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ON THE SCOPE AND ASSESSMENT OF PESTICIDES IN GROUNDWATER IN SKÅNE, SWEDEN

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Paper III: Åkesson M., Sparrenbom C.J., Dahlqvist P. and S.J. Fraser. On the scope and management of pesticide pollution of Swedish groundwater resources: the Scanian example. *Ambio*, in press.

Paper IV: Åkesson M., Suckow A., Visser A., Sültenfuss J., Laier T., Purtschert R. and C.J. Sparrenbom. Constraining age distributions of groundwater from public supply wells in diverse hydrogeological settings by means of environmental tracers and lumped-parameter modelling: a case study from Scania, Sweden. Manuscript submitted to *Journal of Hydrology.*

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Abstract

Pesticides are known to occur in groundwater worldwide. However, long-term pollution concerns and cause-effect relationships for specific regions remain limited. This thesis explores the occurrence of pesticides in south-Swedish groundwater, with the aims of providing a better knowledge basis for assessment and management of present-day and future pollution risks. The investigations are restricted to Skåne, which is a relatively populous, intensively cultivated and geologically diverse region located at the tip of the Scandinavian Peninsula.

The research shows that pesticides are present in very different types of groundwater systems around Skåne, suggesting a wide-ranging, multi-faceted and potentially long-lasting pollution concern. Seemingly, it is only the groundwater environments devoid of influence of waters having recharged since the onset of widespread pesticide use that may be regarded as completely safe and unaffected. Many of the pesticides detected stem from past, less restricted use, primarily for weed control outside of agriculture. Yet, current and future pollution concerns should not be regarded only as a matter of "old sins" as residues from currently used substances manifestly continue to leach towards and into the groundwater system.

Through various analyses of comprehensive data sets both at the regional and the catchment scale, a number of particularly important aspects of regional pesticide occurrence in groundwater and future prediction thereof are inferred and investigated. In addition to application intensities and fundamental physicochemical pesticide properties, these include precipitation and recharge patterns in relation to pesticide application events, (mainly superficial) sorption and degradation processes efficiencies, multiple-scale subsurface physical heterogeneity directing water and solute flow (particularly the presence of preferential flow pathways), and groundwater turnover rates. Environmental tracers show great potential as tools for simple but effective calibration of transport models and for deciphering pollution trends and patterns. However, there are certain tracer-specific complications in need of further attention for future application in Skåne.

For the future, regional as well as nationwide monitoring of pesticides in groundwater needs to be expanded and regulated for sound groundwater and pollution risk management and in order to be able to comply with environmental directives and the EU Water Framework Directive.

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1. Introduction

Groundwater is the underground water that fully saturates voids such as fractures and pore spaces in sediments and rocks of the Earth's subsurface. It constitutes approx. 96% of the planet's liquid freshwater (Shiklomanov 2000) and is accordingly an integral part of the hydrologic cycle. Groundwater sustains ecosystems all over the world, supports industry and global food production and accounts for roughly half of the world's potable water supply (World Water Assessment Programme 2009). It is one of our most important natural resources.

Groundwater forms through the infiltration of precipitation, surface runoff or surface water into the underground. Per definition, groundwater forms as the infiltrating water reaches and passes the groundwater table, which is the level below which the subsurface is saturated with water. On its way, the infiltrating water often percolates through oxygenated and organic-rich soils and sediments which may act as a natural cleansing media, removing entrained pollutants via e.g. filtration, sorption and degradation processes. Groundwater has therefore traditionally been considered a relatively safe and high quality source of freshwater. Gradually, however, it has become obvious that groundwater just as surface water can suffer significant pollution, both through natural processes and sources, and as a result of a variety of human activities. Groundwater environments tend to be dark, cold and deprived of both oxygen and microbial activity which often infers limited scope for pollutant degradation. Further, groundwater is a fluid that is hidden in the subsurface and that exhibits a large storage volume per unit inflow, which connotes turnover rates orders of magnitude lower than those of surface waters. Once a fact, groundwater pollution therefore typically implies a long-lasting environmental concern.

This thesis concerns a particular form of anthropogenic groundwater pollution, namely that of pesticide pollution of groundwater.

2. Background

2.1 Pesticides

Pesticides are substances or mixtures of substances intended to prevent, repel, destroy or lessen the effects of a pest. A pest is basically any organism detrimental to humans or human interests such as crops, livestock and structures. Pesticides are hence designed to interfere with fundamental biogeochemical processes and are inherently toxic, albeit to different degrees depending on type of substance, degree of exposure and type of organism exposed. For humans, epidemiological studies have indicated adverse neurologic (Alavanja et al. 2004, Munoz-Quesada et al. 2013), reproductive (Martenies and Perry 2013), genotoxic (Bolognesi 2003) and cancerogenic (Alavanja et al. 2004) health effects. Common pesticide constituents range from natural organic compounds to metals, petroleum products and a variety of synthetically derived substances such as chlorinated hydrocarbons and organophosphates (Tadeo 2008).

Due to their toxicity, pesticides are unwanted in the groundwater environment. However, both original pesticide parent compounds and transformation products thereof have been observed throughout groundwater reservoirs around the world for decades. This presence is not surprising given that pesticides have been used extensively throughout many parts of the world since the mid-1900s. A relatively recent estimate suggests a yearly global consumption of active pesticide ingredient[1] of about 2.5 billion kg (Grube et al. 2011) and sales figures indicate that this number is increasing (Ly 2013). The paradox is that whereas pesticides pose a threat to human and environmental health on the one hand, they bring, have brought and will likely continue to bring about societal benefits including food security on the other.

[1] *The biologically active ingredient of a pesticide compound is commonly mixed with other ingredients to improve handling, storage and application.*

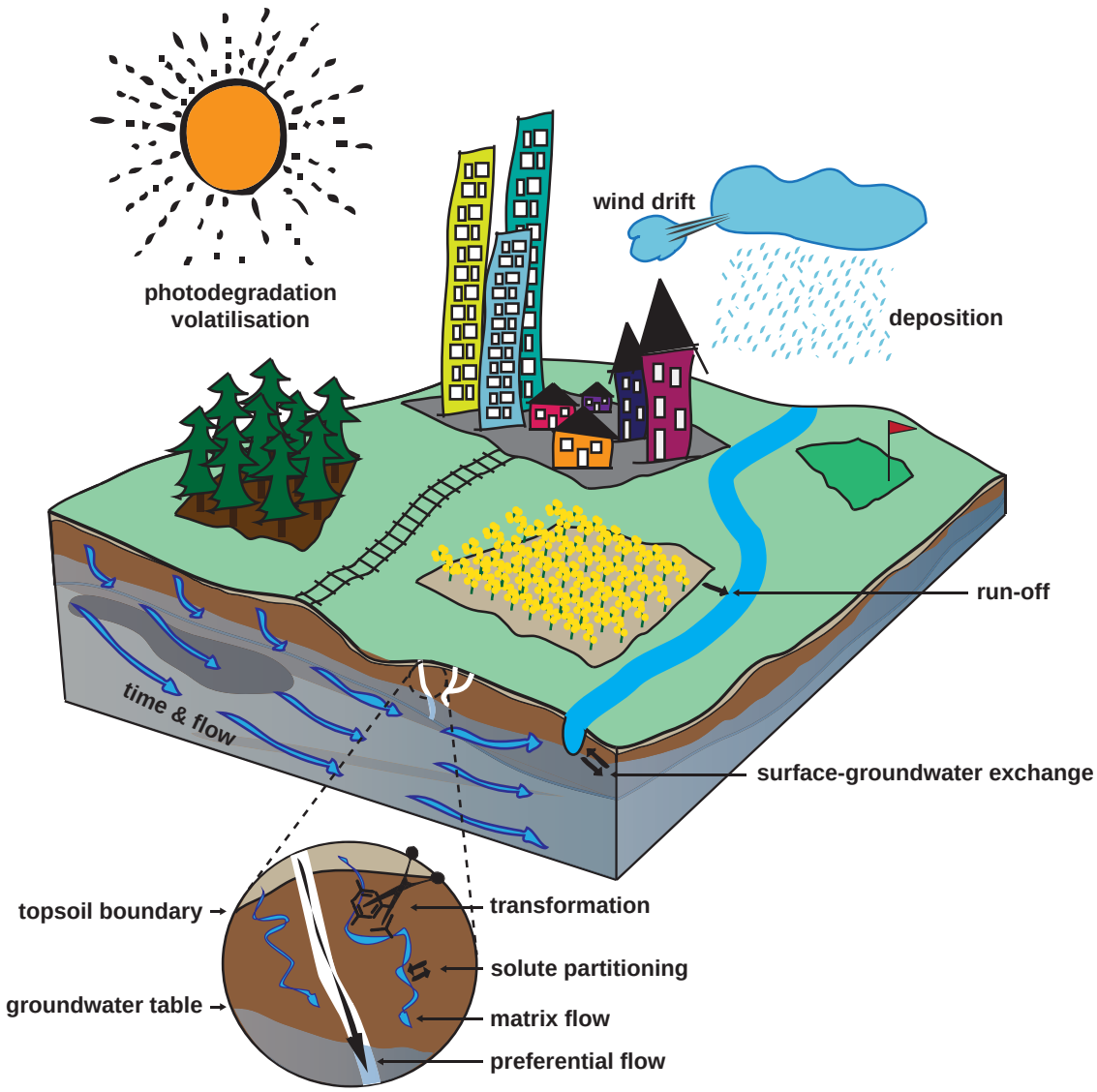

Figure 1. Pesticide-groundwater system conceptualisation including important pollution sources and governing transport, transformation and phase partitioning processes.

2.2 Environmental fate fundamentals

Pesticides are released into the environment from point and non-point (diffuse) sources arising from pesticide production and use (handling, storage and disposal) throughout agriculture, industry, forestry and urban developments including e.g. housing developments, parks, nurseries, sport fields and transport networks (Fig. 1). Subsurface infiltration and transport towards, into and throughout the groundwater environment is fundamentally a matter of solute migration governed by advection, molecular diffusion, mechanical dispersion and often also preferential flow, which involves bypassing of fractions of the subsurface via structural heterogeneities (e.g. fractures, macropores; Jorgensen et al. 2002, Neuman 2005, Jarvis 2007). Adding to this are effects of liquid/solid/gas phase partitioning and transformation.

Phase partitioning may considerably influence pesticide concentrations, rates of movement and overall residence times in the subsurface via retardation and enablement of temporary depositories (Barbash and Resek 1996). Gas phase partitioning tends only to be of relevance at the land surface or in the unsaturated zone, whereas liquid-solid phase partitioning via organic matter

sorption/desorption processes and ion exchange are key phenomena considering overall subsurface pesticide transport (Arias-Estévez et al. 2008).

Pesticide transformation includes both biotic and abiotic processes which may fundamentally alter the structure and physicochemical character of the original pesticide parent compound. Intended toxicity is typically lowered via transformation, yet, the combined toxicological effect of parent compounds and transformation products may still be of concern, as may that of the transformation products alone (Fenner et al. 2013).

Obviously, a range of factors may affect the afore mentioned processes and thus also the transport and occurrence of pesticides to and within groundwater. Extensive reviews on the topic matter can be found in Barbash and Resek (1996), Flury (1996), Gevao et al. (2000) and Arias-Estévez et al. (2008). In short, *land use* is essential, setting the scene in terms of source areas, initial pesticide loadings as well as ground surface and topsoil composition and structure. *Weather and climate* determine the potential for wind drift, volatilisation, run-off and infiltration following application and condition general groundwater recharge rates. *The physical structure of the subsurface* controls the potential and conditions for water and solute flow. *The biogeochemical nature of the subsurface* affects the potential for and character of partitioning and transformation. *The chemical nature of the pesticide* governs affinities for routes of phase partitioning and transformation. Finally, *time* decides to which extent other processes will have progressed. An important aspect to take note of is the scope of variability of these governing factors, meaning it is typically difficult to extrapolate and generalise on pollution risks from one location to another.

2.3 Pesticide occurrence in groundwater

Although there was a time when groundwater was considered shielded from pesticide pollution owing to plant uptake and soil transformation (Sampat 2000), these days are long gone. Initial concerns over the validity of this assumption arose already in the 1950s and since then, a multitude of studies have proven it erroneous. Pesticide residues have been and continue to be observed in groundwater all around the world, time and again (e.g. Leistra and Boesten 1989, Pick et al. 1992, Kolpin et al. 1998, Li and Zhang 1999, Tariq et al. 2004, Brena et al. 2005, Singh et al. 2005, Shomar et al. 2006, Gourcy et al. 2009, Close and Skinner 2012, Malaguerra et al. 2012). The types of substances detected generally cover both parent compounds and transformation products, range from the deemed mobile and thus expected to the deemed immobile and thus unexpected, from the old and banned to the newly introduced. Measured concentrations extend from the just detectable (presently ng/L), to around and sometimes considerably above the general European Union (EU) drinking water threshold of 0.1 µg/L.

Following realisations of widespread pesticide pollution of groundwater, considerable research efforts have been directed towards trying to better understand, predict and avoid the transport of pesticides to groundwater. These research efforts have involved controlled laboratory and field plot experiments (e.g. Boesten and van der Pas 2000, Tuxen 2000, Albrechtsen et al. 2001, Larsbo et al. 2009), regional screening studies (e.g. Kolpin et al. 1998, Close and Skinner 2012, Malaguerra et al. 2012) and the development of a wide range of numerical transport models and pollution risk indicators (see reviews by Dubus and Surdyk 2006, Köhne et al. 2009). International and regional regulations have further been put into place, banning certain particularly persistent pesticides, and setting standards for which pesticides should be allowed for use, and how (e.g. Council Regulation (EC) 1107/2009, the Stockholm Convention on Persistent Organic Pollutants). Industry has followed, adapting to regulations and aiming at more efficient and less persistent compounds. Even so, the pollution concern and the debate on future occurrence of pesticides in groundwater persist, as the understanding of long-term and large-scale fate of pesticides remains limited (Gilliom 2001, Mouvet et al. 2007, Binning et al. 2012).

Basically, compared to the amount of research efforts put into investigations of pesticide leaching through the superficial soil compartment, little has been done in terms of integrated mass-balance and transport assessments at the relevant catchment scale. As noted by Mouvet (2007), "…*literature on*

pesticide fate and transport decreases exponentially with depth below the soil surface."

The major reason for this lack of integrated assessments over multiple environmental compartments is no doubt the fundamental complexity associated with such studies, as they require the consideration, collation, integration and analysis of large amounts of disparate data and a multitude of interacting processes over long periods of time. Another reason is the assumption of limited potential for pesticide reactivity below the upper meter of the subsurface forming the basis for, e.g., pesticide leaching assessments conducted for market registration purposes within the EU (FOCUS 2009). Further, the interdependent and often both temporally and spatially highly variable governing factors for pesticide occurrence in groundwater, as noted, often result in ambiguous outcomes in terms of cause-effect relationships between studies and regions (Barbash & Resek 1996, Flury 1996, Gevao et al. 2000), complicating attempts of extrapolation and generalisation (Arias-Estévez et al. 2008). Accordingly, much remains to be understood in terms of pesticide pollution of groundwater at relevant spatial and temporal scales.

2.4 The Swedish context

In Sweden as in most early industrialised countries, pesticide use became widespread in the 1940s. Usage increased and diversified well into the 1970s, before environmental concerns and public opinion became tangible and the first bans came into place. However, it took another decade until a more profound understanding of the risks associated with pesticide use came about, spurring targeted fees and taxes, as well as more standardised regulations on use and user education (CKB 2013). Following consequential initial reductions, pesticide use appears to have stabilised since the early 1990s, with the exception of the household sector for which use appears to be increasing (Fig. 2). Industrial processing products set aside, herbicides, fungicides and insecticides (in that order) represent the most common groups of pesticides traded (Edell and Würtz 2012). Mordants, growth regulators and repellents are also relatively common. Estimated annual agricultural usage rates average approximately 0.8 kg/ha arable land although in the more intensively cultivated areas of the south, this figure is considerably higher, in the range of 1.5 kg/ha (Sandberg 2011).

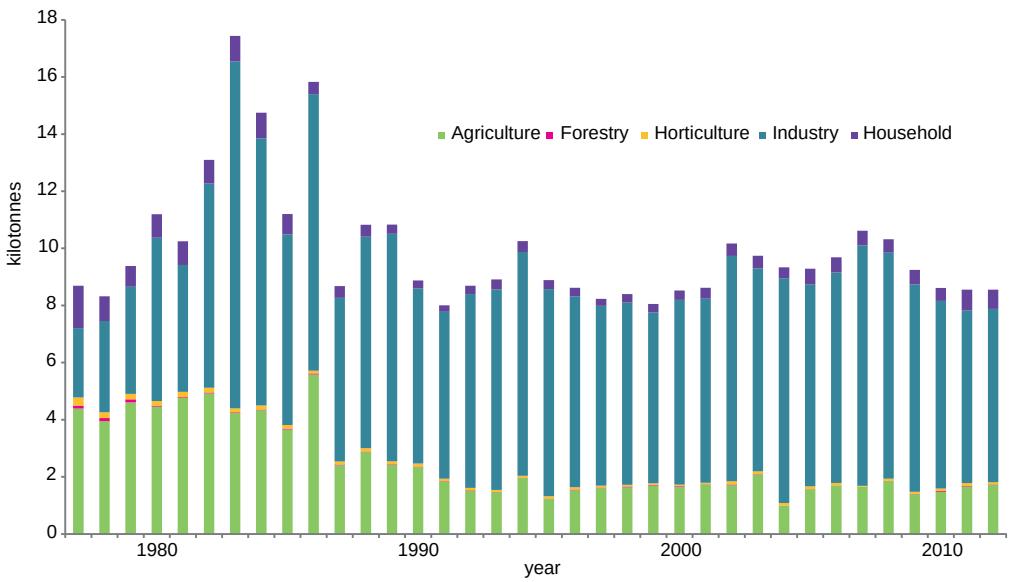

Figure 2. Pesticide sales in Sweden 1977-2012 based on user category (compiled from Andersson 1979, Steckó 1979-1986, KEMI 2013).

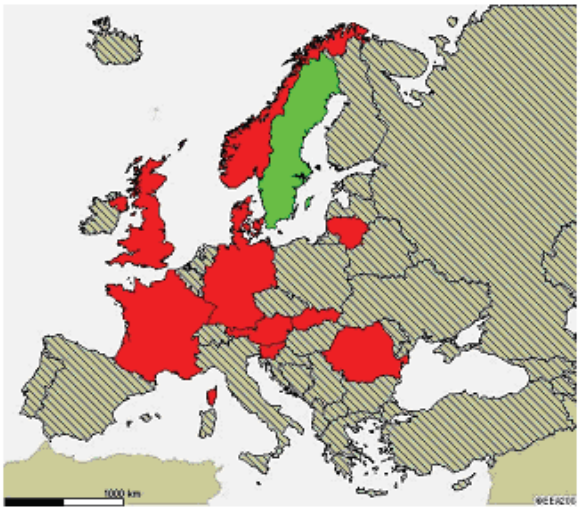

Figure 3. From the 2004 European Environmental Assessment report (EEA 2004), in which Sweden (in green) is the only responding country stating "no danger of pesticide pollution".

Ten years ago, an assessment of the extent of pesticide pollution of European groundwater was conducted as part of a European Environmental Assessment Report (EEA 2004). Out of eleven responding EU member states, Sweden was the only one to state "*no danger of pesticide pollution in groundwater*". Ten years later, pesticides are officially acknowledged as a major concern with regard to Swedish groundwater quality (SEPA 2014). Although the reasons for the change of opinion are not clear-cut, they are likely related to status assessments carried out in response to the Water Framework Directive (2000/60/EC) and the national environmental quality objectives (in particular "*A Non-Toxic Environment*" and "*Good-Quality Groundwater*"; SEPA 2014). The implementation of the Regional Pesticide Database (RPD) of the Swedish University of Agricultural Sciences (SLU) and the Groundwater Bodies and Water Sources Database (DGV) of the Geological Survey of Sweden (SGU), both impelling collection of results of pesticide analyses nationwide, has certainly also played a role, providing unambiguous evidence of pesticide occurrence in groundwater throughout many parts of the country (Ahlström et al. 2008).

In spite of the information brought forward via the above mentioned efforts, the understanding of and the attention given pesticide pollution of Swedish groundwater remains limited. Relevant responsibilities are and have always been split between different authorities, and no formalised comprehensive monitoring of pesticides in groundwater has ever come into place.

National groundwater quality monitoring has been operative since 1978, but has never involved pesticide analyses due to focusing on areas with minimal human impact to constrain background and reference conditions (Nordberg and Persson 1974, SGU 2013). Further, whereas overall quality control of groundwater for drinking water production in Sweden is compulsory and includes pesticide analysis, sampling is only mandated at the end-user and so after potential treatment which infers limited raw water quality control (SLVSF 2001:30). Regional screening efforts occur (e.g. Leander and Jönsson 2003, Andersson et al. 2009, Löfgren and Tollebäck 2012, Virgin 2012), but tend to be infrequent and temporary, shifting with political interest and budgetary constraints.

Effectively, the only regular groundwater sampling of pesticides undertaken within Swedish borders is that of the national monitoring program for pesticides in the agricultural-aquatic environment funded by the Swedish EPA and maintained by SLU. This program encompasses sixteen shallow wells in four agricultural reference areas. As a result, data on pesticide occurrence in Swedish groundwater may be considered much likely to suffer from analytical inconsistencies both in time and space, which potentially limits possibilities for sound status assessments as well as subsequent construction, implementation and evaluation of remedial efforts where such are needed.

3. Research objectives

Building on the lack of understanding of (i) long-term, catchment scale pesticide fate in groundwater systems in general and (ii) extent and reasons for pesticide occurrence in groundwater systems in Sweden specifically, the overarching aim of this PhD thesis is to *increase the understanding of pesticide occurrence in groundwater, focusing on Swedish conditions*. More specifically, the thesis work has involved the assessment of pesticide occurrence in groundwater in Skåne, southern Sweden, at both catchment and regional scale, with specific objectives as follows:

- To test and develop predictive tools for pesticide occurrence in groundwater using long-term, catchment scale monitoring data.
- To investigate pesticide pollution of groundwater at the regional scale, in time and space and in relation to governing factors, using a combination of already existing and new data.
- To identify areas of concern relating to pesticide pollution of groundwater in Skåne and Sweden, including potential pollution trends and patterns, information gaps and management issues.
- To test the applicability and use of environmental tracers within typical groundwater reservoirs throughout Skåne, as well as in relation to studies of pesticide pollution of groundwater.

In the following, chapter 4 introduces and provides necessary background to the regional (4.1) and catchment scale (4.2) study areas. Chapter 5 elaborates on applied methodologies. Chapter 6 summarises partly unpublished material relevant to the catchment scale study. Chapter 7 summarises the scope, approach and main conclusions of the thesis in consecutive order of the appended papers and provides some discussion and suggestions as to further developments of the conducted work. Chapter 8 offers some general reflections with regards to research contributions and inferred management and research needs. Finally, chapter 9 lists the overarching conclusions of this thesis work.

4. Study sites

4.1 Skåne

All work conducted for this thesis has been based in the southernmost province of Sweden called Skåne (or, in English, Scania; Fig. 3). Skåne encompasses roughly 11 000 km^2 at the very tip of the Scandinavian Peninsula (55°48'N, 13°37'E), and currently accommodates approx. 1 250 000 people, which makes it a relatively small but densely populated region. The region experiences the country's mildest climate with average monthly temperatures varying between about -2°C in mid-winter (January), and 17°C in peak summer (July). Annual precipitation varies between 500 and 1 000 mm depending on coastal proximity and topography (SMHI 2014). Regional groundwater recharge rates are estimated at between 150 and 500 mm/yr (Gustafsson 2005).

Compared to other parts of Sweden, Skåne contains relatively little forested land and is rather characterised by its extensive and highly fertile agricultural lands, which cover almost half of the region's total area (Fig. 3). Skåne effectively maintains much of the country's agricultural and horticultural production with main crops including cereals, oilseeds, sugar beet, potatoes, vegetables and fruits. Urban developments cover roughly 10% of the province (SCB 2010).

Geologically, Skåne is situated within a border region between Precambrian crystalline rocks of the Fennoscandian shield to the N-NE and a variety of much younger sedimentary rocks more commonly associated with central Europe to the S-SW (Fig. 3). Repeated movements along a crustal weakness zone known as the Tornquist zone have complicated the stratigraphy along several NW-SE trending fault zones characterized by pronounced horsts and (filled-in) grabens, volcanic remnants and extensive dolerite dykes. Due to repeated ice sheet advances and retreats throughout the Quaternary (2.6 Ma-present), most of the bedrock surface and relief has however been worn down and covered by often thick and complex sediment sequences comprising till plains, esker systems, proglacial delta and lake deposits, clays and postglacial fluvial deposits (Fig. 3). Basically, Skåne contains most of the geological

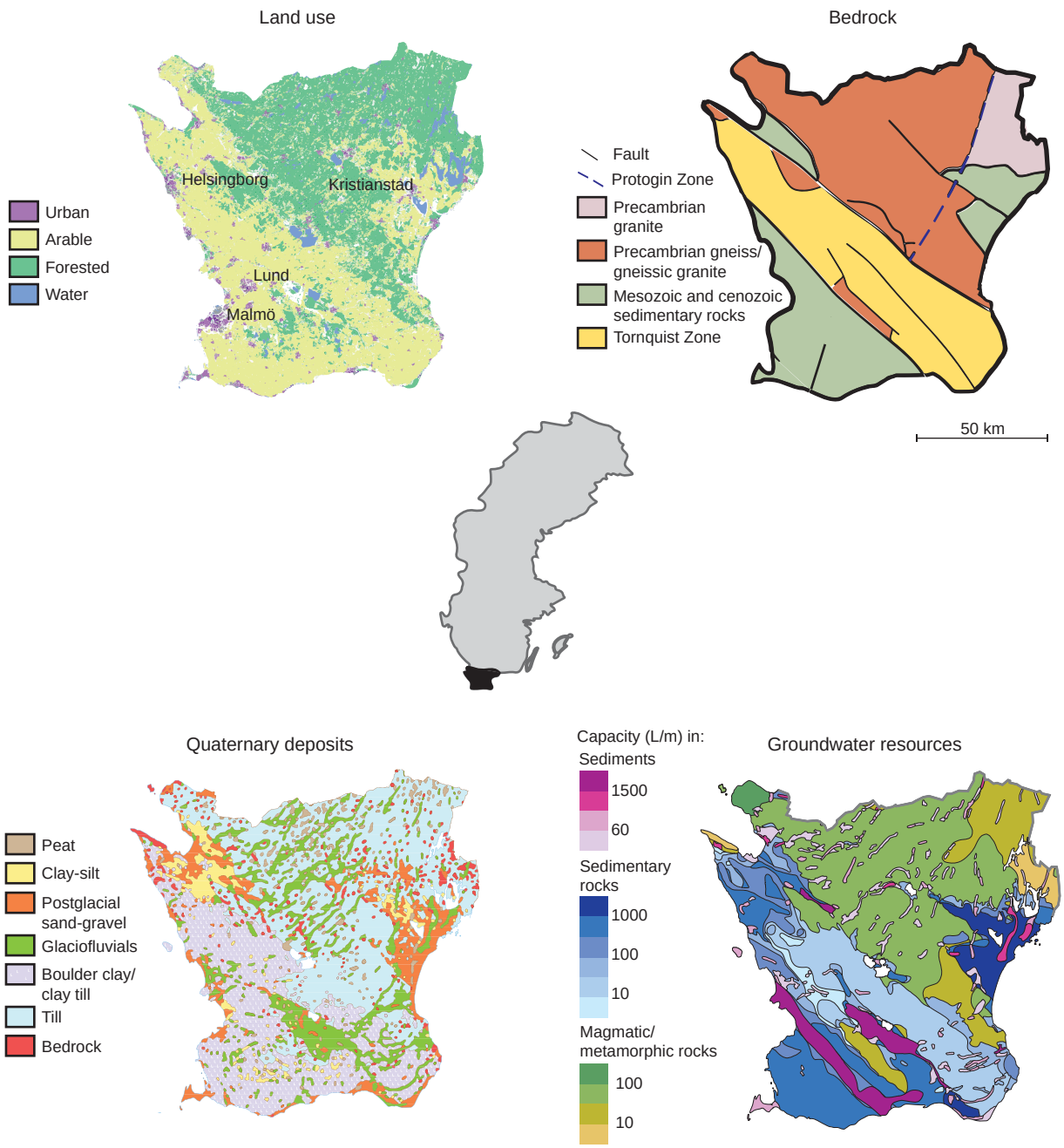

Figure 3. Overview of land use (Lantmäteriet [I2012/00927]), bedrock (adopted from Wastenson et al. 1999), Quaternary deposits (©SGU) and groundwater resources (after Wastenson et al. 1999) in Skåne (black area in the central map of Sweden).

environments present within Sweden as a whole.

As for overall Sweden, about 50% of drinking water in Skåne comes from groundwater. Half of this groundwater is however artificially produced via induced infiltration. Due to the geological diversity, groundwater can be extracted from a variety of aquifer types ranging from superficial or buried fluvial deposits of various compositions, to different types of dual-porosity sedimentary rock aquifers, to fractured crystalline bedrock aquifers (Fig. 3, Gustafsson 2005). Again, Skåne may be considered reflective of Sweden as a whole, comprising most available types of groundwater reservoirs within the country.

Pesticides have been known to occur in groundwater in Skåne for as long as for Sweden overall, i.e. since at least the 1980s and the commencement of related investigations (CKB 2013). In relation to the adaptation of the national environmental quality objectives mentioned in

chapter 2.4, the County Administrative Board of Skåne, recognising the region's urban and agricultural land use pressure, formulated a milestone target stating that by the year 2015, residues of pesticides in use from 2003 onwards should not be detected in the region's groundwater. In relation to the formulation of this target, a first assessment of the extent of the problem was conducted via screening of the data available in the RPD (Maxe et al. 2003). Out of 881 samples from a total of 387 localities reported to the database 1987-2001, 31% were shown to have contained detectable concentrations of one or more of 25 different pesticide residues, one third of which stemmed from substances prohibited at the time of the investigation. BAM (a transformation product of dichlobenil), atrazine and transformation products of atrazine - all prohibited at the time of the investigation - were pointed out as the most frequently detected substances.

In 2007, the County Administrative Board of Skåne pursued the status assessment via a 4-year monitoring program involving 33 substances and 141 sampling sites (Virgin 2012). As with the existing RPD data, about one third of the samples exhibited detectable amounts of the analysed pesticide residues. Nine percent of the samples exhibited pesticide concentrations at or above the EU drinking water threshold. A majority of the detected substances were prohibited at the time of investigation and BAM, atrazine and associated transformation products were again settled as the most commonly occurring substances, although now with the addition of bentazone, which is a substance still in use. However, no convincing patterns as to the extent of the pollution and the causes thereof could be determined, whereby further studies involving a greater number of study sites and a larger number of analysed substances were advised.

4.2 Catchment M42

Catchment M42 is one of the four Swedish reference areas included in the agricultural-aquatic environmental pesticide monitoring program of SLU (see chapter 2.4) and subject to the detailed catchment scale study of this thesis. It constitutes an approx. 9 km^2 area located in the very south of Skåne (Fig. 4). The exact location may not be revealed due to non-disclosure agreements between SLU and the local farmers.

The area is characterised by a gently undulating landscape superficially dominated by tills and boulder clay (Fig. 4; Kreuger 1998). At depth hides an up to 120 m deep sediment sequence deposited into a NW-SE trending valley cut into the limestone bedrock ("Alnarpsdalen"). The deposits reflect glacial dynamics and fluvial activity throughout the Quaternary, resulting in a complex stratigraphy with intercalating tills, clays and sorted sandy-gravelly deposits (Fig. 4; Daniel 1992).

About 95% of the catchment consists of arable land of which most is subject to a 4-year rotational cropping practice dominated by winter rape, winter wheat, sugar beet and spring barley. The mean annual temperature is 7°C, and the mean annual precipitation equals roughly 700 mm. Some 30% of this precipitation is estimated to be available for groundwater recharge (Lewan et al. 2009). The growing season spans about 220 days between May and November (Kreuger 1998).

Monitoring of regular, non-experimental pesticide use in the catchment was initiated already in 1990 via collaboration between SLU and local farmers, resulting in a unique data set enabling long-term studies of environmental pesticide fate. Traditionally, these studies have focused on superficial environmental fate of pesticides, e.g. transport of pesticides to surface water (Kreuger 1998, Kreuger and Törnqvist 1998, Kreuger et al. 1999) or drainage networks via macropore flow (Lindahl et al. 2005, Gärdenäs et al. 2006). In 2000, however, four groundwater monitoring wells (SHG-1 and -2, NAG-1 and -2) were installed in two clusters within the catchment, screening shallow water bearing units underlying the superficial tills (Fig. 4, Table 1). Since 2004, these wells have been sampled four times yearly for analysis of pesticide residues in accordance with known pesticide use. Results of the monitoring program have been reported in annual national reports since 2005 (e.g. Nanos et al. 2012) and are summarised in Table 2 according to SLU (2014a). No further investigations of the groundwater monitoring data with respect to e.g. known

Table 1. Screening depths of monitoring wells in M42.

Well	SHG-1	SHG-2	NAG-1	NAG-2	0901	0902	0904	0905	0906	0907	LIFA
Screen depth (m b.g.s)	*2.9-3.5*	*2.9-3.5*	*4-5*	*6-7*	*26-27**	*6.5-7*	*34-35*	*17.5-18*	*10-10.5*	*5-5.5*	*18-22*

** uncertain due to bending of pipes during drilling.*

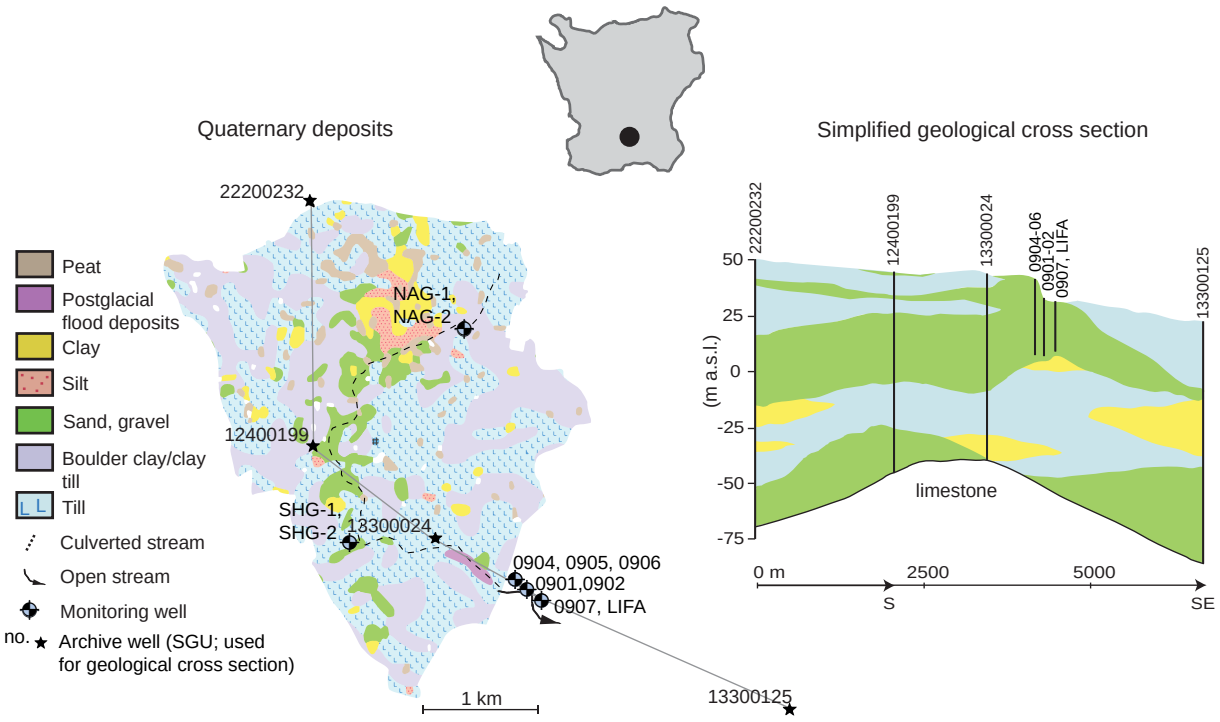

Figure 4. Geolgical overview of catchment M42 (approximate location indicated on the map of Skåne). Left: Quaternary deposits map (adapted from ©SGU). Right: Vertical cross section through the catchment, based on drill logs of specified wells. The plan view extension of the cross section indicated by the grey line on the Quaternary deposits map.

Table 2. Summary of pesticide monitoring results 2004-2012 for the SHG and NAG wells (35 samples totalling about 3 100 individual analyses per well). Bolded substances have been prohibited since 2004 (i.e. since the onset of monitoring).

Well	Max. measured concentration (µg/L)	Detection frequency (including trace level detections*)			
		75-100%	50-<75%	25-<50%	<25%
SHG-1	*0.18*			*chloridazon*	*AMPA, azoxystrobin, clopyralid, dichlorprop, diflufenican, fluroxypyr, glyphosate, imazalil, isoproturon,* ***lindane****, MCPA, methabenzthiazuron, metamitron, metazachlor, propyzamide*
SHG-2	*0.17*			*bentazone, chloridazon*	*clopyralid, imazalil, metazachlor*
NAG-1	*0.035*	***atrazine, HCH-beta***	***atrazine-desethyl, HCH-delta***	*bentazone, chloridazon,* ***HCH-alpha***	*AMPA, clopyralid, diflufenican,* ***diuron****, fluroxypyr, glyphosate, isoproturon,* ***lindane****, MCPA, methabenzthiazuron, metazachlor,* ***terbutylazine-desethyl****, triticonazole*
NAG-2	*0.077*	***atrazine, atrazine-desethyl****, bentazone,* ***lindane****, metazachlor*			*AMPA, azoxystrobin,* ***BAM****, dichlorprop,* ***endosulfansulfate****, fluroxypyr, glyphosate, MCPA, metamitron*

** detections above the limit of detection (LOD) but below the limit of quantification (LOQ).*

pesticide use had been undertaken before this thesis, with the exception of a pilot bachelor thesis study covering restricted monitoring years and restricted portions of the catchment (Lindblad and Lindenbaum 2010).

In late autumn 2009, one pumping well (LIFA) and five monitoring wells (0901-0902, 0904-0907) were drilled just outside the catchment proper as a first step of a research project initiated by the Swedish Geotechnical Institute (SGI), which this PhD project has been part of, in order to capture and enable investigations of pesticide transport also to the deeper parts of the local groundwater system (Fig. 4, Table 1). These wells are located in an exposed sandy deposit described in detail by Andersson (2010).

5. Materials and methods

5.1 Pesticide data acquisition

For investigations conducted in M42, data on pesticide use and monitoring results from the SHG and NAG wells were collated from excerpts of an MS-Access database hosted by SLU. In order to be able to connect documented use to geographical locations, coded field maps constructed as part of the annual monitoring of pesticide use 1990-2010 were digitised using ArcGIS 9.3.

For the newer wells (0901-0905, 0907 and LIFA), groundwater samples were collected for pesticide analysis at five occasions during 2010-2012 (Table 3). 0906 never contained enough water for sampling. Samples were retrieved according to laboratory instructions after purging until standard parameter (temperature, pH, dissolved oxygen, oxidation-reduction potential, electrical conductivity) stabilisation, using permanently installed pumping equipment (Solinst Integra Bladder Pump model 407 SS 1”, Teflon tubing) connected to platinum-cured silicon tubing. Samples were chilled immediately upon retrieval and delivered for analysis at the respective laboratories within 24 hrs. A strict sampling protocol was followed in order to minimise risks of external contamination in association with sampling. Analyses were primarily conducted at the Organic Risks Pollutants Laboratory (OMK) of SLU, according to the standard suited screening package applied for the monitoring of the shallower wells. Each analysis encompassed 114 substances.

At three occasions, additional samples were retrieved for analysis of residues of older pesticide

Table 3. Pesticide sampling and analysis specifications for wells 0901-0905, 0907 and LIFA. OMK = Organic Risks Pollutiants Laboratory, SLU. ALS = ALS Group.

Sampling dates	Analytical laboratory
23-24/3 2010	*OMK*
19-21/7 2010	*OMK*
8-10/11 2010	*ALS*
14-17/4 2012	*OMK, ALS*
30/7-1/8 2012	*OMK, ALS*

compounds which have not been used in the catchment during the monitoring period due to prohibition, but which were considered likely to have been used before 1990 based on discussions with an older local farmer and official national records of previously registered and sold pesticides. These samples were analysed by ALS Group and covered 55 substances.

