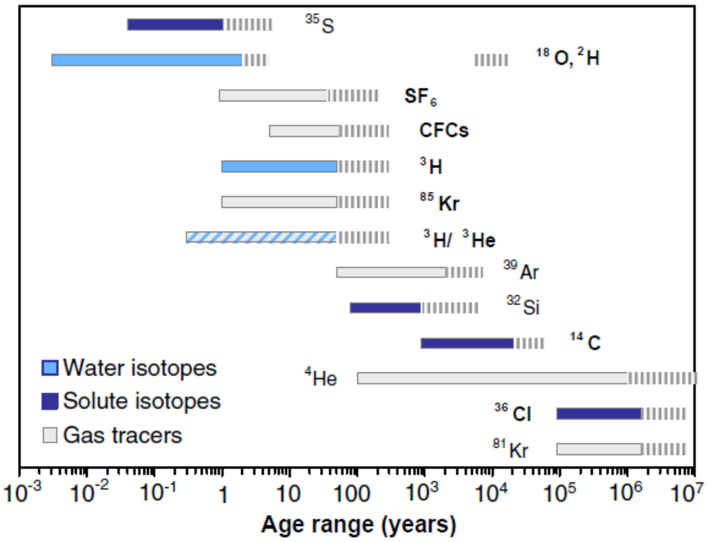

Figure 1. Time ranges and types of selected environmental tracers for groundwater dating. The most commonly used tracers for quantitative dating are indicated by bold labels.

Illustration 3 Time scale of tracers, from Newman et al., 2010, representing the time range applicable for each individual tracer.

A good overview of the range of time each tracer can be used for is given by the synthetic illustration from Newman et al., 2010 (Illustration 3). One should remark where the very wide possibilities of 'dating tools' given the fact that some can help to track information at a monthly scale (seasonal variation of ^{18}O and ^{2}H) some other to a scale of years (tritium, CFC's/SF6, ^{85}Kr), and some in manner of century (^{39}Ar, ^{36}Cl,…).

3.1.2 Need for interpretation : mathematical models and tools

Very early in the description of use of the dating tools, the need for mathematical models has been highlight (Maloszewski and Zuber, 1989; Nir, 1964). The very evident reason for this, is because it is not straightforward to go from a measured concentration from a sample to a valuable information: altitude, temperature, mean residence time, etc. For estimating the 'time' (time from recharge, from equilibrium with atmospheric air, time in the saturated zone,…), it becomes even harder because the tracer concentration at the sampling point could varies with time as well. Mathematical model will then help to compute the evolution of a single (or a set of) tracers in given conditions, and further on, to compare with the measured values.

Most known and popular mathematical models are the one given by Maloszewski and Zuber, 1996, 1989 where the type of flows in aquifers can be approximate by a set of few models (piston flow models-PFM, exponential models-EM, dispersive model-DM and binary mixing model-BMM), Illustration 4.

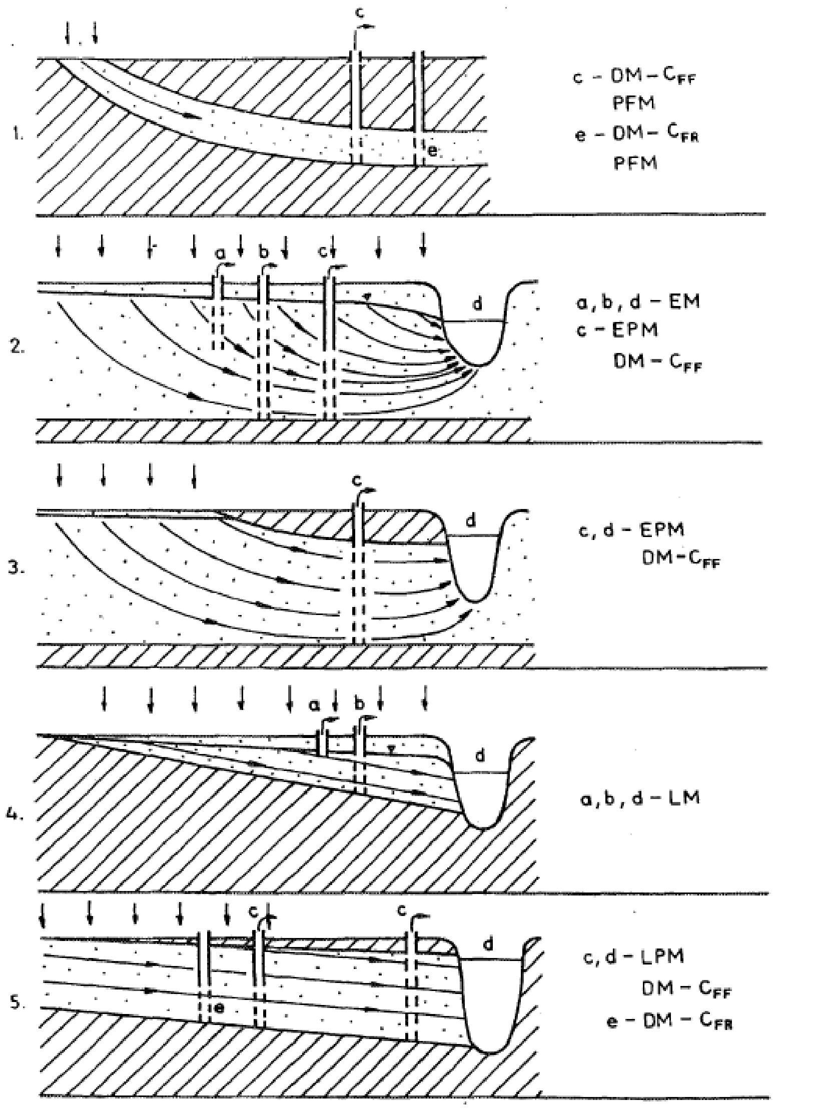

Fig. 5. Schematic situations showing examples of possible applicability of models [3, 6]. Cases a, b, c, and d correspond to sampling in outflowing or abstracted water (the sampling is averaged by the flow rates, C_{FF} mode).
Case e corresponds to samples taken separately at different depths and next averaged by the depth intervals (C_{FR} mode).

