1 Constraining age distributions of groundwater from public supply
2 wells in diverse hydrogeological settings in Scania, Sweden

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16 **Abstract**

17 Twenty-five public supply wells throughout the hydrogeologically diverse region of Scania, southern Sweden
18 are subjected to environmental tracer analysis (^3H - ^3He , ^4He , CFCs, SF_6 and for one well only also ^{85}Kr and ^{39}Ar)
19 to study well and aquifer vulnerability and evaluate possibilities of groundwater age distribution assessment.
20 We find CFC and SF_6 concentrations well above solubility equilibrium with modern atmosphere, indicating local
21 contamination, as well as indications of CFC degradation. The tracer-specific complications considerably
22 constrain possibilities for sound quantitative regional groundwater age distribution assessments and
23 demonstrate the importance of initial qualitative assessment of tracer-specific reliability, as well a need for
24 additional, complementary tracers (e.g. ^{85}Kr , ^{39}Ar and potentially also ^{14}C). Lumped parameter modelling yields
25 credible age distribution assessments for representative wells in four type aquifers. Pollution vulnerability of
26 the aquifer types was based on the selected LPM models and qualitative age characterisation. Most vulnerable
27 are unconfined dual porosity and fractured bedrock aquifers, due to a large component of very young
28 groundwater. Unconfined sedimentary aquifers are vulnerable due to young groundwater and a small pre-
29 modern component. Less vulnerable are semi-confined sedimentary or dual-porosity aquifers, due to older age
30 of the modern component and a larger pre-modern component. Confined aquifers appear least vulnerable,
31 due an entirely pre-modern groundwater age distribution (recharged before 1963). Tracer complications aside,
32 environmental tracer analyses and lumped parameter modelling aid in vulnerability assessment and protection
33 of regional groundwater resources.

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1. Introduction

The southernmost part of Sweden known as Scania relies on groundwater for 50% of its water supply. The understanding of prevalent and future anthropogenic pollution concerns to these water supplies is limited, due to deficient quality monitoring, poorly characterised public supply wells (PSWs) and complex hydrogeological environments.

Scania geology constitutes 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 (Fig. 1). Thus, groundwater extraction for public drinking water supply occurs from a range of different types of aquifers spanning fractured gneisses and sandstones, dual-porosity lime- and sandstones and a wealth of superficial to more or less buried sorted unconsolidated sedimentary deposits of much diverse physical composition (Gustafsson, 2005). Recently, Åkesson et al. (2015) demonstrated pesticide occurrence in 18 of 23 studied regional PSWs, spanning all of the above described aquifer types. Although some deductions on governing factors for observed pollution patterns could be made, the study underlined a need for improved understanding of the age structure of the pumped waters to predict pollution trends, patterns and risks.

Environmental tracer concentrations observed at PSWs represent an integration of the hydrodynamics of the upstream flow-field (Portniaguine and Solomon, 1998) and enable assessment of pollution trends and risks through what is sometimes referred to as groundwater age assessment (Bohlke and Denver, 1995; Tesoriero et al., 2007; Visser et al., 2009; Suckow, 2014; Åkesson et al., 2014). If samples are collected from long screen intervals or in heterogeneous environments (Weissmann et al., 2002; Alvarado et al., 2007; Visser et al., 2013), such as in the case of the PSWs of interest, groundwater age should be considered and assessed as a distribution rather than as having a single mean age (Bethke and Johnson, 2008; Massoudieh et al., 2012). The age distribution is an important aspect for the assessment of intrinsic pollution susceptibility of PSWs (Jurgens et al., In press).

Lumped parameter mixing models (LPMs) reduce the complexity of the groundwater system to a single weight function (Massoudieh et al., 2012; Engdahl and Maxwell, 2014; McCallum et al., 2014) and enable the characterisation of the groundwater age distribution based on observations of multiple tracers, beyond the interpretation of tracer-specific apparent groundwater ages. Each LPM (Table 1) represents a specific hypothetical groundwater flow systems and predicts the concentration of a tracer by a convolution integral:

$$C_{out}(t_{obs}) = \int_0^{\infty} C_{in}(t_{obs} - t)g(t)e^{-\lambda t} dt$$

where C_{in} and C_{out} are the input and output concentrations, t_{obs} the time of observation and t the transit time. The exponential term accounts for first-order decay in case of a radioactive tracer with decay constant λ . The age distribution is reflected in the weight function $g(t)$, specific to the LPM of choice (Maloszewski and Zuber, 1882; 1996). LPMs have proven powerful when compared to more informed and demanding numerical flow and transport modelling efforts (Eberts et al., 2012). Importantly, sound application relies on a multi-tracer approach in order to move toward a unique solution and in order to be able to assess and manage potential tracer-specific complications.

In this study, the age structure of 25 Scanian PSWs was characterised based on the analysis of multiple environmental tracers including tritium-helium (^3H - ^3He ; Schlosser et al., 1988; Poreda et al., 1988), chlorofluorocarbons (CFCs; Busenberg and Plummer, 1992), sulphurhexafluoride (SF_6 ; Busenberg and Plummer, 2000), krypton-85 (^{85}Kr ; Rozanski and Florkowski, 1978; Loosli and Oeschger, 1979) and argon-39 (^{39}Ar ; Loosli, 1983) using lumped parameter models (Eriksson, 1958; Vogel, 1970; Maloszewski and Zuber, 1982; Jurgens et al., 2012). Few tracer-based studies are known from the area (e.g. Persson, 1974; Barmen, 1992; Gustafsson, 1992; Åkesson et al., 2014) and hence this study also serves to test the regional applicability of these tracers.