For the regional Skåne study, past analyses of pesticides in groundwater were collated from regional municipalities and major water authorities, as well as the RPD, the DGV and the County Administrative Board of Skåne. After restricting the assembled data to well-documented analyses of untreated groundwater from single well-defined wells only, twenty-three public supply wells (PSWs) were selected for in-depth investigation based on (i) data availability, (ii) spatial and hydrogeological distribution and (iii) production importance and access. In January 2012, these wells were sampled for complementary pesticide screening via high-resolution analysis at OMK (no. of included substances = 101, median LOD = 0.003 µg/L). Samples were retrieved according to laboratory instructions after purging until standard parameter stabilisation, using permanently installed pumping equipment. Samples were chilled immediately upon retrieval and delivered for analysis at the laboratory within 24 hrs.

5.2 Groundwater geochemistry and levelling

In addition to the in-field standard parameter surveying in connection to pesticide sampling noted above, all studied groundwater were subject to basic geochemical analysis. For the SHG and NAG wells in M42, samples for major ion and nutrient analyses have been collected by SLU in connection to the four-times-yearly pesticide monitoring since 2004. Data can be retrieved from SLU (2014b). For wells 0901-0905, 0907 and LIFA, samples for major ion, nutrient and metal analyses were collected in connection to pesticide sampling in March and July 2010, and analysed by the Geological Survey of Denmark and Greenland (GEUS).

For the regional Skåne study, samples for major ion, nutrient and metal analyses were collected in connection to pesticide sampling and analysed by ALS Scandinavia.

Repeated groundwater levelling was carried out in all wells of the M42 study in connection to sampling. Additionally, wells SHG-1, NAG-1, 0901, 0904 and LIFA were subject to continuous (15 min record interval) level monitoring between March 2012 and June 2013, using Schlumberger Micro-Divers. Also, private wells (n = 40) were surveyed and levelled at an early stage (June 2010) in order to enable assessment of patterns of groundwater flow (see Fig. 5).

5.3 Sorption and degradation experiments

As part of the M42 study, site-specific linear sorption coefficients and first-order degradation rate constants were determined for six pesticides known to have been used and detected in groundwater in the area: bentazone, dichlorprop, glyphosate, isoproturon, MCPA and metamitron. The derived data were aimed for detailed transport modelling within a portion of the catchment (see section 5.6). Experiments were carried out at SGI using ^{14}C-labelled compounds (Izotop, Budapest, Hungary) and soil, sediment and groundwater samples representative of three different depths, i.e. hydrogeological units, of the catchment. Sampling and analytical details are given in Åkesson et al. (in press), appended as paper II.

5.4 Environmental tracer analysis

Environmental tracer analyses were employed throughout all study areas in order to gain insight into the age distributions of the studied groundwater samples and systems. Environmental tracers are basically substances that enter and move through groundwater systems in relatively well-defined manners, meaning that their respective concentrations at any given point within a groundwater system can be used to assess the hydrodynamics of the upstream flow field as well as the time since recharge – the apparent[2] groundwater age – of the associated water molecules

[2] *Apparent, as it is the time since recharge of the tracer rather than the actual water molecules that is estimated.*

Box 1. Groundwater dating with ^{3}H-^{3}He, CFCs, SF_6, ^{39}Ar and ^{85}Kr

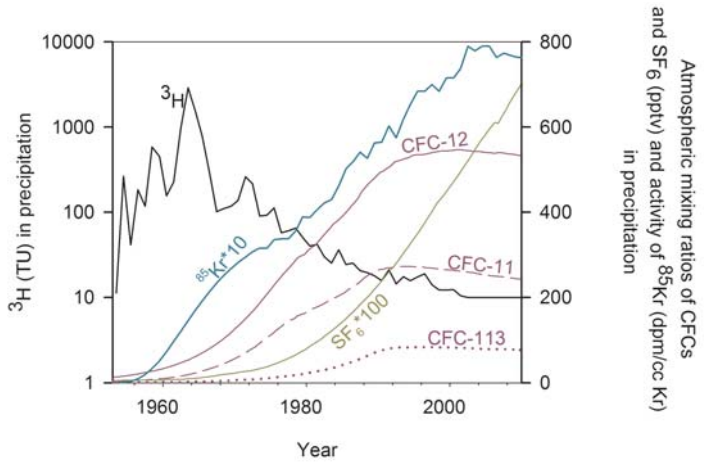

Figure B1. Variation of environmental tracer abundances in precipitation in the Northern Hemisphere.

^{3}H, tritium, is a radioactive hydrogen isotope. As such, it forms part of water molecules and is therefore considered an ideal hydrological tracer. Following nuclear bomb tests in the mid-1900s, large amounts of ^{3}H were introduced to the atmosphere, thereby overwhelming natural background levels and triggering a global hydrological tracer experiment. With a half-life of 12.32 years (Lucas and Unterweger 2000), ^{3}H decays to the stable helium isotope ^{3}He. Upon recharge, any ^{3}He produced through the decay of ^{3}H will be cut off from the atmosphere and have nowhere to go but with water flow. For groundwater forming since the mid-1900s, measured ^{3}H and ^{3}He concentrations can therefore be applied to quantify time since recharge (Schlosser et al. 1988, Solomon and Cook 2000). However, this requires the separation of the tritiogenic fraction of dissolved ^{3}He from (i) a naturally occurring atmospheric equilibrium fraction dependent upon recharge temperature and altitude, (ii) a potential terrigenic fraction (mantle-produced and/or radiogenic resulting from U/Th-decay; Schlosser et al. 1989) and (iii) a potential excess air fraction (Heaton and Vogel 1981).

CFCs and **SF_6** are so called transient tracers for which atmospheric concentrations increased considerably following industrial manufacturing and use since the 1950s and 1970s for CFCs and SF_6, respectively (Fig. B1). These increases are generally well-documented and may, after corrections for substance-specific Henry's Law solubilities, be translated into time-dependent groundwater input functions. Because CFCs and SF_6 are considered relatively stable, measured concentrations thereof are theoretically directly comparable to specific recharge years (Plummer and Busenberg 2000, Busenberg and Plummer 2000). Recharge temperatures and altitudes need also here to be known to allow for credible estimations of solubility equilibrium and (for SF_6 in particular) excess air fractions. Demonstrated application complications include non-conservative behaviour of CFCs in relation to sorption and degradation under low-oxygen conditions (Bauer et al. 2001, Hinsby et al. 2007) and local contamination sources. For CFCs, such contamination sources are presumably only a matter of anthropogenic input. For SF_6, however, natural subsurface production has also been suggested (e.g. Harnisch and Eisenhauer 1998, von Rohden et al. 2010, Friedrich et al. 2013).

^{85}Kr and **^{39}Ar** are noble gas radioisotopes with half-lives of 10.76 and 269 years respectively (Loosli et al. 2000). Assuming equilibrium dissolution of tropospheric activities in recharging groundwater, groundwater ages can be assessed without knowledge of e.g. recharge temperature and excess air by correcting measured specific activities (i.e. ratios of ^{85}Kr to stable Kr and ^{39}Ar to stable Ar) for radioactive decay. Almost all ^{85}Kr present in the environment is of anthropogenic origin, relating to nuclear industry and particularly nuclear fuel bar reprocessing. The atmospheric content of ^{85}Kr has hence been rising since the mid-1900s and hence this substance may be used as an environmental tracer for groundwater recharging since then (Cook and Solomon 1997). Groundwater ages are assessed by finding a match-point on the atmospheric curve (Althaus et al., 2009; Cook and Solomon, 1997). Anthropogenic sources of ^{39}Ar are negligible, but cosmic ray production is largely constant and enough to generate a hydrologic signal that allows for groundwater dating of waters recharging about 50-1000 years ago (Alvarado et al. 2007, Visser et al. 2013). The main issue with ^{85}Kr- and ^{39}Ar-dating is the complicated sampling and analytical procedures required in relation to minor subsurface concentrations. For ^{39}Ar, an additional complication is subsurface production in crystalline bedrock environments (e.g. Andrews et al. 1989, Yokochi 2012).

(Portniaguine and Solomon 1998).

Typically, tracer-derived groundwater ages are computed based on simple piston flow models that assume that all sampled water molecules stem from one single recharge event and that the specific tracer has moved conservatively with those molecules since recharge. These assumptions are hardly ever completely valid, whereby additional efforts may be required to yield credible age and age distribution estimates. Such efforts have here comprised numerical transport modelling (paper II) and lumped-parameter modelling (Maloszewski and Zuber 1996; paper IV).

The environmental tracers applied include tritium-helium (^{3}H-^{3}He), chlorofluorocarbons (CFCs; CFC-11, CFC-12, CFC-113), sulphurhexafluoride (SF_6), argon-39 (^{39}Ar) and krypton-85 (^{85}Kr). Details of the associated dating techniques are given in Box 1.

For the M42 study, wells 0901-0904, 0907 and LIFA were sampled for CFC analysis in March 2010. None of the SHG and NAG wells could be sampled due to limited water availability. Samples were retrieved by T. Laier, GEUS through the bottle-within-can method described by USGS (2013), using a peristaltic pump and polyethylene tubing. Samples were analysed at GEUS according to procedures described by Busenberg and Plummer (1992). SHG-1 and -2, NAG-1 and -2, 0902, 0905, 0907 and LIFA were further sampled for ^{3}H and noble gas (Ar, He, Ne, Kr, Xe) analysis in August 2010, using "Advanced Diffusion Samplers" developed by the Dissolved and Noble Gas Laboratory, Utah University. After purging, samplers were left down-hole at filter depth for 48 hrs to equilibrate with the dissolved gases of the groundwater. Retrieval was preceded by sampler-isolation via a remote-controlled valve to prevent atmospheric contamination and followed by sealing via cold-welding. Analyses were carried out at the Dissolved and Noble Gas Laboratory of Utah University according to procedures described by Bayer et al. (1989) but in an all-metal-system yielding lower blanks. Finally, in April 2012, well LIFA was sampled for ^{39}Ar and ^{85}Kr through in-field degassing of nearly 2.5 m^3 groundwater. Subsequent analyses were conducted at the Physics Institute, University of Bern via gas chromatography separation followed by activity measurements by low level gas proportional counting (Loosli and Purtschert 2005).

The wells of the regional Skåne study were sampled for tracer analysis in January 2012, using permanently installed pumping equipment specific to the well owner. Duplicate ^{3}H-^{3}He samples were collected using glass bottles (^{3}H) and pinch-clamped copper tubes (He, Ne) connected to the well tap through a closed hose system. ^{3}H and noble gas analyses were carried out at the Bremen Mass Spectrometric Facility according to Sültenfuss et al. (2009). CFC sampling and analysis were conducted according to the same procedures as for the catchment scale wells.

Further, SF_6 samples and additional CFC-12 samples were collected from 14 of the regional wells using the headspace technique (see e.g. Friedrich et al. 2013). Failing sampling equipment inhibited such sampling and analysis for the remaining wells. Subsequent analyses were carried out at the Bremen Mass Spectrometric Facility via gas chromatography with electron capture detection based on the method of Bullister and Weiss (1988). Finally, in April 2012, one of the regional wells was sampled for ^{39}Ar and ^{85}Kr according to procedures described above for M42, using roughly 3.5 m^3 of water pumped up via permanently installed pumping equipment.

5.5 Geophysical measurements

Electrical resistivity is a fundamental physical and diagnostic property specific to a given material (Reynolds 1997). In the subsurface, electrical resistivity is a function of e.g. mineralogy, clay and water content whereby analyses of subsurface resistivity variability can be used to help decipher stratigraphy. Two electrical resistivity surveys were employed in M42 to aid in hydro-/geological characterisation.

In June 2011, a continuous roll-along gradient-array vertical electrical sounding survey (CVES; e.g. Dahlin 2013) was conducted for 2D geoelectrical imaging over three transects (Figs. 5 and 6), using an ABEM Terrameter LS system. The applied five-meter electrode spacing yielded information on

apparent[3] electrical resistivity variability down to approximately 75 m depth via measurements of subsurface responses to induced electrical currents. The software Res2dinv was used for inversion of the measured apparent resistivities into 2D models of true resistivities.

In November 2011, an electromagnetic survey along multiple NNW-SSE trending transects (Fig. 5) was conducted in a smaller area within the catchment to yield detailed local information on the character of the shallower subsurface. The survey was made using a portable multiple-frequency electromagnetic sensor (Geophex GEM-2) measuring inductive response of a transmitted primary electromagnetic field averaged down to the practical penetration depth. Inductive responses of the two successfully employed frequencies (15 725 and 27 175 Hz), as measured by the real and imaginary components of the secondary field related to the primary, were transformed into apparent electrical conductivities using the Geophex software EM Inverter. These values were in turn recalculated to yield apparent resistivity values, later interpolated into plan-view maps of apparent resistivity variability down to approximately 10 and 5 m depth respectively.

5.6 Numerical transport modelling

Water flow and pesticide transport was modelled for part of M42 (paper II) using HYDRUS-2D (Simunek et al. 1999), which is a two-dimensional finite element software package for the simulation of water and solute movement in variably saturated media. Water flow is numerically solved via the Richards' equation, and solute transport via Fickian-based advection-dispersion equations capable of accounting for diffusion, phase partitioning and degradation reactions.

A conceptual model was constructed based on available information on stratigraphy and hydrogeology and calibrated against measured ^{3}H and ^{3}He data using recharge flux and associated ^{3}H input 1950-2010 (see paper II for details). Subsequently, pesticide transport modelling was conducted for the six pesticides for which experimental sorption coefficients and degradation rate constants had been derived (bentazone, dichlorprop, glyphosate, isoproturon, MCPA and metamitron; see chapter 5.3) using known input (i.e. spatially and temporally distributed application) 1990-2010. Model output was validated against local groundwater monitoring data.

5.7 Self-Organising Maps

The collated pesticide-groundwater data of the regional scale study was statistically analysed using the Self-Organising Maps (SOM) approach (Kohonen 2001). The SOM is an unsupervised, exploratory neural network analysis approach that allows for the detection and ordered visual representation of natural populations and patterns within complex multi-dimensional data sets. Essentially, input samples are compared based on variable properties according to principles of vector quantisation and measures of vector similarity, then sorted and mapped onto colour-coded graphs (maps) so that similar samples are mapped onto map-cells (nodes) of similar characteristics, and nodes with similar characteristics are positioned close to each other on the map. The maps may then be used for sample and variable pattern recognition, if needed aided by traditional statistical processing procedures such as correlation, principal component and clustering analysis. The SOM handles both categorical, continuous and missing data, as well as nonlinear relationships between variables, and is therefore generally considered much suited for the analysis of (often complex and disparate) geoscientific data (Fraser and Dickson 2007). The potential of the technique for hydrologic system analysis has been reviewed and concluded upon by Kalteh et al. (2008).

[3] *Apparent resistivity = the resistivity of a homogeneous ground which will give the same resistance value for the same electrode arrangement (Loke 1999).*

6. M42: basic characterisation

Groundwater levelling throughout the M42 catchment revealed a relatively shallow groundwater table, generally undulating a few meters below and together with surface topography (Fig. 5). Groundwater divides were demonstrated to roughly correspond with those of surface water and recharge was thus concluded to primarily occur within these borders, justifying the use of the SLU-collated pesticide application data as a starting point for analysis of pesticide occurrence in local groundwater.

The CVES survey enabled confirmation and an extension of the drill log-inferred subsurface stratigraphy of the catchment (Figs. 5 and 6). Based on cross-correlation between the CVES output and the drill logs, the lowest derived electrical resistivity values (up to approx. 60-70 Ωm) were generally interpreted as clay tills or (in places at depth) clays, medium values of between about 70-100 Ωm as silt-rich sands and higher resistivity values (up to >300 Ωm) as increasingly coarse-grained and/or gravelly sands. The most interesting and important information deducted was the proposed spatial continuity of the sandy deposit which wells 0901-0907, LIFA and potentially also the SHG wells are located, suggesting the existence of an extensive and hydraulically rather well-connected groundwater reservoir below the superficially dominating till.

Fluctuations in groundwater heads in the monitoring wells were demonstrated to follow the expected seasonal pattern with recharge occurring in late autumn to early spring (Fig. 7). Groundwater heads in all wells but NAG-1 appeared to respond to precipitation events throughout this period, as

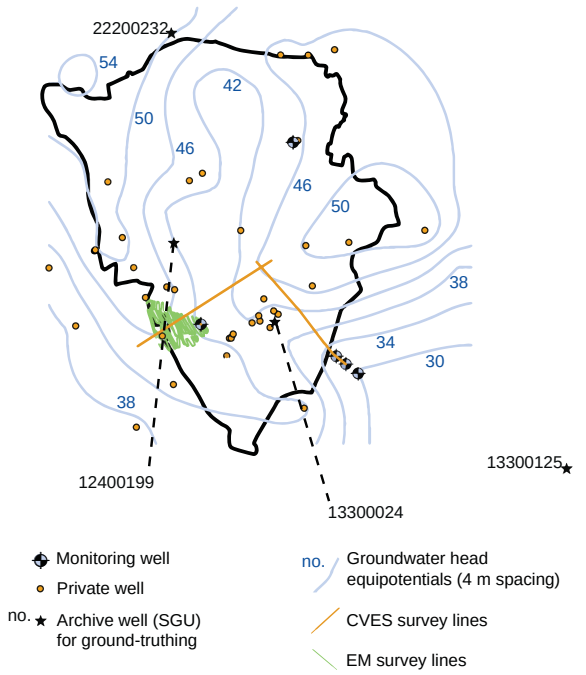

Figure 5. M42: groundwater head equipotentials, geophysical survey lines and wells used for hydro-/geological characterisation.

did the culverted stream (Fig. 4). The superficial till does accordingly not appear truly confining and there is a possibility for recurring ground-drainage water exchange. NAG-1 displayed no noticeable seasonal signal and sustained recovery in association

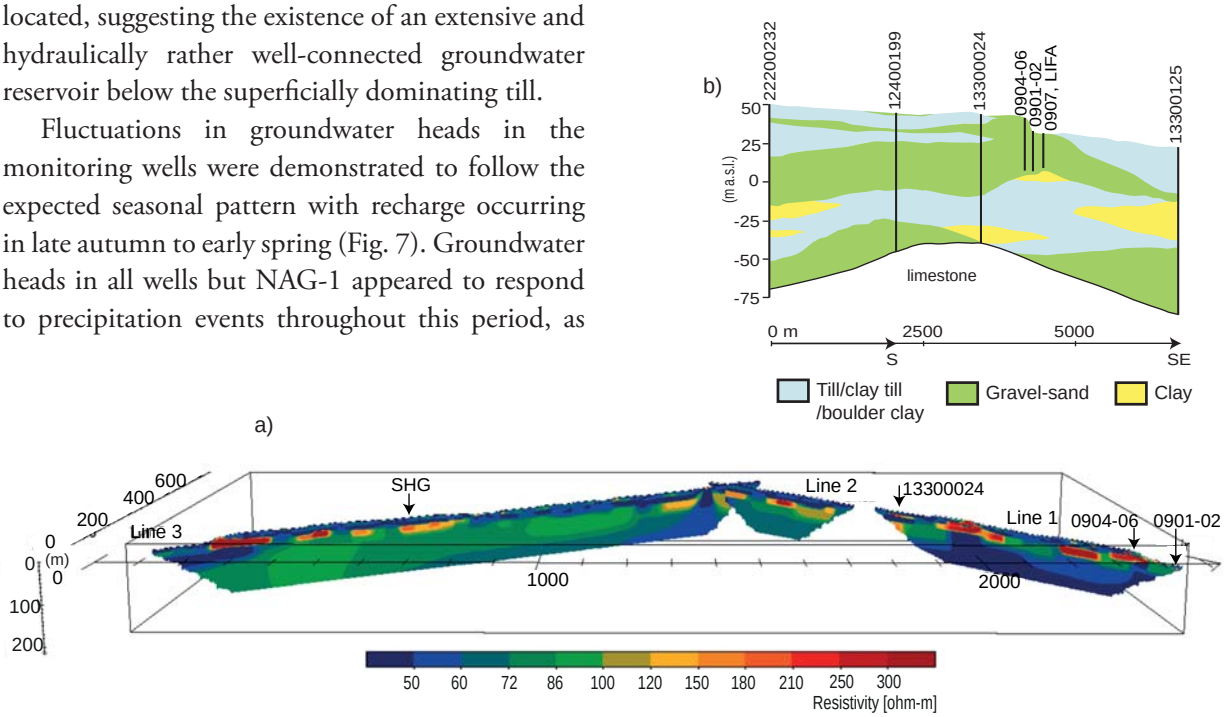

Figure 6. (a) 3D resistivity model (made in EriViz) based on CVES output for the three survey lines (Fig. 5), with approximate locations of nearby wells used for ground-truthing, (b) geological cross-section from Fig. 4 for comparison.

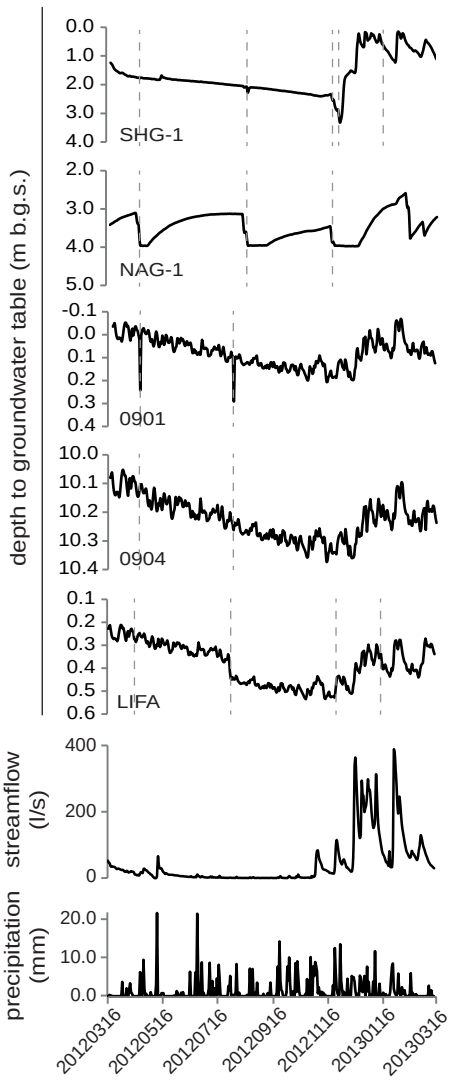

Figure 7. Precipitation (SMHI), streamflow (SLU) and groundwater head variability March 2012-2013, M42. Vertical, dashed grey lines mark known pumping events.

with pumping, suggesting that the associated well cluster draws water from a more confined and overall hydraulically less well-connected unit.

All sampled waters exhibited relatively similar geochemical characteristics (Ca-HCO_3-type with elevated Ca and Mg content; Table 4, Fig. 8) in accordance with the local limestone bedrock and associated chalk-rich sediments. However, wells SHG-1 and 0905 both displayed comparatively elevated SO_4 and Cl contents, so far unexplained. Water from well 0905 further exhibited a relatively high temperature (Table 4). Reducing conditions were shown to prevail for the portion of the aquifer in which wells 0901-0907 and LIFA are located, explanatory for non-detectable NO_3.

Conducted environmental tracer analyses indicated that the deepest monitoring wells 0901, 0904 and LIFA, at the time of sampling, monitored water that primarily recharged around or before the mid-1900s (Table 5). Similar indications applied also to the much shallower well 0907, which may be considered indicative and supportive of the hypothesised discharge location. Indications for wells 0902 and 0905 were that they capture comparatively younger water. However, the difference in apparent ages between tracers for well 0902, as well as the relatively low ^3H content, may be considered indicative of mixing of modern and (tracer-free) pre-modern waters. Mixing between modern and (tracer-free) pre-modern water could also apply to e.g. wells 0901, 0904 and 0905 but is

Table 4. Selected geochemistry data from M42 monitoring wells. Temperature, pH, oxidation-reduction potential (ORP), electrical conductivity (EC), total dissolved solids (TDS) and salinity (Sal.) for wells 0901-0907 and LIFA were measured in field repeatedly and given as artithmetic means over the period March 2010 to February 2013. Other values for the same wells are from laboratory analyses in July 2010. Values for the SHG and NAG wells are from August 2010 (SLU, 2014b).

Well	T (°C)	pH	ORP (mV)	EC (uS/cm)	TDS (mg/L)	Sal. (ppt)	HCO_3 (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO_4 (mg/L)	$NO_3 + NO_2$ (mg/L)
SHG-1		*7.4*					*340*	*195*	*12*	*17*	*3.4*	*140*	*110*	*0.8*
SHG-2		*7.6*					*380*	*160*	*10*	*18*	*2.7*	*36*	*69*	*2.7*
NAG-1		*7.5*					*480*	*180*	*15*	*19*	*3.0*	*27*	*48*	*1.4*
NAG-2		*7.7*					*410*	*160*	*17*	*25*	*5.1*	*30*	*54*	*2.2*
0901	*9.9*	*7.3*	*-220*	*500*	*310*	*0.23*	*380*	*100*	*13*	*15*	*2.8*	*18*	*<0.05*	*<0.05*
0902	*9.8*	*7.2*	*-170*	*540*	*330*	*0.26*	*350*	*120*	*13*	*8*	*2.0*	*15*	*57*	*<0.05*
0904	*9.7*	*7.4*	*-230*	*500*	*290*	*0.22*	*360*	*110*	*12*	*13*	*2.4*	*17*	*8.6*	*<0.05*
0905	*12.1*	*8.0*	*-150*	*340*	*230*	*0.17*	*180*	*91*	*10*	*10*	*3.0*	*45*	*70*	*<0.05*
0907	*9.5*	*6.9*	*-160*	*500*	*310*	*0.24*	*320*	*110*	*9*	*8*	*2.1*	*15*	*16*	*<0.05*
LIFA	*9.5*	*7.3*	*-190*	*520*	*330*	*0.24*	*390*	*110*	*13*	*14*	*2.4*	*19*	*1*	*<0.05*

more difficult to judge on in the absence of multiple tracer (i.e both ^{3}H-^{3}He and CFC) data. One should further note that the prevailing anoxic conditions could allow for CFC degradation, which would serve to increase associated apparent ages. However, no indications of such degradation were observed during analysis.

^{3}H-^{3}He data from the SHG wells both indicated a predominant young water component. The relatively older ^{3}H-^{3}He ages of the NAG wells may be considered further supportive of a more confined setting. The comparatively low ^{3}H contents of NAG-1 and NAG-2 could further be indicative of modern/pre-modern water mixing.

In total, three pesticide detections were derived from wells 0901-0907 and LIFA. Glyphosate (trace level detection) and its transformation product AMPA (0.2 µg/L) were detected in well 0905 during the first sampling round in March 2010. Glyphosate has been used extensively in the catchment throughout the past decades, and was applied onto a neighbouring field closely before the drilling of these wells, which could be the reason for the associated detections.

In the second round of sampling in July 2010, a trace level detection of azoxystrobin was recorded in a sample from well 0902. Azoxystrobin has been used within the catchment since 1997. The in time and space nearest application was conducted almost a month earlier, onto a field located some 2 km N of the well. However, surface water sampling a few meters upstream well 0902 noted an elevated azoxystrobin concentration of 0.16 µg/L the day before groundwater sampling, which may infer a hydraulic connection between well 0902 and the neighbouring stream.

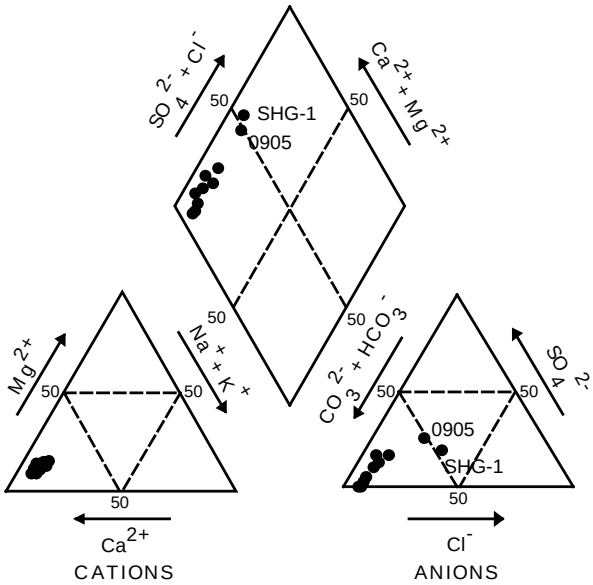

Figure 8. Piper diagram for M42 monitoring wells (values as in Table 5).

It is worth highlighting that the above pesticide detections occurred in those of the newer wells with definite indications of comparatively young water presence. As could be expected, none of the wells seemingly dominated by older water, from the time before pesticide use became widespread, appear to contain any detectable quantities thereof.

Table 5. Environmental tracer analysis results, M42. CFC concentrations are given as arithmetic means of duplicate samples.

Well	^{3}H (TU)	$^{3}He_{trit}$ (TU)	^{3}H-^{3}He age (yrs)	CFC-11 (pg/kg)	CFC-12 (pg/kg)	CFC-113 (pg/kg)	CFC ages (yrs)	^{85}Kr age (activity; dpm/cc Kr)	^{39}Ar age (activity; % modern)
SHG-1	*8.21*	*6.3**	*10*						
SHG-2	*8.66*	*8.0†*	*12*						
NAG-1	*3.81*	*10.9**	*24*						
NAG-2	*5.40*	*13.4**	*22*						
0901				*26.3*	*14.0*	*2.4*	*46+*		
0902	*3.17*	*8.0**	*22*	*9.4*	*3.0*	*0.7*	*56+*		
0904				*4.4*	*6.3*	*0.8*	*58+*		
0905	*6.73*	*7.3‡*	*13*						
0907	*0.10*	*0*	*60+*	*37.5*	*71.8*	*10.1*	*38-50*		
LIFA	*0*	*1.1*	*60+*	*10.0*	*4.3*	*0*	*56+*	*50+ (< 0.5)*	*63 (85)*

*Noble gas dissolution model fit (by A. Visser): *partial re-equilibration (Aeschbach-Hertig et al. 1999), †diffusive degassing (Brennwald et al. 2005), ‡equilibrium degassing (Aeschbach-Hertig et al. 2008; Visser et al. 2007). TU = tritium units.*

7. Summary of papers: scope, results and discussion

Author contributions to the appended and here summarised papers are given in Table 6.

7.1 Paper I

Åkesson M., Sparrenbom C.J., Carlsson C. and J. Kreuger. 2012. Statistical screening for descriptive parameters for pesticide occurrence in a shallow groundwater catchment. Journal of Hydrology 477: 165-174.

Paper I documents a first straightforward attempt at assessing important processes and predictive parameters for pesticide occurrence in groundwater in M42 using the unique long-term monitoring data. The study explores the ability of seventeen different pesticide, site and climate parameters to differentiate between polluting (detected) and non-polluting (non-detected)

Table 6. Author contributions to Papers I-IV. Non-author contributions are bracketed.

	Paper I	Paper II	Paper III	Paper IV
Idea, study design	*C.J. Sparrenbom* *M. Åkesson*	*D. Bendz* *M. Åkesson* *C. Carlsson* *C.J. Sparrenbom*	*M. Åkesson*	*M. Åkesson* *A. Suckow*
Data collation	*M. Åkesson*	*M. Åkesson*	*M. Åkesson*	-
Fieldwork/sampling	*M. Åkesson* *C.J. Sparrenbom*	*M. Åkesson*	*M. Åkesson* *C.J. Sparrenbom*	*M. Åkesson* *C.J. Sparrenbom* *J. Sültenfuss* *T. Laier* *R. Purtschert*
Geophysics	-	*M. Åkesson* *(H. Jeppsson,* *T. Dahlin)*	-	-
Geographic analyses	*M. Åkesson*		*M. Åkesson*	-
Hydrogeologic analyses	*M. Åkesson* *C.J. Sparrenbom*	*M. Åkesson* *D. Bendz* *C.J. Sparrenbom*	*M. Åkesson* *C.J. Sparrenbom*	*M. Åkesson*
Sorption and degradation analyses	-	*C. Carlsson*	-	-
Transport modelling	-	*M. Åkesson* *D. Bendz*	-	-
Statistics	*M. Åkesson* *(C. Bertacchi-Uvo)*	-	*M. Åkesson* *S.J. Fraser*	-
Lumped parameter modelling	-	-	-	*M. Åkesson* *A. Suckow*
Data interpretation and manuscript preparation	*M. Åkesson* *C.J. Sparrenbom* *C. Carlsson* *J. Kreuger*	*M. Åkesson* *D. Bendz* *C. Carlsson* *C.J. Sparrenbom* *J. Kreuger*	*M. Åkesson* *C.J. Sparrenbom* *P. Dahlqvist* *S.J. Fraser*	*M. Åkesson* *A. Suckow* *A. Visser* *J. Sültenfuss* *T. Laier* *C.J. Sparrenbom* *R. Purtschert*

pesticides, as inferred by the monitoring data specific to the well SHG-1 (Fig. 9). The tested parameters were chosen based on previously proposed explanatory ability according to existing literature and risk assessment tools. The specific well was chosen based on the inferred young apparent groundwater age (approx. 10 yrs; Table 1), enabling and justifying comparisons between pesticide application and groundwater data spanning the years 1990-2010 and 2004-2010 respectively.

Parameter averages and bootstrapped confidence intervals thereof were calculated per pesticide group (i.e. polluting and non-polluting) and compared parameter-by-parameter between groups using traditional statistical methods. Six of the seventeen parameters were found to exhibit explanatory ability for pesticide occurrence in groundwater: *applied pesticide dosage* (so that pollution risk increases with increasing dosage), the *Henry's Law Constant* (so that pollution risk increases with decreasing volatility), the *octanol-water partitioning coefficient* (so that pollution risk increases with increasing hydrophilicity), the *substance degradation potential* (so that pollution risk, counter-intuitively, increases with increasing degradability) and *precipitation amounts during the week before and the month after application* (so that pollution risk decreases with increasing amounts of precipitation before and after pesticide application).

We conclude that application intensity is the single most important governing and predictive factor for pesticide occurrence in groundwater and that information thereof therefore is fundamental for associated pollution risk assessments. We further demonstrate the importance of intrinsic physicochemical pesticide properties and that measures of such may be advantageous for predictions of pesticide presence or absence in groundwater when site-specific data of more traditionally applied but strongly site-dependent parameters (such as sorption coefficients and degradation rate constants) are unavailable. Precipitation in connection to application is further

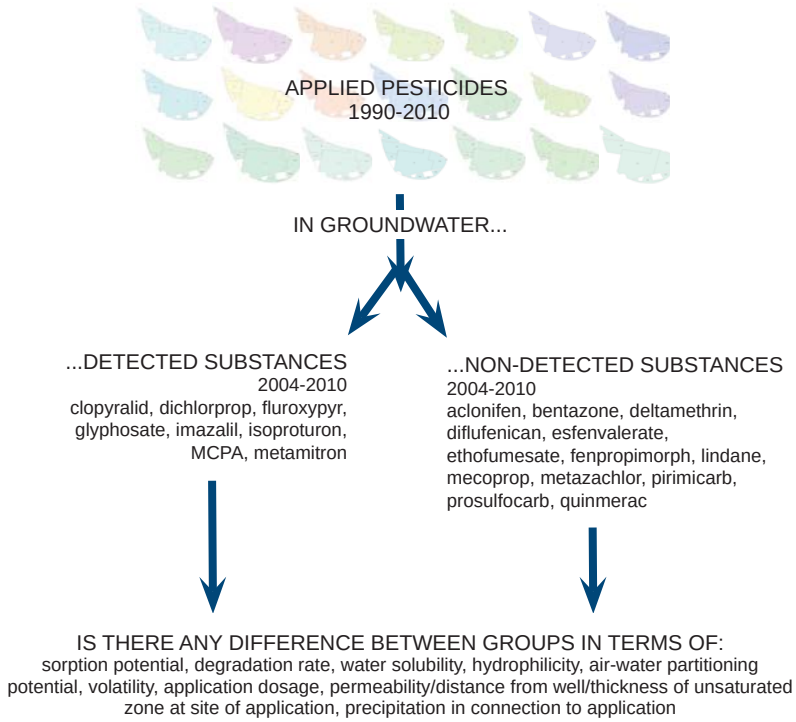

Figure 9. Scope and problem formulation of paper I. Note that corrections for analytical boundary conditions were made before designating particular substances to either the detected or the non-detected group of substances (see paper I for specifications).

indicated as an important and potentially predictive factor for pesticide occurrence in groundwater, with influential processes hypothesised to include e.g. run-off, dilution, soil matrix retainment and top-soil cracking. Presumed site parameter influence, such as e.g. that of permeability and depth to groundwater table, could not be confirmed through the applied approach.

With an improved understanding of local hydrodynamics, including the age distribution of the monitored groundwater and more detailed information of key recharge processes and areas, the undertaken analysis could advantageously be repeated with weighted influence of specific applications accordingly. Then, empirical molecular descriptors, that have been found to exhibit potential for explanatory ability for pesticide occurrence in groundwater (Worrall et al. 2002, Worrall and Kolpin 2004), could also be included.

7.2 Paper II

Åkesson M., Bendz D., Carlsson C., Sparrenbom C.J. and J. Kreuger. Modelling pesticide transport in a shallow groundwater catchment using tritium and helium-3 data. Applied Geochemistry, in press.

Paper II continues on from paper I and describes a process-based analysis of pesticide transport for the very same study area, although now inclusive of monitoring data from both SHG wells. Geological and geophysical data were used to set up a vertical model transect of the study area in HYDRUS-2D (Fig. 10). Hydraulic parameters were set based on a combination of site-specific and best-estimate values. The calibration procedure involved modelling of recharge flux and associated ^{3}H input 1950-2010, followed by tweaking of the porosity of the uppermost layer (the superficial clay till) until

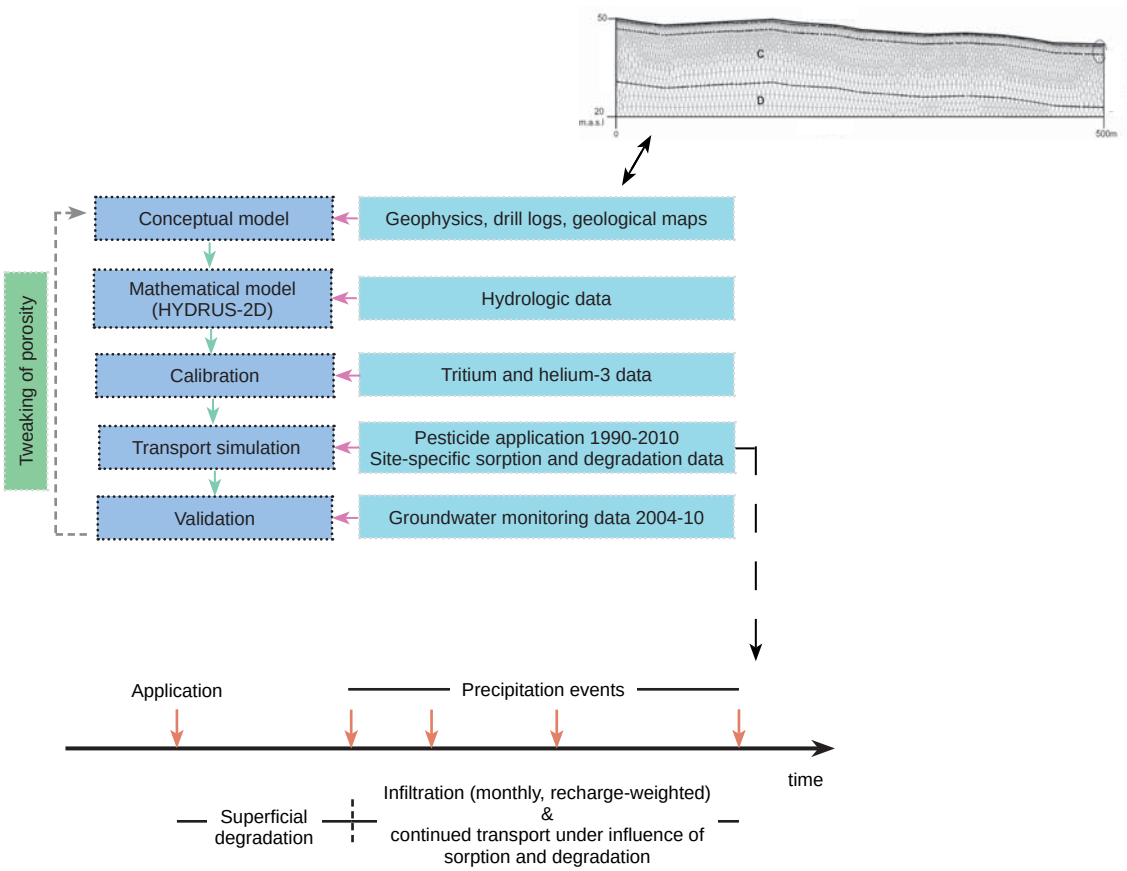

Figure 10. Approach to pesticide transport modelling conducted for paper II.

attaining satisfactory fit between measured and modelled ^3H and ^3He concentrations in the SHG wells for the year 2010. The porosity value had to be considerably decreased in order to yield such a fit, suggesting faster-than-expected water velocities in the superficial clay till, interpreted as indicative of prevailing preferential flow through subsurface heterogeneities not represented in the model.