Illustration 4 Conceptual mathematical models from Maloszewski and Zuber, 1996. It illustrate the link between the mathematical expression of the transfer function and the corresponding geological setting of the aquifer.

Turnadge and Smerdon, 2014 gives a good picture of the state of the art in that domain, almost twenty year later. Three types of models are nowadays available:

3.1.2.1 Lumped parameter models (LPM)

They are base upon a convolution of an tracer input function and a weighting function aiming to reproduce the observed (measured) tracer. Decay function could be taken into account when needed. This lead to the estimation of a mean residence time, for the parameter specific model.

3.1.2.2 Mixing cell models

They are based upon simple instantaneous mixing between discretely defined cells (representing geographical arease) at defined temporal intervals. The volume of fluxes between the cells is a calibration parameter. Coming from the chemical engeneering, this belongs to semi-analytical, semi-distributed Eulerian approach. This models lead to the estimation of a mean residence time, and upon assumption, the recharge rate.

3.1.2.3 Direct age models (DAM)

Recent advances in computing sciences and computing power offer greater possibilities and more complex models have been set up, where tracer transport (advection/dispersion, decay, accumulation) can be computed in combination with hydraulic simulation. For theses authors, this represent the most advanced and promising techniques, but one should stress here that this type of models represents a much greater needs in knowledge (conceptual model), data (geological settings, precipitation, hydraulic heads, …) and in time (time to set and to run the model). They use the governing equations for subsurface solute transport to simulate spatial distributions of the statistical distribution of groundwater age. The concept of age mass is introduced in this models (product of mean groundwater age and groundwater mass), and solution for steady and transient flows are available, as well as for heterogeneous hydraulic conductivity fields. This models requires a high number of different measurement and associated data, within the cross section and in the whole space of definition of the model. They requires also more computing time and a higher level of modeling skills. In contract, they can lead to a highly detailed picture of the flowpaths, spatial distribution of age over space, and can exhibit misconception if using LPM only.

3.1.3 Needs for input functions

As stated before, interpretation of the environmental tracers relies on the possibility to make a link between observations (data) at sampling sites and the history of this tracers before reaching the sampling sites. Two components could be taken into account : the aquifer itself and his related properties to propagate a concentration along flow paths, and the evolution over time of the tracer before entering the aquifer, usually called the 'input function'.s

What should be stressed here is the problematic with the input function, that is tracer dependent, and even sometimes site dependent.

Tracer	Input function	Measured in	Remarks
^{3}H, 85Kr	Site dependant	Rain	Should be measured in the precipitation, or derived from close measurement if not available at the site. Subject to contamination (nuclear plants).

CFC's, SF6	Known everywhere in the globe	air	Well mixed in the atmosphere, but Northern Hemisphere more exhibit higher concentration.
Noble gases	Known for recent years (and estimate for paleo-climate)	air	Needs for specific model to relates concentration in water to equilibrium in air (see Jung and Aeschbach, 2018)
^{14}C, ^{36}Cl	Site dependant	computed	

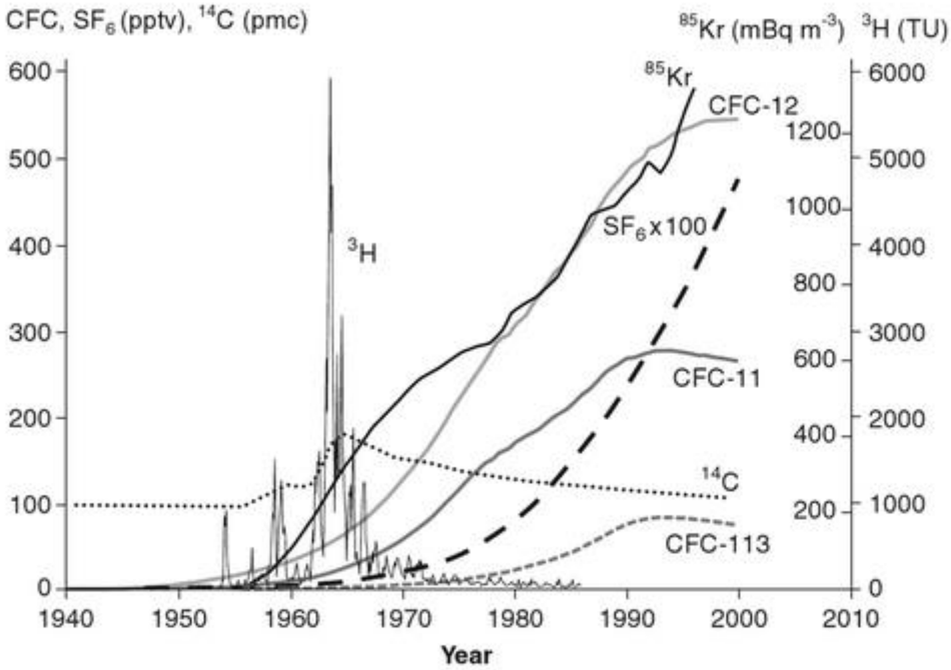

Figure 5.3.1 Concentration trends of selected environmental tracers in the atmosphere applicable for groundwater dating (modified after Hinsby et al.[2]).

Illustration 5 Input functions for environmental tracers, from Hinsby et al., 2008

3.1.4 Need for additional parameters : NG for CFC's and SF6

As certain tracers are found in very small concentrations in ground water due to very low solubility, any factors affecting the water/air partitioning would lead to severe error in interpretation. This is particularly true for CFC's and SF6 and it is of high importance to remember here again the importance of considering that using CFC's and even more SF6 only is not achievable if not taken into account the possible contamination by excess air (Aeschbach-Hertig et al., 1999; Heaton and Vogel, 1981) or degassing. It is usually recommended to sample at the same time the so called Noble gases (He, Ne, Ar, Kr, Xe) as proposed by Aeschbach-Hertig et al., 1999 or at least the Ne alone, which as solubility close the SF6 (Newman et al., 2010).