2. Materials and methods

2.1. Well selection and conceptual hydrogeology

Twenty-five PSWs were included in this study, comprising the 23 of the Åkesson et al. (2015) study and an additional two (Fig. 1, Table 2). The wells are spread out throughout most of Scania, cover varying land use settings and span (ground level) altitudes of 5-120 m. Estimated recharge rates within the studied catchments range between 200 and 500 mm/yr depending on coastal proximity and elevation (Gustafsson, 2005). Average annual temperatures vary between 6 and 10°C (SMHI, 2013). Recharge generally occurs from late autumn to late spring (Gustafsson, 2005). Figure 2 provides simplified and generalised conceptual cross-sections for the different types of aquifers represented.

Seventeen PSWs extract groundwater from unconsolidated sedimentary aquifers. These aquifers range from discrete superficial and relatively thin glaciofluvial (typically esker) deposits generally underlain and

surrounded by tills and flanked by fine-grained and organic deposits (Fig. 2Ai), to thicker glaciofluvial (esker/valley fill) deposits typically buried below semi-/confining tills, silts and clays (Fig. 2Aii). The physical composition of these sedimentary aquifers tend to vary significantly between and within, because of the regional bedrock mosaic and because of diverse sourcing and routing of depositing glacial melt water. Vertical upward groundwater flow from underlying units with higher hydrostatic pressure is commonly observed.

Of the remaining eight studied PSWs, half extract water from a major dual-porosity sedimentary rock aquifer and the other half from fracture-flow dominated bedrock aquifers. The dual-porosity sedimentary rock aquifer consists of a thick sequence of lime- and poorly consolidated sandstones deposited into a several hundred meter deep crystalline bedrock depression (Fig. 2B). Vertical upward leakage is known to occur between the lowermost sandstone-dominated parts and the overlying limestone-dominated parts. Quaternary deposits cover almost the entire aquifer, albeit to different extents in relation to thickness and character. Screening lengths vary (Table 2) and sometimes span multiple lithologies.

The wells in the fracture-flow dominated bedrock aquifers are generally situated at outcrop locations, screening over considerable depths down to >100m, with casing generally only extending down a few meters below the ground surface (Fig. 2C).

2.2. Sampling

Groundwater sampling for ^3H - ^3He , CFCs and SF_6 was carried out in January 2012, using permanently installed pumping equipment specific to the respective well owner. Due to continuous pumping for drinking water production, all wells had been thoroughly flushed before sampling. Samples were collected upon field parameter (pH, conductivity, DO) stabilisation.

Samples for ^3H analysis were collected in duplicate 1 l glass bottles. Samples for dissolved He and Ne isotope analysis were collected in duplicate in clamped-off copper tubes, connected to the well tap through a closed hose system. ^3H and noble gas (He, Ne) analyses were carried out at the Bremen Mass Spectrometric Facility according to Sültenfuß et al. (2009).

Triplicate samples for CFCs were collected according to the bottle-in-can method (Oster 1994) described by USGS (2013). Analyses were carried out at the Geological Survey of Denmark and Greenland (GEUS) according to procedures described by Busenberg and Plummer (1992).

Duplicate samples for SF₆ were collected from 14 wells via headspace sampling (see e.g. Friedrich et al., 2013). Remaining wells could not be sampled accordingly due to failing sampling equipment. These samples were analysed at the Bremen Mass Spectrometric Facility via gas chromatography with electron capture detection based on the method of Bulsiewicz et al. (1998). Follow-up air samples, analysed at the same facility, were collected in duplicate 1 l glass bottles at six of the sampling sites (no. 1-2, 5, 8, 14 and 23) in November 2014.

In April 2012, one of the wells was sampled for ³⁹Ar and ⁸⁵Kr through in-field degassing of approximately 2.5 m³ water. Analyses were conducted at the Physics Institute, University of Bern, Switzerland via gas chromatography separation followed by activity measurements by low level gas proportional counting (Loosli and Purtschert, 2005).

Samples for major ion, metal and nutrient analysis were collected in connection to tracer sampling in January 2012. Analyses were carried out by ALS Scandinavia, Sweden.

2.3. Data analysis

In the absence of a complete set of noble gas data for the calculation of well-specific recharge temperatures, all measured tracer concentrations were interpreted using a single recharge temperature of 9°C, consistent with the temperature of sampled groundwater (8.7±0.6°C; Table A.1). A common arithmetic mean value of 40 metres above sea level (m a.s.l.) was applied as recharge altitude.

After calculating solubility equilibrium fractions for all tracers and samples, potential contributions of excess air were quantified via Ne according to Schlosser et al. (1989). As Ne only has an atmospheric source, offsets between measured and solubility equilibrium concentrations of Ne, expressed as ΔNe, can be used as a proxy for excess air and also for potential degassing. The uncertainty of the recharge elevation and temperature result in a negligible uncertainty in the calculated equilibrium He and Ne concentrations.

The terrigenic He component was calculated as the measured concentration minus the equilibrium and excess air components, assuming a terrigenic ³He/⁴He ratio of 1x10⁻⁸. The terrigenic He isotope ratio was validated on the samples with high terrigenic He and low ³H concentrations (Fig. 3). Tritiogenic He (³He*) was then calculated for each sample, deducting estimated solubility equilibrium, excess air and terrigenic components from measured ³He concentrations. The uncertainty of the tritiogenic He component was

calculated including the uncertainty in the measurements, in the set terrigenic He isotope ratio, the recharge temperature and recharge altitude (Visser et al., 2014).

Atmospheric input records for ^3H , CFCs and SF_6 were obtained from IAEA (1996), IAEA/WMO (1998) and USGS (2014) respectively, to evaluate the measured concentrations against historical mixing ratios and ^3H content of precipitation.