After calibration, the model was used to simulate transport of bentazone, dichlorprop, isoproturon, glyphosate, MCPA and metamitron, using application records for the years 1990-2010 and applying experimentally derived site-specific sorption coefficients and degradation rate constants. Model output was validated against SHG monitoring data for the years 2004-2010.

The model successfully predicted observed breakthrough of bentazone, dichlorprop, isoproturon and MCPA, with offsets attributed to higher-than-accounted-for spatial and temporal variability of sorption coefficients and degradation rate constants.

Occurrences of glyphosate and metamitron were irreproducible. Glyphosate and metamitron exhibit considerably higher sorption coefficients than the other four modelled substances and should not, according to the model, be available for solute transport into the groundwater environment within the modelled time frame. Still, the monitoring data show differently, which is again attributed to the occurrence of preferential flow, which may enable leaching of otherwise strongly sorbed substances (Larsson and Jarvis 2000).

We conclude that the adopted methodological approach is promising not only in terms of pesticide-groundwater transport and pollution risk assessment, but effectively for general groundwater pollution transport and risk assessment. We further corroborate the potential of numerical hydrogeological model calibration by means of ^3H and ^3He data (i.e. actual concentrations) and demonstrate the importance of physical heterogeneity as well as variability in pesticide reactivity for the assessment, conceptualisation and simulation of the pesticide-groundwater system. Last but not least, we demonstrate and stress the importance of long-term monitoring records for holistic assessments of pesticide occurrence in groundwater.

Continued model and analysis improvements first and foremost require additional investigations and subsequent integration of the inferred heterogeneity. In terms of physical heterogeneity, such efforts may include the application of direct push technologies, supplementary geophysical surveys, geostatistical representations of field-derived training images of fracture or sand lens networks (e.g. Kessler et al. 2013) and/or supplementary dual-permeability or macropore flow models (e.g. MACRO; Jarvis et al. 1994). In terms of variability in pesticide reactivity, Ghafoor et al. (2011, 2012) infer promising possibilities for effective analyses and estimates thereof via relatively easily measureable and accessible predictor variables such as pH and organic carbon and clay content.

With an improved conceptual model, it would be particularly interesting to evaluate continued pesticide transport and potential transformation along flow paths towards depth and with increasing travel time. A further step would be to expand the model to include the full M42 catchment, or at least the portions of it subject to monitoring, in order to study larger-scale spatial and temporal patterns in relation to the full set of monitoring data.

7.3 Paper III

Åkesson M., Sparrenbom C.J., Dahlqvist P. and S.J. Fraser. On the scope and management of pesticide pollution of Swedish groundwater resources: the Scanian example. Ambio, in press.

Paper III moves on to the regional scale and investigates pesticide occurrence in a range of different types of groundwater aquifers throughout Skåne (Fig. 11). Existing records and newly acquired data of pesticide occurrence for 23 public supply wells were analysed in relation to land use, abstraction depth, hydrogeological context (aquifer type and confinement), groundwater age (modern/pre-modern) and redox conditions using the self-organising map (SOM) approach (see chapter 5.7).

The collated data revealed pesticide occurrence in 18 of the 23 studied wells, inferring a widespread regional pollution concern. Quantified

concentrations above the drinking water threshold were demonstrated for nine wells. Trend analyses were deemed futile due to (i) inconsistent and limited data availability between wells and over time, (ii) unknown groundwater age distributions and (iii) uncertainty of variability in pesticide reactivity between wells.

The types of pesticides detected suggest that the current pollution situation considerably reflects past, less restricted non-agricultural (i.e. urban) pesticide use. Modern, oxic waters from shallow, unconfined unconsolidated or fracture-type bedrock aquifers appear particularly vulnerable. The least affected waters appear primarily associated with relatively deeper abstraction depths, anoxic conditions and more confined pore-type aquifers largely devoid of urban land use influence. Predominantly pre-modern water does not appear to exclude pollution risk, which implies either pre-modern pesticide use or comparatively small but severely polluted contributions of modern water.

All but one of the studied wells are associated with water protection areas, most of which have been in place for the past 20-30 years, which indicates a need for revaluation of protective measures. Further, conducted pesticide analyses revealed previously undetected pesticides in several wells, implying that the standard analysis packages generally applied and offered by commercial laboratories are not sufficient for thorough pollution status assessment.

Further work should test the suggested inferences of relative pollution vulnerability and main pollution concerns through (i) more comprehensive studies involving additional aquifers and better constrained information on land use and

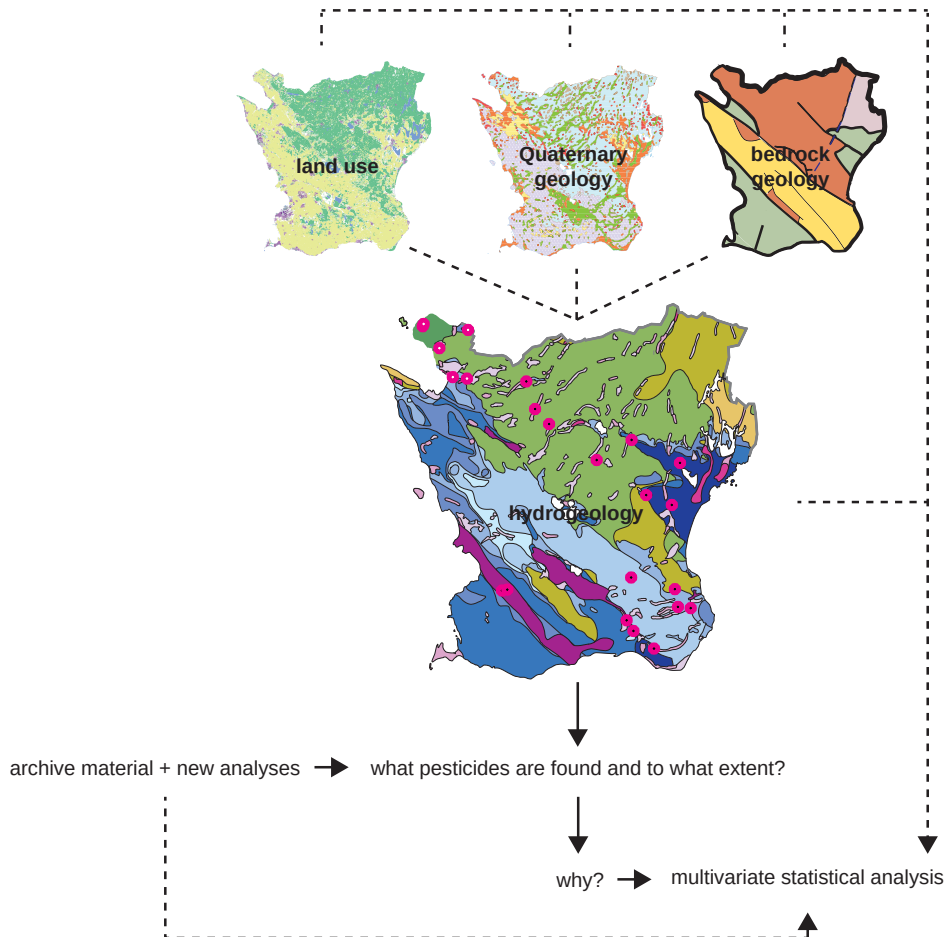

Figure 11. Scope and approach of paper III. Pink dots in the hydrogeology map mark the position of studied wells.

groundwater age distributions and (ii) additional catchment scale studies such as that of M42, but in various hydrogeological and environmental settings. The former is required for the assessment of regional scale pollution patterns, the latter for a more detailed understanding of the same.

Further, in order to be able to develop sound groundwater management plans in accordance with national environmental objectives and the WFD, available data on pesticides in groundwater (regionally and nationally) needs to be collated and structured, and comprehensive and systematic monitoring of pesticides in groundwater needs to be realised.

7.4 Paper IV

Åkesson M., Suckow A., Visser A., Sültenfuss J., Laier T., Purtschert R. and C.J. Sparrenbom. Constraining age distributions of groundwater from public supply wells in diverse hydrogeological settings by means of environmental tracers and lumped-parameter modelling: a case study from Scania, Sweden. Manuscript submitted to Journal of Hydrology.

Leading on from Paper III, Paper IV aims at (i) providing a better basis for assessing (general and pesticide-groundwater) pollution patterns and (ii) testing the applicability of common tracers to hydrogeological studies within Skåne, through exploring possibilities for determining groundwater age distributions for the studied public supply wells by means of environmental tracer analysis. Two additional production wells were added on to the 23 of the previous study.

^{3}H-^{3}He, CFC-11, CFC-12, CFC-113, SF_6 and (for one well only also) ^{39}Ar and ^{85}Kr data derived from the wells revealed (i) indications of frequent CFC degradation, (ii) occasional CFC contamination, (iii) general SF_6 contamination and (iv) overall significantly elevated ^{3}He and ^{4}He concentrations, indicative of a considerable terrigenic source thereof. The tracer-specific complications limited possibilities of sound age distribution assessments as such rely on a sufficient amount of confident, interpretable tracer data.

However, via four examples, broadly representative of the type-aquifers studied, we show that when tracer data do allow, credible age distributions can indeed be accomplished, providing much valuable information both as to associated flow and recharge conditions and enabling temporal pollution pattern analysis. Further, irrespective of the demonstrated tracer-specific limitations, the available data provide a solid basis for determining relative proportions of modern to pre-modern water components for the sampled PSWs, which in its own is valuable information in terms of present day as well as future pollution risks.

As expected, the majority of the wells pump predominantly modern water and hence stand at current and continued risk of anthropogenic pollution. Only two wells appear completely devoid of modern water influence, which 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. For these wells, potential pollution fronts are yet to come. Four wells show signs of significant pre-modern water admixing, which could serve to dilute any pollution front.

In order to enable improved and additional groundwater age distribution and pollution trend assessments, there is a need for (i) additional analyses of ^{85}Kr and ^{39}Ar for more assured assessments of modern as well as pre-modern water components, (ii) complementary sampling of monitoring wells less affected by groundwater mixing and pumping and (iii) investigations of local rates of CFC degradation as well as sources of terrigenic He and SF_6. For some of the studied aquifers, primarily those subject to more detailed age distribution assessments, analysis results should further be compared to those of informed numerical transport models for validation of results and methodology.

8. Synthesising reflections

8.1 Pollution and monitoring concerns

The predominant present-day concern with regard to pesticide pollution of groundwater in Skåne and likely also Sweden as a whole, appears to be considerably attributable to pesticide use during a time characterised by comparatively minor understanding for associated pollution risks and poorly (if at all) constrained use and management. The use of pesticides has clearly changed. However, we know little if anything in terms of consequent effects on groundwater quality, as available data to base such cause-effect assessments on are (i) much limited and (ii) difficult to compare over both time and space. Future research needs to address this matter both with regard to the perseverance of the present-day pollution situation, as well as to impending pollution risks, which are likely to involve many different types of pesticides and span virtually all types of hydrogeological settings.

To some extent, the present knowledge gap can be bridged by extended assessments of existing data, through investigations of the potential occurrence of pools of pesticides in soils and sediments and by experimental assessments of long-term persistence of specific pesticide residues in different types of settings. Nevertheless, there is an inevitable need for the implementation of structured, nationwide monitoring of pesticides in groundwater in order to enable a comprehensive, controlled and consistent source of data for sound and holistic pollution status assessments. In fact, information on pesticide occurrence is significantly deficient from many groundwater environments. Further, almost half of all known analyses of pesticide residues in groundwater in Sweden encompass a mere twenty substances, even though more than 900 active ingredients are known to have been used within the nation's borders (KEMI 2014, SLU 2014c). No doubt, much remains to be found and further investigated in terms of pesticide occurrence in groundwater in Skåne as well as Sweden as a whole. Hence, "monitoring" cannot be restricted to sporadic and analytically restrained investigations from public supply wells, but rather need to (i) include observation points throughout recharge and discharge areas of various type-aquifers and (ii) comprise comprehensive analytical screening packages covering relevant substances and lowest possible detection limits. Increased funding, authorial structuring and judicial incentives are fundamental to such developments.

Two additional aspects of the observed pollution patterns may be further highlighted. One is that pesticide occurrence in regional groundwater to a significant extent appears to result from urban weed control, which underlines the need to consider and regulate not only agricultural but also non-agricultural sources of pesticide pollution. Second, with the exception of groundwater environments characterised by pre-modern waters exclusively, it appears difficult to conclude on "safe spots" for pesticide absence in Skåne. Pre-modern waters will eventually be replenished by modern waters and therefore the contemporary lack of pollution risk for such localities will not persist indefinitely.

8.2 Assessment and prediction of occurrence: thesis contribution, general issues and key variables

One might question the need for further tools or approaches for the assessment and prediction of pesticide occurrence in groundwater. However, the fact remains that most existing tools and approaches only consider the very superficial parts of the pesticide-groundwater system and that few have been tested against non-experimental, long-term monitoring data (Azimonti 2006, Köhne et al. 2009). It is mainly in this regard that this thesis work makes an original contribution. The comprehensive M42 data unambiguously demonstrate the necessity of evaluating and assessing pesticide occurrence and pollution risks based on multiple observation points and in relation to a thorough understanding of recharge areas, groundwater age distributions, transport processes and actual pesticide input to those observation points. The much divergent monitoring results of the two neighbouring SHG wells, subject to in-depth analysis in papers I and II, provide a particularly striking example of the difficulty and uncertainty associated with relying on single

observation points only.

With regard to the simulation of pesticide transport throughout the unsaturated-saturated zone continuum, we apply a much more simple approach than what is generally known from the literature. We make no particular considerations as to the soil-root zone, that normally forms a basis for pesticide leaching models (see reviews by Azimonti 2006, Dubus and Surdyk 2006) and is known to be of major importance in terms of pesticide transport into the subsurface in the M42 area (Lindahl et al. 2005). We adhere to a rather homogenous physical subsurface conceptualisation, when the opposite is known to typically prevail in likewise previously glaciated environments (Sidle et al. 1998, Harrar et al. 2007, Kessler et al. 2012). Likewise, we adhere to a rather homogenous representation of sorption coefficient- and degradation rate variability, well aware of the fact that these parameters also tend to vary significantly over both time and space (Coquet 2003, Rodriguez-Cruz et al. 2003, Larsbo et al. 2009, Hussain et al. 2013) – hence the sensitivity analysis. Finally, as for model calibration, we only use one tweaking parameter (porosity) and two ground-truthing measurements (^{3}H and ^{3}He concentrations), which is quite the opposite to otherwise often complicated calibration schemes dependent on comprehensive laboratory experiments or field observations and typically involving a multitude of calibrated parameters (Christiansen et al. 2004, Jorgensen et al. 2004, Herbst et al. 2005, Stenemo et al. 2005, Bergvall 2007). It may therefore be considered somewhat surprising that the modelling output in most cases show satisfactory agreement with monitoring data (Fig. 12), particularly in terms of timing of pesticide breakthrough. A higher degree of complexity as to the conceptualisation of especially the more superficial parts the modelled system is evidently required to attain a fully satisfactory degree of prediction skill for all types of substances (see chapter 7.2 and paper II for details). However, the

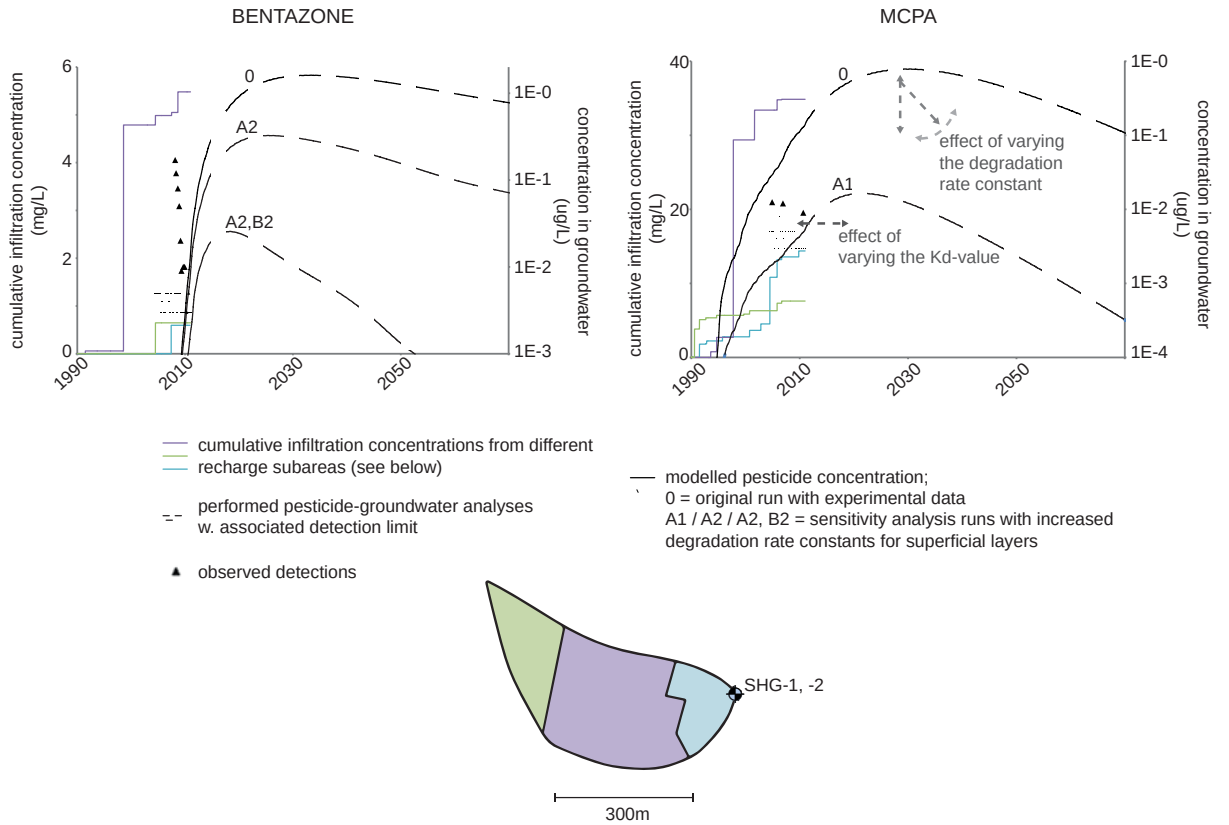

Figure 12. Selected pesticide tranport modelling results from paper II, and an inserted plan-view map of the modelled catchment. Note that recharge and pesticide monitoring data only extend to 2010, hence the dashed lines thereafter.

adopted approach undoubtedly supports the notion of environmental tracers as much powerful calibration tools for groundwater flow and transport models (Portniaguine and Solomon 1992, Zuber 2011) and quite possibly offers a much sought-after rationalising approach to the simulation, prediction and assessment of pesticide occurrence in groundwater (Köhne et al. 2009). With the wealth of tools avaialable for the more detailed characterisation and representation of the pesticide-groundwater system, there is undoubtedly scope for continued, integrated developments of the applied methodological approach. Arguably, the major challenge for the continued development of simulation and prediction tools for pesticide occurrence in groundwater lays in realising relatively straightforward and user-friendly tools that may still account for physical and biogeochemical heterogeneity, at multiple scales.

8.3 Contextual environmental tracer applicability

There are evident challenges to the use of environmental tracers in relation to studies of pesticide pollution of groundwater. As pesticides represent a non-uniform group of substances for which rates of transformation and retardation may vary with orders of magnitude between substances and along flow paths for a single substance, they are generally not subject to conservative (i.e. non-reactive) solute transport, as is generally assumed to be the case for environmental tracers. Hence, tracer-based estimations of groundwater travel times are generally not straightforwardly comparable to those of a given pesticide. In addition to control of potential for groundwater mixing and tracer-groundwater behaviour, successful and sound application of environmental tracer analysis for the assessment of, e.g., temporal patterns of pesticide occurrence thus also require control of pesticide behaviour in the subsurface, which is clearly a rather complex parameter to generalise on. Yet, when such control exists or when key parameters may be estimated and subject to sensitivity analyses, environmental tracers may undoubtedly be highly valuable for the understanding and assessment of variations in pesticide occurrence in groundwater over both time and space. Basically, environmental tracers provide an otherwise rare opportunity to pinpoint and ground-truth observations to particular travel times and recharge year(s). The use of ^{3}H and ^{3}He data to assess and explain pesticide occurrence in the SHG wells provides one example of this. The overall pattern of pesticide occurrence and absence in M42, in good agreement with tracer-derived estimations of modern water influence or not at the respective points of observation, is yet another illustrative case. A few other studies on this topic matter are available from the literature, covering studies of pesticide transformations along flow paths (Tesoriero et al. 2007), trends over time for single observation points (Farlin et al. 2013) as well as of regional pollution patterns (Warner and Morrow 2007, Gourcy et al. 2009).

For Skåne (and likely Sweden as a whole) in particular, the major challenge with regard to the application of environmental tracers for the elucidation of trends and patterns as to pesticide occurrence in groundwater relates to the fact that most available data for such studies come from public supply wells. As further elaborated upon in paper IV, these wells generally abstract water over relatively long screens, resulting in considerable mixing of waters of different origins, ages and potentially also qualities. For a given public supply well, this mix of water is further bound to change in composition in relation to pumping (Zinn and Konikow 2007). It is accordingly particularly difficult to derive sound and durable tracer-based groundwater age distributions for these types of wells, and likewise difficult to properly interpret associated time-series of pesticide occurrences. Again, this highlights the need for tailored monitoring of pesticide occurrence in groundwater in addition to sporadic sampling of production wells only.

Another concern with regard to tracer-based groundwater studies in Skåne are indicated yet so far poorly quantified local sources of CFCs, SF_6 and He (paper IV). Continued research efforts need to assess (i) the extent of anthropogenic CFC contamination of surficial soils and sediments, (ii) explore potential anthropogenic and natural sources of SF_6 and (iii) quantify regional variability of

terrigenic ^{3}He and ^{4}He contributions.

8.5 Continued work: vision for the future

With regard to the understanding of overall environmental pesticide fate, the research community as well as society in general would benefit from continued and more collaborative studies of pesticide occurrence and transport throughout the M42 catchment. Owing to the multi-faceted long-term monitoring data series and the amount of related research already conducted, this particular catchment offers unique possibilities for truly integrated research efforts. Given the questions raised in relation to the outcomes of the presented work, future efforts within the catchment should strive to:

- Intensify groundwater monitoring in time and space, in order to enable high-resolution analyses of pesticide occurrence between and within single observation points in relation to precipitation events and recharge patterns and in order to asses pesticide transformation and trends along specific flow paths (see e.g. Tesoriero et al. 2007). This assumes the continued assessment of groundwater age distributions at the specific observation points.
- Constrain subsurface physical heterogeneity from the scale of macropores to that of shifting geological facies, to improve general system conceptualisation and hence the assessment of potentially variable transport pathways for different types of pesticides into and within the groundwater environment.
- Constrain subsurface biogeochemical variability and related uncertainty ranges for substance-specific sorption coefficients and degradation rate constants over time and space, for the reasons already listed and in order to be able to conclude on long-term pollution risks for the deeper and older parts of the groundwater system.
- Quantify interactions between the different components of the hydrologic cycle, particularly potential exchanges between drainage networks and groundwater.
- Integrate, test and potentially refine existing simulation and prediction tools of environmental pesticide fate. A first logic step would be to link the here constructed 2D unsaturated-saturated zone transport model to the soil-focused MACRO model (Jarvis 1994) already tested and partly developed in the specific area.

Regarding the lack of grounds for holistic status and trend assessments of pesticide occurrence in groundwater in Skåne and Sweden, it is interesting to gaze across the Öresund strait, towards Denmark. There, in a much similar geological and geographical setting as Skåne, public water supply is entirely dependent upon groundwater. Every year or in some cases more often, some almost 1 000 dedicated groundwater intakes, all of which have been subject to CFC dating, are screened for pesticides according to a standardised, state-financed national monitoring program established in the late 1980s (Kjaer and Juhl 2013). The intakes are spread out over 63 catchments, centred on active or previously active public supply wells, with the aim of allowing for high-resolution surveillance of the different parts of hydrogeological and geographically representative groundwater systems (Jorgensen and Stockmarr 2008). Untreated raw water of thousands of public supply wells is further subject to controlled pesticide screening every 3-5 years. By law, all monitoring results are reported to a master database hosted by GEUS. Reported monitoring results do not only cover pesticide screening, but also general chemistry, inorganic trace elements, organic micro-pollutants and more quantitative variables including groundwater levels and (for production wells) abstraction amounts (Jorgensen and Stockmarr 2008). Every year, reported results form the basis for a national status report (e.g. Thorling et al. 2013). Finally, since 1998, five climatically and geologically representative fields (1-3 ha) serve as early warning sites for pesticide leaching to groundwater. These fields are instrumented to allow for high-resolution studies of pesticide transport to the shallow parts of the groundwater system, including soil, drainage and shallow groundwater and are subject to conventional, but controlled, agricultural land and pesticide use (Rosenbom et al. 2010). Results are

used to test and revaluate usage restrictions for specific pesticides as well as for the assessment of potential need of updates to the screening packages applied for nationwide pesticide monitoring (Jorgensen and Stockmarr 2008, Kjaer and Juhl 2013). The efforts undertaken on the subject matter in Denmark are in many ways exceptional and Sweden, where national groundwater monitoring of pesticides is restricted to 16 dedicated monitoring wells, stands short in comparison. Given this and related issues raised by this thesis, the following may be proposed for improving the general understanding and management of pesticide pollution risks in relation to groundwater quality in Sweden:

- An inventory of public groundwater supply wells, including documentation of exact locations, name histories, abstraction depths, hydrogeological contexts (i.e. aquifer types), recharge areas, pumping histories and, in the best of worlds, environmental tracer data. In part, this work is already underway through SGU. Yet, the experience from this thesis work is that readily available information from the respective well owner quite often is limited and uncertain.
- Complementary installation and expanded use of existing monitoring wells along flow paths within the catchments of public supply wells. These wells should be subject to environmental tracer analysis and regular groundwater levelling.
- Legislated requirements of repeated pesticide screening of raw, untreated groundwater from public supply wells and of thereto coupled monitoring wells (see point above). The screening should be conducted in a consistent manner between sampling locations and involve a minimum set of substances with fixed maximum limits of detection and quantification. Complementary substances could be added according to local land use. Reassessments of screening packages should be undertaken repeatedly in relation to findings from the more comprehensive analyses carried out in the four agricultural-aquatic reference areas (of which M42 is one), as well as in relation to new market registrations. Further, parts of the general groundwater quality monitoring network of SGU (totalling 528 wells) could usefully also be extended to cover pesticide screening.
- Structured registration of all pesticide-groundwater sampling locations, including metadata as listed above in relation to public supply wells (e.g. name histories, hydrogeological contexts etc.), into a master database hosted by a single responsible authority. Again, this is partly underway through SGU, although with focus on public supply wells only.
- Collation, structuring and analysis of available data on pesticide occurrence in groundwater from around the country, followed by the construction of a single master database into which all further conducted pesticide analyses of groundwater should be reported. The database should be the responsibility of one authority only and coupled to a registry of sampling locations as specified above. The experience from this thesis work is otherwise that currently available sources of information differ in content and only partly overlap.
- Organised and standardised derivation of yearly approximates of regional pesticide loadings, either via currently available and collated information on annual national pesticide sales and land use, or, through direct reporting from farmers to local authorities.

These developments inevitably require increased funding and also inquiries as to respective authorial responsibilities. One way forward is through general environmental water taxes, which fund much of Denmark's monitoring activities. Another is through application of the Polluter Pays Principle.

Finally, for general safeguarding of national groundwater resources, the delineation of water protection areas and associated regulations often established some 30-40 years ago should be reassessed, as they appear to provide limited groundwater protection (see paper III).

9. Overarching conclusions

>> Pesticides are repeatedly detected in disparate groundwater reservoirs throughout Skåne, pointing towards a potentially long-lasting and multi-faceted pollution concern comparable to that of other early industrialised regions. However, due to insufficient and unstructured monitoring, data on pesticide occurrence in regional as well as national groundwater is inconsistent and limited with regard to sites and types of substances investigated and hence provide a deficient basis for holistic status and trend assessments and sound groundwater management plans in accordance with, e.g., the EU Water Framework Directive.

>> Amongst the most frequently detected pesticide residues in regional as well as national groundwater are those of mainly non-agricultural substances used with little or no restrictions up to c. 10-20 years ago (e.g. atrazine, dichlobenil, terbuthylazine). This pattern is not entirely surprising in view of the fact that most analysed groundwater samples derive from public supply wells for which a certain time lag with regard to transport and arrival of water and associated solutes can be expected. However, residues from currently used substances manifestly continue to leach towards and into the groundwater system whereby current and future pesticide pollution concerns with regard to groundwater cannot and should not only be considered a matter of "old sins".

>> With the exception of those which currently are devoid of any modern (post mid-1900s) water influence, it is difficult to conclude on types of groundwater environments completely unaffected by or safe from pesticide pollution in Skåne. Still, as expected in relative terms, it is those with the most efficient connections to the ground surface which appear to be the most affected and vulnerable. Such groundwater environments include the shallow and oxic portions of unconfined aquifers, or those aquifers influenced by rapid preferential flow through fractures or macropores. In addition to agricultural land use, urban developments within a given recharge area is further indicated to increase the pollution risk.

>> Particularly important aspects of pesticide occurrence in regional groundwater and future assessment and prediction thereof include: fundamental physicochemical properties of applied pesticides, application intensities, precipitation and recharge patterns in relation to application, substance-specific variability of (primarily superficial) sorption and degradation rate efficiencies, subsurface multiple-scale physical heterogeneity and groundwater system turnover rates. Continued research efforts should focus on developing efficient ways of assessing the three latter factors.

>> Environmental multi-tracer analysis exhibits major potential as to the continued assessments of pesticide occurrence in groundwater, both with regard to the development of pollution assessment and prediction tools and with regard to the elucidation of regional pollution trends and patterns. For Sweden, however, a major concern is that most available data on pesticides in groundwater are derived from public supply wells that in view of water mixing and variable pumping rates are not ideal for sustainable groundwater age assessments. For the future, monitoring wells should therefore be favoured and increasingly exposed to pesticide screening as well as environmental tracer analysis to allow for improved status and trend assessments. For Skåne, additional research efforts are further required to better constrain demonstrated common regional tracer-specific complications concerning in particular SF_6 and CFCs, but also terrigenic He.

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Svensk sammanfattning

Grundvatten, det vatten som förekommer i hålrum i underjorden, är en av våra allra viktigaste naturresurser. Grundvattnet utgör den absolut största andelen för oss tillgängligt färskvatten och används för att producera mat och som processvatten inom olika industrier. Ungefär hälften av jordens dricksvattenförsörjning baseras på grundvattenuttag och ekosystem världen över är beroende av grundvatten för sin överlevnad. Eftersom grundvatten generellt omsätts långsamt, via transport genom en mörk och kall miljö där omfattningen av naturlig rening oftast är mycket begränsad, är det ytterst viktigt att försöka undvika att grundvattnet förorenas. Annars riskeras kvaliteten på grundvattnet i generationer framöver.

Forskningen som presenteras i den här avhandlingen har strävat efter att öka kunskapen om i vilken omfattning Skånes grundvatten är förorenat av bekämpningsmedel samt att utreda vilka riskerna för fortsatt förorening är och hur dessa risker bäst kan bedömmas, förutses och i förlängningen även förebyggas. Studier har genomförts både i detaljskala i ett avrinningsområde bland Söderslätts jordbruksmarker och mer brett via kommunala dricksvattenproduktionsbrunnar placerade i olika typer av miljöer runt om i länet. Eftersom Skåne inrymmer de flesta olika typer av såväl markanvändning som grundvattenmagasin som förekommer i Sverige i stort, är resultaten relevanta inte bara ur ett regionalt utan även ur ett större nationellt som internationellt perspektiv.

Bekämpningsmedel är ämnen som är avsedda att reglera tillväxt av för människan eller mänskliga intressen skadliga organismer. Vid exponering kan bekämpningsmedel även vara hälsovådliga för människor och påverka exempelvis nervsystem och reproduktionsförmåga. I Sverige precis som i många andra tidigt industrialiserade länder har bekämpningsmedel sedan mitten av 1900-talet använts i större omfattning inom jordbruket för att säkra och maximera skördar, inom exempelvis trävaruindustri för tryckimpregnering och för ogräsbekämpning längs med trafiknätverk, på offentliga platser och privat mark. I samband med användning finns alltid en risk för spridning av bekämpningsmedel till ej avsedda områden och

objekt, exempelvis till grundvattnet genom infiltration med regn och ytvatten. Insikten om detta har dock dröjt och i Sverige var det först under 1980-talet som restriktioner med avsikt att minska belastningen på miljön initierades. Följden blev en förändrad och i stort minskad bekämpningsmedelsanvändning, men rester av olika ämnen fortsätter att hittas runt om i naturen, så även i grundvatten.

I den första av fyra delstudier undersöktes bekämpningsmedelsförekomst i ytligt grundvatten i det mindre avrinningsområdet i södra Skåne, statistiskt i förhållande till dokumenterad användning. Målet var att få indikationer på vilka faktorer som påverkar huruvida de substanser som används når grundvattnet eller ej och samtidigt undersöka vilka parametrar som skulle kunna användas för att bedöma föroreningsrisk. Som väntat visade sig den absolut viktigaste faktorn vara använd mängd, så att de ämnen som använts med högst intensitet också är de som hittas i grundvattnet. Vidare kunde även substans-specifika kemiska egenskaper konstateras vara av vikt, så att de mer polära och mindre flyktiga ämnena löper större risk att nå grundvattnet. Nederbörd i samband med användning indikerades också vara betydande, så att användning i samband med relativt mindre nederbördsmängder ökar risker för transport till grundvatten, eventuellt på grund av minskad ytavrinning, minskad utspädning och ökad sprickbildning.

I den andra delstudien gjordes en mer process-baserad analys av transport av sex stycken olika bekämpningsmedel till två brunnar inom samma område som undersöktes i den första delstudien. Med hjälp av geofysiska och geologiska data konstruerades en numerisk modell av området. Modellen kalibrerades genom att jämföra simulerade mot uppmätta koncentrationer av spårämnena tritium och helium-3 i de två brunnarna, varpå dokumenterad användning av de sex olika bekämpningsmedlen mellan åren 1990 och 2010 simulerades infiltrera med nederbörd och röra sig i enlighet med grundvattenflödet i området under inverkan av sorption och nedbrytning. På så sätt kunde detektioner av fyra av de sex bekämpningsmedlen rekonstrueras tillfredställande. Enligt modellen borde de två andra bekämpningsmedlen, på grund av sorption, inte kunna transporteras till brunnarna inom den modellerade tidsramen. Att de ändå gjort det tolkas som förekomst av så kallat preferentiellt flöde genom exempelvis sprickor eller makroporer som inte inkluderades i den uppställda modellen. Studien visar på stor potential för användning av tritium och helium-3 som kalibreringsverktyg för flödes- och transportmodeller i grundvattenmiljöer, och på vikten av såväl fysisk som biogeokemisk heterogenitet för simulering och prediktion av transport av bekämpningsmedel till och i grundvatten.

Den tredje studien tar ett mer regionalt grepp och undersöker förekomsten av bekämpningsmedel i en rad olika grundvattenmagasin som används för kommunal dricksvattenproduktion. Äldre bekämpningsmedelsanalysdata från tjugotre brunnar undersöktes i förhållande till markanvändning, hydrogeologi och resultat av nya analyser som omfattade betydligt fler substanser och karaktäriserades av betydligt lägre detektionsgränser än mer konventionella bekämpningsmedelsanalyser. Av de tjugotre brunnarna visade sig arton vid ett eller typiskt upprepade tillfällen ha innehållit bekämpningsmedel, nio av dessa i halter över regionala riktvärden. En betydlig andel av de bekämpningsmedel som hittats visade sig härröra från substanser som sedan ett par decennier varit förbjudna att använda och som framförallt användes utom jordbruket, för ogräsbekämpning inom urbana miljöer. De nya analyserna genererade detektioner av såväl nya substanser som i brunnar i vilka man tidigare aldrig hittat bekämpningsmedelsrester. De kraftigast förorenade och därmed mest känsliga grundvattenmiljöerna verkar som väntat vara de som präglas av relativt god hydraulisk kontakt till markytan, dvs. antingen de grunda, syresatta miljöerna, eller de inom vilka transport kan ske snabbt till relativt stora djup genom sprickor. Resultaten visar att bekämpningsmedel är vanligt förekommande i vitt skilda grundvattenmagasin och miljöer runt om i länet och tyder på en utbredd föroreningsproblematik som potentiellt kan förbli under lång tid framöver. De skyddsområden och skyddsföreskrifter som finns (för alla utom ett av de

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Den fjärde och sista delstudien viker av något från avhandlingens huvudspår och fokuserar istället på att utvärdera möjligheter för att bestämma hur gammalt det vatten som pumpas upp från de i delstudie tre undersökta brunnarna är, det vill säga hur lång tid det tagit för det vatten som pumpas upp att nå brunnen från dess att det infiltrerade markytan. Om man skulle kunna bestämma dessa ”grundvattenåldrar” så skulle det innebära utökade möjligheter till att utföra analyser av regionala föroreningstrender (exempelvis av bekämpningsmedel i grundvatten), eftersom man då får ett verktyg som möjliggör jämförelse mellan provtagningar över tid. Åldersbestämningsförsöken görs via analyser av en rad olika spårämnen som infiltrerat grundvattenmiljöer under decennier på grund av mänsklig produktion och användning: tritium och helium-3, klorfluorkarboner, svavelhexafluorid och krypton-85 samt dessutom argon-39, som finns i grundvattnet av helt naturliga orsaker. Undersökningen visar på att det går att göra kvalificerade bedömningar av grundvattenålder med hjälp av kombinationer av de här spårämnena och att man via sådana bestämningar kan generera mycket ny kunskap om grundvattenmagasinet i fråga. Resultaten tyder vidare på att de flesta vatten som pumpas upp för dricksvattenförsörjning i Skåne är relativt unga och därmed känsliga för förorening. Dock är förutsättningarna för åldersbestämning av flertalet provtagna grundvatten inte optimala. Dels beror detta på att dessa vatten kommer från dricksvattenproduktionsbrunnar som ofta pumpar vatten från flera olika nivåer och med varierande intensitet, vilket försvårar åldersbestämningar. Andra orsaker är dåligt kvantifierade lokala och i vissa fall regionala källor av helium, klorfluorkarboner och svavelhexafluorid samt, ibland, nedbrytning av klorfluorkarboner.

Sammanfattningsvis bidrar den här avhandlingen till ökad förståelse för vilka bekämpningsmedel som förekommer i grundvatten i Skåne, varför de gör det och hur denna förekomst kan förutses och bäst bedömas. Undersökningarna visar också på ett behov av utökade satsningar på övervakning såväl som forskning gällande bekämpningsmedel i grundvatten i Sverige generellt, för att kunna möta uppställda miljömål och för att därmed ha en möjlighet att säkra kvaliteten på framtida grundvattenresurser.

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Paper I

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Statistical screening for descriptive parameters for pesticide occurrence in a shallow groundwater catchment

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SUMMARY

We have assessed the ability of a range of pesticide, site and climate parameters to discriminate between detected and non-detected pesticides as observed by long-term monitoring data of pesticide use and groundwater occurrence in a small catchment in southern Sweden. Of seventeen investigated parameters, six demonstrated such an ability: dosage applied, the Henry's Law Constant (HLC), the octanol–water partitioning coefficient ($\log P_{ow}$), the amount of precipitation the week before application, the amount of precipitation the month after application, and the substance degradation potential (DT_{50}). The apparent influence of the investigated parameters on pesticide occurrence in groundwater, and their apparent suitability as descriptive parameters in terms of assessment of related risks, is accordingly discussed.

We conclude that knowledge of actual pesticide use appear fundamental for risk assessment of groundwater contamination potential. We further suggest that chemical property-parameters of specific pesticides, although clearly valuable, should be applied in groundwater contamination risk assessments with care. If site-specific values are unattainable, tabular values of $\log P_{ow}$, HLC and water solubility (W_s) are demonstrated to exhibit a superior explanatory ability than those of substance adsorption potential (K_{oc}) and DT_{50} which, in the latter case, is shown to be able to lead to misleading conclusions on actual risks.

The demonstrated explanatory ability of precipitation both before and after application suggests that relatively greater precipitation amounts occur in relation to application of non-detected substances. Increased dilution and run-off as well as decreased soil matrix retainment and decreased top-soil cracking are potential explanations although higher-resolution monitoring records are needed in order to confirm these hypotheses.