3.1.5 The concept of 'Age'

The words related to the concept of "*time spent in the aquifer by a particle of water"* have been subject to various interpretation and concepts (see among other Hinsby et al., 2008; Newman et al., 2010; Suckow, 2014).

As stated by Suckow, 2014 the concept of 'age' is familiar for humans but not properly suitable for groundwaters for the following reasons :

- water sample taken at a sampling site represents a potential contributions of different flow paths, of different lengths, velocities, geographical origin and virtually numerous related processes (oxidation, sorption, etc…). What could be estimate is thus a statistical distribution of age, and a good metric to summarize this distribution is often the **mean residence time**;

- the concept behind each tracer could be different, mainly because the 'clock' is not set at the exact same time if dealing with SF6 or water particle itself as with ^{3}H. It is often consider that the **'apparent age'** would be a more appropriate term to use. This concept means that age estimation from different tracers could be inconsistent, each of them representing virtually different processes affecting the conservation and transport of tracers (stagnant zones, diffusive processes,…), this estimation being different to the real age of the water (which is not affected by the previous processes).

Nevertheless it could be assume that the words « groundwater age » if not allways appropriate is meaningfull enough for the majority, and cover more or less the concept of mean residence time in number of studies.

3.1.6 Tools

Interpretation of measured concentrations in environmental tracers relies on both input function and mathematical models. With focus on LPM, tools that are capable of help in that order are given by Suckow, 2014 (see references in that work):

- FlowPC, (Maloszewski and Zuber, 1996, 2000), Multis (Richter et al.,1993) for DOS ;
- QuickCFC (Han, 2006); Boxmodel (Aeschbach-Hertig et al., 2006); TracerLPM (Jurgens et al., 2012) for MS Excel
- Lumped (Ozyurt and Bayari, 2003); LumpedUS (Ozyurt and Bayari, 2005) in Vusal Basic (standalone) ;
- Lumpy (Suckow, 2012) for MS Access

4 WHAT DATING TOOLS COULD TEACH US ?

When dealing with the problematic of make the link between the pressures and their potential effects on groundwater chemistry, time should be taken into account. It takes 'some times' for the nitrates leaching below the root zone to reach the aquifer, and additional time to reach the sample site. But this concept of 'delay' or 'time lag' is not explicit in the 'conceptual model' nor in the 'natural characteristic of groundwater bodies' (§**Erreur ! Signet non défini.**, Illustration 2).

This explain that, by design, the tools that could possibly better explain this time lag are not included in the monitoring programs.

A review paper from Vero et al., 2018 propose an overview of the nitrate-related time lag, over several countries (EU and North America), mainly based on monitored examples, for surface and groundwater. They point out that the correlation between program of measure (i.e. mitigations measures) and water quality improvement is difficult if not impossible when delays is not taken into account.
Evidence of existence of time lag over whole Europe is given, with the most critical exemple of the ‘nitrate bomb model’ from Wang et al., 2013. In this exemple,based on flow equation based models (see §3.1.2.3) and due to a thick unsaturated zone (USZ), actual nitrate concentration are related to waters infiltrated in the last 10 to 50 years !
Modeled (Wang et al., 2013) or observed (Vero et al., 2018), the time lag for nitrate is well documented. But no reference is maid to complementary and integrative tools such as the environmental tracers. The following is trying to show in what order the environmental tracers could be of help is such cases.
Based on selected examples, a trial is made to make the link between the dating tools and the information they can provide, in ordrer to understand the trends.

4.1 Considering the time of recharge

Visser et al., 2007 propose an approach to aggregate data from numerous individual screens, sampled at different depth to deliver an overview of the trend at a regional scale. In some extent, this approach is very comparable to the one achieved when evaluating GW bodies states, trying to compare what could be comparable, and understand what type if information it could exhibit.

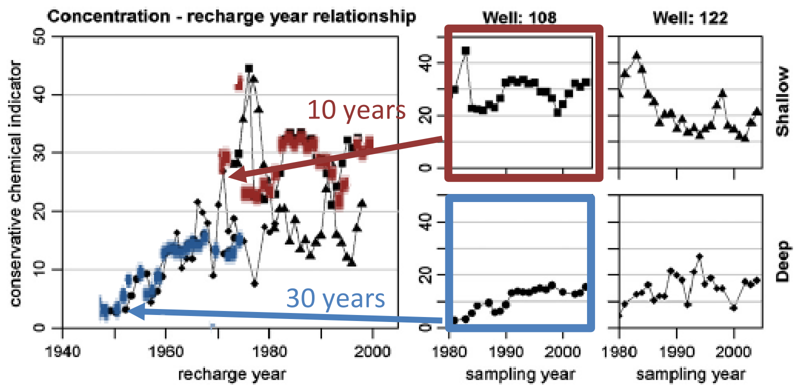

Fig. 2. The concentrations of a conservative chemical indicator (OXC) sampled from the shallow (8 m) and deep (24 m) screens of observation wells 108 and 122 (right) plotted at the recharge year of the sampled groundwater (left). The result is the *concentration − recharge year relationship*, from which a clear trend can be observed that was not visible in the individual time series.

Illustration 6 Observed time series of a 'conservative chemical indicator', and correspondance with the year of recharge. Modified from Visser et al., 2007.

In that work, the $^{3}H/^{3}He$ method is used, but other environmental tracers (capable in the 0-30 years range, such as ^{3}H alone, CFC’s, SF6 ; ^{85}Kr) would be able to deliver a comparable information. Laier, 2005 used a similar approach in Danemark in a chalk aquifer, using CFC’s mean residence time. Tesoriero et al., 2007 propose also a similar approach, on various aquifer systems (alluvial aquifer, fluvial and glacial deposits, alluvial fan, fresh and weathered sandy limestones) and for studying deethylatrazine, atrazine, metolachlor, alachlor Reconstruction of the N input function in the aquifer.