The derived tracer data was analysed in two ways. First, measured data was plotted in selected combinations of tracer-tracer plots, together with predictions of the piston flow model (PM), the exponential model (EM) and a binary mixing (BM) model to evaluate the consistency of the measured tracer concentrations, detect potential tracer-specific complications and to aid in initial qualitative age characterisation. Second, LPMs were fitted to the observed tracer concentrations from four PSWs, one for each end member aquifer type, using Lumpy version 2.9 (Suckow, 2012). Lumpy is a purpose-made software program for simultaneous modelling of multiple tracer concentrations and associated age distributions according to common LPMs. The age distribution is found by minimising weighted residuals between modelled and measured tracer concentrations, referred to as the “Goodness of Fit” (GOF; Suckow, In Review):

$$GOF = \frac{1}{(\sum_{j=1}^k n_j)} \sum_{j=1}^k \sum_{i=1}^{n_j} Abs\left(\frac{C_{0ij} - C_{Mij}}{\sigma C_{0ij}}\right)$$

where i is an index running over the n_j measurements for tracer j , and j is the index running over the k tracers. σC_0 is the absolute uncertainty of the measurement. Table 1 lists tested LPMs.

3. Results

3.1. Measured tracer concentrations

Table 3 lists measured raw tracer data and derived parameters ΔNe , $^4\text{He}_{\text{terr}}$ and $^3\text{He}^*$.

3.1.1. ^3H and noble gases

Ne concentrations indicate modest amounts of excess air in most samples (ΔNe up to 109%; Table 3, Fig. 4). Five samples show Ne concentrations below solubility equilibrium (ΔNe down to -13%), indicating slight

degassing, equilibration at higher temperatures or ion discrimination of Ne in the mass spectrometer due to overwhelming amounts of terrigenous He. All samples show elevated ^4He concentrations, up to 2×10^{-3} ccSTP/kg (Table 3), equivalent to 40 times solubility equilibrium, implying a significant source of terrigenous He. The terrigenous He component is entirely radiogenic, confirmed by the observed He isotope ratio of 1.62×10^{-8} in samples with no ^3H , and the $^3\text{He}^*$ component can therefore be derived with limited uncertainty. $^3\text{He}^*$ was detected and quantified in 23 samples, up to the equivalent of 130 TU ^3H . Two samples from confined sedimentary aquifers (7 and 8) contained less than 0.10 TU ^3H , all other sampled wells contain significant amounts of ^3H (up to 11.9 TU; Table 3).

3.1.2. CFCs and SF_6

Six of the 25 samples show CFC concentrations that do not indicate degradation or contamination for any of the species. GC peaks indicate CFC degradation for eight samples (Table 3). Several samples are contaminated as indicated by measured concentrations higher than possible due to solubility and excess air equilibrium with ambient air: five samples show CFC-11 concentrations above 6 pmol/kg, eight samples have CFC-12 concentrations above 3 pmol/kg and two samples have CFC-113 concentrations above 0.6 pmol/kg. Excessive CFC concentrations appear dictated by local pollution plumes as indicated by concurrent detections of TCE (trichloroethylene) in six samples. Both TCE and CFCs were used extensively throughout a range of industrial processes and for dry-cleaning during several decades in the late 20th century in Sweden (Englöv et al., 2007). Evidently, although the contaminated samples contain a fraction of water recharged after 1950, this fraction cannot be quantified nor can the specific CFC concentration be used as an age tracer.

SF_6 concentrations in all but three samples (no. 7-9) exceed solubility equilibrium with modern air, up to one thousand times (2090 fmol/kg, PSW no. 12). The control air samples show a regional atmospheric concentration of 8.56 ppt ($SD = 0.04$), indicating that the excessive groundwater concentrations derive from a local geogenic source.

3.2. Tracer-tracer plots

Tracer-tracer plots for CFCs, ^3H and $^3\text{He}^*$ are shown in Fig. 5. Plotted tracer concentrations correspond to weighted averages of the duplicate or triplicate samples. For CFCs, error bars correspond to the standard

deviation of the measured values for the given PSW. For ^3H , error bars correspond to measurement uncertainties. Note that contaminated CFC concentrations are outside the plotted area.

Seven samples, all from confined or semi-confined aquifers, have CFC concentrations suggesting primarily pre-modern water contributions (no. 7-8, 14, 18-19, 24-25). These plot near the origin and are consistent within error bars, but they do not provide a good basis for age distribution modelling. The clustering around the origin of the CFC tracer-tracer plots is at least partially a result of CFC degradation, which is more apparent for samples that show near zero concentrations for CFC-11 and CFC-113 but not for CFC-12 (e.g. samples no. 2 and 12). For six of these samples, the ^3H concentrations of up to 2.1 TU also indicate mixing with pre-modern groundwater (no. 7-8, 18-19, 24-25). Nearly all other samples plot outside of the area bordered by the CFC mixing model curves indicating degradation of one or modest contamination of the other species. Few plot in a consistent manner for all three species.

In contrast, nearly all samples without obvious CFC contamination plot within the area of EM, PM or BM mixing model curves for CFCs and ^3H , and could theoretically be explained by binary mixing of EM and PM components. However, the inconsistency on the CFC plots has suggested that most of the CFC concentrations are impacted by degradation or contamination and hence the CFC concentrations have little value for age modelling. All samples also plot within the mixing curves of ^3H and $^3\text{He}^*$, providing no clear indications for inconsistency caused by contamination, sample degassing or loss of $^3\text{He}^*$ due to matrix diffusion. Assuming the ^3H and $^3\text{He}^*$ concentrations are unaffected by those processes and hence reliable, the following can be derived from the ^3H and $^3\text{He}^*$ plot. Samples 7-8 from confined sedimentary aquifers are entirely pre-modern, as observed from ^3H concentrations at or below 0.1 TU. The absence of ^3H and CFCs in well 8 was in line with a ^{85}Kr analysis result of <0.5 dpm/ccKr (disintegrations per minute of ^{85}Kr per cubic centimetre of stable Kr at Standard Temperature and Pressure). The ^{39}Ar activity in this well was $73\pm 7\%$ modern, indicating a mean residence time of about 120 years and thus the absence of large proportions of water younger than 50 years.