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1. Introduction

Pesticide contamination of groundwater is a worldwide concern. Residues of a large variety of compounds are found in aquifers on all inhabited continents, beneath highly variable types of environments (Gaw et al., 2008; Kolpin et al., 1998; Leistra and Boesten, 1989; Li and Zhang, 1999; Pick et al., 1992; Schipper et al., 2008; Shomar et al., 2006; Tariq et al., 2007). The problem is complex since pesticide use, although always involving a risk of unrestrained environmental spread and accumulation, is generally considered necessary in order to sustain worldwide food production (Tadeo, 2008).

During past decades, the understanding of governing parameters and processes for pesticide occurrence in groundwater has increased substantially through laboratory-studies of pesticide behaviour in different soils and sediments (e.g. Clausen et al., 2004; Sprankle et al., 1975; Tuxen et al., 2000), controlled field-scale experiments exploring the rate and pathways of transport (e.g. Boesten and van der Pas, 2000; Funari et al., 1998) and regional and national monitoring programmes comparing the degree and character of contamination between different types of catchments (e.g. Gaw et al., 2008; Steele et al., 2008; Worrall and Kolpin, 2004). Meanwhile and as a result, a range of pesticide environmental fate models (e.g. Carsel et al., 1985; Jarvis et al., 1991; Leonard et al., 1987; Tiktak et al., 2004) and pesticide environmental risk indicators (e.g. Gutsche and Rossberg, 1997; Padovani et al., 2004; Reus and Leendertse, 2000; Sorensen et al., 1998; Vaillant et al., 1995; van der Werf and Zimmer, 1998) have been developed in order to better be able to assess environmental risks associated with pesticide use. In addition to toxicological aspects, pesticide, site and climate parameters are generally considered to constitute the overall building blocks of such fate and risk analyses addressing the issue of groundwater contamination risk. However, actual data requirements may vary significantly between those different models and indicators, as may the weighting of therein applied

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explanatory variables (Dubus and Surdyk, 2006; Reus et al., 2002). This shows a need for further investigation of the individual as well as relative importance of descriptive parameters of pesticide occurrence in groundwater. Not the least, there is a need for such investigations based on long-term monitoring data of pesticide occurrence in groundwater in relation to actual pesticide use (Mouvet, 2007).

1.1. Objective, motivation and hypotheses

The objective of this study is to assess the ability of a range of pesticide, site and climate parameters to discriminate between detected and non-detected pesticides in shallow groundwater beneath an intensively cultivated catchment in southern Sweden. This is done through statistical screening of a local 21-year monitoring data set of pesticide use (1990–2010) in relation to a 7-year monitoring data set of groundwater occurrence of pesticides (2004–2010). Based on the results, the apparent influence of the investigated parameters on pesticide occurrence in groundwater and their apparent suitability as descriptive parameters in terms of assessment of related risks is accordingly discussed. The aim is not to develop yet another risk assessment method, but to independently evaluate the ability of commonly used descriptive variables to explain the presence or absence of pesticides in groundwater as suggested by long-term, non-experimental monitoring data. We hereafter refer to this ability as the "explanatory ability".

The investigated parameters are: substance water solubility (W_s), substance octanol–water partitioning coefficient ($\log P_{ow}$), substance vapour pressure (V_p), substance Henry's Law Constant (HLC), substance adsorption potential (K_{oc}), substance degradation potential (DT_{50}), dosage of applied active substance, total treated area, hydraulic conductivity of treated sediments, depth to water table and distance from well from point of application, and precipitation before, after and at day of pesticide application. The choice of parameters is justified below.

K_{oc}, as measured by the affinity of a given substance to sorb to organic carbon, and DT_{50}, as measured by its soil degradation half-life, have since long been suggested to constitute a sound basis for risk assessment of pesticide contamination of groundwater (e.g. Helling et al., 1971; Hornsby, 1992). Both parameters are commonly used in related risk indicator schemes (Gustafson, 1989; Padovani et al., 2004; Reus and Leendertse, 2000), and for European Union membership states, they form the basis for environmental fate assessment and resultant decisions on authorisation through the Council Directive 91/414/EEC (European Commission, 1991). However, whereas K_{oc} and DT_{50} have been demonstrated an explanatory ability in terms of pesticide contamination of groundwater in certain studies (Gustafson, 1989; Worrall et al., 2000), Barbash and Resek (1996) stressed that this is not always the case. Potentially, K_{oc} and DT_{50} are parameters overly dependent upon surrounding environmental conditions (e.g. organic carbon and clay content of the soil) to be easily applicable as descriptive variables for risk unless site-specific values are or can be made available.

W_s, which gives an indication of the mobility of the pesticide from soil to groundwater; $\log P_{ow}$, representing the ratio of solubility of the pesticide in octanol to its solubility in water; V_p, a relative measure of the volatility of a pesticide in its pure state; and HLC, which measures a pesticide's volatility as a function of both its water solubility and its vapour pressure, are further common chemical property-parameters applied for environmental pesticide fate and risk assessment purposes (e.g. Gutsche and Rossberg, 1997; Padovani et al., 2004; Tiktak et al., 2006; Vaillant et al., 1995). Yet, observational data cast doubts on the degree of applicability of these parameters as descriptors of contamination risk. While some studies have shown a correlation between pesticide detections and compound W_s in both surface water and groundwater (Halfon et al., 1996; Kolpin et al., 1998; Kreuger and Tornqvist, 1998), Worrall and Kolpin (2004) did not manage to find such a relationship in their study of pesticide occurrence in groundwater in the mid-west United States. Furthermore, whereas Kreuger and Tornqvist (1998) found log P_{ow} to be a predictive variable for pesticide contamination of surface water, its potential as a measure of risk of groundwater contamination as suggested by observational data remains to be assessed.

Altenburger et al. (1993) and Halfon et al. (1996) both demonstrated a negative correlation between pesticide detections and compound V_p. However, both studies were conducted on surface water data and the explanatory ability in terms of groundwater contamination risk remains to be studied. HLC has been proven a determinant parameter in terms of pesticide occurrence in a surface water study by Altenburger et al. (1993). However, in a groundwater study, no such observations could be made (Kolpin et al., 1998).

The hydraulic conductivity of the treated sediments is central to many pesticide environmental risk models (e.g. Carsel et al., 1985; Jarvis et al., 1991). In terms of environmental pesticide risk indicator schemes however, this parameter as well as other site parameters such as depth to groundwater table and distance from well to point of application are less commonly adopted. They are, however common vulnerability measures in terms of overall groundwater vulnerability assessment schemes (Aller et al., 1987; Schlosser et al., 2002; Worrall and Kolpin, 2004).

Although an important part of most environmental pesticide fate models (e.g. Carsel et al., 1985; Jarvis et al., 1991; Leonard et al., 1987; Tiktak et al., 2004), the actual influence of precipitation on pesticide occurrence in groundwater, e g. its character and strength, has shown difficult to determine as it is fundamentally related to timing in relation to application (Beulke et al., 1999). This is especially true for soils and sediments exhibiting preferential flow (Gish et al., 1991; Jarvis, 2007). We have accordingly chosen to investigate the explanatory ability of a range of precipitation-parameters covering both the amount of rainfall on the specific application day, as well as the week and month before and after application.

Actual pesticide use is obviously a governing parameter in terms of potential pesticide occurrence in groundwater. However, lack of long-term monitoring data of pesticide has typically hindered real-life, i.e. field-based and non-experimental assessment and validation of actual influence. Here, we employ a unique, 21-year data set to perform such an analysis.

Our hypothesis is that all above mentioned parameters will be able to discriminate between the detected and the non-detected substances although with varying explanatory ability. This would, in turn, indicate various degrees of influence on the occurrence of pesticides in shallow groundwater, as well as various degrees of suitability in terms of use as risk assessment-parameters.

We further hypothesise that the risk of groundwater contamination is the greatest for a soluble and polar pesticide that has a low volatility and degradation potential, and that adsorbs to carbon poorly. Also, we hypothesise that the higher the applied dosage and the greater the area treated, the higher the hydraulic conductivity of the treated sediment, the thinner the unsaturated zone, the lesser the distance to well and the more the precipitation in relation to application, the greater the risk for groundwater contamination.

2. Materials and methods

2.1. Study area

The study area is located within a 9 km^2 catchment located in the southernmost part of Sweden, in one of Europe's most fertile

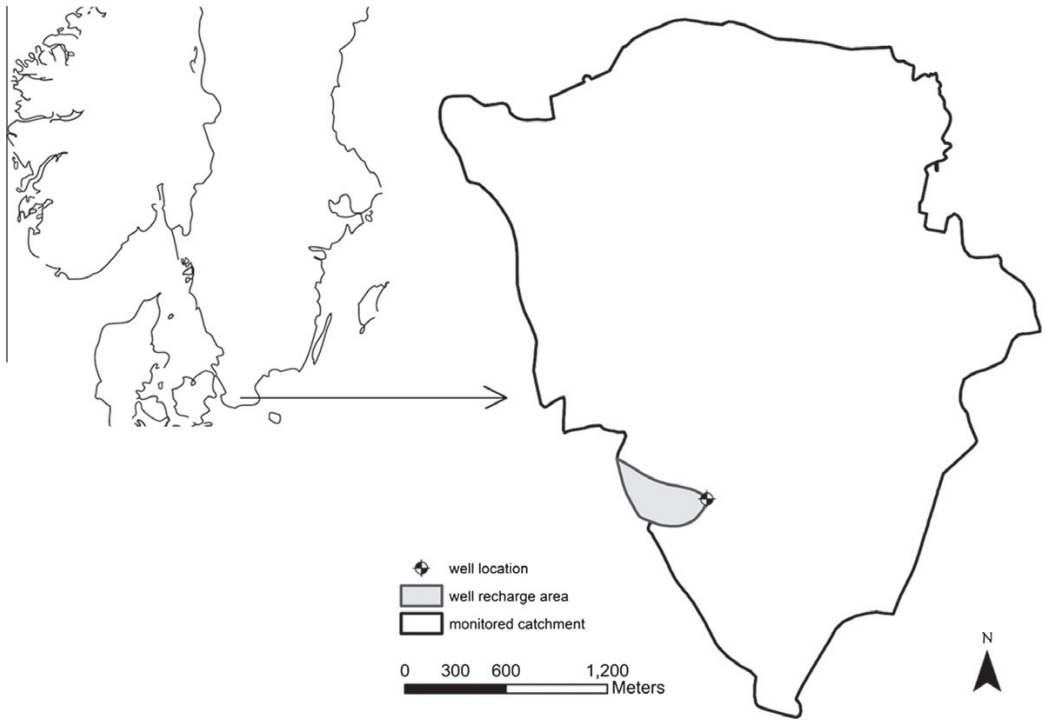

Fig. 1. Overview of study area. Right; the surface water catchment monitored for pesticide usage by the Swedish University of Agricultural Sciences, the here studied well and its estimated recharge area. *Left*: regional location.

and most intensely cultivated areas (Fig. 1). About 95% of the catchment consists of arable land, of which most is subject to a 4-year rotational cropping practice dominated by winter rape, winter wheat, sugar beet and spring barley (Kreuger, 1998). The climate is maritime with a mean annual temperature of about 7 °C and an average annual precipitation of roughly 700 mm, of which approximately 30% is available for groundwater recharge (Lewan et al., 2009). The growing season equals about 220 days.

Geologically, the region is characterised by gently undulating, glacially derived Quaternary sediments deposited within a buried Tertiary limestone bedrock valley. The thickness of the infill varies between 60 and 120 m, with a major sandy glacifluvial deposit at depth overlain by intercalating clay- and chalk-rich tills and lenses and sequences of sorted, fine-grained sediments. In the specific catchment studied, surficial sediments are dominated by a sandy loam soil consisting of 51–59% sand, 26–32% silt and 12–21% clay (Kreuger, 1998). Soil pH averages 7.2 (Svensson, 1999), surface and drainage water 7.5–8.0 (Kreuger, 1998), and shallow groundwater 7.5.

The catchment has been monitored in terms of pesticide use since 1990 through standardised documentation by the Swedish University of Agricultural Sciences in collaboration with local farmers. Since 2004, two shallow groundwater wells (filter depths: 2.9–3.5 m) located *c.* 5 m apart in the western part of the catchment have been sampled four times yearly for analysis of pesticide residues. Analyses have been adapted to known application to incorporate as many of the used substances as possible. Results from the groundwater monitoring program have been reported in annual national reports starting 2005 (Adielsson et al., 2009; Adielsson and Kreuger, 2008; Adielsson et al., 2006, 2007; Graaf et al., 2010, 2011; Tornquist et al., 2005). These reports also detail specific sampling protocols and analytical procedures.

$^3H/^3He$-analyses conducted by the Dissolved and Noble Gas Laboratory at Utah University indicate residence times of approximately 10 years for water from the so called well A, and approximately 11 years for water from the so called well B. The $^3H/^3He$-analyses were conducted according to the procedures described by Bayer et al. (1989) but in an all-metal-system yielding lower blanks. Gas model fits and resultant ages were obtained using the partial re-equilibration model (Stute et al., 1995) for well A, and the diffusive degassing model (Brennwald et al., 2005) for well B. Specific pesticide detections in well A suggest that mixing of water of residence times between at least <1 to $\geqslant$17 years occur in that well. A similar conclusion could not be drawn from the pesticide occurrence registered from well B.

2.2. Data compilation

2.2.1. Pesticide data

For retrieval of relevant pesticide data within the study area, a best-estimate recharge area of the two wells was delineated based on a groundwater surface constructed through a co-Kriging-analysis using 49 local groundwater head-measurements as a main variable, and a laser-derived national digital elevation model (©Lantmäteriet; SE < 0.5 m) as a covariate. Annual coded field maps, constructed as part of the monitoring program, were then digitalised for the recharge area permitting derivation of information on the exact timing, location and intensity of local pesticide use for the years 1990–2010.

Since analytical scope and detection limits within the groundwater monitoring program have varied over time and between substances, a correction of the data set was considered necessary in order to avoid analytical bias. Comparative studies between detected and non-detected substances can only be justified if

Table 1
Studied substances, documented detections and chemical data used in the analysis. S_w = solubility in water; log P_{ow} = octanol–water partitioning coefficient; V_p = vapour pressure; HLC = Henry's Law Constant; DT_{50} = mean soil half-life over a range of studies; K_{oc} = soil sorption coefficient.

Substance	Detected (year-month, well)	S_w (mg/L)	Log P_{ow}	V_p (mPa)	HLC (Pa m^3/mol)	DT_{50} (days)	K_{oc} (ml/g)
Aclonifen	–	1.4	4.37	0.016	3.03E−03	117	5318[b]
Bentazone	2008–02, B; 2008–04, B; 2008–08, B; 2008–11, B; 2009–02, B; 2009–08, B; 2009–11, B	570	−0.46	0.17	7.2E−05	13	55.3
Clopyralid	2006–11, A	143,000	−2.63	1.36	1.8E−11	34	5
Deltamethrin	–	0.0002	4.6	1.24E−05	3.1E−02	13	10,240,000
Dichlorprop-P	2004–11, A	590	−0.56	0.056	5.6E−05	14	44
Diflufenican	–	0.05	4.2	4.25E−03	0.0118	180	1995.5[b]
Esfenvalerate	–	0.001	6.24	1.2E−06	4.9E−04	44	5300
Ethofumesate	–	50	2.7	0.65	6.8E−04	70	166[a]
Fenpropimorph	–	4.32	4.5	3.9	2.74E−04	35	4382[a]
Fluroxypyr	2004–11, A 2007–04, A	6500	0.04	3.8E−06	1.6E−10	1	68[a]
Glyphosate	2004–11, A 2005–02, A	10,500	−3.2	0.0131	2.1E−07	12	1435
Imazalil	2009–04, A + B 2009–08, A + B	184	2.56	0.158	1.08E−04	50	3606[b]
Isoproturon	2006–11, A 2007–02, A 2007–04, A	70.2	2.5	5.5E−03	1.46E−05	12	123[a]
Lindane	–	8.52	3.69	4.34	0.15	121	1100
MCPA	2004–11, A 2006–11, A	29,390	−0.81	0.4	5.5E−05	15	31[a]
Mecoprop-P	–	860	0.02	0.23	5.7E−05	8	17[a]
Metamitron	2004–11, A	1770	0.85	7.44E−04	8.95E−08	30	77.7
Metazachlor	–	450	2.49	0.093	5.9E−05	8.6	54
Pirimicarb	–	3100	1.7	0.43	3.3E−05	86	1387[a]
Prosulfocarb	–	13.2	4.48	0.79	0.0152	31	1855[b]
Quinmerac	–	107,000	−1.41	1E−07	1E−10	30	86

All values from the FOOTPRINT PPDB database (2009).
[a] Exception: Kreuger and Tornqvist (1998).
[b] Exception: Average values from dossiers prepared by the Swedish Chemicals Agency (KEMI).

fundamental analytical boundary conditions for those substances are equivalent. Therefore, in accordance with methodology used by Kolpin et al. (1998) and Worrall et al. (2002), groundwater monitoring data was corrected to a common detection threshold of 0.01 μg/L, so that for substances with a lower specified analytical detection limit concentrations less than 0.01 μg/L were set to zero. Substances applied within the catchment and throughout the entire groundwater monitoring program detectable but never detected in concentrations ⩾0.01 μg/L were accordingly defined as non-detected substances. Substances applied within the catchment and detected once or more in concentrations ⩾0.01 μg/L were correspondingly defined as detected substances. Substances applied within the catchment and never detected but neither throughout the entire monitoring program detectable in concentrations ⩾0.01 μg/L were excluded from further study since it cannot be ascertained that they never have occurred in concentrations at or above the defined detection threshold in one or more of the analysed samples. Whilst decreasing the sample population available for analysis, this correction ensures that only substances truly comparable in terms fundamental analytical boundary conditions are included in the analysis.

For well B, the data set correction meant too heavy a reduction of data for sound quantitative statistical investigation. For well A, the correction constrained the data set to 19 of 58 substances applied in the recharge area since 1990 (Table 1). Two additional substances for which there are no records of use met the above analytical criteria and were accordingly incorporated into the study. One of these is the seed treatment substance imazalil, which has probably been used in the area along with sowing at multiple occasions without documentation. The other is lindane, which was phased out during the 1980s in Sweden suggesting either non-documented or pre-1990-application.

For the 21 substances, dosage and total area treated per application was calculated. Typical tabular values of chemical properties (W_s, log P_{ow}, V_p, HLC, DT_{50} and K_{oc}) were collected from the comprehensive, relational FOOTPRINT Pesticide Properties Database (PPDB, 2009). Values which could not be attained from the PPDB were collected from Kreuger and Tornqvist (1998) and the Swedish Chemicals Agency (KEMI, 2012). Using tabular values from a widely available relational database is a conscious choice made by the authors; partly due to economical restrictions impeding determination of site-specific values, mainly however, in order to study the explanatory ability of readily accessible data as it is commonly this type of data that is used for general risk assessment purposes (e.g. Guerbet and Jouany, 2002; Padovani et al., 2004).

2.2.2. Site data

The hydraulic conductivity of the sediments within the study area was estimated based on a digital version of the Swedish Geological Survey's Quaternary deposits map (scale 1:50,000, mapping-depth: 50 cm). Three areas of varying sedimentary character were recognised: clayey till, silty-sandy till and postglacial sand. The areas were digitalised using ArcGIS, and given a hydraulic conductivity-index of 0, 1 and 2 respectively. The indexing acknowledges the theoretical concept of increasing conductivity (and permeability) with increasing average grain-size and increasing degree of sorting (Fetter, 2001). However, it does not consider the potential for preferential flow which can be significant in clayey till deposits (Jarvis et al., 2007). Calculations of an average conductivity-index for each application were conducted through automated spatial analyses of the digitalised field and sedimentary maps in ArcGIS.

The average distance from site of application to well was calculated for all applications using ArcGIS and the digitalised field

Table 2
Results of statistical analyses for investigated parameters (two significant figures). Bootstrapped confidence intervals (CI) were compared at significance-level-intervals of 0.05 down to the 0.4-level. If two or more analyses of a specific parameter demonstrate a significant difference at a level of ⩽0.1 between the two groups, the parameter is considered to be statistically significant in terms of risk for pesticide contamination of groundwater. Applied dosage of active substance, amount of precipitation week before and month after application, log P_{ow}, HLC and soil DT_{50} are accordingly indicated to constitute explanatory ability for risk of pesticide contamination of groundwater in the studied catchment.

Parameter	Group 0		Group 1		*t*-Test for equality of means (*p*)	Independent-samples median test (*p*)	Bootstrapped level of significance; means (*p*) [CI group 0];[CI group 1]	Bootstrapped level of significance; medians (*p*) [CI group 0]; [CI group 1]
	Mean	Median	Mean	Median				
Dosage (g/ha) per app.	200	100	600	600	<0.0001	<0.0001	0.01 [160–250]; [520–670]	0.01 [94–130]; [400–700]
Tot. area (ha) treated per app.	1.1	0.47	1.3	0.68	0.24	0.019	>0.4	>0.4
Hydraulic conductivity-index per app.	1.0	1.0	1.0	1.0	0.37	0.53	>0.4	>0.4
Av. distance (m) from well per app.	250	250	230	250	0.34	0.51	>0.4	>0.4
Av. distance (m) to gw-surface per app.	2.9	3.0	3.0	3.0	0.13	0.86	0.4 [2.9–2.9]; [3.0–3.0]	>0.4
Rain (mm) per day of app.	1.5	0	0.92	0	0.25	0.96	>0.4	>0.4
Rain (mm) week before app.	10	6.5	8.9	3.5	0.20	0.006	>0.4	0.1 [5.3–8.5]; [2.9–4.8]
Rain (mm) week after app.	12	6.6	10	5.5	0.38	0.34	>0.4	>0.4
Rain (mm) month before app.	45	37	44	38	0.75	0.83	>0.4	>0.4
Rain (mm) month after app.	56	49	49	42	0.017	0.13	0.1 [52–59]; [45–51]	0.25 [46–52]; [39–46]
Rain-lag (days) if 0 rain on day of app.	3.9	2.0	3.9	2.0	0.98	0.72	>0.4	>0.4
W_s (mg/L)	8600	13	2.4E4	4100	0.38	0.08	>0.4	0.2 [4.3–450]; [590–18,000]
Log P_{ow}	2.9	3.7	−0.16	−0.26	0.007	0.18	0.05 [1.7–4.0]; [−1.5–1.2]	0.1 [1.7–4.5]; [−1.7–1.7]
V_p (mPa)	0.82	0.17	0.25	0.035	0.31	0.66	0.3 [0.43–1.2]; [0.12–0.41]	>0.4
HLC (Pa m^3/mol)	0.016	4.9E−4	2.9E−5	7.4E−6	0.28	0.024	0.01 [4.6E−4–0.048]; [1.9E−6–7.0E−5]	0.01 [3.3E−5–0.015]; [8.9E−11–8.2E−5]
Soil DT_{50}	58	35	21	15	0.073	0.18	0.1 [37–83]; [13–30]	0.40 [31–44]; [13–23]
K_{oc}	7.9E5	1400	760	73	0.45	0.18	0.25 [1500–1.6E6]; [240–1400]	0.35 [190–2000]; [76–160]

maps. The laser-derived national digital elevation model and the interpolated groundwater surface were used to calculate average depth to groundwater table at site of application.

2.2.3. Climate data

Precipitation data was collected from a weather station located *c.* 2 km NE of the wells. For all applications, calculations were made for amount of precipitation per application day, per week before and after application and per month before and after application. Further, a rain-lag index defined as amount of days until rainfall after application was calculated based on the assumption that if no rain falls on the day of application, the time-lag until rain will be negatively correlated to the risk for groundwater contamination. That is, the longer the time until rainfall, the lesser the risk for contamination.

2.3. Statistical analysis

In accordance with the general methodology outlined in the objective-section, compiled pesticide, site and climate data were sorted into two groups; group 0 containing all data concerning the non-detected substances, and group 1 containing all data concerning the detected substances. Data on pesticide use, site and climate conditions relating to applications of detected substances occurring *after* the last detection of the respective substances were discarded. I.e., for a given detection of a specific substance, only the applications of that substance occurring *before* that detection can have resulted in the detection. Pesticide, site and climate data relating to a total of 211 applications for the seven substances in group 1 could accordingly be compared to those of 233 applications for the twelve substances in group 0.

Group-wise means and medians were calculated for all investigated parameters, i.e. dosage per application, total treated area per application, average hydraulic conductivity per application, average distance from well per application, average depth to water table per application, amount of precipitation at day of application, amount of precipitation during the week and month before and after application, rain-lag (if 0 precipitation on day of application), W_s, log P_{ow}, V_p, HLC, DT_{50} and K_{oc}. The means for the two groups were then compared, parameter by parameter, using the independent samples *t*-test to test the null hypothesis that the means were equal. Further, group-wise medians were compared, and the null hypothesis that the medians were equal was tested using the independent-samples median test.

Next, confidence intervals for the respective data set means and medians were estimated and compared through bootstrapping (Efron, 1979), again parameter by parameter and group-wise. The bootstrap process was conducted in MATLAB R2010b and involved 1000 repetitions of random resampling with replacement of the original data sets. The resulting 1000 means and medians for each data set were used to better understand and constrain the distribution of the various sample populations, providing a more robust basis for comparison than only the basic sample summary statistics independently.

All results were analysed jointly, and when two or more analyses indicated a statistically significant difference between groups for a certain parameter at a level of $\leqslant 0.1$, the difference and hence the explanatory ability of that parameter was considered to be statistically validated.

3. Results

Table 2 lists the results of all statistical analyses.

3.1. Pesticide parameters

All statistical analyses demonstrate a significant difference in applied dosage between the non-detected and the detected substances. The detected substances are generally applied in higher dosages ($\bar{x} = 600$ g/ha,$M = 600$ g/ha) than the non-detected substances ($\bar{x} = 200$ g/ha,$M = 100$ g/ha). None of the other investigated parameters show a similar magnitude of difference.

For total area treated, the analyses demonstrate a tendency for the detected substances to have been applied over larger areas ($\bar{x} = 1.3$ ha/app,$M = 0.68$ ha/app) than the non-detected substances ($\bar{x} = 1.1$ ha/app,$M = 0.47$ ha/app). However, the difference is too small to yield any statistical significance with the exception of the independent-samples median test.

Three of the chemical parameters studied, $\log P_{ow}$, HLC and DT_{50}, demonstrate statistically significant differences in property values between the two groups. Overall, the non-detected substances exhibit larger values for all three properties than the detected substances. This suggests that the detected substances are more polar, less volatile and more degradable in soil than non-detected substances.

None of the other chemical parameters tested (W_s,V_p,K_{oc}) show significant differences between groups.

3.2. Site parameters

None of the investigated site parameters, i.e. hydraulic conductivity, depth to water table and distance from well to point of application, demonstrate any statistically significant difference between groups. Yielded sample populations are virtually identical.

3.3. Climate parameters

The statistical analyses of precipitation amounts in relation to pesticide application demonstrate a statistically significant difference between groups with regard to the amount of rain falling the week before application and the amount of rain falling the month after application. The amount of precipitation the week before application of detected substances is overall less ($\bar{x} = 8.9$ mm,$M = 3.5$ mm) than the amount of precipitation the week before application of non-detected substances ($\bar{x} = 10$ mm,$M = 6.5$ mm). Likewise, the amount of precipitation the month after application of detected substances is overall less ($\bar{x} = 49$ mm,$M = 42$ mm) than the amount of precipitation the month after application of non-detected substances ($\bar{x} = 56$ mm,$M = 49$ mm).

None of the other precipitation variables show any statistically significant differences between groups.

4. Discussion

4.1. Quality of the monitoring data set

The key data set forming the basis of this study is that of pesticide use as documented and reported by the local farmers to the Swedish University of Agricultural Sciences 1990–2010. This data set is inevitably subject to uncertainties as the documentation relies on the honesty of the farmers, and their willingness to collaborate. Overall the data is considered of high quality and probably unique in its kind. With one exception, all farmers within the catchment have been part of the research programme since its start, continuously documenting their pesticide use according to standardised protocols. Even illegal use of banned substances has been reported, and the same data set has further proven valuable for studies of pesticide contamination of surface water (Kreuger, 1998; Kreuger et al., 1999; Kreuger and Tornqvist, 1998).

Of greater concern is the groundwater monitoring data with regard to quantity. Even though samples are being and have been taken four times yearly, the amount of data generated is relatively limited. More frequent sampling would allow for a higher resolution-record which would constitute a better basis for analysis as the sample population would increase. However, in this respect, the methodological approach taken is considered robust as it takes into consideration four statistical analyses per investigated parameter; two of which explores and compares the distribution of the sample populations.

4.2. Results vs. hypotheses: explanatory ability and apparent influence of the investigated parameters

Of the seventeen parameters investigated, only six were able to discriminate between the detected and the non-detected substances; dosage, HLC, log P_{ow}, amount of rain the week before application, amount of rain the month after application, and DT_{50} (ranked according to explanatory ability). For the remaining eleven parameters; total treated area, average soil hydraulic conductivity and distance from well, average depth to water table, amount of precipitation at day of application, amount of precipitation the week after and the month before application, rain-lag, W_s, V_p and K_{oc}, differences between the two groups were too small to yield statistical significance. That is, they exhibited no satisfactory explanatory ability in terms of pesticide contamination of groundwater within the studied catchment.

4.2.1. Pesticide parameters

As hypothesised, the results suggest that the risk of groundwater contamination is fundamentally dependent upon dosage; the larger the amount of a specific pesticide applied over a certain area, the higher the risk. Whilst expected, as to our understanding, no previous studies have been able to so directly demonstrate this based on detailed long-term, non-experimental data of actual use (as opposed to estimations on use based on land-use or pesticide sales (e.g. Bartos et al., 2009; Kolpin et al., 1998)). It is clear that in order to assess the risk of groundwater contamination of pesticides, knowledge of actual pesticide loading is essential. Dosage alone exhibits the greatest explanatory ability of all studied parameters.

The size of the treated area alone is clearly not as good a discriminator. Although the results do show the expected tendency of detected substances to have been applied over relatively larger areas than the non-detected substances, the difference is not statistically significant. As the comparison is made based on 21 years of monitoring data of pesticide use within a single and relatively small rotational-cropping catchment that has roughly exhibited the same field-configuration throughout, spatial differences are likely averaged out over time. There is likely more potential for using total treated area as a descriptive variable for assessment of relative risk of pesticide contamination between or within catchments that exhibit widely varying land-use, as it would introduce more pronounced spatial disparity (e.g. Barbash and Resek, 1996; Sorensen et al., 1998).

The screening for chemical property-parameters indicates that HLC, log P_{ow} and DT_{50} independently all exhibit an explanatory ability in terms of pesticide contamination of groundwater. As for HLC and log P_{ow}, results confirm the original hypothesis suggesting that the less volatile and the more polar a substance, the more likely it is to contaminate groundwater. The findings of Altenburger et al. (1993) and Kreuger and Tornqvist (1998) of correlations between surface water pesticide detections and HLC and log P_{ow} respectively are hence suggested to apply also for groundwater environments. Accordingly, HLC and log P_{ow} appear as suitable chemical-property parameters for risk assessment of pesticide contamination of groundwater.

However, for DT_{50}, results indicate that detected substances would be more easily degradable than non-detected substances. This opposes the original hypothesis. There are, however, potential explanations for this outcome. Firstly, it could be a result of using tabular instead of site-specific values. If so, this indicates the necessity of the latter, and the inappropriateness of the former with regard to the applicability of DT_{50} as a descriptive variable for risk assessment of pesticide contamination of groundwater. Secondly, the outcome could be an indication of the presence of preferential flows, which would serve to increase the transport and contamination potential of otherwise rapidly degrading substances (Elliott et al., 2000; Jarvis, 2007). Theoretically, however, this would only serve to minimise the differences in contamination potential of substances with varying degrading potential and not to increase the risk of contamination of otherwise easily degradable substances. Thirdly, as suggested in a study by Kreuger and Tornqvist (1998), it could also be that the overall poorer ability of the detected substances to sorb to soil compensates their overall greater degradability. The fact that the detected substances overall exhibit a greater degradation-potential than the non-detected substances could potentially be explained by the fact that the detected substances overall exhibit a relatively poorer ability to sorb to soil which infers a relatively greater potential for leaching. This would then mean that K_{oc} is a more important parameter in terms of pesticide contamination risk of groundwater than DT_{50}. However, it should then be noted that the difference between the detected and the non-detected substances in terms of sorption coefficients is not statistically significant.

Why then, are neither W_s, V_p nor K_{oc}, able to discriminate between the detected and non-detected substances in this study? All three are chemical property-parameters commonly used for environmental pesticide risk assessment-purposes (e.g. Carsel et al., 1985; Guerbet and Jouany, 2002; Gutsche and Rossberg, 1997) and have, as noted, shown to exhibit a descriptive ability in terms of pesticide contamination of surface (V_p: Altenburger et al., 1993; Halfon et al., 1996) and groundwater (W_s, K_{oc}: e.g. Kolpin et al., 1998). Inevitably, using tabular values instead of site-specific values is an issue relevant also here and could be a reason for the lack of explanatory ability. Further, it is clear that the analyses conducted with regard to the chemical property-parameters are sensitive to extreme values due to the relatively low sample population. For example, quinmerac, which sorts under the non-detected substances, has an extremely high solubility value that disproportionately affects the summary statistics of its group. Upon removal of quinmerac from the analysis, the difference in W_s between the detected and non-detected substances becomes statistically significant thus supporting the findings of earlier studies (Kolpin et al., 1998). Quinmerac is by far the least used pesticide in the data set, i.e. it is only applied twice in the area throughout the entire monitoring program hence this might be considered a valid exclusion. It should also be noted that HLC – a combination of W_s and V_p – does exhibit an explanatory ability thereby indicating a certain degree of *joint* explanatory ability of W_s and V_p. In order for V_p to matter in terms of groundwater contamination potential, possibly, much greater values than those exhibited by the substances studied here are needed.

Lastly, preferential flow minimising differences in contamination potential of substances with varying chemical properties, could be the reason for the lack of explanatory ability of W_s, V_p or K_{oc} as was discussed in relation to DT_{50}.

4.2.2. Site parameters

For the investigated site parameters, group-wise means and medians are, as noted, virtually identical which suggest a lack of explanatory ability for those parameters. However, this does not necessarily imply that they are unsuitable as descriptive variables for estimation of risk of groundwater contamination. First, since the site parameters studied are dependent upon field-configuration, the concerns raised regarding the treated area-parameter are also relevant here. I.e., spatial differences can be expected to average out over time when the comparisons are made based on monitoring data from a single and relatively small rotational-cropping catchment that roughly exhibits the same field-configuration throughout the studied time period. The hydraulic conductivity of the treated sediments, the distance to well and to the groundwater surface from the point of application may likely constitute suitable descriptive variables in terms of relative risk assessment of groundwater contamination with regard to comparisons between catchments of varying physical and land-use properties, or between single pesticide applications (e.g. Barbash and Resek, 1996; Schlosser et al., 2002; Tiktak et al., 2004). However, this is likely not the case when attempting relative environmental risk assessment for the use of specific pesticides within relatively small areas dominated by rotational cropping practices such as the catchment studied. Consideration needs then (and overall) be given the long-term perspective.

Furthermore, it is plausible that at least part of the inability of the studied site parameters to discriminate between the detected and the non-detected substances could relate to the presence of fractures and preferential flow within the more clayey parts of the catchment. This would lessen the hypothesised differences in hydraulic conductivity with average grain-size within the catchment (Nilsson et al., 2001) and therefore also decrease the importance of distance to well and groundwater surface from application. Based on detailed investigations of modes of pesticide transport to groundwater in similar Danish environments (Jorgensen et al., 2002), this appears very reasonable. The marked difference in detected substances between close-lying well A and well B (Table 1), as well as the indicated mixing of water of residence times between at least <1 to $\geqslant$17 years in the studied well A, further corroborates the hypothesis that preferential flow constitutes an important pathway for pesticide transport to groundwater in the studied catchment.

4.2.3. Climate parameters

Of the precipitation-parameters studied, it is only the amount of rain falling the week before application and the amount of rain falling the month after application that demonstrated an ability to discriminate between the detected and the non-detected substances, indicating that the detected substances experience significantly less precipitation both before and after application than the non-detected substances. Although none of the other precipitation indices show any overall statistically significant differences between groups, the tendency for relatively less precipitation to occur both before and after the application of the detected substances is present throughout with the exception of the rain-lag index and the median amount of precipitation the month before application for which differences are minor. The outcome is against the original hypothesis assuming that relatively high amounts of rainfall before and after application should favour pesticide transport to

groundwater as potential recharge rates would increase. Why is the exact opposite relationship suggested here?

Firstly, it should be noted that in absolute terms, the statistically significant differences in precipitation amounts between the two groups of substances are only a few millimetres and perhaps an insufficient amount to matter in terms of actual transport potential. Also, sources of errors regarding the precipitation data exist since e.g. wind-loss and evapotranspiration has not been accounted for. Local measurements thereof do not exist. As a test, analyses were however carried out accounting for regional evapotranspiration-losses as suggested by back-modelled data from the regional hydrological HYPE-model (Lindström et al., 2010). The results smooth out group-wise differences throughout and no statistical significance remain. Since the evapotranspiration data is modelled over a 23 km^2 area with generalised input data, it however inherently also suffers from sources of error. This is demonstrated in Lindström et al. (2010), where the HYPE-modelled evapotranspiration managed to explain slightly more than half of measured evaporation at a specified test-site. Accordingly, it is not necessarily the case that the precipitation data adjusted for evapotranspiration is more correct than the unadjusted data. Hence, we think it is viable to discuss potential inferences of the statistically significant differences as indicated by the only site-measured data available. The concerns ought, however, to be acknowledged, and the inferences made should be considered with caution.

A simple yet plausible explanation for the indicated tendencies of the non-detected substances to overall experience relatively greater precipitation amounts is that the greater precipitation amounts serve to dilute the applied pesticide amounts and thereby also lessen potential groundwater concentrations. Whilst potentially explaining the presence or absence of pesticides as recorded in groundwater samples it is worth emphasising that dilution would not, however, serve to infer a lesser or greater groundwater contamination risk per se, only resulting concentrations. Whether or not the absolute difference in amounts of precipitation between the two groups is big enough to cause major differences in terms of these two processes is questionable. A higher-resolution pesticide monitoring record would be needed in order to resolve this, i.e. in order to study transport and resultant groundwater concentrations in relation to singe applications.

Other studies who have reported relatively less pesticide transport from wet than from dry soils have further suggested increased soil matrix incorporation and retainment in relatively wetter soils (Shipitalo et al., 1990), and increased top-soil cracking allowing for increased downward flow of water and associated solutes during relatively drier periods of time (Brown et al., 1995) as plausible explanations. It could also be the case that increased run-off in relation to greater precipitation amounts could result in decreased groundwater contamination potential.

4.3. Overall implications and issues

As stated in the introduction, the aim of this study was to evaluate the individual and relative ability of a range of pesticide, site and climate parameters commonly used as descriptive variables in existing pesticide environmental risk assessment schemes, to explain the presence or absence of pesticides in groundwater as suggested by long-term, non-experimental monitoring data (corrected for variable analytical boundary conditions). Although the data set has the potential for validation of specific risk models and indicators, we opted for an independent evaluation with a relatively broad approach aimed at providing an "observational data fundament" for prospective discussions on strengths and weaknesses of a number of existing models and indicators (e.g. SYNOPS: Gutsche and Rossberg, 1997; MACRO: Jarvis et al., 1991; EPRIP: Padovani et al., 2004; FOOT-CRS: Reichenberger et al., 2008; EYP: Reus and Leendertse, 2000; HD: Sorensen et al., 1998; SIRIS:Vaillant et al., 1995). Covering all variables and aspects of these models and indicators is beyond the scope of this study, as is therefore also judgments on their overall set-up and potential performance. Yet, some general inferences can be made.

Overall, it seems appropriate to suggest that applied pesticide dosage has the greatest explanatory potential in terms of pesticide presence or absence in groundwater. As such, with regard to related risk assessment, knowledge of pesticide loading is fundamental and ought to be treated as a key variable as is the case for most existing risk models and indicators (e.g. Gutsche and Rossberg, 1997; Padovani et al., 2004; Reus and Leendertse, 2000; Sorensen et al., 1998; Vaillant et al., 1995; van der Werf and Zimmer, 1998).

Chemical property-parameters of specific pesticides further undoubtedly exhibit explanatory ability in terms of pesticide contamination of groundwater. However this study highlights some important issues concerning their applicability for related risk assessment. As demonstrated, the use of tabular values always introduces analytical uncertainty potentially leading to misleading conclusions as discussed in relation to analysis outcomes regarding DT_{50}. If possible, site-specific values should therefore be used. In the absence of such values, which is often the case due to economical restrictions, this study indicates that tabular values of relatively less site-dependent parameters such as log P_{ow}, HLC and likely also W_s exhibit a relatively greater explanatory ability and as such are preferable for risk assessment. Similar inferences have been the starting-point of other studies taking things further and demonstrating, based on observations of pesticide occurrence or absence in groundwater, that there is even scope for applying empirical molecular descriptors obtainable without measurement error or site-specific variability as descriptive variables in related risk assessment models and indicators (e.g. Worrall and Kolpin, 2004; Worrall and Thomsen, 2004).