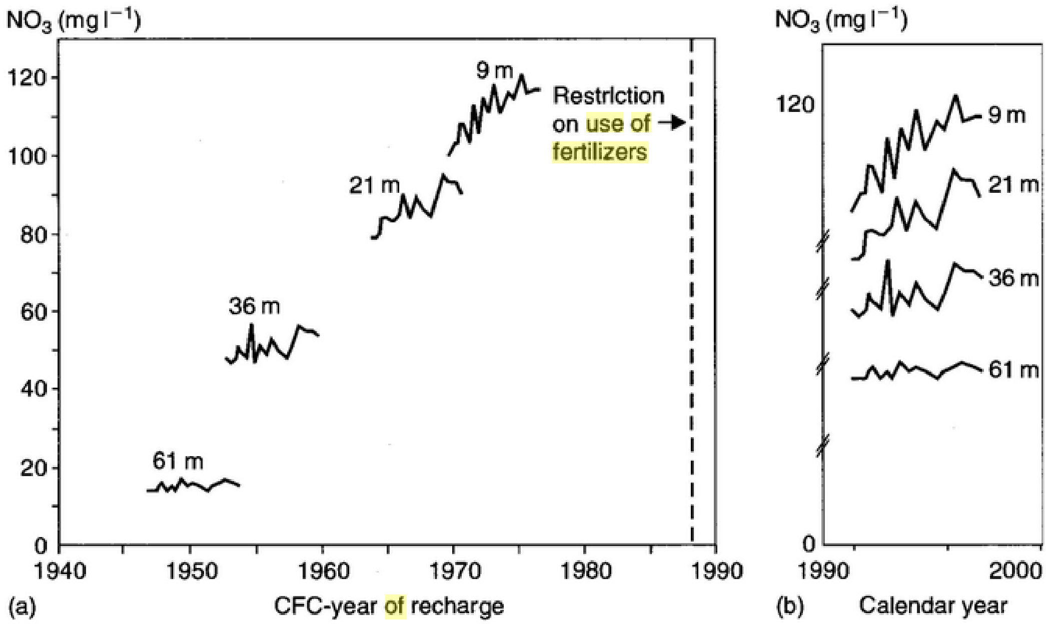

Figure 5. Increase in groundwater nitrate concentration with time in the chalk aquifer at Drastrup, location B on Figure 4. (a) Groundwater age has been subtracted from the time of sampling in May 1997 to obtain the real change in nitrate with time. (b) Nitrate concentrations at sampling dates for the four levels.

Illustration 7 Evolution of nitrate at different depth : observed time series (b) and time series with time-axis alignement, based on CFC's ages, from Laier, 2005

The key idea is to make the informations comparable over a region, and over the depth. The way to do so is to link any observed hydrochemical time serie with the time of recharge (Illustration 6, Illustration 7). In simple words, this means : "At that point/depth, the evolution I see now, is what appens X years ago". The original illustration from Visser et al., 2007 as been modified (Illustration 6) to better illustrate that i) based on information of 'age', ii) the information at each sample site/depth could think as look in the past. The greater is the 'age', the deeper we can look in the past.
In this work, reconstruction of the historical inputs on nitrogen (leaching of the N surplus) based on aggregation of numerous data sources lead to a complete validation of the approach. This have been possible because of sufficient constraints on N sources, and time-relative information given by the environmental tracers

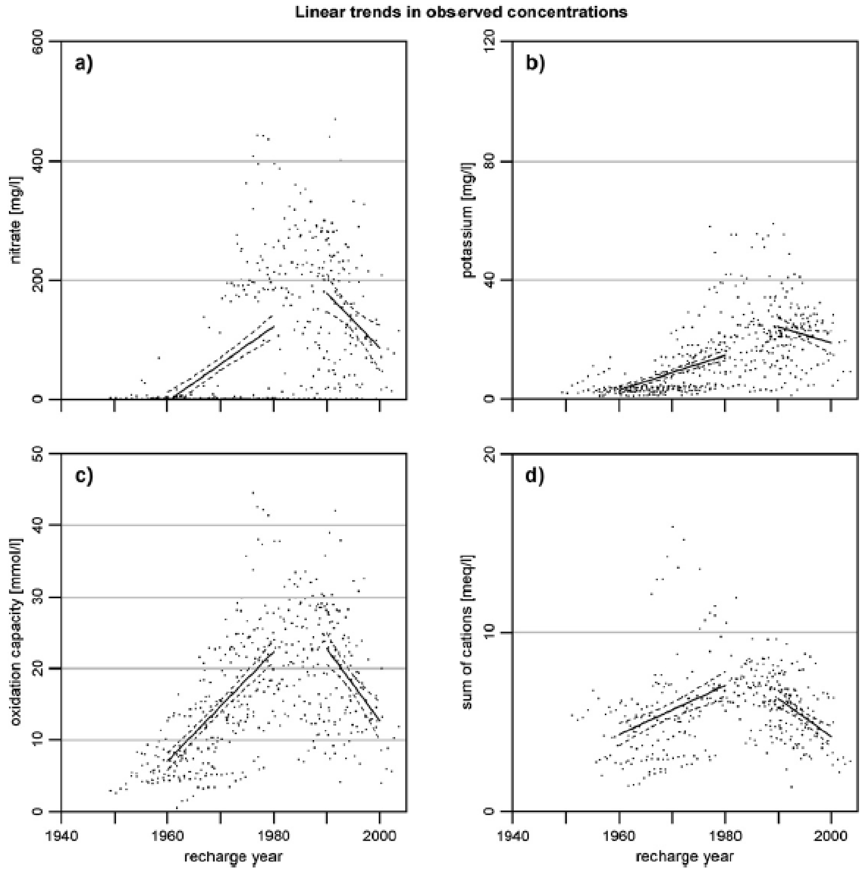

Fig. 6. Linear trends through *concentration − recharge year* data show significant trend reversal between 1980 and 1990 for nitrate (a); oxidation capacity (b); showed no significant trend reversal (c); and sum of cations (d). Potassium.