Four samples from semi-confined aquifers (samples no. 18-19, 24-25) plot near the beginning of the bomb-pulse, and probably contain a significant fraction of pre-modern groundwater. Sample 17 from an unconfined sedimentary aquifer contains a fraction of groundwater recharged during the bomb pulse (1960-1980) and a fraction of pre-modern groundwater, resulting in dilution of the modern component while preserving its ^3H - $^3\text{He}^*$ ratio. Samples 20 and 22, from unconfined sedimentary and fractured aquifers, appear to be a mixture of groundwater components recharged between present and 30 years ago. Samples 4 and 14 from semi-confined

sedimentary aquifers and sample 12 from an unconfined fractured aquifer plot very close to the PM model line with ages between 20 and 30 years. However, due to the location on the curve, a mixture between somewhat older groundwater and pre-modern groundwater is also possible. All other samples plot near the PM model line with ages between 5 and 20 years. Due to the shape of the ^3H input curve, it is impossible to assess the width of the age distribution (age spread) for these samples, but significant components of pre-modern or bomb pulse groundwater are not plausible.

Based on the observed tracer-specific complications, one may assign different reliability and weight to the different tracers for further analysis. ^3H is part of the water molecule, does not observe chemical degradation and could therefore be considered the most reliable tracer. While the concentrations of ^3H in historical precipitation are not accurately known for the study location, the consistency with $^3\text{He}^*$ lends credibility that the reconstructed curve is valid. While calculation of $^3\text{He}^*$ relies on several other measured concentrations (He isotope ratio, He and Ne concentrations) and calculated parameters (excess air, terrigenic He concentration and isotope ratio), associated uncertainties have at large been accounted for through error propagation. A main concern is rather small degrees of CFC contamination or degradation, for which judgement and handling is more difficult and ambiguous, particularly when results lie in the possible range but not within the areas of model curves (e.g., PSWs 2, 10-13, 16; Fig. 5).

The tracer-tracer plots show that a combination of LPMs will be able to fit to combinations of two tracers (e.g. ^3H vs. CFC plots; Fig. 5), but few samples show concentrations that are consistent when including more than two tracer species. The implication is that few of the analysed samples allow for quantitative groundwater age distribution assessments using LPMs. Exceptions include samples from PSWs no. 1, 4, 16 and 23, and these wells were chosen to represent the four different aquifer types in a more quantitative age analysis.

3.3. LPM modelling of age distributions

3.3.1. *Unconfined sedimentary aquifer*

PSW 23 extracts water from 7 to 10 metres below ground surface (m b.g.s.), from an up to 15 m thick, elongate and unconfined esker deposit representative of an unconfined sedimentary aquifer (Fig. 2Ai). Relatively permeable tills and fine-grained postglacial material flank this particular esker ridge, and till is known to occur in between the esker deposits and the underlying gneissic bedrock. Measured CFC-12 and SF_6 concentrations are higher than peak solubility equilibria and are excluded from the LPM analysis.

The tracer-tracer plots including combinations of ^3H , CFC-11 and CFC-113 (Fig. 5) suggest that PSW 23 pumps water according to a model somewhere in between a PM and an EM, possibly with a minor proportion of a tracer-free component. CFC-11 and CFC-113 concentrations correspond to PM ages of 27 and 25 years. The ^3H - $^3\text{He}^*$ plot points towards a PM age of 8 ± 3 years.

A satisfactory LPM fit was derived for a combination of 11% tracer-free water and 89% of a partial exponential model (PEM; Table 1) corresponding to the conceptual model (screening depth: 7-10 m b.g.s., aquifer depth: 15 m) and with an aquifer MRT of 10 years (GOF = 5.0). The solution is sensible in view of the available hydrogeological information, with an older component attributed to upward leakage from underlying units. The presence of an older component is also supported by the presence of terrigenic ^4He at 2.2×10^{-4} ccSTP/kg ($\Delta^4\text{He}_{\text{terr}} = 480\%$). The relatively high GOF is primarily a result of an offset between the modelled and the measured CFC-113 value (0.50 vs. 0.43 pmol/kg), as well as the low analytical uncertainty of CFCs, and is potentially indicative of sorption and/or degradation.

Fig. 6 (PSW 23) displays resulting fits and age distribution. In agreement with what would be expected for a relatively short screen installed in an unconfined and relatively shallow aquifer, the resulting age distribution is narrow and young, almost entirely dominated by water between 6-11 years old. As such, the well should be considered very vulnerable to pollution. While the LPM predicts no contribution of water younger than 6 years, only tracers that are sensitive to very young groundwater (e.g. ^{35}S ($t_{1/2} = 87$ days) or ^{22}Na ($t_{1/2} = 2.6$ years)) would be able to confirm whether the well is not vulnerable on an even shorter time scale.

3.3.2. *Semi-confined sedimentary aquifer*

PSW 4 extracts water over two screens, between 28-32 and 36-40 m b.g.s., from an up to 60 m thick esker deposit covered by clay and/or postglacial sand representative of a semi-confined sediment aquifer (Fig. 2Aii). The thickness of the overburden varies from a few metres along the esker ridge, up to more than 40 m along its sides. Till occurs between at least part of the esker sediments and the underlying limestone bedrock. Recharge is thought to occur both through the overburden and from the underlying bedrock. CFC-12 is excluded because of obvious contamination (Table 3).

Interpretable tracer data, including CFC-11, CFC-113, ^3H and $^3\text{He}^*$, all suggest PM ages around 27-35 years (Table 3). However, the tracer-tracer plots including ^3H and CFC-11 or CFC-113 suggest pre-modern water admixing (Fig. 5).

A reasonable LPM fit was derived when mixing 25% tracer-free water with 75% of a diffusion model (DM; Table 1) with a sample MRT of 30 years and a Peclet number of 0.4 (GOF = 1.3). This mixing model results in a wide yet significantly skewed age distribution (Fig. 6), suggesting that almost half of the pumped water would have recharged less than twenty years ago. This in turn invokes a notable degree of pollution vulnerability, yet, the proportion of older and also pre-modern water is significant, whereby pollutant concentrations are likely to be considerably diluted.