Further, V_p as an independent measure of groundwater contamination risk cannot be supported by this study. However, its joint influence together with W_s is demonstrated through the explanatory ability of HLC. This highlights the importance of estimating and appropriately addressing not only the independent but also the joint influence of chemical property-parameters. Especially, as discussed in relation to K_{oc} and $DT_{50,}$ since one property may affect the potential influence and hence explanatory ability of another.

Another point to be made is the importance of risk assessment of pesticide contamination of groundwater to be able to account for the occurrence of preferential flow. This is hardly news to the modelling-community (Dubus and Surdyk, 2006; Jarvis et al., 1991; Vanclooster et al., 2000). In terms of environmental pesticide risk indicator-schemes however, this appears to be a seldom considered parameter. If preferential flow is a plausible means of pesticide transport to the subsurface, then dominant mechanisms of overall transport of pesticides to groundwater may alter together with the explanatory ability of otherwise descriptive variables. Not accounting for preferential flow when this is a plausible means of transport into the groundwater environment may therefore deteriorate risk assessments made.

Precipitation is clearly an important variable to consider in terms of risk assessment of pesticide contamination of groundwater. However, it is evident that a simple, general conclusion on the strength and character of its influence is proving difficult to constrain as it may alter according to prevailing site conditions and local pesticide use patterns. Obviously, precipitation is necessary for infiltration, groundwater recharge and contamination to occur. Hence, on a large regional or national scale, relative precipitation amounts as a positively correlated measure of groundwater contamination risk might be valid (e.g. Tiktak et al., 2004). However,

on a more detailed note, it might be that dilution and run-off in relation to relatively larger amounts of precipitation, enhanced soil matrix incorporation and retainment in relatively wetter soils (Shipitalo et al., 1990), as well as increased top-soil cracking allowing for increased downward transport of water and associated solutes during relatively drier periods of time (Brown et al., 1995) need to be considered in terms of contamination potential.

5. Conclusions

The overall findings of this study demonstrate an ability of pesticide use and -chemistry parameters, as well as precipitation parameters, to discriminate between detected and non-detected substances as suggested by long-term, non-experimental monitoring data corrected for variable analytical boundary conditions. Spatially-dependent parameters such as total treated area, hydraulic conductivity of the treated sediments and distance to groundwater surface and well to point of application did not exhibit a similar ability. This might, however, be a result of spatial differences averaging out over time when the presence and absence data is a result of multiple applications from within a rotational-cropping catchment that has roughly exhibited the same field-configuration throughout the studied time interval. Specific conclusions are as follows:

- Of the studied parameters, applied dosage exhibits the overall greatest explanatory ability in terms of pesticide presence or absence in groundwater. Knowledge thereof consequently appears fundamental for related risk assessment and should be treated as a key parameter.
- Whilst valuable, chemical property-parameters of specific pesticides should be applied in groundwater contamination risk assessments with care. If site-specific values are unattainable, tabular values of log P_{ow}, HLC and W_s appear to exhibit a greater explanatory ability than those of K_{oc} and DT_{50}. Potential effects of one chemical property-parameter on the explanatory ability another further need to be considered.
- Whilst a prerequisite for estimation of overall contamination potential, in more detail, relatively more precipitation both before and after pesticide application may serve to decrease resultant groundwater concentrations and thus likelihood for detection. Dilution, increased run-off, decreased soil matrix retainment (Shipitalo et al., 1990) and decreased top-soil cracking (Brown et al., 1995) are potential explanations. More and higher-resolution studies of the effects of precipitation on pesticide contamination potential of groundwater in different environments and in relation to actual pesticide use are needed in order to be able to better and more accurately account for the resultant effects in terms of risk assessment of pesticide contamination of groundwater on different scales.
- If preferential flow is a plausible means of transport of pesticides into the groundwater environment, this is a parameter that needs to be considered for risk assessment purposes as it may alter the strength and character of the explanatory ability of otherwise descriptive variables.

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Paper II

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Modelling pesticide transport in a shallow groundwater catchment using tritium and helium-3 data

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ABSTRACT

Using tritium and helium-3 data for calibration, a 2-D transport model was set up to explain the occurrence of bentazone, dichlorprop, glyphosate, isoproturon, MCPA and metamitron in a small groundwater catchment in southern Sweden. The model was parameterised with site-specific degradation and sorption data to enable transport simulations. Local climatological data and a 21-year record of agricultural pesticide use within the study area were used as boundary conditions. Model output was evaluated against a 7-year long pesticide monitoring data-series from two monitoring wells within the study area. The model successfully predicts observed breakthrough of bentazone, dichlorprop, isoproturon and MCPA. However, it fails to simulate observed occurrences of glyphosate and metamitron. Glyphosate and metamitron exhibit relatively high sorption potential, and their occurrence is suggested to be the result of non-equilibrium preferential flow paths which the model cannot reproduce due the conceptualisation of the system as homogenous and isotropic. The results indicate a promising methodological approach applicable to groundwater contamination risk assessment, and demonstrate the potential for transport model calibration by means of tritium and helium-3 data. Main constraints of the study relate to the relatively simple system conceptualisation, indicating a need for further consideration of physical and chemical heterogeneity.

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1. Introduction

Past and present widespread use of pesticides constitutes a threat to surface- and groundwater resources. Pesticides are developed to protect crops from disease and harmful organisms, but can affect non-target organisms and cause both acute and long-term effects in the environment.

The fate and transport of pesticides to and within groundwater is governed by a myriad of more or less interdependent factors including land-use, chemical properties of the pesticides, climatological and hydrological conditions and soil/sediment biogeochemistry (such as pH, organic carbon content and microbial biomass and activity) and structure (Barbash and Resek, 1996; Arias-Estevez et al., 2008). Sorption and degradation processes, and their governing modelling parameters, should preferably be parameterised with site-specific data to account for local conditions (e.g. Dann et al., 2006). In addition, it is common knowledge that physical and chemical heterogeneity are characteristic features of geological formations and that they may have a large impact on the fate of contaminants. Local parameter variability can be considerable in both time and space (Sudicky, 1986; Mallants et al., 1996; Walker et al., 2001; Rodriguez-Cruz et al., 2006; Ghafoor et al., 2011). The particular influence of any underlying chemical heterogeneity (e.g. pH, mineral surfaces) is difficult to identify because its manifestation depends on the hydraulic and physical properties of the system as well as the chemical components involved (Valocchi, 1989; Tompson et al., 1996). The physical heterogeneity of the soil results in a non-uniform flow field, e.g. through preferential transport pathways (Jarvis, 2007) which have been shown to be a prominent characteristic of glacial clay tills (Klint and Gravesen, 1999; Jorgensen et al., 2002).

Multiple transport models have been developed in order to simulate and evaluate risks of pesticide contamination of groundwater (see reviews by Dubus and Surdyk, 2006; Kohne et al., 2009). Most of these are small-scale, one-dimensional models focusing on the upper parts of the system to around 1 m depth (Azimonti, 2006). With few exceptions (e.g. Herbst et al., 2005; Stuart et al., 2006), comprehensive and integrated efforts to model pesticide transport throughout both the vadose and the saturated zones at the full catchment scale are rare.

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Throughout the past few decades, environmental tracers and the associated concept of groundwater age have come to make their way into the general hydrogeological modelling community (Newman et al., 2010). At any given point within a groundwater system, the groundwater age of a water sample represents an integrated value of the subsurface travel times of the water molecules of that sample, dictated by advection, hydrodynamic dispersion and diffusion (Goode, 1996; Portniaguine and Solomon, 1998). An estimation of the travel times through measurements of concentrations of specific environmental tracers with known system input-functions can therefore provide a powerful and independent parameterisation tool for associated flow and transport models (Solomon et al., 1992; Portniaguine and Solomon, 1998; Bethke and Johnson, 2002; Ginn et al., 2009; Zuber et al., 2011), and has further shown potential for facilitating contaminant fate analyses for specific groundwater systems (Bohlke and Denver, 1995).

One of the more commonly applied environmental tracers for superficial aquifers is tritium (^{3}H). The atmospheric concentration of tritium rose substantially as an effect of nuclear bomb tests in the 1950s and early 1960s. This resulted in a corresponding global groundwater recharge signal which together with information on concentrations of the ^{3}H decay product helium-3 (^{3}He) can be used to deduct information on groundwater travel times (Solomon and Cook, 2000).

Up to this date, only a few studies have been reported where environmental tracers have been used for evaluating the occurrence of pesticides in groundwater (Tesoriero et al., 2007; Warner and Morrow, 2007; Gourcy et al., 2009; Farlin et al., 2013). To our knowledge, no studies have previously been reported where environmental tracers have been used for the parameterisation of numerical groundwater-pesticide flow- and transport models.

1.1. Objective

In this study, we seek to investigate the fate and explain the occurrence of six pesticides (bentazone, dichlorprop, glyphosate, isoproturon, MCPA and metamitron) in a groundwater system in southern Sweden, taking long-term recharge and pesticide use into consideration on full catchment scale. The pesticides were chosen due to their observed occurrence within a local groundwater monitoring program, thus enabling model verification.

We argue that the concentrations of ^{3}H and ^{3}He at a given point within a groundwater system carry information about the physical processes that acted on the water present at that point since its entry into the specific groundwater system. As atmospheric ^{3}H concentrations have levelled off since the 1980s, ^{3}He concentrations may be considered particularly valuable in order to assess travel times in relatively young groundwater systems. We hypothesise that a groundwater transport model calibrated against observed ^{3}H and ^{3}He concentrations, and parameterised with site-specific chemical pesticide properties, constitute a powerful basis for explaining the occurrence of pesticides at a given sampling location.

A unique, 21-year long pesticide application record was used in this study together with experimental data on sorption and degradation parameters.

2. Data and study area

The study area constitutes an approximately 11 ha groundwater catchment located in the very south of Sweden (Fig. 1). About 90% of the catchment is cultivated with agricultural crops, and information on pesticide activities including timing, intensity and location of pesticide applications has been collected from the farmers operating in the catchment since 1990. Since 2004, pesticide occurrence in the shallow groundwater environment of the catchment has been monitored through quarterly sampling of two neighbouring wells located *c.* 5 m apart, both with filter depths of *c.* 2.9–3.5 m. ^{3}H–^{3}He analyses indicate radiometric groundwater ages of *c.* 10.1 and 11.7 years for these wells respectively. Specific pesticide detections in one of these wells suggest mixing of water of ages between at least <1 and ⩾17 years (Akesson et al., 2013). Results from the groundwater monitoring program have been published since its start in annual reports that also detail specific sampling protocols and analytical procedures (CKB, 2012).

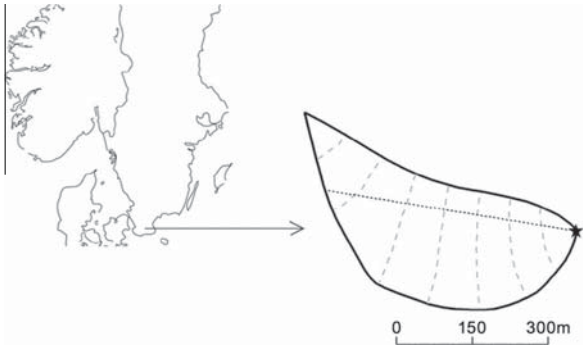

Fig. 1. Regional location (left) and plan-view (right) of the study area. The star marks the location of the monitoring wells, and the solid black line delineates the boundary of their potential recharge area (i.e. the study area). The dashed grey lines are hydraulic head equipotential lines (1 m spacing) indicating the direction of groundwater flow towards the wells. The dotted black line denotes the spatial (plan-view) extent of the modelled transect.

The region is characterised by (up to 100 m) thick, gently undulating, glacially derived Quaternary deposits characterised by a typically complex stratigraphy of tills and more sorted interbedded sediment formations (Daniel, 1992). The climate is maritime with a mean annual temperature of about 7 °C and an average annual precipitation of roughly 700 mm. The growing season typically equals about 220 days between May and November (Kreuger, 1998).

3. Methodology

3.1. Model parameterisation: conceptualisation of the study area and definition of initial and boundary conditions

A conceptual model of the study area was constructed based on published literature from the area (Daniel, 1992; Svensson, 1999; Andersson, 2010), well-logs from the monitoring wells (unpublished), and through geophysical surveying. The latter included (i) a continuous vertical electrical sounding (CVES) survey yielding electrical resistivity variability over *c.* 5–70 m depth along a vertical 2-D NE–SW-trending transect (Fig. 2a) and (ii) an electromagnetic (EM) survey along multiple vertical W–E-trending transects yielding information of apparent electrical resistivity variability from the ground surface down to practical penetration depths of *c.* 5 and 10 m for two different frequencies respectively (Fig. 2b and c). Subsurface electrical resistivity is a function of e.g. mineralogy, clay- and water-content and its variability can therefore be used to interpret subsurface stratigraphy. The geophysical surveys indicate the presence of a largely continuous, higher-resistivity formation interbedded between less resistive materials. Together with literature and well-log data, this higher-resistivity formation is interpreted as a sorted sandy deposit, interbedded between two clayey till units of which the upper is likely significantly fractured.

At the location of the monitoring wells, the border between the upper till and the sand is located at *c.* 3 m below ground surface

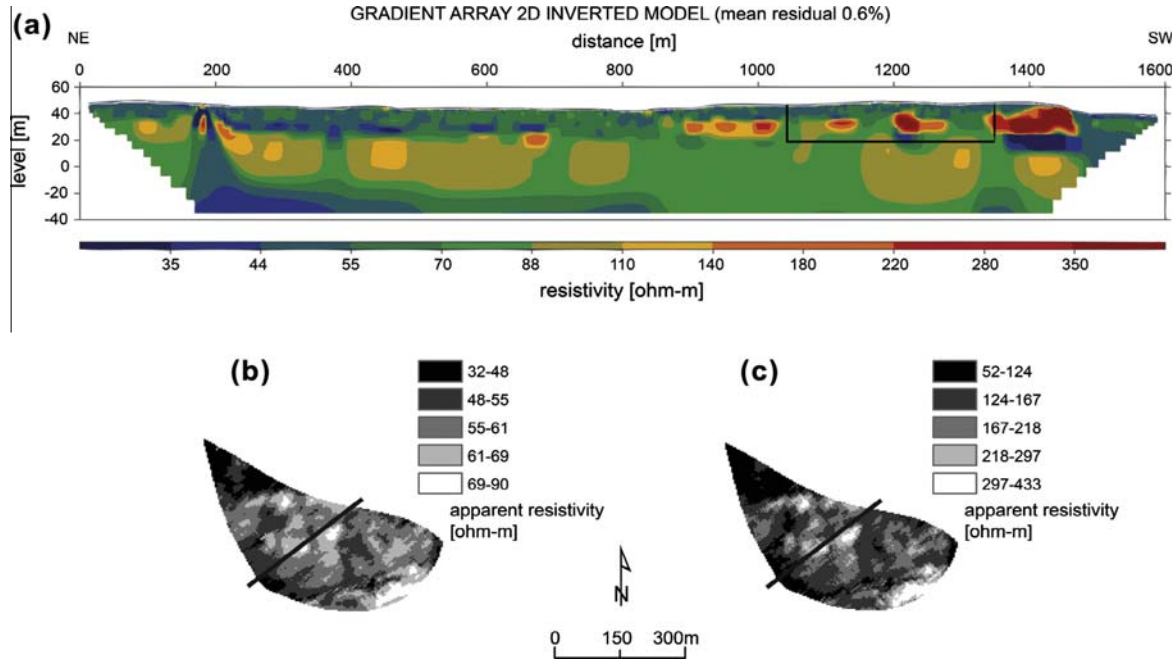

Fig. 2. (a) Inverted CVES results demonstrating electrical resistivity variability over a 1600 m long vertical 2-D transect passing through the studied catchment (boxed). (b) Results of the 27 kHz-EM-survey showing apparent resistivity variability over 0 to *c.* 5 m depth throughout the study area. The black line denotes the position of the CVES-transect. (c) Results of the 16 kHz-EM-survey showing apparent resistivity variability over 0 to *c.* 10 m depth throughout the study area. The geophysical surveys indicate the presence of a higher-resistivity formation interbedded between two lower-resistivity formations. The higher-resistivity formation is present already at 0–5 m depth as indicated by (b). The higher-resistivity formation is interpreted as a sorted, sandy deposit. The lower-resistivity formations are interpreted as clay tills.

(mbgs). This was held as a good approximation for its average position throughout the entire catchment based on the higher-frequency EM-survey which indicates the presence of the higher-resistivity formation between 0 and 5 m depth. In order to realistically reflect expected differing biogeochemical properties of a cultivated vs. a non-cultivated soil, the upper till was divided into two layers (cultivated: 0–0.4 mbgs, non-cultivated: 0.4–3 mbgs). The border between the lower till and the sand was estimated at *c.* 20 mbgs as suggested by the CVES-survey.

In accordance with the conceptual model, a numerical vertical 2-D model (Fig. 3) was set up in HYDRUS-2D (Simunek et al., 1999), which is a finite element software package for simulating water and solute movement in two- and three-dimensional variably saturated media. The program numerically solves the Richards' equation for saturated–unsaturated water flow and Fickian-based advection–dispersion equations for solute transport. The transport equations also include simple reactions between the solid and liquid phases and degradation reactions. The unsaturated soil hydraulic properties are described using analytical functions, here the function by van Genuchten (1980) is used. A finite element grid of 13,637 triangular elements and 8143 nodes was generated by the HYDRUS/MeshGen2D.

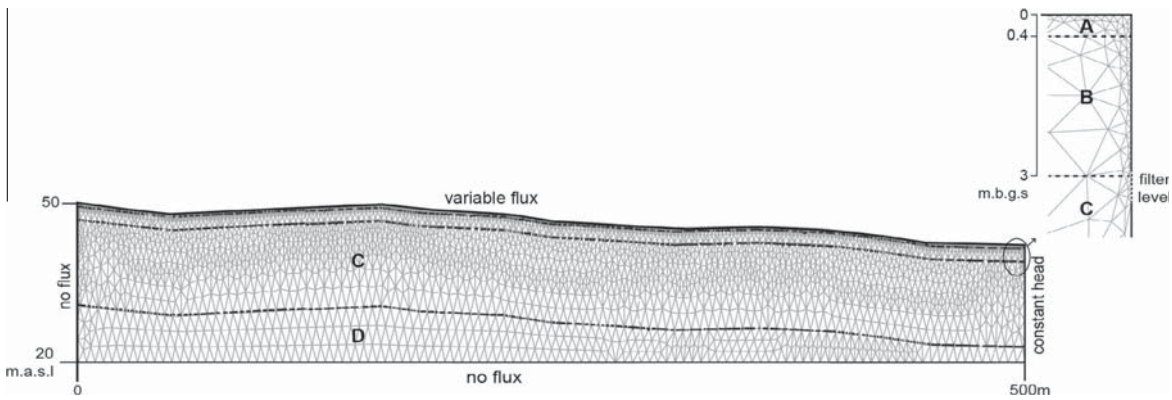

Fig. 3. Conceptual 2-D vertical model of the study area as set up in HYDRUS. The figure shows the grid mesh (grey), stratigraphic boundaries (darker), layers (letters), location and filter depth of the monitoring wells (also magnified), and boundary types (no flux/constant head/variable flux). Note that the vertical scale is exaggerated.

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The hydraulic conductivity of the upper till (layers A and B, Fig. 3) was set at $1 * 10^{-7}$ m/s based on values reported from detailed studies of expected similar till-formations (Jorgensen et al., 1998; Nilsson et al., 2001; Harrar et al., 2007). The hydraulic conductivity of the sand (layer C, Fig. 3) was set at $1 * 10^{-5}$ m/s based on experimental studies and slug tests of a likely analogous deposit located *c.* 1 km from the specific study area (Andersson, 2010). The hydraulic conductivity of the lower till (layer D, Fig. 3) was set to a standard value of $1 * 10^{-10}$ m/s (Fredericia, 1990). Default model values for comparable standard HYDRUS-soils were applied for the remaining hydraulic parameters (Table 1).

The bottom and the western boundaries of the model domain were assigned no-flux boundary conditions. The western boundary is considered a groundwater divide based on hydraulic head measurements. The eastern boundary, at the well location, was set as a constant head boundary with a hydrostatic pressure distribution from the lowest located nodal point on the boundary, extending all through the unsaturated zone, as determined from field measurements of groundwater heads. The *initial* pressure distribution for the full model domain, defining starting conditions only, was specified using the same approach. The upper boundary of the model domain was given variable flux boundary conditions, defined by precipitation and evapotranspiration flux as derived through local fine-tuning of the Swedish Meteorological and Hydrological Institute's regional S-HYPE model (Lindström et al., 2010), which was calibrated against two decades of local run-off measurements.

Although pesticide detections have been shown to vary between the two adjacent monitoring wells, our 2-D conceptualisation of groundwater system does not allow for their spatial differentiation and so here, they are represented by one spatial point.

3.2. Model calibration and determination of groundwater age

For calibration, input and transport of ^{3}H and ^{3}He into and throughout the groundwater system was modelled for the period 1950–2010. A local ^{3}H-input function was generated through linear interpolation between continuous monthly measurements from Ottawa and irregular measurements from Odense, Taastrup (Denmark) and Skurup (Sweden; IAEA, 2012). Average yearly concentrations for the modelled period were calculated through monthly recharge-weighting against the derived hydrologic data. As the HYPE-model only covers the period 1960–2010, average values of precipitation and evaporation flux for the standard climatic averaging period 1961–1990 was used to calculate recharge for the period 1950–1959.

Subsurface transport was modelled under the radioactive decay of ^{3}H into tritiogenic ^{3}He according to a first-order process with a half-life of 12.43 years (Solomon and Cook, 2000). Input of ^{3}He was set to begin at the groundwater surface as a product of ^{3}H-decay. The atmospheric component of ^{3}He was thus neglected.

The model was manually calibrated against measured concentrations of ^{3}H and ^{3}He in the two monitoring wells to obtain the lowest root mean squared error (RMSE). Only the porosity of the upper till (layers A and B, Fig. 3) was used as a calibration parameter.

After calibration, the average groundwater age and the associated groundwater age distribution at the sampling location was estimated through modelling constant-flux infiltration of a conservative tracer over the entire model domain. The recharge component was set at 200 mm/year based on the 1950–2010 average. The model was run five initial years with recharge as the only input, after which a conservative tracer of constant concentration was set to infiltrate continuously together with recharge for another 61 years corresponding to the length of the ^{3}H model-run applied for calibration. The average groundwater age and its distribution were calculated as the first and second moments of arrival times of the solute front at the location of the well screen.

Table 1
Applied hydraulic model parameter values. Φ_r and Φ_s denote the residual and saturated water contents respectively, α and n are empirical coefficients affecting the shape of the governing hydraulic functions, K_s (m/s) is the saturated hydraulic conductivity, and l is a pore-connectivity parameter (van Genuchten, 1980). Uncalibrated (default) Φ_s-values are bracketed and italicised.

Layers	Φ_r	Φ_s	α	n	K_s	l
A	0.095	0.22 (*0.41*)	1.9	1.31	10^{-7}	0.5
B	0.095	0.22 (*0.41*)	1.9	1.31	10^{-7}	0.5
C	0.045	0.43	14.5	2.68	10^{-5}	0.5
D	0.095	0.41	1.9	1.31	10^{-10}	0.5

3.3. Experimental determination of sorption and degradation properties of the pesticides

Linear sorption coefficients and first-order degradation rate coefficients for the six pesticides in soil samples representative of layers A, B and C were determined in laboratory experiments using ^{14}C-labelled pesticides together with groundwater and soil material from the site.

3.3.1. Pesticides

The following radiolabelled pesticides were used in sorption and degradation experiments: [carbonyl-^{14}C]-bentazone (99.6% radiochemical purity), [ring-U-^{14}C]-dichlorprop (96.9% radiochemical purity), [P-methylene-^{14}C]-glyphosate (95.0% radiochemical purity), [carboxyl-^{14}C]-MCPA (96.0% radiochemical purity), [phenyl ring-U-^{14}C]-metamitron (99.1% radiochemical purity), and [ring-U-^{14}C]-isoproturon (97.7% radiochemical purity). All ^{14}C-substances were obtained from Izotop, Budapest, Hungary.

3.3.2. Soil and groundwater

Groundwater representative of an aqueous phase in layers A and B was collected from the two monitoring wells. Groundwater representative of layer C was collected from a monitoring well SE of the modelled area with a filter depth ranging from 18 to 22 mbgs located within the deposit mentioned in Section 3.1. All wells were purged before sampling. Waters were collected in glass bottles without any headspace and refrigerated until use within 7 days.

Representative soil samples for layers A and B were collected at a depth of 0.2–0.3 mbgs and 0.5–0.9 mbgs respectively, at a site about 100 m from the monitoring wells (within the modelled catchment). The soil samples were transferred to clean polyethene bags and stored at 4 °C until use within 2 weeks. Soil samples representative of layer C were collected from three different depths (8.0–8.5, 10.5–11.0 and 16.5–17.0 mbgs) during the drilling of the deeper monitoring well. The samples were stored slightly aerated at 4 °C for several months before use within the experiments.

Selected soil and groundwater data are shown in Table 2.

3.3.3. Sorption experiment (modified ASTM D4646-03)

The three samples from different depths in layer C were mixed in equal proportions to give a representative sample C. All soil samples A to C were dried and sieved (<2 mm) before use. For each combination of pesticide and soil material, five different concentrations of radiolabelled pesticide ranging from *c.* 1 to 100 μg/l were equilibrated on an end-over-end shaker with 2.5 g of soil and 5.0 ml of groundwater in Teflon test tubes at 4 °C for 24 h. After centrifugation at 20 000 rpm for 30 min, the ^{14}C-activity in three ml of the supernatant was analysed by scintillation (Tri-Carb 2810 TR, Perkin Elmer) after addition of 10 ml of Ultima Gold

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Table 2
Selected soil and groundwater data.

Parameter	Soil A	Soil B	Soil C	Water A	Water B	Water C
pH	6.8	7.2	7.9	8.1	8.1	8.2
TOC (%DW for soil, mg/l for water)	2.35	0.816	<0.350	35.7	63.2	35.9[a]
Conductivity (mS/m)	–	–	–	96	83	40
Dissolved oxygen (%)	–	–	–	n.a.	n.a.	0
Redox potential (mV)	–	–	–	n.a.	n.a.	−200

[a] Remarkably high value for (relatively) deep groundwater. Earlier analyses of the same water have yielded concentrations of *c.* 3 mg/l indicating variability and/or measurement error.

scintillation cocktail (Perkin Elmer). Controls without soil were included in the study to calculate the loss due to sorption on the test tube surface. No significant adsorption to the test tubes occurred. The equilibrium sorption isotherms of the pesticides for the different soils were described with a linear sorption isotherm: $S = K_d * C$, where S is the concentration of pesticide in the solid phase (μg/g), C is the pesticide concentration in the aqueous phase (μg/ml) and (ml/g) the linear sorption coefficient.

3.3.4. Degradation experiment

The soils were prepared as described for the sorption experiment. For each combination of pesticide and soil material, mineralisation was tracked over 98 days in 350 ml septum-sealed glass vials using 30 g of soil and 300 ml of groundwater with an initial headspace of about 30 ml. After initial shaking of the samples by hand, the bottles were left to equilibrate for 24 h before the labelled pesticide (dissolved in ethanol) was added to give an initial concentration of 100 μg/l. During the incubation the vials were kept in the dark at 7 °C to mimic the field conditions, and sampled at five occasions by withdrawing 5 ml of the aqueous phase with a syringe after the vials had been shaken and the sediment settled. The aqueous sample was transferred to a 20 ml scintillation vial, in which a 4 ml plastic scintillation vial containing 1 ml of 1 M KOH was placed together with a drop (50 μl) of 10 M NaOH. The 20 ml vial was closed after the addition of 1 ml of 2 M HCl, and the released $^{14}CO_2$ was collected for 48 h. Four ml of (Ultima Gold) scintillation cocktail (Perkin–Elmer) was added to the KOH solution and the sample ^{14}C-activity counted in a liquid scintillator (Tri-Carb 2810 TR, Perkin Elmer). First-order degradation rate constants were estimated by linear regression (using the entire data set) from the equation: $\ln C_t = \ln C_0 - k * t$, where C_0 is the initial pesticide concentration (μg/l), C_t is the pesticide concentration at time t (μg/l; day) and k is the first-order rate constant (day^{-1}). C_t was estimated from the difference between initial pesticide concentration and the cumulative $^{14}CO_2$ evolved at time t.

3.4. Pesticide transport modelling

For the pesticide transport modelling, monthly hydrological- and pesticide application data for the period 1990–2010 were used.

The catchment area was discretised into three subareas (Fig. 4), each corresponding to a given length of the variable flux-boundary (Fig. 3) in order to account for the distributed application of pesticides over the model domain. The discretisation was made in rough accordance with agricultural field boundaries, and with regard to the direction of groundwater flow (thus also with regard to the model transect).

Information on the timing, location and intensity of applications of the six pesticides for the considered period was collected from a database hosted by the Swedish University of Agricultural Sciences as part of the monitoring program. Each application was assigned to one of the flux-boundaries according to application location,

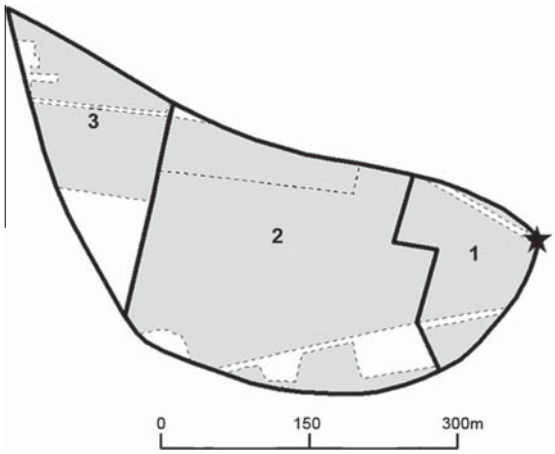

Fig. 4. Catchment discretisation. For the pesticide modelling, the catchment area was discretised into three subareas (1–3) each corresponding to a particular segment of the variable flux boundary of the model. Grey areas separated by dashed lines delineate field locations (for an example-year).

and assumed to infiltrate over that entire boundary with a concentration c calculated according to the formula: $c = m_i/(A_d * R_d)$, where A_d is the area of the associated subarea (m^2) and R_d is the amount of recharge (mm) of the first subsequent month with positive effective precipitation. m_i is the total amount of active substance made available for infiltration through application and calculated as: $m_i = m_a * e^{-k * \Delta t}$, where m_a is the total amount of pesticide applied, k is the experimentally yielded degradation constant derived for layer A (day^{-1}), and Δt is the time (day) elapsed between the application of a certain pesticide and the next subsequent positive effective precipitation event.

The HYDRUS model was parameterised with the experimentally derived sorption coefficients and degradation rate constants for layers A, B and C. The experimental data for layer C were applied also for layer D (which was not subject to any sorption/degradation analyses).

Pesticide degradation rates may vary considerably in both time and space (Albrechtsen et al., 2001; Charnay et al., 2005). The experimentally derived degradation rate constants are therefore considered to be subject of significant uncertainty and variability. Hence, a sensitivity analysis with regard to the degradation rate of the three least adsorptive substances was conducted through a systematic variation of the degradation constants for layer A and (for one substance) layer B within intervals defined by the experimentally derived value and common literature values. To better investigate and visualise the effects of the tweaking of the degradation rate constant, the sensitivity analyses runs were extended a further 60 years in time. After the year 2010, no further pesticide

infiltration was simulated, and average values for (water) recharge were applied.

The experimentally derived sorption coefficients are also subject to uncertainty, but since the sorption coefficient only affects the arrival time of the breakthrough curve by predictably scaling the retardation factor, no sensitivity analysis with regard to the sorption coefficients was undertaken.

4. Results

4.1. Model calibration and groundwater age modelling

A satisfactory fit between modelled and measured ^{3}H and ^{3}He concentrations was attained by decreasing the porosity of the upper clay till from the default-value of 0.41 to an effective value of 0.22 (Table 3). This calibrated effective porosity value lies close to porosity values reported from studies of fractured clay tills in Denmark (Jorgensen et al., 1998, 2002; Klint and Gravesen, 1999), and is suggested to confirm the expected heterogeneity and associated preferential flow in the upper till.

The calibrated model yields an average groundwater age of 10.9 years at the filter level (layer C) of the wells, corresponding closely to the radiometric ^{3}H–^{3}He ages. The modelled groundwater age distribution (Fig. 5) is, however, considerable and suggests significant contributions of both younger and older water. Almost 50% of the water is suggested to reach the well within 5 years of infiltration, yet, contributions of waters with travel times of up to *c.* 40 years are clearly significant. The modelled groundwater age distribution can be assumed to represent a minimum distribution of travel times since exchange with stagnant zones (Zuber et al., 2011), physical heterogeneity and the resulting spatially variable flow field is not considered in the transport model.

4.2. Sorption and degradation properties of the pesticides

The results of the sorption and degradation analyses are listed in Table 4.

Equilibrium sorption of the six pesticides for the different soils were well-described by a linear isotherm within the concentration range used (correlation coefficient r is generally $\geqslant 0.99$). As expected, sorption varied both between pesticides within the same soil, and between soils for the same pesticide. Linear sorption coefficients, K_d, were highest for glyphosate and lowest for bentazone (Table 4). For all six substances, sorption was highest for the cultivated, surficial soil (layer A) with an overall tendency for decreasing sorption with increasing depth.

First-order degradation rate coefficients, k, were generally very low for all pesticides in all types of soils, and varied between 10^{-4} and 10^{-6} day^{-1} corresponding to half-lives of about 4–200 years (Table 4). These low rates of degradation are expected for the relatively deeper soil layers having a low carbon content, and consequently low biomass existing at relatively cold, oxygen-deprived conditions. For surficial soils, however, reported values of degradation rate constants for the studied substances are typically 2–5 orders of magnitude higher than those derived here (PPDB, 2013).

Table 3
Measured and modelled ^{3}H and ^{3}He concentrations (TU), and groundwater ages (years). The root mean squared error (RMSE) of the measured vs. modelled ^{3}H and ^{3}He concentrations equals 0.89. For ^{3}H and ^{3}He sampling and analysis specifications, see Akesson et al. (2013).

	^{3}H	^{3}He	Age
Measured well A	8.21	6.32	10.1
Measured well B	8.66	8.04	11.7
Modelled	8.99	7.89	10.9

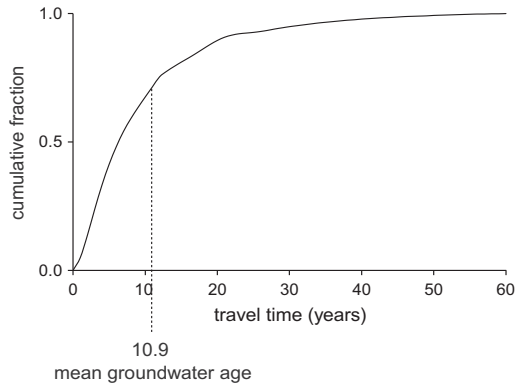

Fig. 5. The modelled distribution of travel times. The modelled mean groundwater age is represented by the curve's first-order moment.

Table 4
Experimentally derived linear sorption coefficients (K_d; ml/g) and degradation rate constants (k; day^{-1}).

Substance	Layer	K_d	k
Bentazone	A	0.073	$1.2 \cdot 10^{-5}$
	B	0.022	$1.0 \cdot 10^{-5}$
	C	0.041	$1.3 \cdot 10^{-5}$
Dichlorprop	A	0.29	$8.0 \cdot 10^{-6}$
	B	0.047	$6.4 \cdot 10^{-6}$
	C	0.056	$9.7 \cdot 10^{-6}$
Glyphosate	A	140	$4.2 \cdot 10^{-4}$
	B	58	$2.2 \cdot 10^{-4}$
	C	25	$5.3 \cdot 10^{-4}$
Isoproturon	A	1.7	$8.9 \cdot 10^{-6}$
	B	0.42	$5.7 \cdot 10^{-6}$
	C	0.89	$8.7 \cdot 10^{-6}$
MCPA	A	0.53	$2.0 \cdot 10^{-4}$
	B	0.18	$1.2 \cdot 10^{-4}$
	C	0.15	$4.0 \cdot 10^{-4}$
Metamitron	A	4.0	$1.7 \cdot 10^{-5}$
	B	2.0	$2.1 \cdot 10^{-5}$
	C	1.2	$2.7 \cdot 10^{-5}$

One plausible explanation is differences in experimental set-up, where we aimed to resemble aquifer conditions whereas most other studies are conducted at superficial conditions.

4.3. Pesticide transport modelling

Fig. 6a–f illustrates the results of the pesticide transport model runs. The modelled pesticide concentration in the well at filter depth (right y-axis) is plotted together with cumulative infiltration concentrations for the three different subareas (left y-axis), performed analyses and associated detection limits (right y-axis) and observed detections (right y-axis). Year 0 equals the start of the monitoring program, i.e. 1990. Particle tracking simulations showed that only subarea 1 contributes to the recharge of the wells. In reality however, it cannot be ruled out that there is a possibility for contributions from subarea 2 or 3 due to physical heterogeneities and anisotropy in the subsurface not captured by the model. Therefore, the applications of pesticides from all subareas are displayed in the figures to allow for alternative and wider interpretations in relation to observed detections.

A clear distinction can be made between substances exhibiting relatively high sorption coefficients (glyphosate and metamitron),

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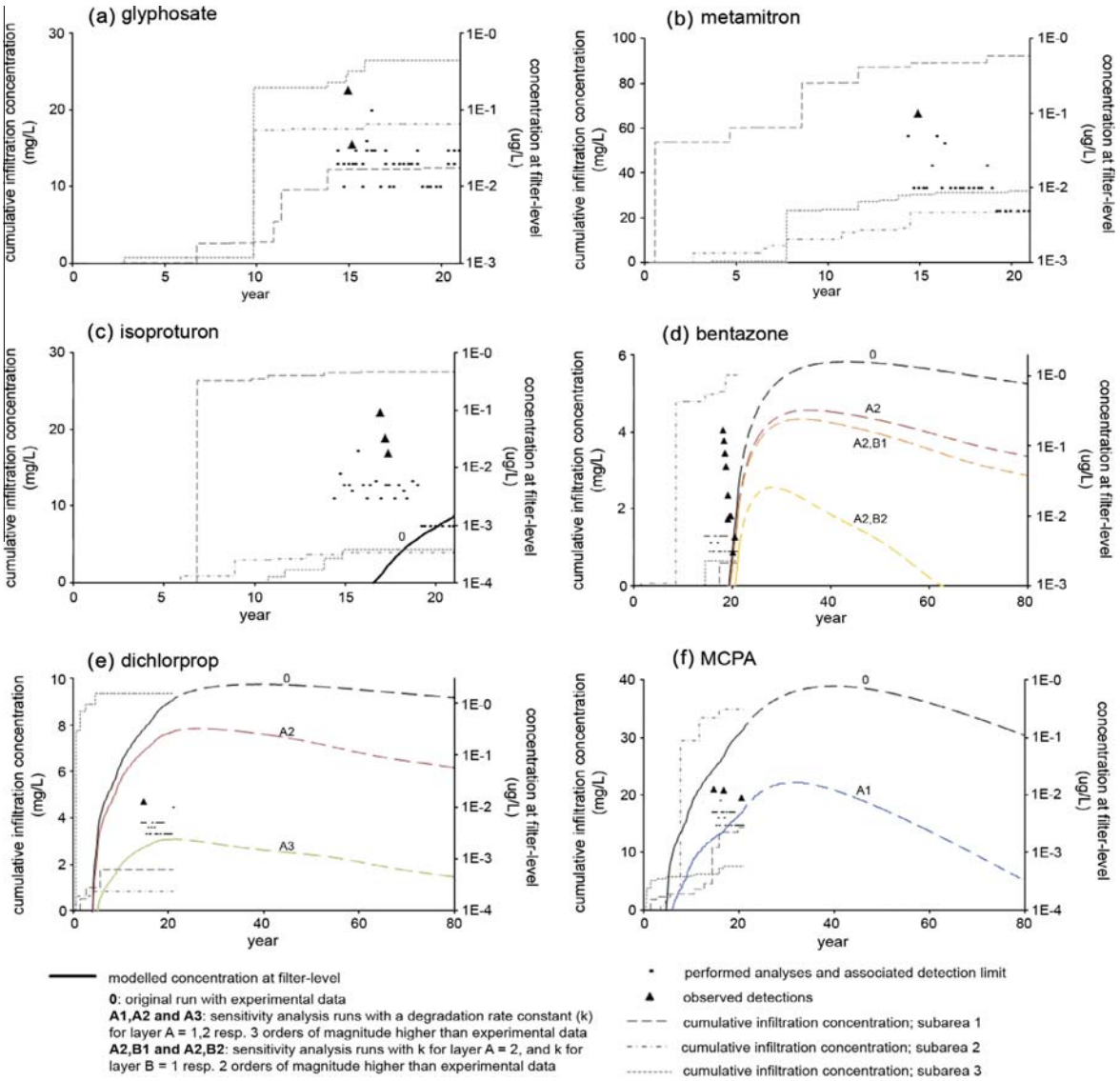

Fig. 6. Modelled pesticide concentrations at filter level in relation to accumulated infiltration concentrations for the three different subareas, performed analyses and associated detection limits, and observed detections. Year 0 equals the start of the monitoring program, i.e. 1990. Bentazone, dichlorprop and MCPA transport is modelled over a period of 80 years in order to clarify effects of the sensitivity analyses concerning adopted degradation rate constants, conducted for these three substances only. Note that information on recharge and pesticide application only exist for the period 1990–2010, hence the dashed lines after year 21.

and those with relatively lower sorption coefficients (bentazone, dichlorprop, isoproturon and MCPA). Derived sorption coefficients for glyphosate and metamitron do not allow for any significant subsurface transport of these substances within the modelled time frame. Still, they have been detected in the monitoring wells (Fig. 6a and b). This might relate to pre-1990 applications, but may also be a result of non-equilibrium transport along preferential flow paths.