Illustration 8 Calculating trends on hydrochemical time series after considering the 'year of recharge', i.e. the 'age of the water' (from Visser et al., 2007).

In practical use, this work provide a clear evidence that the use of GW dating tools can disambiguate the comprehension of trends in aligning the time axis. Authors have identified for different reason that usually make the trend calculation hard if not impossible: (1) the uncertainty of the travel time of groundwater and contaminants to the monitoring screens; (2) attenuating processes retarding the arrival of contaminants at the monitoring screen, such as sorption or chemical reactions with the subsurface; (3) noise caused by short term temporal variation of concentrations, for example as a result of crop rotation; and (4) variation of concentrations in separate monitoring screens as a result of large scale spatial variation in inputs.
Similar approach can be found in (Hansen et al., 2012), where authors shows that even if trend reversal took place around the 80's, significant amount of wells (1/3 of the studied wells) still have upward nitrate trends (Illustration 9).

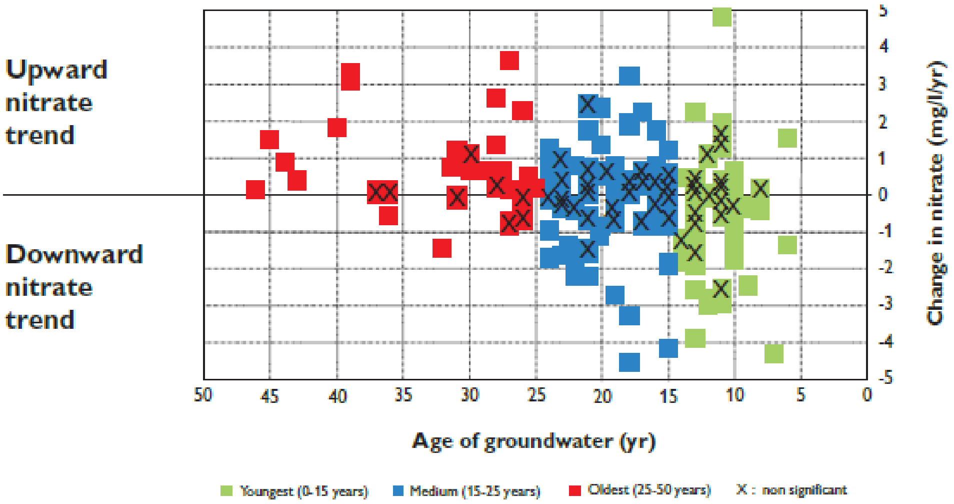

Illustration 9 Relation of the nitrate trends to the age of water, based on CFC's, from Hansen et. al. 2012.

But using information on groundwater age, and especially considering the 'year of recharge' makes possible to demonstrate a trend reversal in groundwater quality; and to correlate the concentration - recharge year relation to the historical concentrations of agricultural contamination in recharging groundwater.

If year of recharge would not have been considered, upward trends would be calculated at greater depth, in that case meaning at greater 'ages', and downward trends would be calculated for shallower depth, in that case meaning at low 'ages'. That illustrate in a clear manner the concept of 'time lag': it takes time to water to flow downwards. This means that the upward trends are greater depth are reflecting the input N function 10,20 of 30 years ago, and will then takes an other 10;20 or 30 years to see actual changes.

An other example of this can be found in Hansen et al., 2017, where nitrate trends have been separate among for periods depending of the year of recharge (Illustration 10).

It is made evident that one would made a strong misinterpretation of the general trend evaluation over the whole set of data without the information on the age. In this example, waters infiltrate before 1985 exhibit upward trends, whereas waters infiltrate after that date exhibit downward trends. Interpretating this data as a whole would mix this two different dynamics.

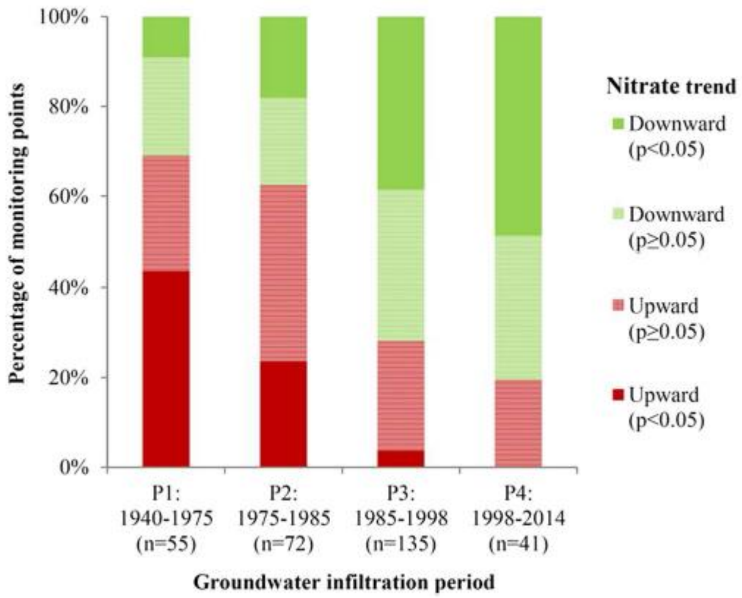

Illustration 10 Repartition of the trends in nitrate, based on the year of recharge, from Hansen et. al., 2017.

As a consequence, evolution of hydrochemical at each sampling site/depth should be consider with respect to this time-lag (the time it takes for water to flow from surface (recharge) to the sampling depth).

Method presented by this authors is to align the time-axis. But the concept is exactly the same as for the PistonFlowModel (PFM): on observation a time *t* with an 'age' of 10 years is related with the input function at time *t-10*, with no modification of the signal in between. One should remarks that the LPM approach could be of help to improve the relation between input function (recharge and N leaching) and observed time series as other transfer function than Piston Flow exists (Dispersive model, gamma model, mixing,etc.).