3.3.3. *Unconfined dual-porosity bedrock aquifer*

PSW 16 is located in the NW border area of the dual-porosity sedimentary bedrock aquifer described in chapter 2.1 (Fig. 2B). Tracer analyses show indications of CFC degradation as well as some minor degassing (Table 3). The well pumps water from 20-27 m b.g.s., from a 10-20 m thick limestone unit covered by about 10 m of rather permeable sands/sandy-silty tills. Recharge may occur both from the overburden and the underlying unconsolidated sandstone.

All interpretable tracer data suggest a predominantly modern water component (Table 3). CFC PM ages range from 29-35 years. The ^3H - $^3\text{He}^*$ plot points to a PM age of 10 ± 3 years. This discrepancy can result from a highly mixed sample, or possibly diffusion of $^3\text{He}^*$ into the matrix (LaBolle et al., 2006; Neumann et al. 2008).

The tracer concentrations indicate the majority of the water to have recharged well after the bomb-pulse. If diffusive exchange with the matrix was relevant, one would expect diffusion of bomb-pulse $^3\text{He}^*$ out of the matrix into the mobile water, rather than diffusion of $^3\text{He}^*$ into the matrix, leading to older ^3H - $^3\text{He}^*$ PM ages (Fig. 5A; Neumann et al., 2008). Because CFC PM ages are older than ^3H - $^3\text{He}^*$ PM ages, we consider matrix diffusion to be insignificant and the $^3\text{He}^*$ concentration to be robust. The ^3H -CFC plots indicate pre-modern water admixing or confirm degradation of CFCs (Fig. 5).

Trials using combinations of all LPMs listed in Table 1 suggest that it is impossible to fit all CFC species and ^3H . Due to the indications of CFC degradation, a satisfactory fit was derived using ^3H , $^3\text{He}^*$ and CFC-12, because CFC-12 is considered the most stable CFC species. The fitted age distribution contained a fraction of 27% of a tracer free component and 73% of a dispersion model with an MRT of 4 years and a Peclet number of 0.6 (GOF = 0.9). The model is reasonable in view of the hydrogeological context, where the dual-porosity flow system (i) is affected by upward leakage of older water from underlying units and (ii) allows both for a rapid fracture- and a slow matrix flow component. It should be noted that in this case the dispersion model does not represent

Fickian dispersion along a flow path in a sedimentary aquifer but the combined effect of fast macro-pore and slow micro-pore flow. The derived model was used to assess indicated loss of CFC-11 and CFC-113 due to degradation, which was estimated at 28% and 45% respectively. Fig. 6 (PSW 16) displays resulting fits and age distribution, with indicated degrees of CFC-11 and -113 losses accounted for. The well is clearly very vulnerable to pollution, with a large proportion of the abstracted water reaching the well within a few years. The shape of the age distribution derived from ^3H , $^3\text{He}^*$ and CFC-12 shows the importance of including multiple tracers, because the ^3H - $^3\text{He}^*$ plot did not reveal the large proportion of very young water and the width of the age distribution.

3.3.4. *Unconfined fracture-flow bedrock aquifer*

PSW 1 screens water over nearly its entire depth, from 2 to 54 m b.g.s., from an unconfined aquifer within a fractured and weathered gneiss representative of an unconfined bedrock aquifer (Fig. 2C). CFC-12 and SF_6 contents are higher than peak solubility equilibria (Table 3) and excluded from the LPM modelling. $^3\text{He}^*$ was not detected.

Representative LPMs of fracture-flow dominated aquifers are typically difficult to presume because of the wide variety of possible flow paths. Whereas CFC PM ages range from 24-28 years, the non-detectable $^3\text{He}^*$ rather suggest a predominant very young water component, which is also supported by the tracer-tracer plots including combinations of the quantitatively interpretable tracers (^3H , CFC-11 and CFC-113; Fig. 5), indicating binary mixing between recent and pre-modern water.

Using ^3H , CFC-11 and CFC-113, a satisfactory fit was attained when mixing 90% of a PM of 0.5 years with 10% tracer-free water. This model implies that the absolute majority of the pumped water is conveyed from the surface to the screen within months, through one or more major fractures and that the remaining water component connects to a deeper fracture system. The large component of very young water in the mixture makes the well very vulnerable to pollution. Fig. 6 (PSW 1) displays resulting fits. Surprisingly, the 10% tracer free water does not contain terrigenic He from the fractured gneiss, possibly indicating that the tracer-free component is comparably young, i.e. recharged before 1960 but less than several centuries ago.

4. Discussion

4.1. Aquifer types, age distributions and vulnerability

Age tracer data from PSWs in different aquifer types of Scania were evaluated by tracer-tracer plots, qualitative characterisation and quantitative LPM modelling.

PSWs in unconfined sedimentary aquifers generally pump young groundwater with a possible but comparatively minor pre-modern component. The representative well was modelled with a PEM and a 10% pre-modern fraction. The mean age for nearly all PSWs in unconfined sedimentary aquifers is less than 30 years, based on the ^3H - $^3\text{He}^*$ plot. PSWs in unconfined sedimentary aquifers should be considered vulnerable to pollution.

PSWs in semi-confined sedimentary aquifers show a mixture of young and pre-modern groundwater. The mean age of the young component is often older than in unconfined settings, and the fraction of pre-modern water is larger. The representative well was modelled with a combination of a DM and a pure pre-modern component, indicating a wide but significantly skewed age distribution. Because of a relatively large pre-modern component, PSWs in semi-confined sedimentary aquifers are considered less vulnerable to pollution than those of completely unconfined sedimentary aquifers.

PSWs in confined aquifers, of which two samples are available, appear to pump entirely pre-modern groundwater and are therefore considered least vulnerable to pollution.