For the less strongly sorbing pesticides bentazone, dichlorprop, isoproturon and MCPA, the model output show breakthrough comparable with the observed detections (Fig. 6c–f). The arrival times of isoproturon and bentazone is in accordance with the field data (Fig. 6c and d). For dichlorprop and MCPA (Fig. 6e and f), the model seems to predict a somewhat early arrival, however, whether this is truly the case cannot be validated due to the lack of earlier monitoring data. Modelled concentrations of bentazone, dichlorprop and MCPA deviate less than one order of magnitude relative to those observed. For isoproturon, that deviation is in the range of two orders of magnitude.

Conducted sensitivity analyses confirm the major importance of adopted degradation rate constants, both in terms of pulse shape (breakthrough, decay and extent), and pulse magnitude.

5. Discussion

Transport modelling based on (i) model calibration with respect to measured groundwater ^{3}H and ^{3}He concentrations and (ii)

parameterisation with experimental data of site-specific sorption isotherms and degradation rate constants seems a promising approach to explain the occurrence of pesticides in groundwater. With a basic understanding of the subsurface stratigraphy, only one parameter (the effective porosity) had to be tweaked during calibration in order to (i) simulate the ^{3}H and ^{3}He observations in the wells and (ii) satisfactorily predict breakthrough of pesticides with a relatively low sorption potential. This indicates methodological potential and further serves to confirm the applicability of ^{3}H and ^{3}He measurements in terms of flow and transport model parameterisation. As for the pesticide transport modelling, the deviations in model output vs. field observations can mainly be attributed to (i) the conceptualisation of the aquifer, (ii) the boundary conditions, and (iii) the chemical model parameters.

The adopted methodological approach and the resulting transport model successfully links application to occurrence and satisfactorily predicts the arrival times of bentazone, dichlorprop, isoproturon, and MCPA. However, model results for glyphosate and metamitron deviate significantly from field observations. The observed occurrence of glyphosate and metamitron relative to the model results is likely to indicate rapid, non-equilibrium transport along preferential flow paths governed by heterogenic soil structures and hydrological conditions which would require a detailed characterisation and finer spatial representation to be appropriately reflected (Jarvis, 2007). This is supported by findings in previous studies showing that retardation of substances in preferential transport pathways, such as macropores and fractures, is generally less than in the soil matrix. This phenomena has been observed both in laboratory and field experiments (e.g. Jarvis, 2007 and references therein) and is commonly attributed to small available surface areas in the preferential pathways (compared to the soil matrix), matrix diffusion, kinetically controlled sorption reactions and colloidal and particle transport. Model simulations have shown that the influence of pesticide properties are minor if preferential transport is occurring. Thus, the effect of preferential transport becomes relatively larger for moderate-strongly sorbing compounds compared to low sorbing compounds (Larsson and Jarvis, 2000).

The groundwater system is conceptualised as homogenous and isotropic and the physical heterogeneity of the soil is only indirectly taken into account in the calibration procedure by treating the porosity of the upper clay till as an effective parameter. By decreasing the porosity values of the clay till the overall hydraulic effect of preferential transport pathways on the system is simulated. However, the reactive transport in the field is an inherent nonlinear system and by not directly considering the field scale heterogeneity, important information is lost. Therefore, our transport model cannot simulate the resulting effects of such features. Prominent features of the system such as the biochemical heterogeneity, reflected in spatially varying sorption and degradation rate constants (Walker et al., 2001; Coquet, 2003; Rodriguez-Cruz et al., 2006; Ghafoor et al., 2011), and variations over time in relation to season, cropping and tillage (Gaston et al., 1996; Larsbo et al., 2009; Hussain et al., 2013) are neither accounted for, but may play a significant role.

Despite the constraints in the conceptual model, we see major potential of the overall methodological approach not only for explaining and predicting pesticide occurrence in groundwater, but also in general for groundwater contamination risk analysis purposes. Considering the physical and biogeochemical heterogeneity, the most pressing need in further studies is that of a refined system conceptualisation via further characterisation through, e.g. direct push technologies in combination with geophysical methods. Further work would also benefit from an enhanced model calibration procedure via additional ^{3}H and ^{3}He measurements from multiple locations within the study area. Adopted boundary conditions could additionally be elaborated to include surficial processes such as plant uptake and volatilisation which would affect infiltrating concentrations.

Lastly, this study demonstrates the importance of a long-term and larger-scale perspective when seeking explanations of the occurrence of pesticides in groundwater environments. Although observed occurrences overall mainly seem to stem from applications occurring relatively close in time and space, temporally distant applications are the only viable explanations for the detection of e.g. dichlorprop as it was last applied *c.* 10 years before that detection.

6. Conclusions

Pesticide transport modelling based on ^{3}H–^{3}He calibration of the hydrogeological transport model and site-specific sorption isotherms and degradation rate parameters, appears to be a promising approach for explaining the occurrence of pesticides in groundwater and for risk assessment of groundwater contamination.

Using this methodological approach, we can successfully link recorded application to observed occurrence of bentazone, dichlorprop, isoproturon and MCPA. However, our conceptual model and its mathematical representation is too simplistic (i.e. homogenous) to accurately simulate the transport of the relatively strongly sorbing substances glyphosate and metamitron, whose observed occurrence is expected to be the results of physical heterogeneity and non-equilibrium transport along preferential flow paths.

In order to improve model performance, a more detailed conceptual model accurately reflecting physical and chemical heterogeneity is needed.

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Paper III

On the scope and management of pesticide pollution of Swedish groundwater resources: the Scanian example

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Abstract

Twenty-three south-Swedish public supply wells were studied to assess pesticide pollution of regional groundwater resources. Relations between pesticide occurrence, hydrogeology and land use were analyzed using Kohonen's Self-Organizing Maps approach. Pesticides are demonstrated to be substantially present throughout the studied aquifers with detections in 18 wells. Concentrations above the drinking water threshold are confirmed for nine wells. Observations indicate considerable urban influence, and lagged effects of past, less restricted use. Modern, oxic waters from shallow, unconfined unconsolidated or fracture-type bedrock aquifers appear particularly vulnerable. Least affected waters appear primarily associated with deeper wells, anoxic conditions and more confined sediment aquifers lacking urban influence. Comprehensive, standardized monitoring of pesticides in groundwater need to be implemented nationwide to enable sound assessments of pollution status and trends, and to develop sound groundwater management plans in accordance with the Water Framework Directive. Further, existing water protection areas and associated regulations need to be reassessed.

Keywords: *pesticides, groundwater, Sweden, water framework directive, monitoring, self-organizing maps.*

1. Introduction

Pesticides occur in groundwater worldwide. As groundwater tends to cycle slowly with limited potential for natural attenuation, and because pesticide use predictably will remain as global population and food demand increases, this occurrence is likely to persist well into the foreseeable future. It is a troublesome prospect, as pesticides can be toxic, and as groundwater supports ecosystems and food production worldwide, and accounts for about half of the world's potable water supply (WWAP 2009).

Upon use, pesticide transport into and throughout groundwater is essentially a matter of solute migration, transformation and phase partitioning as governed by interactions between pesticide chemistry, soil biogeochemistry and hydrogeological conditions dictating surface-groundwater connections, transport rates and groundwater biogeochemistry (Barbash and Resek 1996). These are variable factors, as is pesticide use, and hence it is generally difficult to infer pollution status and extrapolate primary concerns from one setting to another. Regional studies of pesticide occurrence in groundwater are accordingly necessary to assess site-specific aquifer vulnerability and pollution risks, and to develop sound groundwater management plans. For EU member states, such assessments are mandatory under the Water Framework Directive (WFD; European Union 2000).

Comprehensive screening studies for pesticide occurrence in groundwater have been undertaken in many regions, e.g. the US (Gilliom 2007), Denmark (Thorling et al. 2012), New Zealand (Close and Skinner 2012), Norway (Haarstad and Ludvigsen 2007) and the Netherlands (Schipper et al. 2008). Between as well as within these studies, over time and space, measured pesticide concentrations can range orders of magnitudes, from the just detectable (currently ng L^{-1}) to several µg L^{-1}. Total detection frequencies (DFs) commonly range between 25-50%, whereas DFs for concentrations at or above general environmental or health threshold criteria (e.g., the EC drinking water limit of 0.1 µg L^{-1}) tend to be considerably lower, around 5-10% (Schipper et al. 2008; Thorling et al. 2012). Differences in pollution extent are often noted between different types of wells, e.g., Haarstad and Ludvigsen (2007) showed considerably lower DFs for pesticides in public supply wells (PSWs), than in farm- and shallow monitoring wells. Commonly detected substances include triazines such as atrazine and metabolites thereof (Gilliom 2007; Close and Skinner 2012; Thorling et al. 2012), and, at least in Europe, 2,6-dichlorobenzamide (BAM; a metabolite of dichlobenil), aminomethylphosphonic acid (AMPA; metabolite of glyphosate) and bentazone (Schipper et al. 2008; Thorling et al. 2012). Both total and substance-specific DFs tend to be much dependent

upon land use, national pesticide regulations, and subsurface stratigraphy. In addition to agricultural pesticide use, urban weed control has also proven a much potent pollution contributor (Gilliom 2007; Malaguerra 2012). Permeable and unconfined porous groundwater environments are typically found to be particularly vulnerable, however, for oxidizable pesticides, these types of environments have been found to provide better protection against leaching than semi-/confining layers (Malaguerra et al. 2012). Local comparisons of pesticide pollution between completely different types of hydrogeological settings, i.e. sediment vs. bedrock aquifers, are rare. Sampling depth, as a proxy of lag time between infiltration and observation, is commonly found to be inversely correlated to pesticide DF (e.g. Thorling et al. 2012). Relationships between estimates of this lag time through environmental tracer-based groundwater dating (Newman et al. 2010) and pesticide DF are generally more dubious, which is likely due to the fact that such ages, without detailed scrutiny, may be little representative of actual pesticide travel times, as that would require (i) negligible groundwater mixing and (ii) identical tracer and pesticide transport. Nevertheless, groundwater dating via e.g. tritium analysis (Solomon and Cook 2000) has proven useful for understanding general patterns of pesticide occurrence and absence (Kolpin et al. 1995), as it enables discrimination of predominantly modern groundwater which infiltrated before the onset of widespread pesticide use (post mid-1900 recharge), from predominantly old (pre mid-1900 recharge) groundwater.

In Sweden, about 50% of drinking water is provided by groundwater (half artificially produced via surface water infiltration). The same figure is valid for the southernmost province of Sweden, Scania (Skåne), an intensively cultivated region for which groundwater resources have been known to suffer from pesticide pollution since long (Maxe et al. 2003). Recently, results from a regional screening study (n = 141) initiated by the County Administrative Board of Scania proved pesticide occurrence in about half of the aquifers investigated, spurring questions as to potential trends and causal conditions, and highlighting a need for further investigations (Virgin 2012). However, to thoroughly assess the character and cause of pesticide pollution of Scanian, and effectively overall Swedish groundwater resources, is challenging due to a nationwide lack of comprehensive and consistent long-term groundwater monitoring data relevant to anthropogenic pollution concerns. This monitoring deficiency has previously been highlighted in relation to nutrient and pollutant loads in coastal areas (Destouni et al. 2008), with regard to heavy metal drainage from mining areas (Baresel and Destouni 2009), and most recently in view of general groundwater status and quality assessment in accordance with national environmental objectives and the WFD (European Commission 2012; SEPA 2013). Basically, the national groundwater monitoring network as set up and maintained by the national groundwater authority (SGU; the Geological Survey of Sweden), focuses on areas with minimal human impact to constrain background/reference conditions and does not involve pesticide analyses (Nordberg and Persson 1974; SGU 2013a). Quality control of groundwater used for drinking water is only mandated at the end-user, after potential treatment (SLVSF 2001:30). The only regular groundwater sampling of pesticides undertaken in Sweden is that of the national agricultural-aquatic environmental pesticide monitoring program of the Swedish University of Agricultural Sciences (SLU), encompassing sixteen shallow wells in four agricultural reference areas. The deficiency of comprehensive monitoring potentially hinders not just sound quality and status assessment, but also the construction, implementation and evaluation of remedial efforts where such are needed.

The aim of this study is to explore the character and causal conditions of pesticide pollution of Scanian groundwater resources, and from that address related management and policy issues applying to the wider, national and general scale. We conduct an in-depth analysis of 23 municipal PSWs, studying their pesticide content as far back in time as possible, and in relation to land use and hydrogeological contexts. Specifically, the following questions are addressed:

- What is the extent and character of pesticide pollution of the investigated groundwater systems as inferred via the PSWs?
- Are there indications of differences in the degree and character of pollution between different types of aquifers and if so, what is generating these differences?
- Are existing monitoring practices sufficient to provide a sound knowledge basis for status- and trend analysis? If not, how can they be improved?

It may be argued that PSWs can be unrepresentative of regional pollution status, as groundwater resources associated with such wells tend to be subject to safeguarding via local regulations on use of potentially hazardous substances and so reflect comparatively less polluted settings. Further, PSWs are generally not ideal for deciphering trends as they generally extract groundwater over long filter screens and hence mix and integrate waters of varying origin and quality. Nevertheless, most existing analytical data on pesticide occurrence in groundwater in Sweden stem from such wells, and hence it is both inevitable and relevant to use and study this data for the specified purpose.

2. Materials and methods

2.1 Study area

Scania encompasses roughly 11 000 km^2 at the tip of the Scandinavian Peninsula (55°48'N, 13°37'E; Fig. 1), and experiences Sweden's mildest climate with an average annual temperature of about 8°C. Precipitation varies between 500 and 1000 mm yr^{-1}, depending on coastal proximity and topography (SMHI 2014). Effective precipitation varies between 150 and 500 mm yr^{-1} (Gustafsson 2005).

Compared to other parts of Sweden, Scania comprises relatively little forested land, and is rather characterized by extensive and highly fertile lands, which cover almost half of the region's total area, and maintains much of Sweden's agricultural and horticultural production (SCB 2010). Main crops include cereals, oilseeds, sugar beet, potatoes and fodder. Pesticide use is common practice throughout the agricultural sector, with a current annual active pesticide ingredient application intensity of about 1.5 kg ha^{-1} dominated by herbicides, fungicides and insecticides (in that order, Sandberg 2011). Commonly applied active ingredients throughout past decades include bentazone, isoproturon, metazachlor, simazine and phenoxy acids such as 2,4-dichlorophenoxyacetic acid (2,4-D), dichlorprop, mecoprop and MCPA. Urban developments cover about 10% of the total area.

Scania's geological record spans thousands of millions of years and comprises Precambrian crystalline bedrock, various younger sedimentary rocks, and sediment deposits associated with previously glaciated settings. Accordingly, groundwater reservoirs are manifold, spanning fractured gneisses and sandstones, dual-porosity lime- and sandstones, and a wealth of sorted porous unconsolidated sediment deposits of, primarily, glaciofluvial provenance (Fig. 1; Gustafsson 2005).

Basically, Scania comprises most types of land uses and hydrogeological settings comprised within Sweden as a whole, and is accordingly an interesting area for assessments of both regional and potential national pollution patterns and concerns.

2.2 Data collection

The studied PSWs (Fig. 1, Table 1) were chosen after consultation with all Scanian municipalities, the Regional Pesticide Database (RPD), and the Groundwater Bodies and Water Sources Database (DGV). Selection criteria included overall spatial and hydrogeological distribution, availability of past pesticide analysis records, well metadata availability, and production importance and access. Approval from well

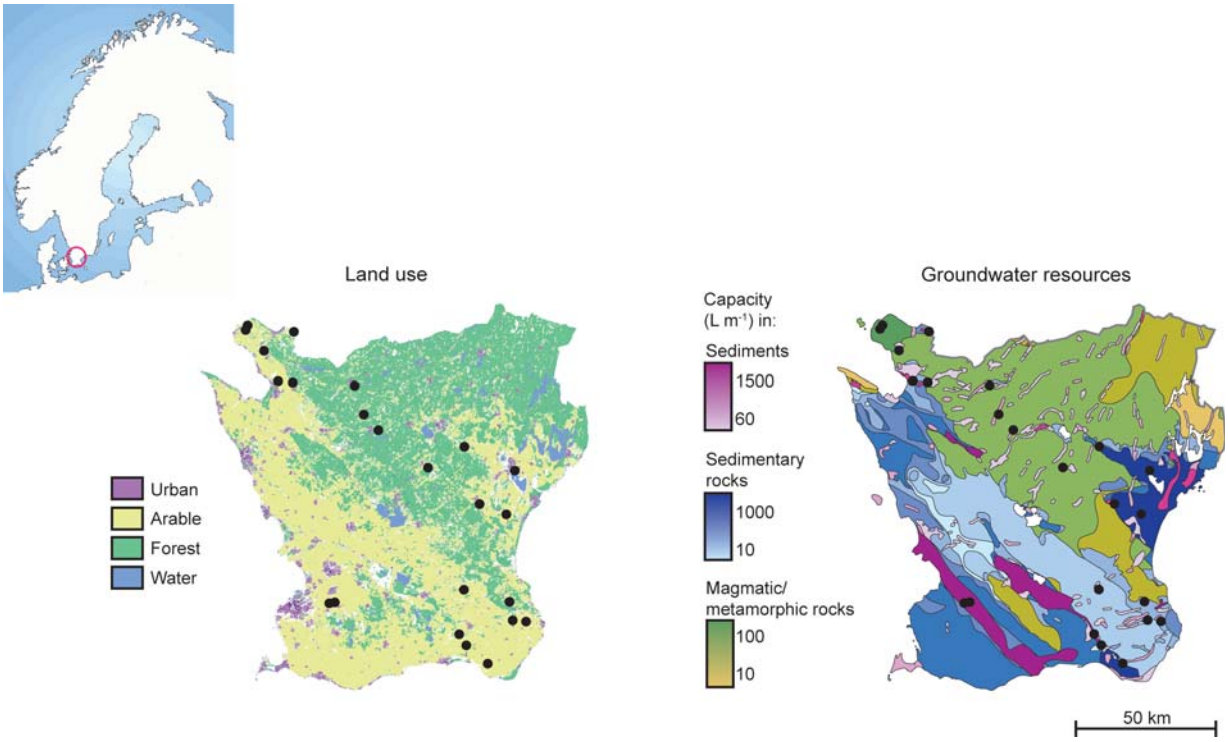

Figure 1. Location of study area (encircled in the top left-hand corner), associated land use (© Lantmäteriet [I2012/00927]) and overview of regional groundwater resources (after Wastenson et al. 1999). Black dots mark the locations of the studied PSWs, for which exact locations cannot be revealed due to non-disclosure agreements with the owners.

Table 1. Characteristics of studied wells: filter depth (in meters below ground surface; m b.g.s.), water age group, redox state, aquifer confinement and type, land use and whether (Y) or not (N) the specific aquifer is associated with a water protection area.

Well	Filter depth	Water age group	Redox state[a]	Aquifer confinement	Aquifer type	Land use	Water protection area (since)
1	*2-54*	*Modern*	*Oxic*	*Unconfined*	*Fracture*	*Arable, urban*	*Y (1974)*
2	*15-114*	*Modern*	*Suboxic*	*Unconfined*	*Fracture*	*Arable, urban*	*Y (1974)*
3	*18-22*	*Modern*	*Oxic*	*Unconfined*	*Pore*	*Arable, urban*	*Y (1974)*
4	*28-40*	*Modern*	*Oxic*	*Leaky*	*Pore*	*Arable, urban*	*Y (1978)*
5	*6-11*	*Modern*	*Oxic*	*Unconfined*	*Pore*	*-*	*Y (1976)*
6	*11-23*	*Modern*	*Oxic*	*Leaky*	*Pore*	*Arable, urban*	*Y (2000)*
7	*74-75*	*Old*	*Anoxic*	*Confined*	*Pore*	*Arable, urban*	*Y (1977)*
8	*71-72*	*Old*	*Anoxic*	*Confined*	*Pore*	*Arable, urban*	*Y (1977)*
9	*13-17*	*Modern*	*Anoxic*	*Unconfined*	*Pore*	*Arable*	*N*
10	*9-12*	*Modern*	*Suboxic*	*Unconfined*	*Pore*	*Arable, urban*	*Y (1977)*
11	*9-12*	*Modern*	*Suboxic*	*Unconfined*	*Pore*	*Arable, urban*	*Y (2008)*
12	*5-90*	*Modern*	*Suboxic*	*Unconfined*	*Fracture*	*Arable, urban*	*Y (1980)*
13	*6-10*	*Modern*	*Oxic*	*Unconfined*	*Pore*	*Arable, urban*	*Y (1973)*
14	*29-43*	*Modern*	*Anoxic*	*Leaky*	*Pore*	*Arable*	*Y (1987)*
15	*29-39*	*Modern*	*Anoxic*	*Leaky*	*Pore*	*Arable*	*Y (1990)*
16	*20-27*	*Modern*	*Oxic*	*Unconfined*	*Dual porosity*	*Arable*	*Y (2008)*
17	*14-20*	*Modern*	*Oxic*	*Leaky*	*Pore*	*Arable, urban*	*Y (1971)*
18	*49-69*	*Old*	*Oxic*	*Leaky*	*Dual porosity*	*Arable, urban*	*Y (1980)*
19	*47-96*	*Old*	*Oxic*	*Leaky*	*Dual porosity*	*Arable, urban*	*Y (1973)*
20	*14-19*	*Modern*	*Oxic*	*Unconfined*	*Pore*	*Urban*	*Y (1970)*
21	*9-12*	*Modern*	*Suboxic*	*Unconfined*	*Pore*	*Arable*	*Y (1977)*
22	*?-57*	*Modern*	*Anoxic*	*Unconfined*	*Fracture*	*Arable, urban*	*Y (1991)*
23	*7-10*	*Modern*	*Oxic*	*Unconfined*	*Pore*	*Arable, urban*	*Y (1989)*

[a] *Classification according to SGU (2013b). Oxic = class 1, suboxic = class 2, anoxic = class 3.*

owners was a further requirement.

Results of past pesticide analyses were compiled from drinking water producers, municipalities, the County Administrative Board, relevant commercial laboratories, RPD and DGV, and digitized together with information on analyzed substances and corresponding reporting limits per analysis. The hydrogeological context of each well was determined through studies of geological maps and hydrogeological reports provided by the SGU and the respective local authorities. All wells were classified in terms of aquifer confinement (unconfined, leaky or confined) and type (pore, fracture or dual porosity). The presence or absence of arable land and urban areas within the expected recharge area was determined through the Swedish mapping, cadastral and land registration authority's terrain map (1:50 000). Whether or not the studied aquifers were associated with water protection areas, i.e. judicial protection areas for which environmentally hazardous activities (generally including pesticide use) are controlled to safeguard potable water supply, was determined via the Swedish Environmental Protection Agency's VicNatur-database.

In January 2012, all wells were sampled for metals, nutrients, pesticides, and tritium-helium-3 (^3H-^3He) for groundwater age assessment. Permanently installed pumping-equipment was used throughout. As active production wells, all had been thoroughly flushed upon sampling. Nevertheless, samples were first retrieved upon field parameter (pH, conductivity, DO) stabilization, as measured in a flow-through cell connected to an Aquameter AP-800.

Metal and nutrient samples were collected from the tap in plastic bottles provided by the analytical laboratory ALS Scandinavia. Samples were chilled upon retrieval. Fe, Mn and SO_4 concentrations were used for redox classification according to SGU (2013b).

Pesticide samples were collected from the tap in glass bottles provided by the Organic Risk Pollutants Laboratory, SLU. Samples were chilled upon retrieval, immediately forwarded to the laboratory and screened for 101 types of pesticide residues (including metabolites) using LC-MS/MS according to Jansson and Kreuger (2010). The median limit of detection (LOD) was 0.003 µg L^{-1}, and the median limit of quantification (LOQ) was 0.01 µg L^{-1}.

Samples for ^3H analysis were collected in duplicate 1 l glass bottles, and samples for He isotope analysis in duplicate clamped-off copper tubes connected to the well

tap through a closed hose system. Subsequent analyses were carried out at the Bremen Mass Spectrometric Facility according to Sültenfuss et al. (2009). Sampled waters were classified as either (predominantly) modern or old according to ^{3}H concentrations, and after testing for large-scale mixing via comparing initial-^{3}H to historical records of ^{3}H local concentrations in precipitation during year-of-recharge as suggested by the radiometric ^{3}H-^{3}He age (Aeschbach-Hertig et al. 1998). ^{3}H-^{3}He analysis results are specified in Table S1.

2.3 Self-Organizing Maps

Data patterns and variable relations were assessed using Kohonen's Self-Organizing Maps (SOM) approach (Kohonen 2001). The SOM is an unsupervised, exploratory neural network analysis approach that finds natural populations and patterns within multi-dimensional data sets and allows relationships to be displayed visually. Input samples are compared based on variable properties, then sorted and mapped onto a set of color-coded 2D graphs (maps) so that similar samples are mapped onto "nodes" with similar characteristics, and nodes with similar characteristics are positioned close to each other on the "map". Both sample and variable similarity and patterns can be assessed through these maps, by the naked eye, and by traditional statistical processing procedures, such as correlation, principal component and clustering analysis. The SOM handles categorical, continuous and missing data, and non-linear relationships between variables. The SOM approach is therefore suited for the analysis of often complex and disparate geoscientific data (Fraser and Dickson 2007). The potential of the technique for hydrologic system analysis has been reviewed and concluded upon by Kalteh et al. (2008), with recent examples including, e.g., investigations of heavy rainfall patterns (Nishiyama et al. 2007) and groundwater exploration (Friedel et al. 2012).

Table 2. Variables included in the SOM analysis. DF 0.01 = detection frequency for the 0.01 µg L^{-1}-threshold data set. DF 0.1 = detection frequency for the 0.1 µg L^{-1}-threshold data set (see "Materials and methods").

Category	Variable	Type	
Pesticide pollution degree	*DF 0.01*	*Continuous*	*(%)*
	DF 0.1	*Continuous*	*(%)*
Well filter	*Top*	*Continuous*	*(m b.g.s.)*
	Bottom	*Continuous*	*(m b.g.s.)*
Water age group	*Modern*	*Categorical*	*(1/0)*
Redox state	*Oxic*	*Categorical*	*(1/0)*
	Suboxic	*Categorical*	*(1/0)*
	Anoxic	*Categorical*	*(1/0)*
Aquifer confinement	*Unconfined*	*Categorical*	*(1/0)*
	Leaky	*Categorical*	*(1/0)*
	Confined	*Categorical*	*(1/0)*
Aquifer type	*Pore*	*Categorical*	*(1/0)*
	Fracture	*Categorical*	*(1/0)*
	Dual porosity	*Categorical*	*(1/0)*
Land use	*NO_3[a]*	*Continuous*	*(mg L^{-1})*
	Urban	*Categorical*	*(1/0)*

[a] Arable land is present in all but two of the expected recharge areas inferring a limited basis for statistical analysis of influence based on presence/absence data. Instead, NO_3 concentrations were used as a proxy for agricultural land use.

The SiroSOM software developed by the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO) was used for the analysis. Included variables are listed in table 2. After various trials, we found that 1365 iterations (65 for rough training, 1300 for fine training) onto a 9*6 sized (54 nodes) toroidal map, with a hexagonal lattice, was optimum for displaying the variability within the data set. Interpretation was augmented by the use of correlation and principal component analyses of the SOM output.

Due to inconsistencies between compiled pesticide analyses, for the SOM only, collected pesticide data were adjusted with respect to analytical boundary conditions to enable comparative studies between wells. The adjustment was conducted with regard to analyzed substances so that the data set would only include analyses covering the same residues, and reporting limits so that the meaning of detection would be equal for all included analyses. Adjustments were implemented to preserve as much of the data as possible, resulting in an adjusted data set restricted to analyses covering the twenty most commonly analyzed substances (Table S2). A common detection threshold of 0.01 µg L^{-1} was applied so that for substances with a lower specified analytical detection limit, concentrations less than 0.01 µg L^{-1} were set to 0 (see e.g. Kolpin et al. 1995). A 2nd adjusted pesticide data set was created with a common detection threshold set to the environmental threshold criteria of the EC; 0.1 µg L^{-1} (European Union 2006). Subsequently, DFs were calculated per well for both data sets.

3. Results

3.1 Pesticide occurrence and analysis records

Altogether, 255 pesticide analyses were collated from the various sources noted in the methodology section, including our own analyses. Considerable discrepancies between the different data sources were noted both in terms of data quantity and type of data stored. No single source provided a complete record. The frequency and analytical scope of conducted analyses varied both

between wells and for single wells over time. The overall sampling frequency per well averaged just below 1 yr^{-1}, but varied between 0.4 and 2.4. The number of analyzed substances ranged between 1 and 122 per analysis. LOQ-variation spanned between 0.001 and 5 µg L^{-1}. Some wells demonstrated analysis records covering just over two decades, others only covered the past few years.

In total and when including trace amounts, pesticides can be concluded to have occurred in 18 of the 23 wells, i.e. approx. 80% of the study sites. If considering above-LOQ detections only, the figure is reduced to about 60% (14 wells). Detected substances are listed in table 3. Atrazine (and metabolites), BAM, bentazone and terbuthylazine (and metabolites) represent the most common substances both with regard to overall DF and in terms of number of wells affected (Table 3). The remaining substances listed have been detected once or more in one or two wells only. Over half of the detected substances stem from prohibited compounds, and compounds mainly or partly used outside of the agricultural sector. Of the four most common substances, only bentazone is (i) currently granted usage and (ii) used solely for agricultural purposes. Metabolites account for more than half of the total number of detections.

DFs for polluted wells range between 13 and 100%, with an average of about 60%. Single, isolated detections are rare, suggesting that if a pesticide is detected in a well at a given point in time, repeated pesticide detections in the same well can be expected. More than one type of substance further tends to be detected in a given polluted well throughout its analysis record, suggesting that a well in which one type of pesticide is detected at a given point in time, likely is at risk of pollution of additional types of substances. However, there are wells in which only single substances are detected repeatedly. Recurrent substances in such wells include BAM, bentazone and mecoprop.

Documented concentrations of individual substances range between estimated trace amounts of 0.001 µg L^{-1}, to measured concentrations of up to 0.64 µg L^{-1}. Concentrations above the EU-threshold of 0.1 µg L^{-1} for a single substance have been measured one or more times in nine wells. Bentazone is the substance most commonly detected in above-threshold concentrations. Atrazine-desethyl, BAM, clopyralid, isoproturon and quinmerac, which are all relatively mobile herbicides, have also been detected in concentrations ≥0.1 µg L^{-1}.

The results of the comprehensive low-LOQ-analyses conducted as part of this study are presented in Table S3. These revealed (i) pesticides in three wells wherein pesticides had not been detected previously, (ii) for the specific well previously undetected pesticides in fifteen wells, and (iii) three pesticides which had never before been detected in any of the wells. The latter three included imidacloprid (1 well), simazine (1 well)

Table 3. Detected substances with information on type (H = herbicide. F = fungicide. I = insecticide), detection frequency in %, no. of wells affected, median concentration (c) and range of documented detections in µg L^{-1}, median LOQ (limit of quantification) and range of documented analyses in µg L^{-1}, main use (A = agricultural. Non-A = non-agricultural), and year of prohibition (if applicable).

Substance	Type	Detection frequency (incl. trace detections)	No. of wells affected	Median *c.* (range)	Median LOQ (range)	Main use	Prohibited since
Atrazine	*H*	*6.4 (9.2)*	*12*	*0.008 (0.002-0.06)*	*0.01 (0.001-0.1)*	*Non-A*	*1989*
Atrazine-desethyl	*H*	*6.3 (10)*	*10*	*0.03 (0.01-0.2)*	*0.01 (0.002-0.2)*	*Non-A*	*1989*
Atrazine-desethyl-desisopropyl	*H*	*4.8 (4.8)*	*2*	*0.02 (0.01-0.02)*	*0.01*	*Non-A*	*1989*
BAM	*H*	*24 (29)*	*12*	*0.05 (0.01-0.7)*	*0.01 (0.003-0.1)*	*Non-A*	*1990*
Bentazone	*H*	*14 (15)*	*8*	*0.09 (0.01-0.4)*	*0.01 (0.003-0.1)*	*A*	*-*
Carbendazim	*F*	*2.4 (2.4)*	*1*	*0.01*	*0.002 (0.002-0.01)*	*A*	*1998*
Clopyralid	*H*	*0.61 (0.61)*	*1*	*0.1*	*0.1 (0.01-0.3)*	*A*	*-*
Imazapyr	*H*	*1.7 (1.7)*	*1*	*0.01*	*0.01 (0.01-0.1)*	*Non-A*	*2002*
Imidacloprid	*I*	*4.3 (4.3)*	*1*	*0.07*	*0.002*	*Both*	*-*
Isoproturon	*H*	*0.84 (0.84)*	*1*	*0.2 (0.1-0.2)*	*0.01 (0.001-0.2)*	*A*	*2012*
Mecoprop	*H*	*2.4 (2.8)*	*1*	*0.01*	*0.01 (0.003-0.1)*	*Both*[a]	*-*
Metalaxyl	*F*	*0 (5.3)*	*2*		*0.001 (0.001-0.3)*	*A*	*-*
Quinmerac	*H*	*0.43 (0.87)*	*2*	*0.1*	*0.01 (0.001-0.1)*	*A*	*-*
Simazine	*H*	*0 (0.41)*	*1*		*0.01 (0.001-0.2)*	*Non-A*	*1994*
Terbuthylazine	*H*	*1.6 (1.6)*	*2*	*0.02 (0.002-0.03)*	*0.01 (0.001-0.1)*	*Both*	*2003*
Terbutyhlazine-desethyl	*H*	*6.4 (11)*	*5*	*0.005 (0.003-0.005)*	*0.01 (0.001-0.01)*	*Both*	*2003*
Terbuthylazine-hydroxy	*H*	*17 (17)*	*1*	*0.04*	*0.01*	*Both*	*2003*

[a] *Agricultural use prohibited since 2011.*

and metalaxyl (2 wells). Simazine, a herbicide, has been prohibited for use in Sweden since 1994, while imidacloprid (insecticide) and metalaxyl (fungicide) are currently allowed. Only metalaxyl is exclusively used within the agricultural sector.

The variability in analytical scope between samples and wells, combined with the uncertainty relating to (i) potential offsets between groundwater and pesticide travel times, and (ii) representativeness of derived groundwater ages in view of expected groundwater mixing, currently precludes trend analyses both regionally (between wells) and locally (for an individual well).

3.2 SOM-results: data patterns and variable relations

SOM-outputs are given in figures 2a-c and table 4.

Figure 2a is the "Unified distance matrix" (U-matrix – Ultsch and Siemon 1990; Ultsch 2004) representation of the self-organized map. It is an overall and composite visualization of the SOM that displays nodes grouped or distributed across the map according to overall similarity. The white nodes are so called "hit nodes" representative of the location of actual input samples within the data space. The size of a hit node is proportional to the number of input samples represented by it. Fourteen hit nodes were sufficient to represent the variability of the 23 input samples within the given data space. Dis-/similarity between neighboring nodes is indicated via color-coding; the cooler the color of a node, the greater the similarity to surrounding nodes (and vice versa).

Figure 2b shows the component (plane) plots derived from the SOM analysis. These plots are basically slices of the self-organized map, showing each variable's contribution across it. The location of input samples is the same as for the U-matrix as both are derived from the same SOM analysis. On the component plots, cool colors (blue) represent low variable values, and warm colors (red) represent high variable values. Coinciding patterns between two or more variables indicate positive correlation (such as between DF 0.1 and DF 0.01), and inverse patterns indicate inverse correlation (such as between filter top depth and modern water). Results of image processing procedures applied to the component plots are given in figure 2c (principal component analysis; PCA conducted on all nodes) and table 4 (correlation analysis conducted on hit nodes only).

The patterns of the component plots (Fig. 2b) indicate that severe, high concentration pesticide pollution (the elevated yellow-red regions of the DF 0.1 plot) is related to modern, oxic-suboxic waters with high NO_3 concentrations from wells with relatively shallow filter tops in unconfined fracture or pore-type aquifers exhibiting urban land use influence. The PCA (Fig. 2c) and the correlation analysis (Table 4) expectedly corroborate these indications, and further suggest particular strong associations between DF 0.1, modern water, fracture-type aquifers, urban land use and filter top depth (such that the shallower the filter top, the more polluted the water).

Table 4. SOM component plot (Spearman rho-) correlation analysis results (hit nodes only). Bolded r-values are significant at >90%. Bolded and underlined r-values are significant at >95%.

Category	Variable	DF 0.01 (r)	DF 0.1 (r)
Well filter	*Top*	***-0.604***	***-0.609***
	Bottom	*-0.009*	*0.125*
Water age group	*Modern*	*0.351*	***0.504***
Redox state	*Oxic*	***0.551***	*0.149*
	Suboxic	*-0.079*	*0.193*
	Anoxic	***-0.559***	*-0.325*
Aquifer confinement	*Unconfined*	*0.384*	*0.371*
	Leaky	*-0.109*	*-0.194*
	Confined	***-0.540***	*-0.375*
Aquifer type	*Pore*	*-0.478*	*-0.317*
	Fracture	***0.566***	***0.741***
	Dual porosity	*0.015*	*-0.379*
Land use	*NO_3[a]*	***0.656***	*0.412*
	Urban	***0.545***	***0.469***

Similarly, the least polluted waters (represented by the depressed blue region on the DF 0.01 plot) appear to be primarily associated with deeper and more confined groundwater environments, suboxic-anoxic redox states, pore-type aquifers, and low NO_3 concentrations (Fig. 2b-c, Table 4). Because of correlation between anoxic conditions and low NO_3 concentrations, it is difficult to interpret the latter as an actual sign of low agricultural influence, as it is rather likely to primarily relate to nitrate reduction. Interestingly, there is no convincing correlation between overall pesticide presence/absence and predominantly modern/old groundwater. Arguably, some of the so classified old waters still contain a large enough proportion of modern water to allow for pesticide detection, albeit not for high concentration pesticide presence.