4.2 Transit time in the USZ

Transit time in the USZ is one of the main problem when dealing with time lag, especially for nitrate (see for example Wang et al., 2013). Some methods have been proposed (Ascott et al., 2017), based on extensive estimation of all possible sources of nitrate, and budget methods, accounting for recharge rate. As it is usually not possible to sample water at the bottom of the USZ, more integrated methods are still needed.

Use of environmental tracers to estimate the time spent in the USZ by water is usually not feasible because of the principle of the tools: the clock is set only when the system become 'close', that is to say at the bottom of the USZ, when no exchange with the atmosphere is further possible. Tracers such as CFC's, SF6 or ^{85}Kr, ^{39}Ar will be affected by such a problem, but not ^{3}H, or conservative tracers (or other conservative solute depending of the matrix). Gerber et al., 2018 shows that a multitracers approach can lead to a good estimate of the transit time in the USZ. In this case, the combination of ^{85}Kr, ^{39}Ar, ^{3}H and [NO_3^-] where used, and combination of several LPM where used.

Several cases where considered, considering or not the USZ, and modelling all tracers together, only nitrates, or only the environmental tracers. Several of them achieve to reproduce the measured concentrations, but the one considering the USZ shows better results.

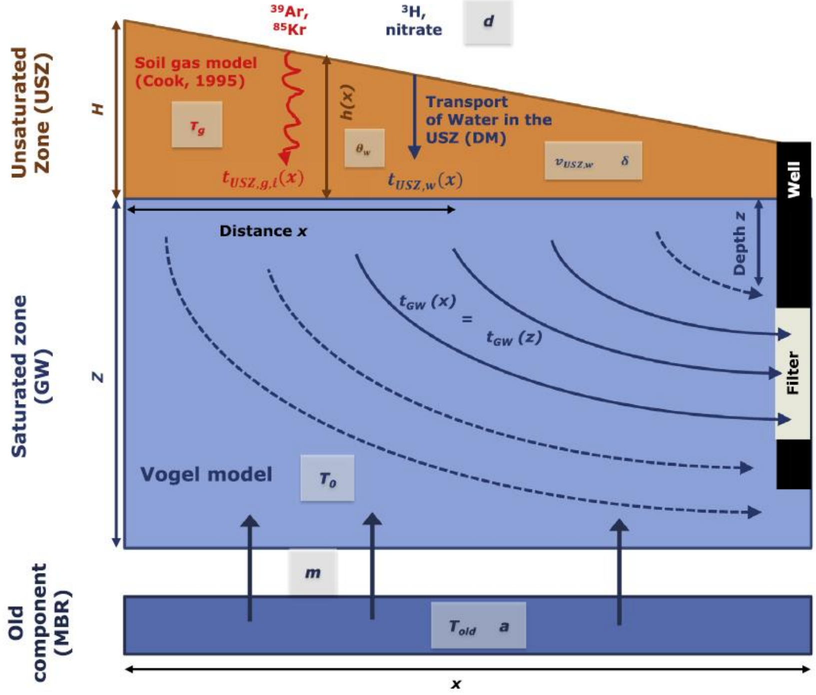

Fig. 3. A cross section along the main flow direction of the conceptual model used for deriving model ages with the three parts unsaturated zone, saturated zone, and old component. The scheme only shows a subsection of the study area from the upstream boundary of the aquifer to an arbitrary well. Fitted model parameters (see also Table 2) are shown in grey boxes in the model segment where they are relevant.

Illustration 11 Illustration of the conceptual model and the associated LPM, Gerber et al., 2018

The model used (or combination of models) is rather simple, even if depending of 9 parameters. But the low computation cost of such simple models authorize a thorough assessment of the associated uncertainties.

Calculation of the transit time in the USZ is only possible if a set of tracers are monitored, in that case dissolved gases (^{85}Kr, ^{39}Ar) and water molecule tight (^{3}H) or dissolved ion (nitrate). One should argue that CFC's or SF6 could certainly lead to a similar conclusion. But a conceptual and mathematical model is also needed (LPM, or combination of LPM) and more complex models as presented by Gerber et al., 2018 are not available to our knowledge. Simple model for USZ only however could be found (Schwientek et al., 2009).

4.3 Structure of age, mixing

Osenbrück et al., 2006 demonstrate an other use of environmental tracers using a combination of different tracers, sampled in only two campaigns in 1992 and 2002. Based on prior knowledge of the hydrogeological structure and functioning, they set a combination of LPM Illustration 12to understand and simulate the measured concentration in CFC's, ^{3}H and ^{3}He and a tritium free end member, corresponding to

mixing with old waters. After calibration, a set of possible calibration parameters have been found, showing that the dispersive model (DM) is the more suitable for interpretation of measured data, with high mean residence time (25-50 years), and significant dispersion value. The DM have been preferred to the PFM and PEM based on the agreement with the observed data. The contribution of tritium free flows is estimate in the range of 15 to 25 %. This is in contradiction with the existence of preferential recharge areas that could have been proposed based on geological knowledge only. This helps to lead to a revised conceptual model, highlighting the dispersive character of the flows, in good agreement with the geological settings. This implies a larger range of age, as many contribution of different flow paths.
Based on this founding, and on reconstruction of the N input historical input function, the LPM have been used to simulate the nitrate concentration (considering nitrate as a conservative tracer) which reveals a good agreement between the synthetic input function and the observed values.

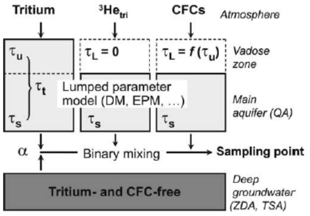

Figure 3. Schematic representation of the lumped parameter concept. Symbols represent fitting and related parameters. Parameters τ_t, τ_s, and τ_u are the mean residence times of the young groundwater end-member of the total system, the saturated zone, and the vadose zone, respectively, α is the fraction of young groundwater, and τ_L is the time lag of gas tracers in the vadose zone, which is negligible in case of $^3He_{tri}$, and related to τ_u by equation (3) in case of the CFCs.