PSWs in dual-porosity aquifers pump water with a distinctly different age distribution. While the ^3H - $^3\text{He}^*$ plot of the representative unconfined dual-porosity well indicated a PM age of 10 years, including CFC-12 in the analysis shows that the majority of the pumped water is much younger, mixed with a 27% pre-modern component. In contrast, three PSWs in semi-confined dual-porosity aquifers plot near the beginning of the bomb-pulse with large proportions of pre-modern water. PSWs in unconfined dual-porosity aquifers are therefore extremely vulnerable to pollution, while PSWs in semi-confined dual-porosity aquifers are less vulnerable.

PSWs in fractured bedrock aquifers pump water from long screens reaching 50 to 100 meter depth. The representative PSW was modelled with a binary mixture of 90% water with an age of 0.5 years and 10% pre-modern water, demonstrating that in spite of the long screen, the majority of the water is very young and that PSWs in fractured bedrock aquifers are also extremely vulnerable.

4.2. Tracer-specific complications

The analysed data set is demonstrative of most known complications of the applied tracers, including contaminated and degraded CFCs, abundant but poorly constrained terrigenous sources of He as well as abundant but poorly constrained sources of SF₆. Whilst complicating in terms of groundwater age assessments, it is illustrative of common tracer-specific limitations and point towards a need to include additional tracer analyses to constrain the PSW age distributions.

Calculating the tritiogenic ³He component involves separating it from the equilibrium, excess air and terrigenous sourced components. Associated uncertainties are calculated through error propagation. The effect of the uncertainty in the adopted recharge temperature and altitude, due to the lack of a complete noble gas data set, is limited. The most significant source of uncertainty is the terrigenous ³He component. In this case, ³H-free samples confirmed that the terrigenous He isotope ratio was near the production ratio of the upper crust (1x10⁻⁸), allowing for accurate calculations of the tritiogenic He component. The possibility of diffusive ³He* exchange with the matrix of dual-porosity aquifers further complicates the interpretation of observed ³He* concentrations. Due to the possible degradation of CFC, this could not be ruled out but was regarded negligible.

The observed high concentrations of He render Scania as a particular area of interest for studies into the mechanisms and rates of radiogenic ⁴He release in mixed young groundwater, by either incubation of aquifer materials (Solomon et al., 1996) or additional tracers to further constrain the age distribution of the pre-modern groundwater fraction (Plummer et al., 2012). Within this study, no clear correlation between He concentration and aquifer type was found, except for a tendency of increased ⁴He with screening depth (Fig. 7). The concentrations in predominantly modern groundwater are higher than can be supported by U/Th-decay only. Release of He from old U- and Th-bearing aquifer (Solomon et al., 1996) or aquitard (Sheldon et al., 2003) solids, is the most likely source for the sedimentary aquifers sampled. For the sampled bedrock aquifers, long-standing diffusion of He through fractures and micropores from below may be part of the explanation (Andrews et al., 1982; Neretnieks, 2013).

The measured SF₆ concentrations are among the highest ever reported for groundwater (Koh et al., 2007; von Rohden et al., 2010; Friedrich et al., 2013). As analysed air samples show no indications of local atmospheric contamination, natural sourcing is the most likely explanation. Potential sources include fluorite- and sulphur-bearing mineralisations which are known to occur in veins, fractures and rock matrices throughout

much of the region (Johansson, 1982; Bergerat et al., 2007). The lack of correlation between SF₆ and ⁴He (R² = 0.0038) suggest divergent terrigenic sourcing.

In addition to degradation, the collected CFC data indicate considerable regional extent of local contamination sources. CFC-12 appears to be more commonly contaminated than CFC-11 and CFC-113. However, this could also be an effect of degradation of the two latter species. CFC contamination, retardation and degradation have been observed in several European studies before (e.g. Bauer et al., 2001; Hinsby et al., 2007; Visser et al., 2009). To investigate the indicated contamination sources and degradation rates, additional samples are required, ideally from clusters of monitoring wells, with restricted screens at different levels, nested along flow paths towards the PSW of interest (Hofmann et al., 2010). Pumping wells are less suitable because of heavily disturbed and unpredictable flow conditions and water mixing (Zinn & Konikow, 2007).

In order to arrive at rigorous groundwater age distribution assessments using LPMs, environmental tracer analyses cannot be interpreted blindly, but require initial qualitative assessment of potential tracer-specific concerns, and at least some conceptual model of flow conditions and general stratigraphy. The conceptual model is needed to compare and judge on the respective probability of one LPM fit to another, as it is rare to find a unique solution. Conversely, LPMs allow for tests and re-evaluations of assumed flow patterns.

What is primarily lacking for this study is knowledge on unsaturated zone thicknesses and time-series of variations in pump rates and of environmental tracers. This may undermine the long-term representativeness of the derived age assessment.

5. Conclusions for regional groundwater pollution vulnerability

The studied PSWs jointly span most types of groundwater aquifers subject to drinking water production in Scania and may thus be considered representative and indicative of regional scale conditions. In terms of regional groundwater management, the most apparent and arguably also most important deductions from this study are that most of these PSWs are dominated by modern water. Effectively, it is only wells 7 and 8 that appear entirely deficient of modern water. This is consistent with the hydrogeology, as these wells are the only ones that extract water from a very narrow portion of a deep, confined aquifer. The implication is that all other studied groundwater environments exhibit relatively short travel times to the ground surface and hence stand at current and continued risk of anthropogenic pollution.