4. Discussion

4.1 Pollution extent, character and vulnerability

Repeated pesticide occurrence applies to a majority of the studied PSWs. Because PSWs generally integrate water quality over large recharge areas, pesticide occurrence in these types of wells is likely to reflect either large-scale pollution in terms of volume, or in terms of source-concentrations (Brüsch 2007). All but one of the studied aquifers are further subject to regulated safeguarding measures (Table 1), whereby they may effectively be non- (i.e. under-) representative of general

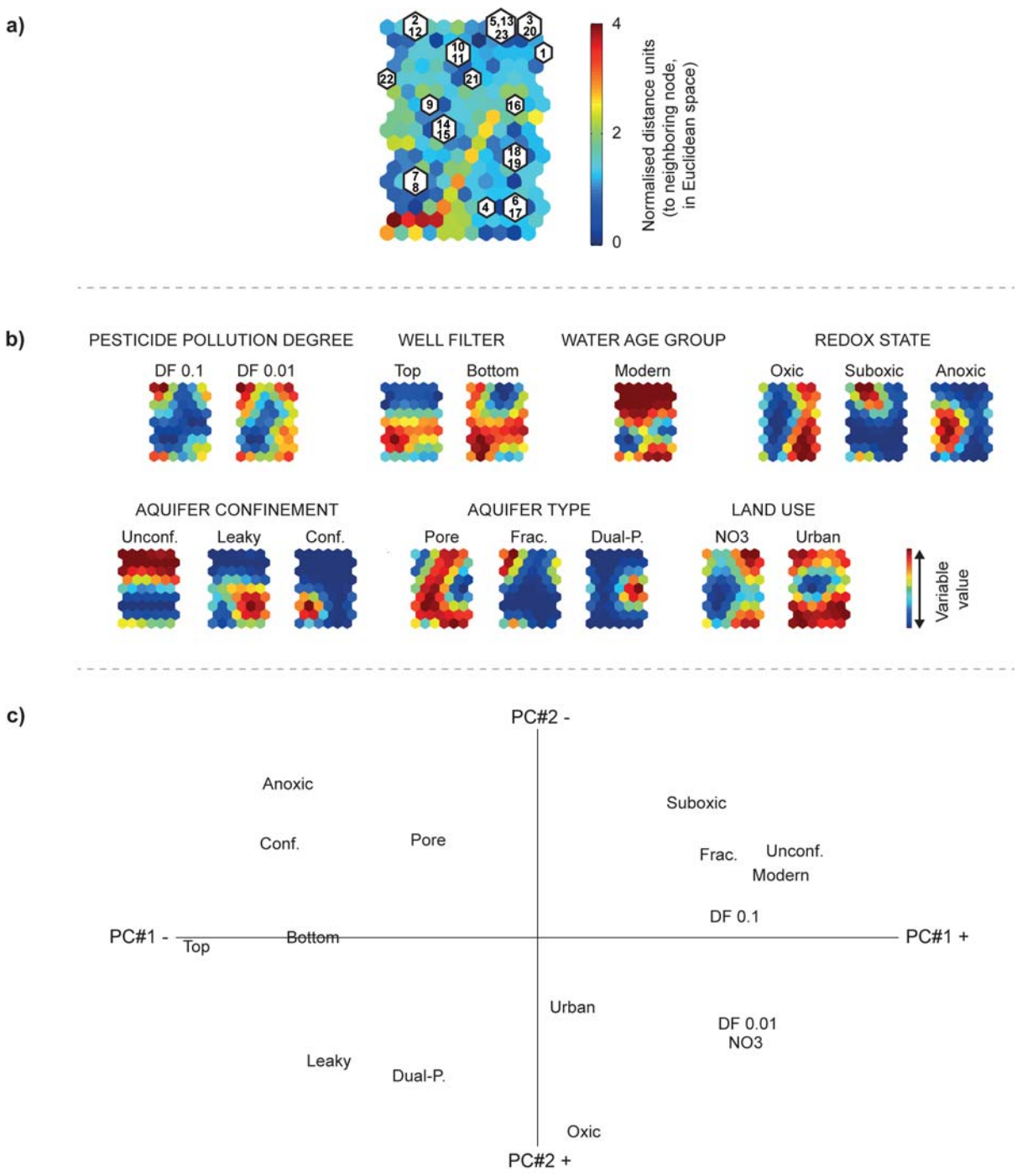

Figure 2. SOM outputs. Maps are toroidal and so wrap top-to-bottom and side-to-side. Note the different color schemes.
a) The U-matrix. Input sample locations in the map are represented by the (well no.-) annotated white nodes with black encircling (the bigger the node, the more input samples represented by it). Colors represent degree of dis-/similarity between neighboring nodes: warmer colors equal larger distance and dissimilarity, cooler colors equal smaller distance and similarity.
b) Component plots, sorted according to variable category, demonstrating the contribution of each variable to the composite U-matrix and hence variable variation over the data space. Warm colors correspond to high values (for binary variables; 1), cool colors correspond to low values (for binary variables; 0). Similar patterns between variables indicate positive correlation, inverse patterns indicate inverse correlation.
c) A "similarity plot" based on a principal component analysis of SOM component plots (Fig. 2b). Proximity indicates similarity.

conditions.

On the other hand, as the PSWs were chosen partly based on pesticide analysis record length, there is potential for bias towards the relatively more polluted examples of regional groundwater reservoirs used for drinking water production, as these in the absence of a general sampling prerequisite, may have demanded relatively more attention than others. This could be a valid reasoning as previous studies have indicated lower pesticide DFs, in the range of 30 to 50%, for Scanian groundwater reservoirs (Maxe et al. 2003; Virgin 2012), as compared to the derived 80% of this study. However, it is difficult to compare these numbers directly in view of varying investigative scope and approach, and this study arguably allows for a relatively more thorough assessment in view of the detailed analysis records compiled (including conducted low-LOQ analyses). Either way, pesticide pollution of Scanian groundwater seems a genuine concern on par with established situations in many other industrial countries, both in terms of overall DF, concentration levels and frequently occurring substances (Kolpin et al. 1998; Haarstad and Ludvigsen 2007; Schipper et al. 2008; Close and Skinner 2012; Thorling et al. 2012), and questions previous reports of no danger of pesticide pollution of groundwater for Sweden as a whole (European Environment Agency 2004).

Whilst agriculture is undoubtedly one important source of pesticide pollution of the sampled waters, the collated data clearly indicate that non-agricultural pesticide use also exerts a major influence. As noted earlier, similar indications have been demonstrated also in other regions including e.g. the US (Kolpin et al. 1998) and Denmark (Thorling et al. 2012). One could speculate whether the major urban influence might result from a relative lack of restrictions in terms of non-agricultural compared to agricultural pesticide use. In Sweden however, large efforts have been put into the restriction of non-agricultural pesticide use since the end of the 1980s, when studies started to indicate significant environmental impact thereof. Potent weed killers such as atrazine and dichlobenil (the parent compound of BAM) were effectively prohibited for use by 1990, and thus many of the observations made likely stem from a time during which overall restrictions were absent or less strongly enforced. One part of the explanation for the extensive occurrence of these types of substances in the studied aquifers is certainly inherent and generally valid hydrogeological system time lags (e.g. Destouni et al. 2010). Gradual leach-out of built-up pools of recalcitrant substances within the soil could be yet another concern. In comparable hydrogeological settings in Denmark, BAM is recognized as a potential long-term groundwater pollution threat in view of documented soil loading (Clausen et al. 2007). Similar indications have been made in relation to atrazine and associated metabolites in e.g. Germany (Tappe et al. 2002) and France (Morvan et al. 2006). No comparable studies are known from Sweden.

In terms of pollution vulnerability, the results confirm the expected importance of connectivity between the ground surface and the point of observation within the groundwater system. According to the SOM output, vulnerability and thus pollution risk generally increases with modern and oxic waters, with decreasing minimum extraction depth, and with decreasing degree of aquifer confinement. These findings are typical (e.g. Close and Skinner 2012; Malaguerra et al. 2012), expected and in agreement with the long-standing general consensus (Barbash and Resek 1996). Indications are further that groundwater systems dominated by fracture flow are particularly vulnerable to pesticide pollution. Likely, fracture flow increases pollution vulnerability via an overall reduction in both travel time and natural remediation-potential relative to matrix flow, thereby allowing for comparatively rapid transfer of infiltrating water and pesticides. This proposal is theoretically valid (Freeze and Cherry 1979) and well-established regarding fracture and macropore flow and associated pollutant transport in e.g. clay tills (Jorgensen et al. 1998; Jarvis 2007). However, few studies comparing pesticide pollution in aquifers dominated by matrix flow to those dominated by fracture flow have been able to support such a hypothesis (Neil et al. 1989; Barbash & Resek 1996). Crystalline fracture-type aquifers are present throughout much of Sweden (and much of Scandinavia), and hence, this pollution concern is in need of further investigation.

Finally, it is interesting to note that a majority of the studied aquifers are polluted even though all but one have water protection areas. Many of these areas were installed in the mid-1970s and so should have served to protect the associated groundwater quality since then. Thus, there appears to be a need for re-evaluation of (i) the location of the areas in relation to actual recharge areas, and (ii) the scope of associated regulations.

4.2 Data and management limitations and requirements

Whilst this study fills an important role in indicating regional concerns of pesticide pollution of groundwater and the causes of those, the underlying data set is limited which constrains possibilities for confident, general conclusions. Whether or not the above inferences are valid also in a wider context requires extended studies encompassing more wells and desirably also more comprehensive and detailed metadata concerning e.g. land use patterns over time and space within well-defined recharge areas, and groundwater age distributions of extracted waters. The lack of coordinated pesticide-groundwater monitoring,

as well as the lack of a comprehensive database of conducted analyses, is a palpable concern in this regard, as it constrains possibilities for rigorous status assessments over both space and time. Regional temporal and spatial comparisons currently require data collation from a wide range of separate authorities and databases followed by data quality assessment and -leveling. This approach is neither efficient nor ideal as it is excessively time-consuming and jeopardizes objectivity. The limited availability of well- and sample metadata including information on e.g. filter depths, recharge areas and stratigraphy is a further concern.

For now, an effort to collate and structure all documented pesticide analyses of groundwater in Scania and overall Sweden from the variety of information sources to a single master database should be made, to enable a wider test of the hypotheses put forward here, and to further assess the current pollution situation. Such a database needs to contain fundamental well and sample metadata, and should be continuously maintained and updated. Requirements for automated submission of conducted analyses of pesticides in groundwater, inclusive of analytical boundary conditions and specified metadata, to this database should be implemented. Further, multiple catchment-scale field studies should be undertaken in various type settings to study governing transport processes in detail (e.g. Åkesson et al. 2013, in press), to further explore the extent and effects of system time lags on pesticide fate in the groundwater system (e.g. Tesoriero et al. 2007), and to investigate the potential presence, extent and effects of pesticide residues within soils. Such studies are fundamental both in terms of enhancing pollution prediction skill, and for the development of sound management policies including remedial efforts where needed.

In order to secure WFD compliance and thereby also future groundwater quality, Sweden further needs to develop and implement statutory regulations enforcing adequate monitoring and assessment of the occurrence of not only pesticides but as previously noted also other anthropogenic pollutants (Destouni et al. 2008; Baresel and Destouni 2009; European Commission 2012; SEPA 2013) in groundwater nationwide. As for general groundwater quality monitoring and assessment, precepts effectively already exist (e.g. SGU 2013:1). However, these lack distinct pesticide monitoring and assessment specifications, and appear poorly followed overall. Based on experiences from neighboring Denmark, a country well ahead of Sweden as to this matter (Jorgensen and Stockmarr 2009), adequate monitoring and assessment should span both untreated groundwater from PSWs, and groundwater from an independent and comprehensive purpose-made monitoring network, in order to secure a sustained, geographically and hydrogeological well-distributed, controlled source of data.

5. Conclusions

- Analysis records from 23 public supply wells reveal pesticide occurrence in all but five, which suggests that pesticides are substantially present in groundwater throughout much of Scania, southern Sweden. Collected data indicate considerable influence of both agricultural and non-agricultural (urban) pesticide use, and lagged effects of past, less restricted pesticide use. Modern (post-1950), oxic waters from shallow, unconfined unconsolidated or fracture-type bedrock aquifers appear particularly affected and vulnerable. Least affected waters appear primarily associated with relatively deeper extraction depths, anoxic conditions and more confined sediment aquifers largely devoid of urban land use influence. Predominantly old (pre-1950) water does not appear to exclude pollution risk, which could be due to earlier pesticide use, and/or relatively minor proportions of modern, severely polluted water.
- Pesticide residues that had not previously been observed via more standard analyses were detected throughout many of the studied aquifers when applying a comparatively generous screening analysis package covering an ample range of residues detectable at relatively low concentrations. This implies that the standard analysis packages are not sufficient for thorough pesticide-groundwater pollution status assessment.
- As a majority of the studied aquifers are affected by pesticide pollution even though all but one are associated with water protection areas, the positioning of and pesticide use regulations associated with these areas should be reassessed.
- Due to the relatively limited data set explored, further studies are required to test the above inferences of primary pollution concerns in more detail and in a wider context. Such studies are currently hampered by a lack of comprehensive and consistent data on pesticide occurrence in Swedish groundwater, resulting from nationally deficient statutory monitoring of anthropogenic pollutants in groundwater (Destouni et al. 2008; Barsesel and Destouni 2009).
- For Sweden, comprehensive monitoring of the occurrence of pesticides (and other anthropogenic pollutants) in groundwater needs to be realized, and available data need to be collated and structured to allow for comprehensive nationwide status assessment, identify problem areas, direct research efforts and develop and implement sound management plans in accordance with the WFD.

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Supplementary material

Table S1. ^{3}H-^{3}He analysis results. Tritiogenic ^{3}He is calculated based on an estimated recharge temperature (8°C) and altitude (40 m a.s.l.).

Well	^{3}H (TU)	Tritiogenic ^{3}He (TU)	^{3}H-^{3}He age (years)
1	8.27	[a]	n.a. (but ^{3}H alone indicates predominantly modern water)
2	7.19	2.8	6
3	7.00	2.0	5
4	6.26	22.4	27
5	6.92	9.5	15
6	6.78	7.6	13
7	0.10	[a]	n.a. (but ^{3}H alone indicates old water)
8	0.02	[a]	n.a. (but ^{3}H alone indicates old water)
9	6.86	5.7	11
10	5.96	6.2	13
11	7.60	0.5	1
12	5.23	15.0	24
13	7.62	0.8	2
14	5.32	14.6	23
15	6.28	6.6	13
16	6.67	4.1	9
17	11.94	130.1	44
18	0.53	3.7	37 (but ^{3}H alone indicates predominantly old water)
19	0.30	[a]	n.a. (but ^{3}H alone indicates predominantly old water)
20	7.52	15.5	21
21	7.94	3.0	6
22	7.63	[a]	n.a. (but ^{3}H alone indicates predominantly modern water)
23	6.98	2.9	6

[a] *Non-quantifiable.*

Table S2. Substances included in the adjusted data set, with information of type (H = herbicide, I = insecticide) and use (N = prohibited and not in use, Y = permitted and in use at time of sampling).

Substance	Type	In use
2,4-D	*H*	*N*
Atrazine	*H*	*N*
Atrazine-desethyl	*H*	*N*
Atrazine-desisopropyl	*H*	*N*
BAM	*H*	*N*
Bentazone	*H*	*Y*
Cyanazine	*H*	*N*
Dichlorprop	*H*	*N*
Dimethoate	*I*	*N*
Ethofumesate	*H*	*Y*
Fenoxaprop	*H*	*Y*
Isoproturon	*H*	*Y*
MCPA	*H*	*Y*
Mecoprop	*H*	*Y*
Metamitron	*H*	*Y*
Metazachlor	*H*	*Y*
Metribuzin	*H*	*Y*
Quinmerac	*H*	*Y*
Simazine	*H*	*N*
Terbuthylazine	*H*	*N*

Table S3. Results of the pesticide analyses conducted as part of this study.

Well	Detection (concentration; µg L^{-1})
1	*atrazine (0.001[a]), metalaxyl (0.002[a])*
2	*atrazine (0.003), BAM (0.009[a]), bentazone (0.069)*
3	*atrazine (0.018), atrazine-desethyl (0.023), BAM (0.017), terbuthylazine (0.002), terbuthylazine-desethyl (0.005)*
4	*atrazine (0.004), BAM (0.007[a])*
5	*atrazine (0.002), atrazine-desethyl (0.009[a]), BAM (0.024)*
6	*atrazine (0.006), atrazine-desethyl (0.006[a]), BAM (0.006[a])*
7	-
8	-
9	*bentazone (0.008[a])*
10	-
11	*BAM (0.007[a])*
12	*atrazine (0.003), atrazine-desethyl (0.004[a]), bentazone (0.15), terbuthylazine (0.006), terbuthylazine-desethyl (0.001[a])*
13	*bentazone (0.026)*
14	-
15	*bentazone (0.004[a]), quinmerac (0.001[a])*
16	*atrazine (0.001[a]), atrazine-desethyl (0.002[a]), metalaxyl (0.001[a]), terbuthylazine-desethyl (0.005)*
17	*atrazine (0.005), atrazine-desethyl (0.1), BAM (0.051), terbuthylazine-desethyl (0.001[a])*
18	*atrazine (0.004), atrazine-desethyl (0.009[a]), BAM (0.008[a]), bentazone (0.04)*
19	*BAM (0.003[a]), mecoprop (0.006[a])*
20	*atrazine-desethyl (0.008[a]), BAM (0.065), terbuthylazine-desethyl (0.003)*
21	-
22	*atrazine (0.005), atrazine-desethyl (0.006[a]), BAM (0.019)*
23	*BAM (0.006[a]), imidacloprid (0.067), simazine (0.001[a])*

[a] *Estimated trace amount.*

Paper IV

Constraining age distributions of groundwater from public supply wells in diverse hydrogeological settings by means of environmental tracers and lumped-parameter modelling: a case study from Scania, southern Sweden

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Abstract

Twenty-five public supply wells throughout the hydrogeologically diverse region of Scania, southern Sweden are subjected to environmental tracer analysis (^{3}H-^{3}He, CFCs, SF_6 and for one selected well only also ^{85}Kr and ^{39}Ar) to study well vulnerability and evaluate possibilities of groundwater age distribution assessment. We find elevated ^{4}He and SF_6 content throughout, with maximum concentrations equivalent of up to 40 and 1000 times solubility equilibrium respectively. Further, CFC degradation is indicated for a large proportion of the samples, as is CFC contamination. These tracer-specific complications constrain possibilities for sound age distribution assessments. Nevertheless, we are able to conclude that only two wells, the only ones abstracting water from a confined aquifer, are completely devoid of modern tracer residues. Four wells show indications of significant pre-modern water admixing. Remaining wells, i.e. the absolute majority, appear dominated by relatively young water and should as such be considered much vulnerable to pollution. Lumped parameter modelling validated on seemingly sound multi-tracer analysis results from wells from four type aquifers yield credible age distribution assessments, which may be used to asses pollution patterns and trends. In order to enable improved and additional age distribution and associated pollution vulnerability assessments, there is a need for (i) additional ^{85}Kr and ^{39}Ar measurements, (ii) complementary sampling of monitoring wells and (iii) investigations of local rates of CFC degradation as well as sources of terrigenic He and SF_6.

Keywords: *groundwater age, public supply wells, lumped-parameter modelling.*

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 sedimentary deposits of much diverse physical composition (Gustafsson, 2005).

Recently, Åkesson et al. (Accepted) 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 source of pumped waters in order to be able to better constrain potential pollution trends, patterns and risks.

This study aims to improve the understanding of these water sources by applying a set of environmental tracers including tritium-helium (^{3}H-^{3}He; (Schlosser et al., 1988), chlorofluorocarbons (CFCs; Busenberg and Plummer, 1992), sulphurhexafluoride (SF_6; Busenberg and Plummer, 2000), krypton-85 (^{85}Kr; Loosli and Oeschger, 1979; Rozanski and Florkowski, 1978) and argon-39 (^{39}Ar; Loosli, 1983). Few tracer-based studies are known from the area (e.g. Barmen, 1992; Gustafsson, 1992; Persson, 1974) and hence this study also serves to test the regional applicability of these tracers.

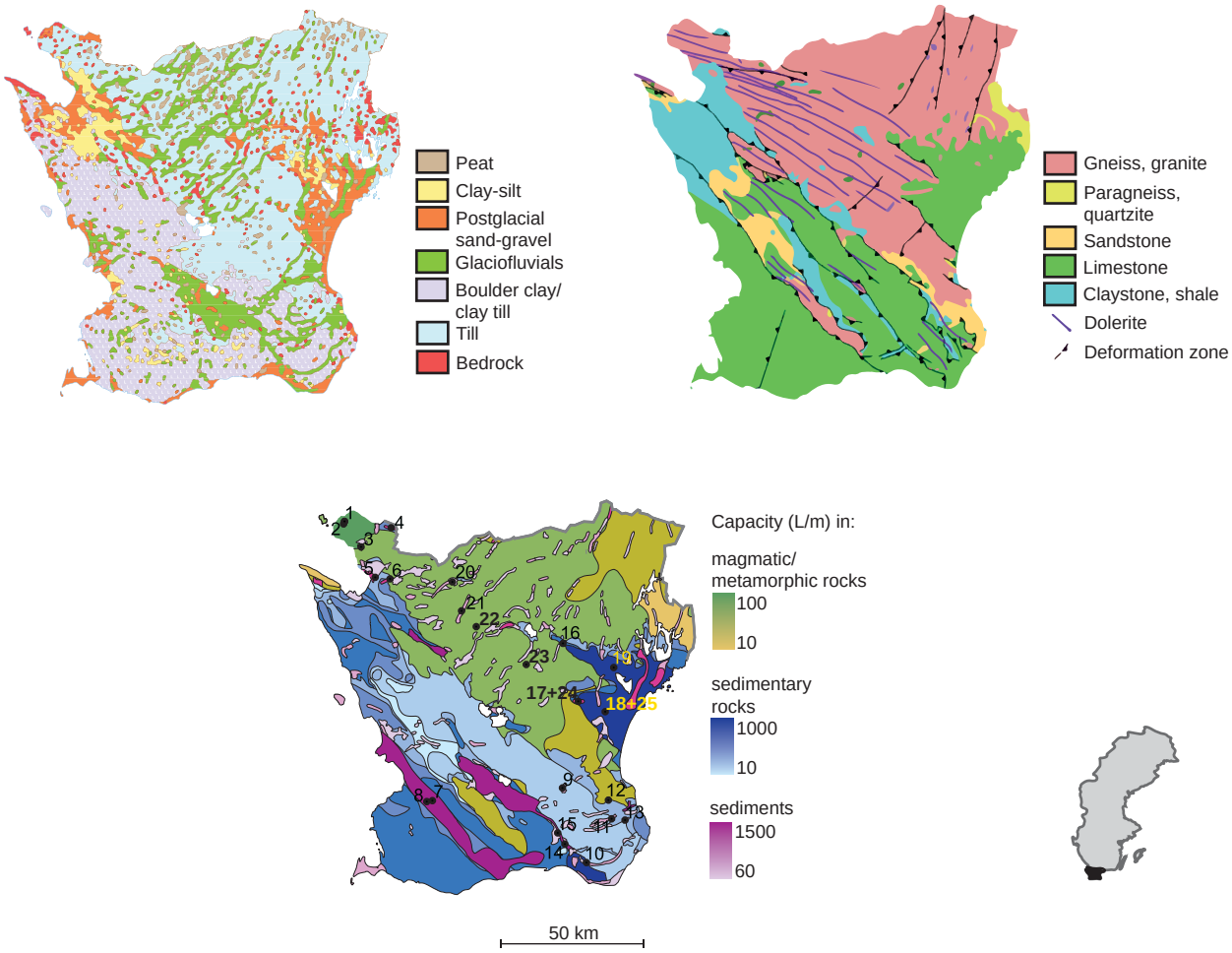

Figure 1. Overview of geology and hydrogeology of Scania (adopted from ©SGU and Wastenson et al. 1999). Study locations are indicated by the annotated black dots (see Table 1 for further information). The location of Scania is shown on the map of Sweden in the lower right hand corner.lower right hand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

2. Theoretical framework

2.1 Groundwater "age": concept and modelling

Sustainable groundwater management relies on an understanding of the hydrogeological systems in question. In this regard, global environmental trace substances that enter and move through groundwater systems in significantly well-defined manners, such as the tracers listed above, have time and again proven highly valuable, because they may serve as proxies for actual water flow, thus enabling investigations of prevailing hydrodynamics and any other related questions raised, e.g. those of pollution trends and risks (Bohlke and Denver, 1995; Tesoriero et al., 2007; Visser et al., 2009; Åkesson et al., In press).

At any given point of observation within a groundwater system, the sampled concentration of an environmental tracer will represent an integration of the hydrodynamics of the upstream flow-field (Portniaguine and Solomon, 1998). If the assumed criterion of well-constrained tracer-groundwater conveyance is fulfilled, the measured tracer concentration can be used to assess the time elapsed since recharge of the associated water molecules. This time interval is often referred to as the "groundwater age", although this is a much debated concept (Etcheverry and Perrochet, 2000; Goode, 1996; Suckow, In press; Varni and Carrera, 1998), as such an age implies that a given groundwater sample consists of water molecules that all recharged at one single point in time. This is seldom a valid assumption, especially when sampling over long screen intervals or in heterogeneous environments (Alvarado et al., 2007; Weissmann et al., 2002; Visser et al., 2013), such as in the case of the PSWs of interest. In such situations, it is generally more appropriate to consider groundwater age as a distribution with a mean residence time (MRT) of the water molecules in the saturated zone, rather than

anything else (Bethke and Johnson, 2008; Massoudieh et al., 2012). Arguably, this distribution represents the most important feature for the assessment of intrinsic pollution susceptibility of PSWs (Jurgens et al., In press).

One way of constraining groundwater age distributions is via tests of measured to modelled tracer concentrations according to mathematical lumped parameter mixing models (LPMs) reflecting hypothetical groundwater flow systems. This approach assumes that the concentration of a tracer at a point of observation within a groundwater system can be described by the convolution integral:

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

where the exponential term accounts for first-order decay in case of a radioactive tracer, C_{in} and C_{out} are the input and output concentrations of the specific tracer respectively, t_{obs} the time of observation and t the transit time. The age distribution is reflected in the weight function $g(t)$, specific to the LPM of choice (Maloszewski and Zuber, 1996). Examples of such LPMs include the piston flow model (PM) for which no mixing at all is assumed, the exponential model (EM) for which an exponential age distribution is assumed, the linear model (LM) for which a linear age distribution is a assumed and the dispersion model (DM) for which hydrodynamic dispersion during transport is taken to account, allowing for the close coexistence of water molecules of varying ages (Maloszewski and Zuber, 1996).

Although a somewhat simplified approach (Engdahl and Maxwell, 2014; Massoudieh et al., 2012; McCallum et al., 2014), lumped parameter modelling is easily accessible, has proven powerful when compared to more informed and demanding numerical flow and transport modelling efforts (Eberts et al., 2012) and is arguably a natural first line of attack in and for cases like the one presented. 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.

2.2 Tracer fundamentals

^{3}H is a radioactive hydrogen isotope which forms part of water molecules. Hence, ^{3}H is generally considered an ideal hydrological tracer. Following nuclear bomb tests in the mid-1900s, large amounts of ^{3}H were introduced to the atmosphere, thereby overwhelming natural background levels and triggering a global hydrological tracer experiment. With a half-life of 12.32 years (Lucas and Unterweger, 2000), ^{3}H decays to the stable helium isotope ^{3}He. Upon recharge, any ^{3}He produced through the decay of ^{3}H will be cut off from the atmosphere and have nowhere to go but with water flow. For groundwater forming since the mid-1900s, measured ^{3}H and ^{3}He concentrations can therefore be applied to quantify time since recharge (Schlosser et al., 1988; Solomon and Cook, 2000). This however requires the separation of the tritiogenic fraction of dissolved ^{3}He (^{3}He*) from (i) a naturally occurring atmospheric equilibrium fraction dependent upon recharge temperature and altitude, (ii) a potential terrigenic fraction (mantle-produced and/or radiogenic resulting from U/Th-decay; Schlosser et al., 1989) and (iii) a potential excess air fraction (Heaton and Vogel, 1981). Degassing (Solomon et al., 1992; Visser et al., 2007) is a further potentially complicating issue.

CFCs (here: CFC-11, -12 and -113) and SF_6 are transient tracers for which atmospheric concentrations increased considerably following industrial manufacturing and use since the 1950s (CFCs) and 1970s (SF_6). This increase is generally well-documented and can, after corrections for tracer-specific Henry's Law solubilities, be translated into a time-dependent groundwater input function. Both CFCs and SF_6 are generally considered stable (i.e. non-reactive) and measured groundwater concentrations are, in theory, directly comparable to specific recharge years (Busenberg and Plummer, 2000; Plummer and Busenberg, 2000). Recharge altitudes and temperatures in particular[1] need to be known to allow for estimations of solubility equilibrium fractions and potential influences of excess air and/or degassing. However, it should be noted that the effects of excess air on CFC is very small when compared that on 3He* and SF_6 due to comparatively high Henry's law solubilities (Beyerle et al., 1999). Demonstrated complications include non-conservative behaviour of CFCs (particularly CFC-11 and -113) in relation to sorption and degradation under reducing conditions (Bauer et al., 2001; Hinsby et al., 2007), and local contamination sources. For CFCs, such contamination sources are presumably only a matter of anthropogenic input. However, for SF_6, natural subsurface production has also been suggested (Friedrich et al., 2013; Harnisch and Eisenhauer, 1998; von Rohden et al., 2010). Further, as a result of usage restrictions in the 1990s, atmospheric concentrations of CFC-11 and CFC-12 have ceased and decreased, resulting in dating ambiguity for waters infiltrating since the past twenty years.

^{85}Kr and ^{39}Ar are noble gas radioisotopes with half-lives of 10.76 and 269 years respectively (Loosli et al., 2000). Assuming equilibrium dissolution of tropospheric activities in recharging groundwater, groundwater ages can be assessed without knowledge of e.g. recharge temperature and excess air by correcting measured specific activities (i.e. ratios of ^{85}Kr to stable Kr and ^{39}Ar to stable Ar) for radioactive decay. Almost all atmospheric ^{85}Kr

[1] *CFCs and SF_6 solubilities are more dependent upon infiltration temperature than He and Ne (±>10%/°C vs. ±1%/°C).*

is of anthropogenic origin, relating to nuclear industry and particularly nuclear fuel bar reprocessing. The atmospheric concentration of ^{85}Kr has accordingly been rising since the mid-1900s (Winger et al., 2005) and it may be used as an environmental tracer for groundwater recharging since then (Cook and Solomon, 1997). Groundwater ages are assessed by finding a match-point on the atmospheric curve (Althaus et al., 2009; Cook and Solomon, 1997). Anthropogenic sources of ^{39}Ar are negligible, but cosmic ray production is largely constant and enough to generate a hydrologic signal that allows for groundwater dating of waters recharging some 50-1000 years ago (Alvarado et al., 2007; Visser et al., 2013). The main issue with regard to ^{85}Kr- and ^{39}Ar-based groundwater dating is the complicated sampling and analytical procedures necessitated due to minor subsurface concentrations. A further issue with regard to ^{39}Ar specifically, is subsurface production in crystalline bedrock environments (Andrews et al., 1989; Edmunds et al., 2014; Yokochi et al., 2012).

3. Materials and methods

3.1 Well selection and conceptual hydrogeology

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

Table 1. Altitudes, screening depths, aquifer types and local lithology of studied wells.

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: sediment aquifer, B: dual-porosity bedrock aquifer, C: fracture-flow bedrock aquifer.*
[b] *For wells in sediment aquifers ("A-wells"): underlying bedrock.*
[c] *Uncertain.*

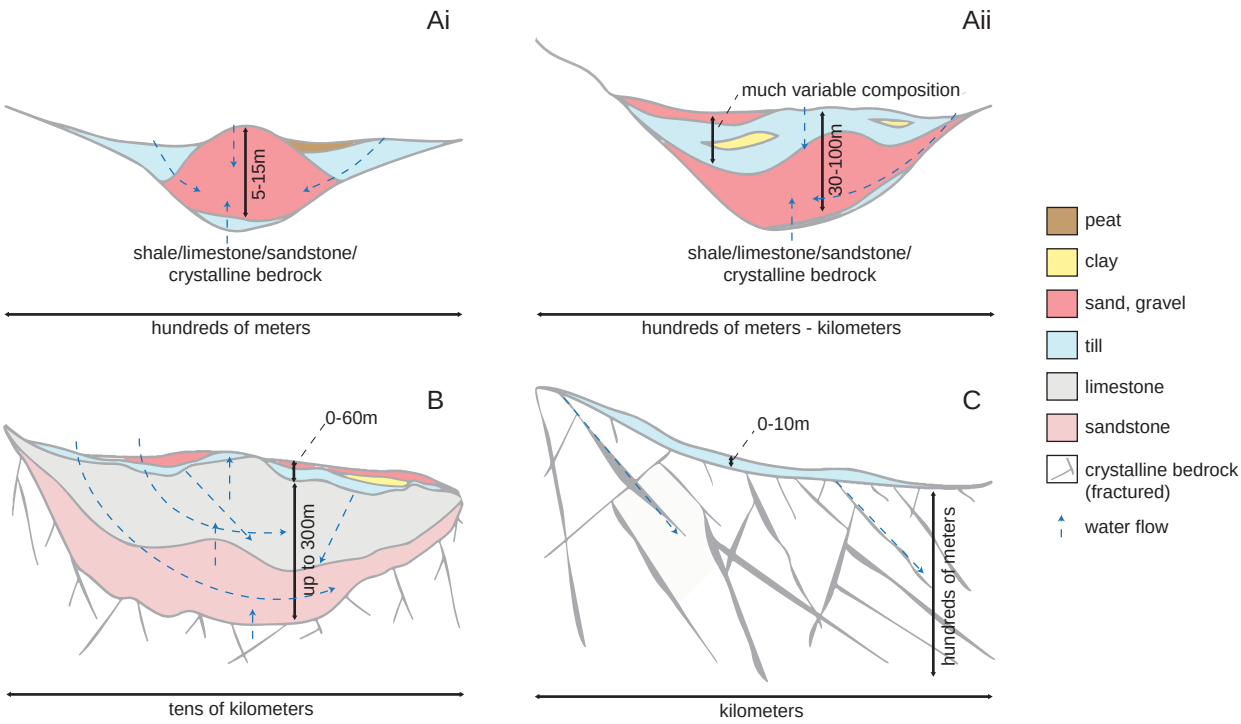

Figure 2. Generalised cross-sections for the four end member aquifer types studied: (Ai) unconfined sediment aquifer, (Aii) semi-confined/confined sediment aquifer, (B) unconfined/semi-confined dual-porosity bedrock aquifer, (C) unconfined fracture-flow bedrock aquifer.

bedrock aquifers and unconfined bedrock aquifers dominated by fracture flow.

Seventeen PSWs extract groundwater from sediment 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 sediment 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 are located in a dual-porosity sedimentary rock aquifer and half in fracture-flow dominated bedrock aquifers. The dual-porosity sedimentary rock aquifer is one of a thick sequence of poorly consolidated lime- and sandstones deposited into a several hundred meter deep crystalline bedrock depression in NE Scania (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 1) and sometimes span multiple lithologies. The fracture-flow dominated bedrock aquifers generally consist of heavily weathered and fractured gneisses or granites with associated PSWs 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). PSW 12 is located along a deformation zone between gneiss and massive but fractured Cambrian sandstone, and may span both lithologies.

3.2 Sampling

Sampling for ^{3}H-^{3}He, 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 ^{3}H analysis were collected in duplicate 1 l glass bottles. Samples for dissolved helium and neon isotope analysis were collected in duplicate in clamped-off copper tubes, connected to the well tap through a closed hose system. Tritium and noble gas 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, 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 CFC-12 and SF_6 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 Bullister and Weiss (1988).

In April 2012, one of the wells was sampled for ^{39}Ar and ^{85}Kr through in-field degassing of approximately 2.5 m^3 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.

3.3 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 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). Because Ne only has an atmospheric source, offsets between measured and solubility equilibrium concentrations of Ne can be used as a proxy for excess air and also for potential degassing.

The terrigenic helium component was calculated as the measured concentration minus the equilibrium and excess air components, assuming a terrigenic $^3He/^4He$ ratio of $1*10^{-8}$. The terrigenic helium isotope ratio was validated on the samples with high terrigenic helium and low tritium concentrations (Fig. 3). Tritiogenic helium ($^3He^*$) was then calculated for each sample, deducting estimated solubility equilibrium, excess air and terrigenic components from measured ^3He concentrations. The uncertainty of the tritiogenic helium component was calculated including the uncertainty in the measurements, in the set terrigenic helium isotope ratio, the recharge temperature and recharge altitude.

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 tritium content of precipitation. To evaluate the consistency of the measured tracer concentrations and detect potential tracer-specific complications, measured data was plotted in selected combinations of tracer-tracer plots, together with predictions of the PM, EM and a binary mixing (BM) model. Finally, groundwater age distribution modelling was conducted for four PSWs, one for each end member aquifer type, using Lumpy version 2.3 (Suckow, 2012), which is a purpose-made software program for the modelling of tracer concentrations and associated age distributions according to specified MRTs of common LPMs. Simultaneous modelling of multiple tracers is possible, as is parallel modelling of up to two LPMs at specified ratios. Derived offsets between modelled and measured tracer concentrations are quantified as a "Goodness of Fit" (GOF), calculated as:

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

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 2 lists tested LPMs.

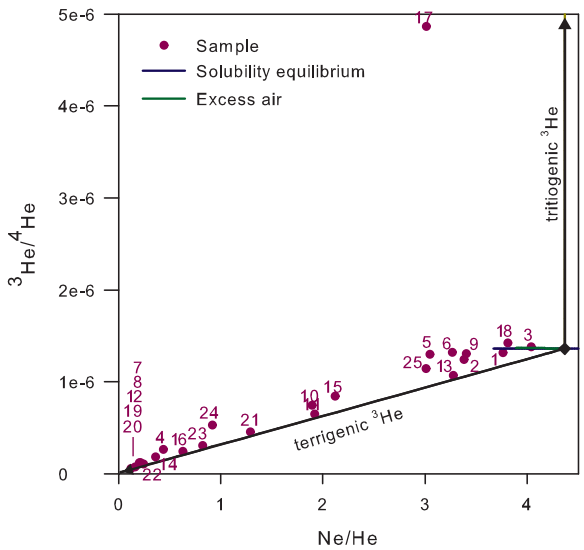

Figure 3. Helium isotope mixing plot. The vertical line demonstrates ratio alterations as a result of increasing ^3He owing to ^3H decay. The inclined line demonstrates ratio alterations as a result of increasing ^3He owing to terrigenic production according to a $^3He/^4He$ ratio of $1*10^{-8}$. The 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 $^3He/^4He$ isotopic ratio of air and the Ne/He ratio in equilibrium with the atmosphere. For a given sample, $^3He^*$ can be estimated through the offset of the measured $^3He/^4He$ ratio to the terrigenic component, if Ne allows and if assuming no mantle contribution.

Table 2. Tested lumped parameter models (LPMs), with associated parameter variables (in Lumpy).

LPM	Basic concept	Parameter variables
Piston flow model (PM)	*No mixing*	*Sample mean residence time (MRT)*
Exponential model (EM)	*Exponential mixing of ages between 0 and ∞*	*Sample MRT*
Exponential piston flow model (EPM)	*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)	*Partial exponential mixing*	*Aquifer MRT, screening depth and aquifer depth*
Dispersion model (DM)	*Mixing according to the advection-dispersion equation*	*Sample MRT and peclet number*

4. Results

4.1 Measured tracer concentrations

Table 3 lists measured raw tracer data and derived parameters ΔNe and ^{3}He*. Due to the incompleteness of the Bremen CFC-12 data set, the GEUS CFC-12 data was favoured for further analysis. However, as can be seen, significant differences occur.

4.1.1 Tritium and helium

Neon concentrations indicate some yet relatively modest amounts of excess air in most samples (ΔNe up to 108%; Table 3, Fig. 4). Five samples show neon concentrations below solubility equilibrium (ΔNe down to -13%), indicating slight degassing or equilibration at higher temperatures. All samples further contain considerably elevated ^{4}He, up to $2*10^{-3}$ ccSTP/kg (Table 3), equivalent to 40 times solubility equilibrium, implying a significant source of terrigenic He. Tritiogenic helium was detected and quantified in 23 samples.

All but two sampled wells (no. 7 & 8) contain significant amounts of tritium (up to 11.9 TU; Table 3). Eighteen samples show ^{3}H/^{3}He ages and tritium concentrations consistent with waters having predominantly recharged since the 1980s (Fig. 5). Exceptions, in addition to PSWs 7 and 8, are no. 18-19 and 24-25 that display tritium concentrations indicative of a considerable pre-modern component, and no. 17, that seem to contain mostly water from the late 1960s. This agrees rather well with known hydrogeological conditions: PSWs 7 and 8 are the only ones abstracting water from a confined setting, wells 18-19 and 25 pump water over long screens in leaky dual-porosity systems and wells 17 and 24 pump water from a leaky sediment aquifer known to be influenced by significant vertical upward flow from the underlying dual-porosity bedrock (Table 1).

The absence of tritium, CFCs and SF_6 in well 8 was confirmed by a ^{85}Kr analysis result of < 0.5 dpm/ccKr. The ^{39}Ar activity in this well was 73±7% modern, equivalent to an age of about 120 years (Table 3).