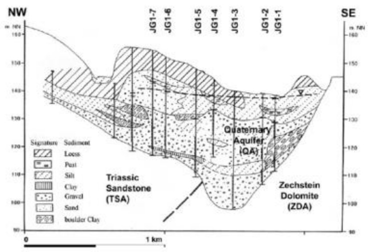

Figure 2. Geological cross section through the Quaternary aquifer (QA) following the orientation of the well gallery JG1 [after *GEOS Freiberg Ingenieurgesellschaft mbH*, 1999]. The dashed line indicates the potentiometric surface (without pumping) of the QA.

Illustration 12 Conceptual model of the aquifer (right), and corresponding Lumped Parameter Model (LPM), including old component (tritium free) mixing with younger component, Osenbrück et al., 2006

Osenbrück et al., 2006 demonstrates the usefulness of environmental tracers in different ways:
When several tracers are used (CFC's, ^3H, ^3He), the confidence in the calibrated parameters for LPM is better. Once set, the LPM can be extended for using with other tracers, and in particular, with assumption, for nitrates. If not fully documented, the N-input function can be calibrated using the existing model, and when done, this model could provide projection for the future evolution on NO3-. This modeled evolution of nitrate can be used to understand the actual and future trend, and eventually the reversal of trend. Here, calibration of the LPM helps to constrain an historical reconstruction of the N leaching, and thus to better understand the potential N stock of the aquifer.
More, the contribution of old water can been reveal, explaining the relatively low concentration in NO3- due to dilution by the old water (low nitrate). Change in the pumping regime, if adding more young water would instead lead to increase in nitrate concentration.
Finally, because of the long residence time, nitrate concentration in the groundwater will be achieved only after a long time span

4.4 What consequences for monitoring programs ?

Based on selected studies, three main advantages of considering environmental travers have been presented: i) a better knowledge of the year of recharge, ii) a better knowledge of the delay due to unsaturated zone, and iii) a better knowledge of the distribution of the residence time and possible mixing with 'old' water. In addition when models are set up, and when nitrate can be considered as conservative, or with appropriate model to take degradation of nitrate into account, the LPM can be extended for nitrate simulation, which helps to understand the observed evolution of nitrate, and simulate the future evolution. Trends in nitrate could be interpreted with respect to theses simulation.

Considering those information, what should be recommended for monitoring programs in order to calculate trends (in regards to the WFD) ?

A general flowchart is proposed, in order to better integrate: knowledge based on environmental tracer in the groundwater bodies description. This tend to estimate for example, the fraction of young/old water, the time spent in the USZ and the distribution of residence time when possible.

The main logic is based on :

- If priori knowledge on mean residence time (MRT), fraction of old waters, year of recharge,etc… are already known:
    - Publishing this information on a specific database (to be create);
    - Compute and analyze trends in relation to the information on i) year of recharge, ii) estimated future evolution (modeled from LPM for example)
- If no information exists on groundwater age :
    - Sampling for minimum set of tracers:
        - Those identifying young waters:
            - CFC's, SF6 (including noble gases for assumption on air excess, temperature of recharge,etc.)
            - ^{85}Kr
            - ^{3}H
        - Those identifying old water : ^{39}Ar or ^{36}Cl
    - Interpreting the results in term of old (CFC's free)/'young' waters
    - Consider the effect of USZ
    - Implement a model to interpret the results
    - Publish data, interpretation and associated model (see specific database above)
    - Compute and analyze trends in relation to the information on i) year of recharge, ii) estimated future evolution (modeled from LPM for example).