Because of the established complications for deriving groundwater age distributions from the measured tracers for many of the studied PSWs, it is so far not possible to precisely predict time-scales of risks of pollution and potential pollutant breakthrough and evolution for the full data set. Still, it is clearly the case that pollution risks are prevalent for the characteristic unconfined sedimentary aquifers for which modern water appears to be completely dominating (e.g. PSWs 3, 11, 21 and the modelled 23). The same appears to be true for the unconfined bedrock aquifers dominated by fracture flow (e.g. the modelled PSW 1), as well as for unconfined dual-porosity aquifers (e.g. PSW 16), where water and solutes appear to be able to be conveyed relatively long distances over relatively short time scales. Semi-confined aquifers show larger pre-modern water components (e.g. PSWs 18, 19, 24) and pollution breakthrough might be yet to come and/or significantly diluted. The PM ^{39}Ar groundwater age of 120 years in well 8 indicates the time scale of pollution risk to this well, but without additional tracer data to constrain the age distribution, this should by no means be interpreted that transport of pollution to this well will be delayed by at least 120 years. The absence of ^{85}Kr , however, defines a minimum delay time.

Environmental tracer analysis coupled to lumped parameter modelling undoubtedly has the potential to further aid in the protection of regional groundwater resources, both through constraining time frames of recharge and hence pollution concerns and through providing additional information as to overall flow patterns. Several software programs have recently been developed to make lumped parameter modelling accessible (Suckow, 2012; Jurgens et al., 2012; Suckow, In review). The complications presented here show that real world cases require expert knowledge of tracer behaviour. Because of the local tracer-specific complications revealed by this study, future groundwater age investigation in Scania should aim to include age tracers that are not subject to these complications, e.g. ^{85}Kr . Furthermore, additional age tracers which apply to the older time range should also be included. In view of regional abundance of carbonate-rich rocks and tills, ^{39}Ar may in this regard be preferable to ^{14}C .

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443

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Table 1. Common and applied lumped parameter models (LPMs), with associated parameter variables (in Lumpy).

LPM	Basic concept	Parameter variables
Piston flow model (PM)^{a, b}	No mixing	Sample mean residence time (MRT)
Exponential model (EM)^{a, b, c}	Exponential mixing of ages between 0 and ∞	Sample MRT
Exponential piston flow model (EPM)^b	A PM and EM in series	Sample MRT and a volume ratio specifying the volume with exponential age distribution as compared to the total volume of the model
Partial exponential model (PEM)^d	Partial exponential mixing	Aquifer MRT, screening depth and aquifer depth
Dispersion model (DM)^{a, b}	Mixing according to the advection-dispersion equation	Sample MRT and Peclet number

^a Eriksson, 1958
^b Maloszewski and Zuber, 1982
^c Vogel, 1970
^d Jurgens et al., 2012

Table 2. Altitudes, screening depths, aquifer types and local lithology of studied wells.

Well	Well altitude (m a.s.l.)	Screening depth (m b.g.s.)	Screen length (m)	Aquifer type ^a (confining layer/-s?)	Bedrock ^b
1	23	2-54	52	C (no)	Gneiss
2	40	15-114	99	C (no)	Gneiss
3	60	18-22	4	A (no)	Gneiss
4	9	28-32, 36-40	4+4	A (semi)	Limestone
5	9	6-11	5	A (no)	Sandstone
6	22	11-23	12	A (semi)	Clay-/sandstone, gneiss
7	12	74-75	1	A (yes)	Limestone
8	9	71-72	1	A (yes)	Limestone
9	82	13-17	4	A (no)	Shale
10	17	9-12	3	A (no)	Limestone ^c
11	67	9-12	3	A (no)	Crystalline, shale, sand-/limestone
12	121	5-90 ^c	85	C (no)	Sandstone, gneiss
13	57	6-10	4	A (no)	Clay-/sandstone, shale
14	17	29-43	14	A (semi)	Clay-/sandstone, shale, limestone
15	22	29-39	10	A (semi)	Clay-/sandstone, shale, limestone
16	40	20-27	7	B (no)	Limestone
17	32	14-20	6	A (semi)	Lime-/sandstone
18	23	49-69	20	B (semi)	Lime-/sandstone
19	4	47-96	49	B (semi)	Lime-/sandstone
20	71	14-19	5	A (no)	Gneiss
21	80	9-12	3	A (no)	Gneiss
22	88	5-57 ^c	52	C (no)	Gneissic granite
23	92	7-10	3	A (no)	Gneiss
24	31	24-31	7	A (semi)	Lime-/sandstone
25	17	15-54	39	B (semi)	Lime-/sandstone

^a A: sedimentary aquifer; B: dual-porosity bedrock aquifer; C: fracture-flow bedrock aquifer.

^b For wells in sedimentary aquifers ("A-wells"): underlying bedrock.

^c Uncertain.

Table 3. Measured tracer concentrations and derived parameters excess air (ΔNe), $^4\text{He}_{\text{terr}}$ and $^3\text{He}^*$.