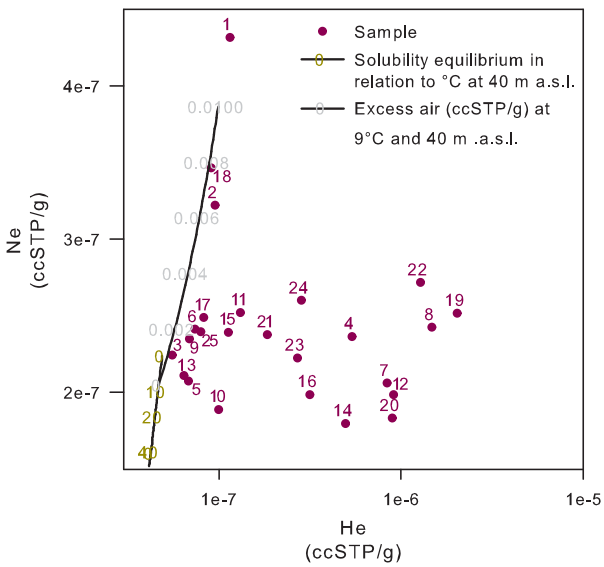

Figure 4. He vs. Ne, demonstrative of relative amounts of excess air and terrigenic He. Most of the wells exhibit excess air (>0 along the excess air curve). Some wells have a Ne-deficit (e.g. PSWs 10, 12, 14, 16 and 20) which could be due to higher-than-assumed infiltration temperature or degassing.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

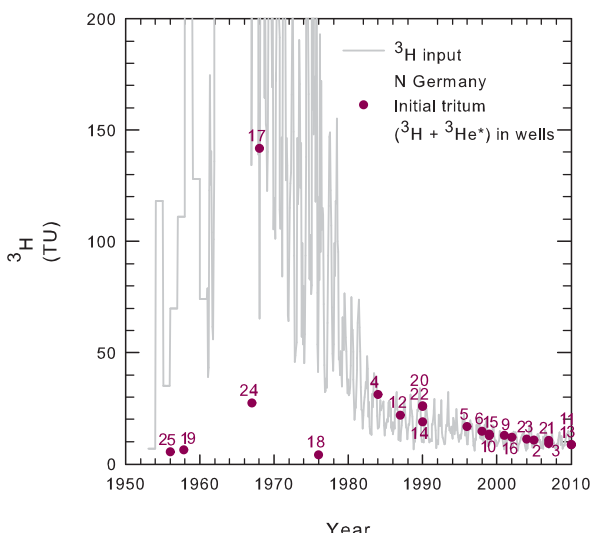

Figure 5. Comparison of recorded tritium input history for N Germany to initial tritium concentrations of the samples.

4.1.2 CFCs and SF_6

Most CFC samples contain concentrations that are internally consistent with mixing of modern and pre-modern water along one of the simple mixing models. However, there are indications of degradation for eight wells (Table 3) and some samples are contaminated as indicated by measured concentrations higher than possible due to solubility and excess air equilibrium with ambient air. Excessive CFC concentrations appear dictated by local pollution plumes as indicated by common concurrence of TCE (trichloroethylene; Table 3), which just as CFCs was 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 these contaminated samples also contain a fraction of water recharged later than 1950, but this fraction cannot be quantified. Apparent CFC ages are generally somewhat older than $^3H/^3He$ ages, which may be an effect of admixing of some pre-modern water and/or due to degradation.

Derived SF_6 concentrations reach up to one thousand times solubility equilibrium. Effectively, all but three samples (no. 7-9) exhibit SF_6 concentrations outside an interpretable range, indicative of a major local contamination source.

4.2 Tracer-tracer plots

Selected tracer-tracer plots are shown in Fig. 6. Plotted tracer concentrations correspond to weighted averages of the duplicate samples. For CFCs, error bars correspond to the standard deviation of the measured values for the given PSW. For ^3H, error bars correspond

Table 3. Measured tracer concentrations and derived parameters excess air (ΔNe) and $^3He^*$.

Well	^3H	^3He	^4He	Ne	ΔNe	$^3He^*$	CFC				SF_6	^{85}Kr	^{39}Ar
								GEUS		Bremen			
		x 10^{-11}	x 10^{-4}	x 10^{-4}			-11	-113	-12	-12			
	(TU)		(ccSTP/kg)		(%)	(TU)		(pmol/kg)			(fmol/kg)	(dpm/ccKr)	(% modern)
1	8.27	15.1	1.15	4.33	108	0	4.79	0.46	4.34	3.45	574		
2[b]	7.19	11.9	0.953	3.22	56	3.5±1.9	0.16	0	1.51	1.15	4210		
3[c]	7.00	7.66	0.555	2.24	8	2.2±1.3	6.38	0.51	4.52				
4[b]	6.26	14.2	5.36	2.36	14	24.8±2.8	3.40	0.19	6.76				
5[c]	6.92	8.85	0.681	2.07	0	9.7±1.4	21.33	0.88	29.66	37.56	78.5		
6[c]	6.78	9.73	0.739	2.41	16	7.8±1.5	9.28	0.32	3.22	2.52	7.74		
7[a,b]	0.10	8.73	8.37	2.06	0	6.3±3.5	0.10	0	0.04	0.05	0.39		
8[a,b]	0.02	10.9	14.8	2.43	17	0	0.13	0	0.05	0.03	0.14	< 0.5	73
9[a,b]	6.86	9.03	0.690	2.35	14	6.0±1.5	0.10	0.01	0.22	0.12	0.94		
10[b]	5.96	7.43	0.998	1.89	-9	6.7±1.2	0.84	0.06	1.18	0.79	7.49		
11[b]	7.60	8.54	1.31	2.52	22	1.0±1.5	5.01	0.14	2.64	1.94	596		
12[b]	5.23	11.1	9.10	1.99	-4	16.7±3.8	0.26	0.02	1.03	0.65	2090		
13	7.62	6.88	0.644	2.11	2	1.1±1.2	0.53	0.04	1.24	0.90	509		
14[a,b]	5.32	9.14	4.96	1.80	-13	13.5±2.3	0.11	0.01	0.05	0.05	11.6		
15[a,b]	6.28	9.50	1.13	2.39	15	7.1±1.5	0.09	0.06	0.24				
16[a]	6.67	7.68	3.15	1.99	-4	5.3±1.7	2.81	0.20	2.14	1.64	4.47		
17	11.94	40.2	0.826	2.49	20	129.8±5.1	1.38	0	0.33				
18	0.53	12.9	0.909	3.47	68	3.6±2.1	0.92	0.11	0.95				
19[a,b]	0.30	11.7	20.3	2.52	22	6.1±8.2	0.12	0	0.05				
20[c]	7.52	10.9	8.92	1.83	-12	18.5±3.8	21.38	1.77	28.25				
21[b,c]	7.94	8.41	1.84	2.38	15	2.5±1.5	5.30	0.34	2.95				
22[b,c]	7.63	14.7	12.7	2.72	31	18.1±5.3	21.30	0	8.83				
23	6.98	8.25	2.69	2.22	7	4.1±1.6	5.10	0.43	3.96	3.06	11.2		
24	2.12	15.0	2.83	2.60	26	25.3±2.3	0.22	0.02	0.13				
25[a,b]	0.25	9.13	0.796	2.40	16	5.7±1.5	0.34	0.02	0.19				

[a] *CFC-degradation indicated during analysis.*
[b] *Indications of oxic-anoxic water mixing by redox sensitive species (see Table A.1), potential for CFC-degradation.*
[c] *TCE (trichloroethylene) present, potentially indicative of CFC-contamination.*

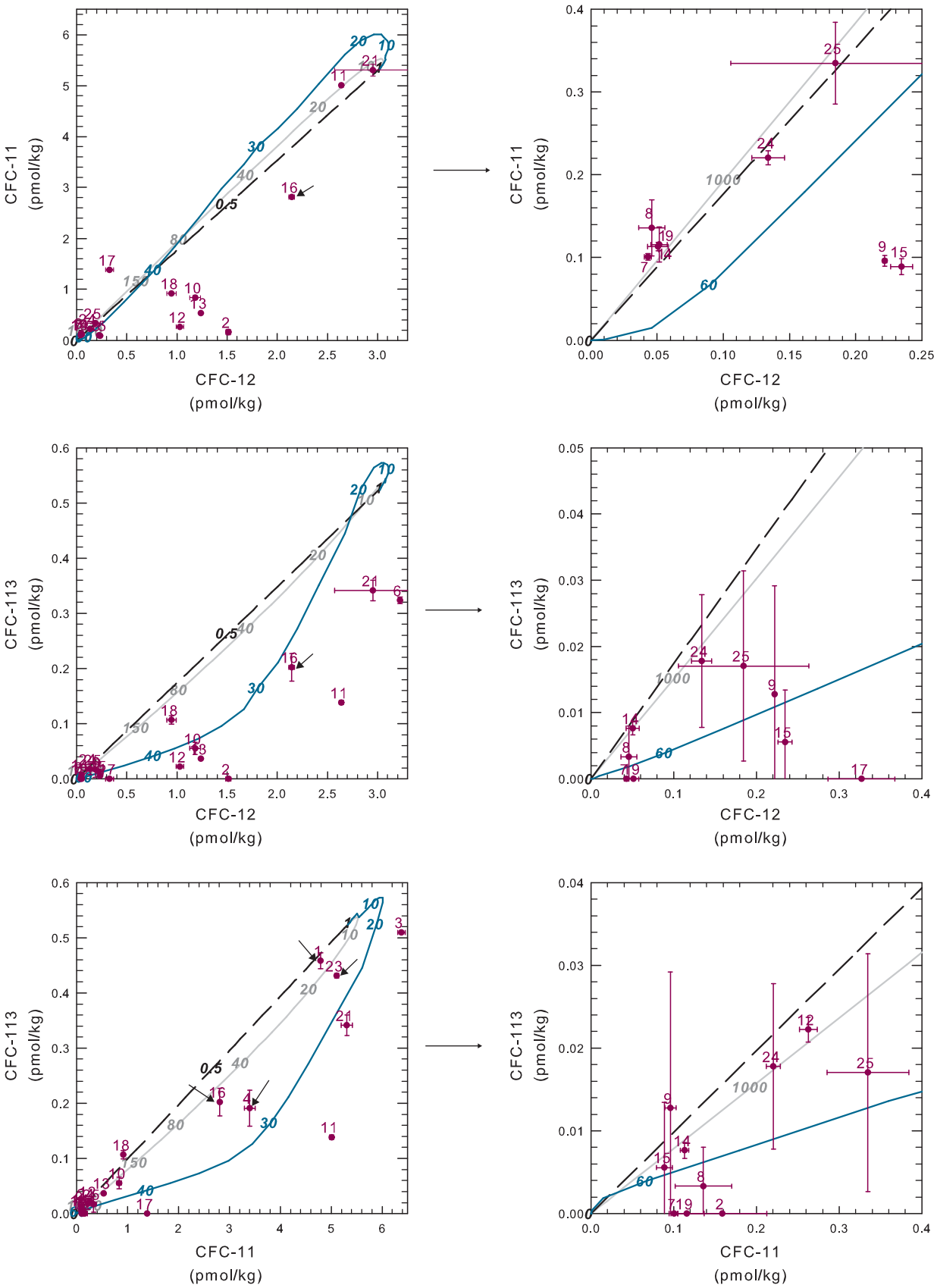

Figure 6. Tracer-tracer plots comparing measured to modelled tracer concentrations for selected LPMs (legend on other side). Wells subjected to age distribution modelling are marked by arrows. Note that some samples are outside the figure borders due to CFC contamination.

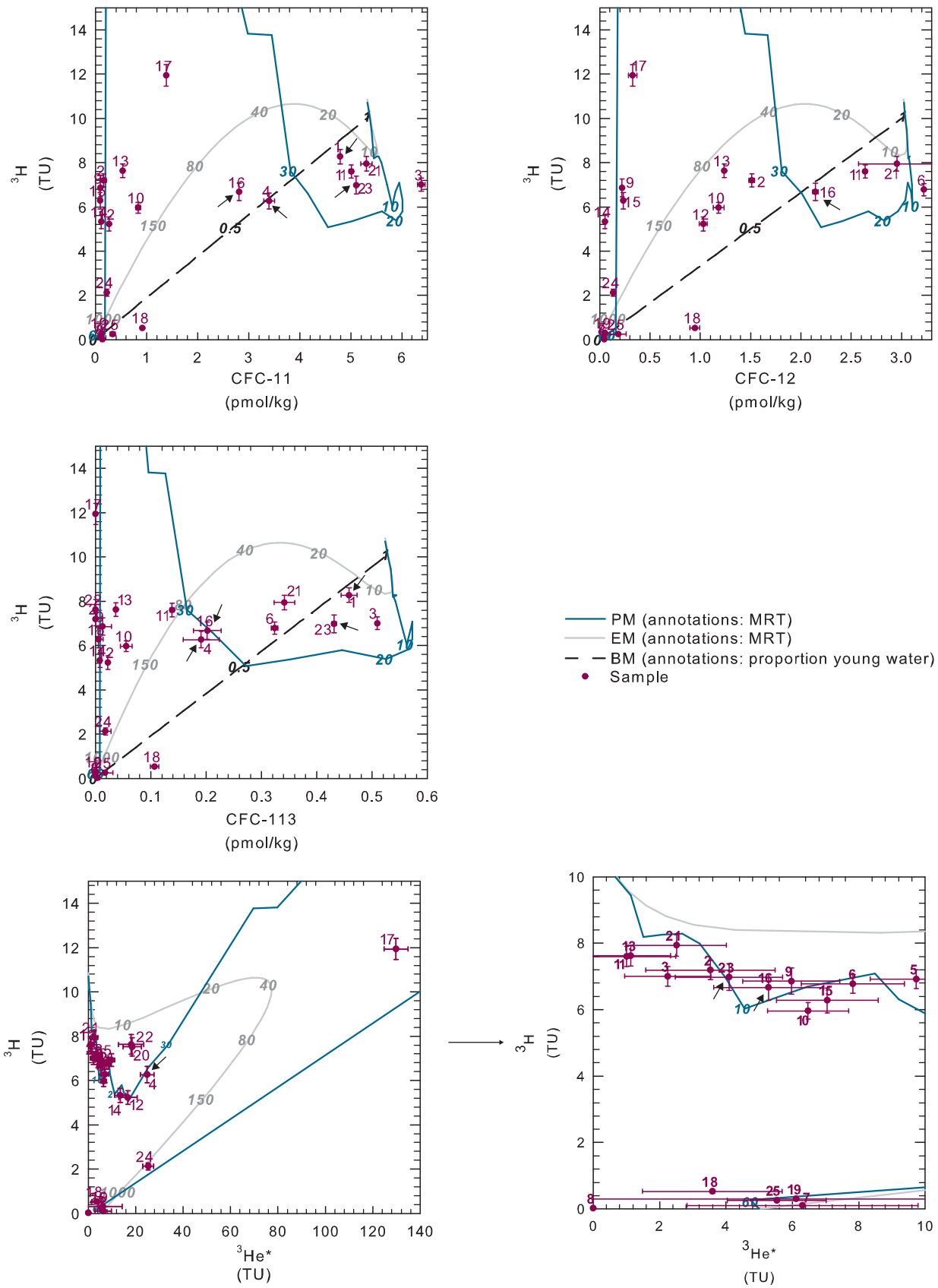

Figure 6 cont.

to measurement uncertainties. Note that samples falling off but within the EM and/or PM mixing model curves in the ^3H-$^3He^*$ plot can be explained by binary mixing, resulting in gradual dilution of the modern component of the water whilst preserving its ^3H-$^3He^*$ ratio.

Ideally, in these plots, samples should (i) fall within the areas bordered by the mixing model curves and (ii) reproduce in a consistent manner in relation to these. Whilst necessary for enablement of tracer data interpretation using LPMs, these conditions do not guarantee that a good fit or unique solution can be obtained from LPMs. Considering the dating range of the applied tracers, samples should further preferably plot as to indicate modern era MRTs, in order for age distribution modelling to at all be viable.

The tracer data analysed do not represent such an ideal case. Several samples plot outside of the area bordered by the mixing model curves in multiple plots and few reproduce in a consistent manner between plots. Further, of those samples that demonstrate plausible consistency with regard to locations within the plots, several suggest primarily pre-modern water contributions which, as noted above, do not constitute a good basis for age distribution modelling by means of the applied tracers (e.g., no. 7-8, 14-15, 18-19, 24-25). In light of the sampling conditions detailed in the previous section, these observations are not surprising. The scatter is an inevitable result of groundwater mixing, CFC degradation and contamination and to some extent also $^3He^*$ uncertainties. The clustering around the origin of the CFC tracer-tracer plots is at least partially a result of CFC degradation.

However, based on the observed tracer-specific complications, one may assign different reliability and weight to the different tracers for further analysis. Tritium is part of the water molecule, was introduced into the environment earlier than CFCs and SF_6, does not observe chemical degradation, cannot be contaminated and should therefore be considered the most reliable tracer. Whereas $^3He^*$ deduction relies on several assumptions, 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 in Fig. 6).

Accordingly, although groundwater age distributions are demonstratively derivable for most samples via a combination of generally adopted mixing models (most apparently by a combination of PM, EM and/or BM models; e.g. ^3H vs. CFC plots; Fig. 6), few are so when including more than two tracer species or when excluding uncertain data. The implication is that few of the analysed samples allow an assessment of groundwater age distribution from the available data. The necessity of multiple tracers for appropriate groundwater age and groundwater age distribution assessment is evident.

4.3 Age modelling

4.3.1 Unconfined sediment reservoir

PSW 23 extracts water from 7 to 10 m b.g.s., from an up to 15 m thick, elongate and unconfined esker deposit (Fig. 2Ai). Relatively permeable tills and fine-grained postglacial material flank the 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.

The tracer-tracer plots including combinations of ^3H, CFC-11 and CFC-113 (Fig. 6) suggest that PSW 23 pump water according to a model somewhere in between a PM and an EM, possibly with a minor proportion of a tracer-free component. The apparent CFC-11 and CFC-113 ages are 27 and 25 years respectively. The ^3H-$^3He^*$ plot points towards a PM with a somewhat younger age (8±3 y).

A satisfactory LPM fit was derived for a combination of 11% tracer-free water and 89% of a partial exponential model (PEM; Table 2) corresponding to the conceptual model (screening depth: 7-10 m b.g.s., aquifer depth: 15 m) and with an aquifer MRT of 10.5 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 (Δ^4Heter = 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), potentially indicative of sorption and/or degradation.

Fig. 7 (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.

4.3.2 Semi-confined sediment reservoir

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 postglacial sand (Fig. 2Aii). The thickness of the overburden varies from a few meters 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, ^{3}H and $^{3}He^{*}$, all suggest apparent ages around 27-35 years (Table 3). However, the tracer-tracer plots including CFC-11 and/or CFC-113 suggest pre-modern water admixing (Fig. 6).

Assuming that the 4 m separating the screens is impermeable enough to prevent the well from capturing everything from 28-40 m b.g.s., a reasonable age distribution solution should result from a mixture of two LPMs. A satisfactory fit was derived for a combination of a mixture of 80% of a PEM with a sample MRT of 29 years and 20% of a PEM with a sample MRT of 75 years (GOF = 0.8). Both PEMs had a total aquifer depth of 42 m.

Fig. 7 (PSW 4) displays resulting fits and age distribution. The major proportion of the abstracted water is suggested to be about 25-35 years old.

4.3.3 Unconfined dual-porosity bedrock reservoir

PSW 16 is located in the NW border area of the dual-porosity sedimentary bedrock aquifer described in chapter 3.1 (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.

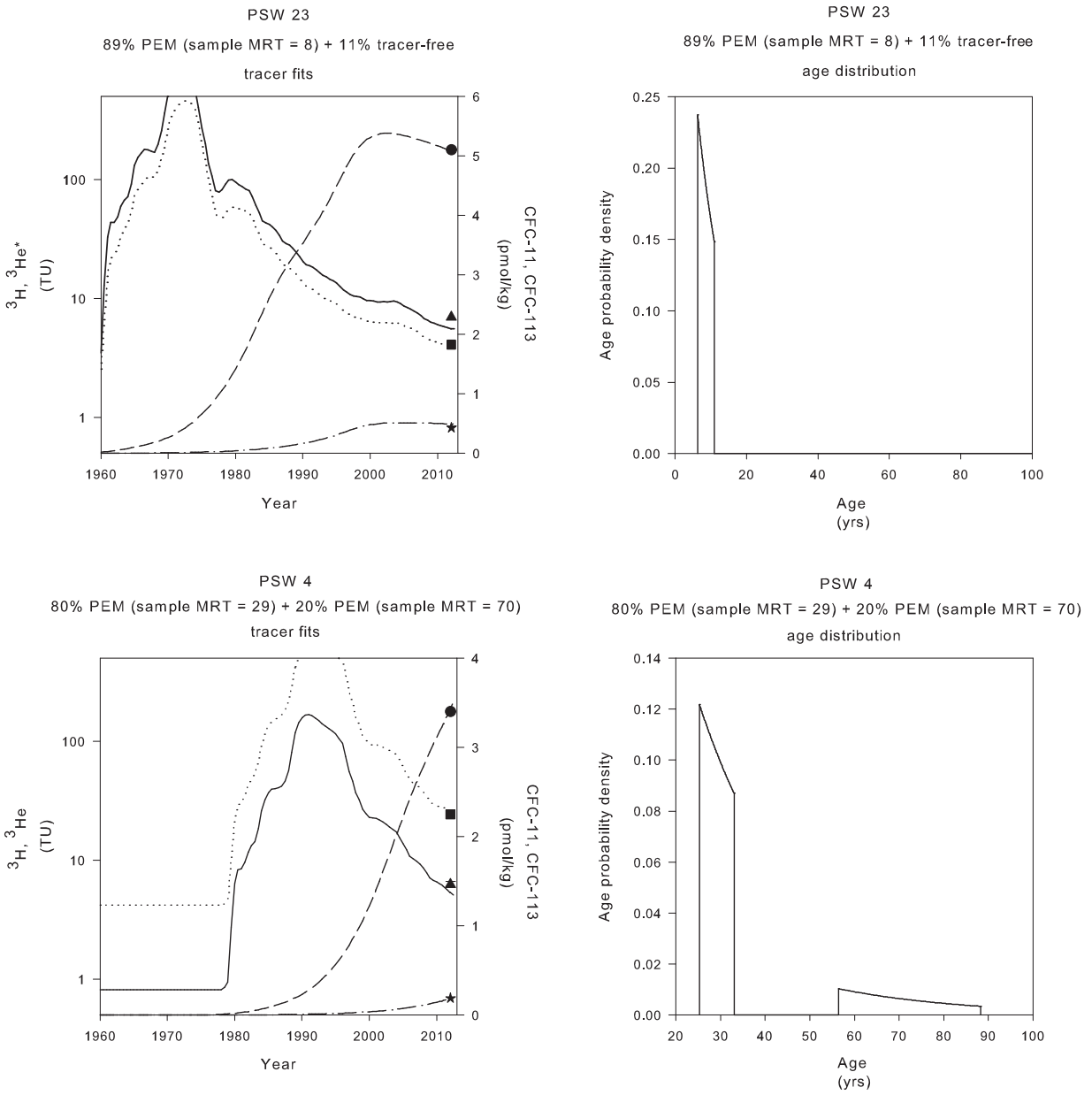

Figure 7. LPM-modelled fits and resultant age distributions for PSWs 23, 4, 16 and 1.

All interpretable tracer data suggest a predominantly modern water component (Table 3). Apparent CFC ages range from 29-35 years. Again, the ^{3}H-^{3}He* apparent age is younger: 10±3 y. The ^{3}H-CFC plots indicate pre-modern water admixing or confirm degradation of CFCs (Fig. 6).

Trials using combinations of all LPMs listed in Table 2 suggest that it is impossible to (with these) aptly fit all CFC species and ^{3}H. Due to the indications of CFC degradation, CFC-12, generally regarded as the more stable of the three species, was favored for fitting over CFC-11 and -113. Using ^{3}H, ^{3}He* and CFC-12, a satisfactory fit was derived for 27% of a tracer free component and 73% of a dispersion model (DM; Table 2) with an MRT of 4 years and a Peclet number of 0.6 (GOF = 1.0). 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. 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. 7 (PSW 16) displays resulting fits and age distribution, with indicated degrees of CFC-11 and -113 loss 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.

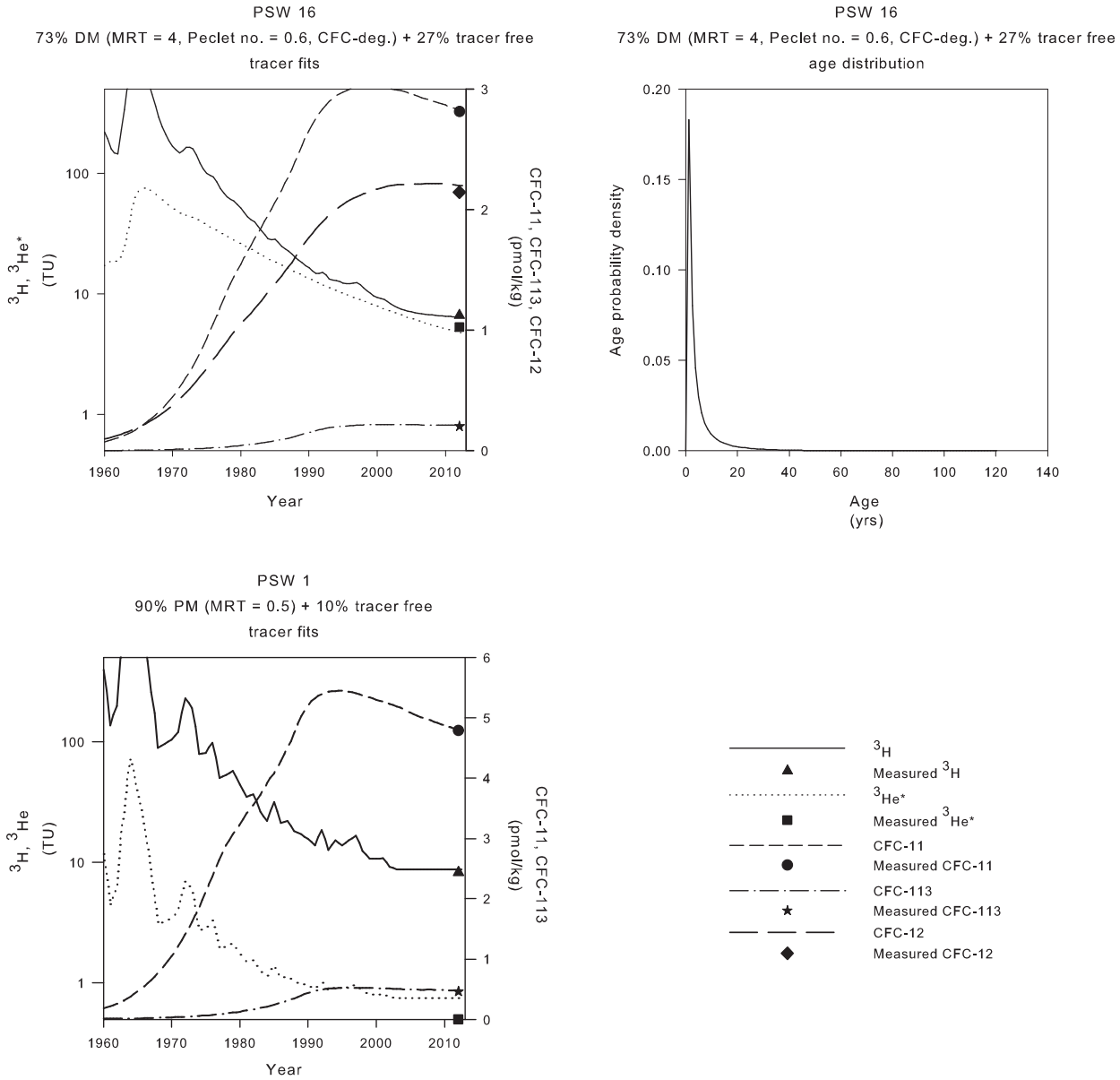

Figure 7 cont.

4.3.4 Unconfined fracture-flow bedrock reservoir

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 (Fig. 2C). CFC-12 and SF_6 contents are higher than peak solubility equilibria. $^3He^*$ cannot be detected.

Representative LPMs of fracture-flow dominated aquifers are typically difficult to presume because of the wide variety of possible flow paths. CFC apparent ages range from 24-28 years. However, the non-detectable $^3He^*$ 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. 6), indicating binary mixing between about 80% recent water and 20% tracer free, 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/-s connects to a deeper fracture system. Clearly, the well is much vulnerable to pollution.

Fig. 7 (PSW 1) displays resulting fits. Surprisingly, the 10% tracer free water does not contain terrigenic helium from the fractured gneiss.

5. Discussion

5.1 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 terrigenic sources of He and contaminated SF_6. Whilst complicating in terms of groundwater age assessments, it is illustrative of common tracer-specific limitations and point towards Scania as a particular area of interest for continued studies into, e.g., natural ^4He and SF_6 sourcing. There is also an evident need for additional ^{85}Kr and ^{39}Ar analyses.

5.1.1 $^3He^*$ and ^4He

Calculating the tritiogenic ^3He component involves separating it from the equilibrium, excess air and terrigenic sourced components. If excess air and terrigenic contributions are small, associated uncertainties may well be negligible. If not, $^3He^*$ calculations should be supplemented by thorough uncertainty estimations, as is the case here. Although the adopted recharge temperature and altitude matters, the most important variable is undoubtedly the terrigenic ^3He component. In this case, tritium free samples confirmed that the terrigenic helium isotope ratio was convincingly close to the radiogenic ratio (1*10-8). This allows for accurate calculations of the tritiogenic helium component, despite the overwhelming terrigenic component that consists almost entirely of ^4He.

The presence of the large component of terrigenic helium in groundwater samples which are largely modern needs to be further investigated in order to allow for improved regional groundwater age assessments. The question is where, how and to what extent the terrigenic He is sourced, and how this sourcing varies between the various hydrogeological settings of the region. A tendency of increased ^4He with screening depth can be noted for the full data set (Fig. 8), however, further work should involve multiple samples from different depths within specific aquifers to come to terms with this matter. Nonetheless, accumulation rates are orders of magnitude higher than can be supported by U/Th-decay only, and terrigenic contributions are hence bound to be diffusion- rather than production controlled. Typically, ^4He concentrations like the ones measured are otherwise only reported for tritium-free waters. An explanation model according to that of Solomon et al. (1996), of internal release from old U- and Th-bearing aquifer (or aquitard; Sheldon et al., 2003) solids, is plausible for the sedimentary aquifers sampled. For the sampled bedrock aquifers, long-standing diffusion of helium through fractures and micropores from below may be part of the explanation (Andrews et al., 1982; Neretnieks, 2013).

5.1.2 SF_6

The measured SF_6 concentrations are among the highest ever reported for groundwater. The reported

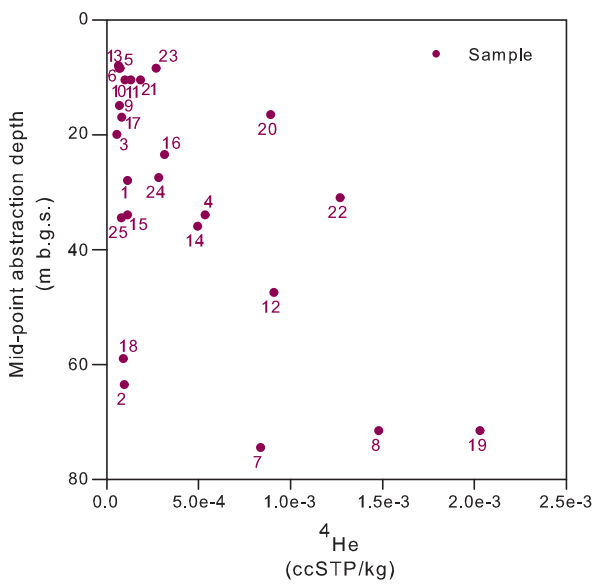

Figure 8. ^4He vs. mid-point abstraction depth, demonstrating a weak tendency of increasing ^4He with increasing abstraction depth.

contents could be due to analytical errors, to local enrichment owing to anthropogenic sources and/or to natural sourcing. Anthropogenic sourcing could be explained through localised leakage from e.g. high-voltage switchgear. Such an explanation is supported by realistically low values for the tritium-free waters (PSWs 7 and 8). Natural sourcing could potentially be explained by fluorite- and sulphur-bearing mineralisations which are known to occur in veins, fractures and rock matrices throughout much of the region (Bergerat et al., 2007; Johansson, 1982) and hence likely also throughout much of aquifer and aquitard solids. Comparing the locations of sampled PSWs with associated types of bedrock and deformation zones, it appears as though there might be some relationship. For example, the well with the highest measured concentration (PSW 2) is located within a deformation zone and the three next-highest-SF_6-concentration wells (no. 11-13) are all located within a region from which fluorite has been mined from local bedrock. With good will, one might argue some correlation between measured F and SF_6 concentrations over the full data set (Fig. 9). However, the absence of SF6 in the tritium free samples from PSWs 7 and 8 and absence of correlation between SF_6 and ^4He (Fig. 10) are arguments against natural production and suggest divergent sourcing of ^4He and SF_6. Further work is clearly needed in order to resolve this matter.

5.1.3 CFCs

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 (in that order). However, this could also be an effect of commonly indicated degradation of the two latter species. CFC contamination, retardation and degradation has been observed in several European studies before (e.g. Bauer et al., 2001; Hinsby et al., 2007). Future studies would benefit from an investigation of the extent of CFC use within different types of industries and localities, which might help assess observed patterns and support relative reliability and accordingly promote the use of the different species.

5.2 Lessons learnt: how to and how not to approach environmental tracer analysis for groundwater age assessment in hydrogeologically heterogeneous regions

5.2.1 Multiple tracers

Groundwater age assessment by means of environmental tracer analysis should always involve as many relevant tracers as feasible. Restricting analytical efforts to one tracer only is precarious as it limits possibilities of assessing and managing potential tracer-specific complications, and as it limits possibilities for assessments of groundwater mixing and associated age distributions. If this study had adhered to any single tracer species only, one would either be in lack of interpretable data (SF_6), or, only be able to tell part of the story (CFCs, ^3H-$^3He^*$). ^{39}Ar and ^{85}Kr offer great opportunities both in terms of covered dating ranges and in terms of relatively few methodological constraints. However, it is a relatively expensive technique and sampling is still tedious and not easily accessible for

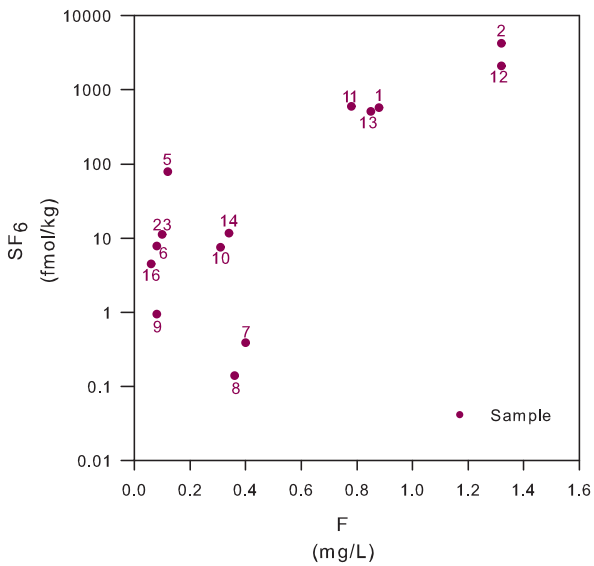

Figure 9. F vs. SF_6, indicating a potential relation which would infer natural sourcing of SF_6.

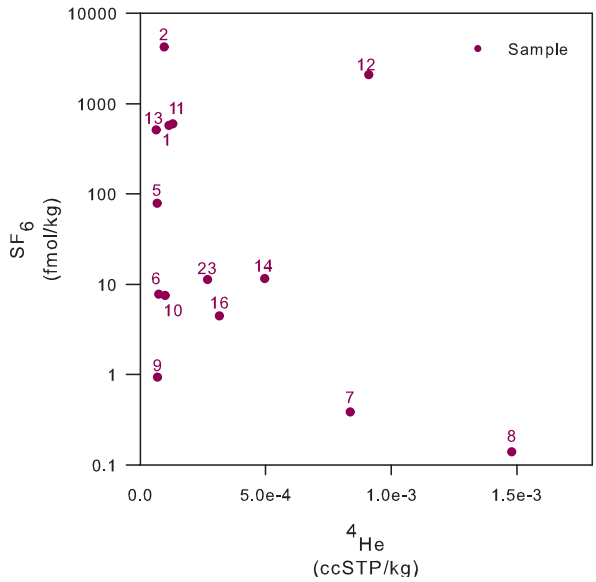

Figure 10. ^4He vs. SF_6. Samples scatter which suggest differing sourcing of the two substances.

everyday practitioners.

5.2.2 Complementary analyses

Environmental tracer analyses should always be complemented by simultaneous sampling and analysis of additional parameters. This includes a full set of noble gases to allow for sample-specific estimations of recharge temperature, and, redox reactive species to allow for assessment of groundwater mixing in general and of anoxic water admixing and thus potential for CFC degradation in particular. For the same reasons, sampling should always be preceded by measurements of (particularly) O_2, oxidation-reduction potential and temperature. The yielded information will help reduce uncertainties of subsequent age interpretations and help understand potentially deviant measured tracer concentrations.

5.2.3 Multiple wells and well types

In order to allow for assessments of tracer sources and sinks for specific groundwater environments, multiple samples from different outtakes and depths from one and the same aquifer should be collected where possible. Preferably, these samples should not be taken from pumping wells in view of associated analytical complications, including heavily disturbed and unpredictable flow conditions and water mixing (Zinn and Konikow, 2007). Clusters of monitoring wells, with restricted screens at different levels, nested along flow paths towards the PSW of interest are ideal in this regard (Hofmann et al., 2010).

5.2.4 Hydrogeological basis

In order to arrive at rigorous groundwater age distribution assessments, environmental tracer analyses cannot be interpreted blindly, but require at least some conceptual model of flow conditions and general stratigraphy. Such a model is needed to compare and judge on the respective probability of one model 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.

5.3 Implications 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 presence. 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 sediment 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. For the few wells and aquifers associated with more substantial pre-modern water components (e.g. PSWs 18, 19, 24), pollution breakthrough might be yet to come and/or significantly diluted. The ^{39}Ar groundwater age of 120 years in well 8 indicates the time scale of pollution risk to this well.

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. LPM fitting of the four type wells is demonstrative of this fact. However, because of the local tracer-specific complications revealed by this study, future groundwater age investigation should aim to include age tracers (e.g. ^{85}Kr) that are not subject to these complications. Further, future work should favour monitoring rather than pumping wells.

6. Conclusions

- Of twenty-five studied public supply wells (PSWs), largely representative of the types of groundwater aquifers present within Scania, southern Sweden, the absolute majority was demonstrated to be dominated by modern water, likely having recharged

since the last few decades. Only two wells, the only in a confined setting, pump solely older water without indications of any post-1950 component. This implies a prevailing and continued anthropogenic pollution risk for many of the region's groundwater resources.

- Comparing multiple measured tracer concentrations to equivalent basic lumped parameter modelled concentrations allows for rigorous assessment of groundwater mixing and potential tracer-specific complications.
- If such mixing and complications is limited, further lumped parameter modelling and fitting against measured concentrations allow estimating groundwater age distributions for a given sample. This may aid in assessing vulnerability to pollution and help understanding the hydrodynamics of the studied system.
- PSWs are generally not well-suited for environmental tracer analysis as these types of wells typically imply extensive groundwater mixing and as they tend to significantly disturb and alter the groundwater levels in the surrounding aquifer and thus flow conditions over time. Although taken under sampling conditions far from optimal, this study shows that age assessment of water from PSWs may still yield much valuable information in terms of associated hydrodynamics.
- Further work is needed to improve the understanding of turnover rates and pollution vulnerability of Scanian groundwater aquifers. Environmental tracers may help in this respect, if the applied tracers are not subject to complications like degradation or contamination, or if those complications can be overcome by a better understanding of the contamination source and transport characteristics.

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Appendix

Table A.1. Temperature readings and selected water chemistry data from the studied wells for interpreting oxic-anoxic water mixing.

Well	Temp. (°C)	DO (% sat.)	Mn (ug/L.)	Fe (mg/L)	FeO(OH) (precipitate)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)
1	8.8	41	0.041	0.0029		35.2	31.7
2	8.8	5.7	492	0.0582		123	3.04
3	8.5	59	3.52	0.0010		25.6	38.4
4	8.6	15	1.49	0.0033	x	29.5	6.69
5	8.9	31	0.255	0.0199		60.6	22.9
6	8.6	46	<0.030	0.0031		27.5	28.9
7	9.0	12	238	4.57		28.2	<0.040
8	9.0	15	262	4.60	x	19.3	<0.040
9	8.2	12	322	2.95	x	40.9	0.055
10	9.2	51	111	0.094		138	0.728
11	8.1	7.1	54	0.0214		58.5	2.27
12	8.3	13	159	0.0055		39.0	1.24
13	8.4	19	21.1	0.0015		82.5	62
14	8.1	37	93	1.19	x	67.7	<0.080
15	8.5	21	247	1.85	x	80.9	<0.080
16	7.8	22	0.21	<0.0004		14.9	14.8
17	8.8	15	28.3	0.0018		68.0	13.7
18	8.7	39	10.9	0.0085		11.3	2.32
19	11	11	4.53	0.0439	x	20.7	0.056
20	8.4	37	41.7	0.0229		18.0	11.3
21	8.8	0.9	1000	0.084		13.1	4.43
22	7.7	18	647	0.141		43.5	1.78
23	9.0	45	1.18	0.0689		17.0	22.2
24	9.2	11	24.8	0.0579		25.5	1.66
25	9.4	2.4	135	0.0017		8.0	0.985

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