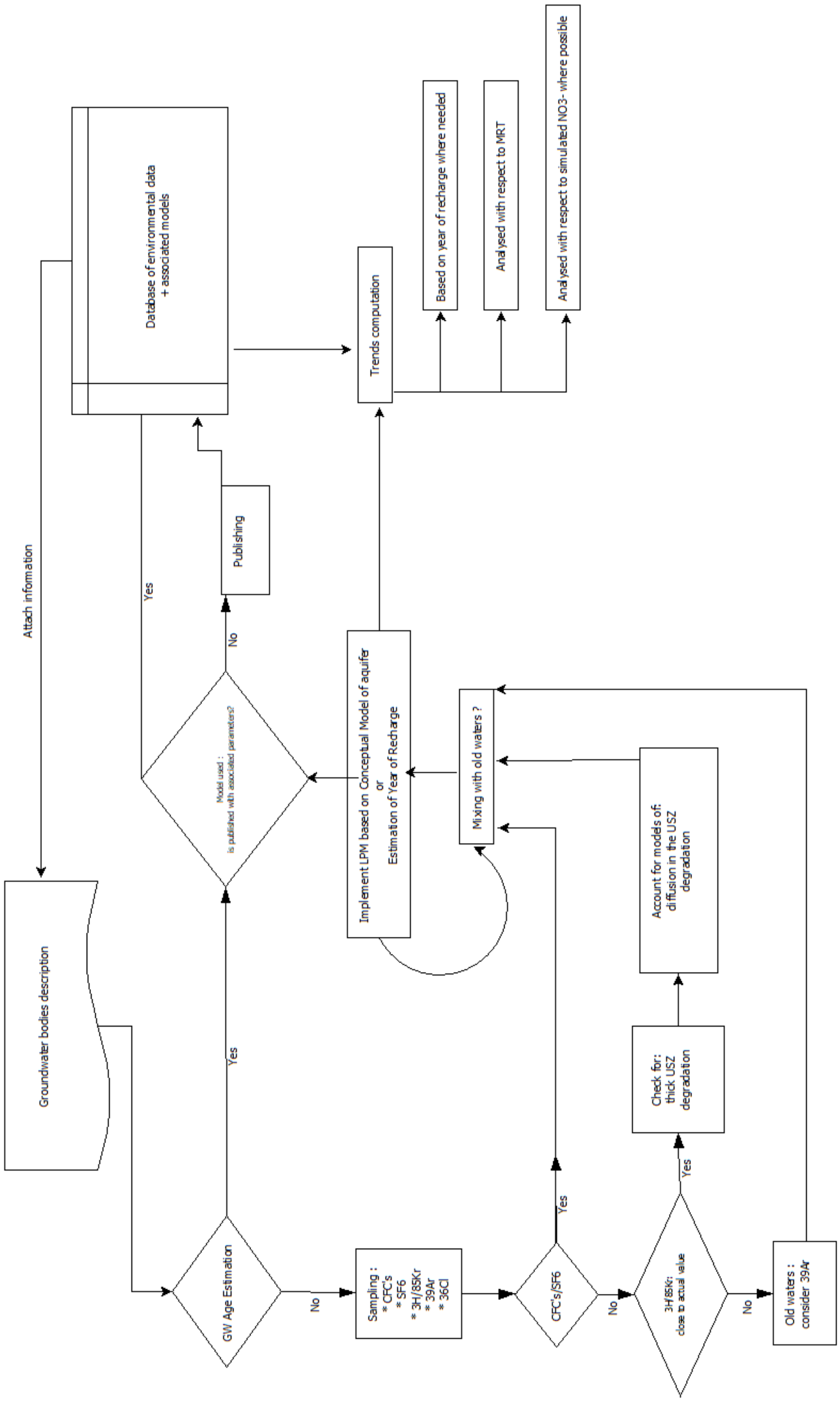

Illustration 13 Proposal for integration of the envrionmental tracers.based knowledge to the groundwater bodies description.

A key proposal is to add to groundwater bodies description an information about the mean residence time based on several tracers, and at least based on both water molecule tight and solute tracers. Best would be to provide a first estimation of the 'age-profile' of the groundwater based on a first sampling campaign, followed by a confirmation campaign, few years later. An outcome of these procedure could be:

-an estimate mean residence time (MRT), leading to an estimate of the 'year of recharge';

- using LPM: an estimate of the distribution of MRT and possible mixing of different waters (young/old);

- the corresponding LPM model, with it's parameters.

This informations could be store in a specific database. This database as to be created.

When talking to sampling frequency, even if implementation of monitoring is made at national scale and a lot of discrepancies exists over Europe, a general recommendation would be to adapt the sampling frequency to the dynamics of groundwaters. An example of implementation in Europe can be found for Danemark in Jørgensen and Stockmarr, 2009,were the sampling frequency is dependant of two categories: young (main components sampled every year) and old (main components sampled every 6 years). The old water meaning groundwater without CFC's, that is recharged before 1940.

But as only few example of monitoring implementation have been found in literature, and this one being the only one considering the MRT as a controlling parameter to implement the monitoring, this appear as a middle term perspective at a European scale, as the heterogeneity of the existing monitoring and geological contexts are not consider here.

5 CONCLUSION

Through a selection of published examples, benefits of integrating environmental tracers is the comprehension of the structure and functioning of the aquifer has been documented.

A key objective of the WFD it to reach a good chemical status for groundwater bodies (GWB). This cannot be achieve without a good comprehension of the time needed for a certain pressure to have an effect on the state of GWB.

Nevertheless, the conceptual model of GWB does not include explicitely concept of 'age' or information related to age, even if a mention of 'understanding of potential effects of pressure' is made. We thus propose to work in such a direction, with linking information on residence time to the GWB.

To do so, both raw data and interpretation have to be attached and a minimum set of tracers appears is recommended (CFC's,^{3}H or ^{85}Kr, ^{39}Ar). It is also proposed to describe the way data where interpreted, most likely using a LPM, and in such a case, the type of model (PFM, EM, PEM, DM, BMM) and related parameters.

All studies highlight the crucial importance to interpret a range of complementary environmental tracers as whole data set. Each of them is based on slightly different principles and they are capable of capturing different phenomenon. The integration of all gives a general and clearer picture.

Considering environmental tracers can exhibit the existence of mixing of waters of different ages, and any mitigation measure would then have an answer depending of this mixing. Evaluating the aquifer answer as a uniform transfer function would here lead to erroneous conclusion.

Under certain conditions, environmental tracer could help to evaluate the time spent in the USZ, which could be significant enough to delay the arrival of the nitrate peak by 10 to 30 years. As flows in the USZ are completely different than flows in the saturated zone, this partition could be of high importance in groundwater management.

Evaluation the heterogeneity of 'ages' is possible using mathematical models, and this could be of great help when evaluating the effect of mitigation measure (a wide distribution of age would lead to a rather low and diffuse answer to a strong stimulus).

Good estimation of age at sampling point can lead to interesting consideration when looking at hydrochemical time series. It can be possible to express the time-evolution of a parameter in relation to the time the water has been infiltrating. Doing so, it makes more significant to calculate trends on this "shifted in time" data, which exhibit possible reversal only on recent waters.

There are already available tools to interpret the environmental tracers data, but they are not always as complex as it should be to interpret slightly complex dataset such as combination of models, effect of the USZ. A further work in that direction could be of interest.

The need of database for tracers data at a European scale is emphasis as it appears to a highly valuable approach to better understand the functioning of the aquifer, and thus effect of pressure on it, such as the nitrate provider activities.

A concluding remark would be the paradox linking the concept of mean residence time and the measurable effects of any pressure change on the aquifer. As it is may appear to be urgent to see the effect of a mitigation measure, it should be kept in mind that aquifers with long residence time will have a long and delay answer to this change. In some extent, it could be think that it is more urgent to act on 'old' groundwater, as effects will be longer to be seen, and pollution would stay longer in the USZ/aquifer. Appreciation of this memory effect of the aquifer is exactly the goal of the environmental tracers, and a certainly good motivation to use them.

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