Well	^3H (TU)	^3He $\times 10^{-11}$ (ccSTP/kg)	^4He $\times 10^{-4}$ (ccSTP/kg)	Ne $\times 10^{-4}$	ΔNe (%)	$^4\text{He}_{\text{terr}}$ $\times 10^{-4}$ (ccSTP/kg)	$^3\text{He}^*$ (TU)	CFC-11	CFC-113 GEUS (pmol/kg)	CFC-12	SF_6^{d} (fmol/kg)	^{85}Kr (dpm/cc Kr)	^{39}Ar (% modern)
1	8.27	15.1	1.15	4.33	109	0.0264	0	4.79	0.46	4.34	574		
2 ^b	7.19	11.9	0.953	3.22	56	0.149	3.5 $\pm$ 1.9	0.16	0	1.51	4210		
3 ^c	7.00	7.66	0.555	2.24	8	0.0338	2.2 $\pm$ 1.3	6.38	0.51	4.52			
4 ^b	6.26	14.2	5.36	2.36	14	4.80	24.8 $\pm$ 2.8	3.40	0.19	6.76			
5 ^c	6.92	8.85	0.681	2.07	0	0.209	9.7 $\pm$ 1.4	21.33	0.88	29.66	78.5		
6 ^c	6.78	9.73	0.739	2.41	16	0.169	7.8 $\pm$ 1.5	9.28	0.32	3.22	7.74		
7 ^{a,b}	0.10	8.73	8.37	2.06	0	7.90	6.3 $\pm$ 3.5	0.10	0	0.04	0.39		
8 ^{a,b}	0.02	10.9	14.8	2.43	17	14.2	0	0.13	0	0.05	0.14	< 0.5	73
9 ^{a,b}	6.86	9.03	0.690	2.35	14	0.137	6.0 $\pm$ 1.5	0.10	0.01	0.22	0.94		
10 ^b	5.96	7.43	0.998	1.89	-9	0.578	6.7 $\pm$ 1.2	0.84	0.06	1.18	7.49		
11 ^b	7.60	8.54	1.31	2.52	22	0.708	1.0 $\pm$ 1.5	5.01	0.14	2.64	596		
12 ^b	5.23	11.1	9.10	1.99	-4	8.65	16.7 $\pm$ 3.8	0.26	0.02	1.03	2090		
13	7.62	6.88	0.644	2.11	2	0.160	1.1 $\pm$ 1.2	0.53	0.04	1.24	509		
14 ^{a,b}	5.32	9.14	4.96	1.80	-13	4.57	13.5 $\pm$ 2.3	0.11	0.01	0.05	11.6		
15 ^{a,b}	6.28	9.50	1.13	2.39	16	0.566	7.1 $\pm$ 1.5	0.09	0.06	0.24			
16 ^a	6.67	7.68	3.15	1.99	-4	2.70	5.3 $\pm$ 1.7	2.81	0.20	2.14	4.47		
17	11.94	40.2	0.826	2.49	20	0.233	129.8 $\pm$ 5.1	1.38	0	0.33			
18	0.52	12.9	0.909	3.47	68	0.0333	3.6 $\pm$ 2.1	0.92	0.11	0.95			
19 ^{a,b}	0.30	11.7	20.3	2.52	22	19.7	6.1 $\pm$ 8.2	0.12	0	0.05			
20 ^c	7.52	10.9	8.92	1.83	-12	8.52	18.5 $\pm$ 3.8	21.38	1.77	28.25			
21 ^{b,c}	7.94	8.41	1.84	2.38	15	1.28	2.5 $\pm$ 1.5	5.30	0.34	2.95			
22 ^{b,c}	7.63	14.7	12.7	2.72	31	12.0	18.1 $\pm$ 5.3	21.30	0	8.83			
23	6.98	8.25	2.69	2.22	7	2.17	4.1 $\pm$ 1.6	5.10	0.43	3.96	11.2		
24	2.12	15.0	2.83	2.60	26	2.21	25.3 $\pm$ 2.3	0.22	0.02	0.13			
25 ^{a,b}	0.25	9.13	0.796	2.39	16	0.229	5.7 $\pm$ 1.5	0.34	0.02	0.19			

^a CFC-degradation indicated during analysis via GC peaks.^b Indications of oxic-anoxic water mixing by redox sensitive species (see Table A.1), potential for degradation.^c TCE (trichloroethylene) present.^d Measurement uncertainty for SF_6 -concentrations of several hundreds of fmol/kg or more is estimated at $\pm 20\%$.

Figure captions

Figure 1. Overview of geology and hydrogeology of Scania (adopted from ©SGU and Wastenson et al. 1999). Study locations are indicated by the annotated black dots (see Table 2 for further information). The location of Scania is shown on the map of Sweden in the lower right hand corner.

Figure 2. Generalised cross-sections for the four end member aquifer types studied: (Ai) unconfined sedimentary aquifer, (Aii) semi-confined/confined sedimentary aquifer, (B) unconfined/semi-confined dual-porosity bedrock aquifer, (C) unconfined fracture-flow bedrock aquifer.

Figure 3. Helium isotope mixing plot. The vertical line demonstrates ratio alterations as a result of increasing ^3He owing to ^3H decay. The inclined line demonstrates ratio alterations as a result of increasing ^3He owing to terrigenic production according to a $^3\text{He}/^4\text{He}$ ratio of $1 \cdot 10^{-8}$. The blue and green lines demonstrate ratios of solubility equilibrium and excess air respectively. Fractionation during solution is hardly visible at the scale of this plot, thus the overlap of the green and blue lines. The diamond points out the $^3\text{He}/^4\text{He}$ isotopic ratio of air and the Ne/He ratio in equilibrium with the atmosphere. For a given sample, $^3\text{He}^*$ can be estimated through the offset of the measured $^3\text{He}/^4\text{He}$ ratio to the terrigenic component, if Ne allows and if assuming no mantle contribution.

Figure 4. He vs. Ne , demonstrative of relative amounts of excess air and terrigenic He . Most of the wells exhibit excess air (>0 along the excess air curve). Some wells have a Ne -deficit (e.g. PSWs 10, 12, 14, 16 and 20) which could be due to higher-than-assumed infiltration temperature, degassing or ion discrimination of Ne in the mass spectrometer due to overwhelming amounts of terrigenic He . All wells exhibit elevated He .

Figure 5. Tracer-tracer plots comparing measured to modelled tracer concentrations for selected LPMs. Wells subjected to age distribution modelling are marked by arrows. Note that some samples are outside the figure borders due to CFC contamination.

26

27 **Figure 6.** LPM-modelled fits and resultant age distributions for PSWs 23, 4, 16 and 1.

28

29 **Figure 7.** ^4He vs. mid-point abstraction depth, demonstrating a weak tendency of increasing ^4He with increasing
30 abstraction depth.

Figure 1

Figure 1.

Figure 2

Figure 2.

Figure 3

Figure 3.

Figure 4

Figure 4.

Figure 5

Figure 5.

Figure 5 cont.

Figure 6

Figure 6.

Figure 6 cont.

Figure 7

Figure 7.