Proposal for the use of regular groundwater monitoring results for the authorisation of plant protection products in the Netherlands

Working Group Groundwater Atlas

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WAGENINGEN UNIVERSITY & RESEARCH

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In Nederland wordt 60% van het drinkwater gemaakt uit grondwater. Het grondwater wordt door provincies en waterbedrijven regulier gemonitord op de aanwezigheid van residuen van gewasbeschermingsmiddelen en biociden. Het doel van de Grondwateratlas is om de monitoringresultaten te ontsluiten voor gebruik in de toelatingsprocedure. De ontwikkelde methodiek omvat de selectie van meetresultaten voor een specifieke stof, periode en diepte, en beoogt een verband te laten zien tussen het voorkomen van die stof in het grondwater en het toegelaten gebruik in de Nederlandse land- en tuinbouw. De uitkomsten worden samengevat in een rapport. De voorgestelde methodiek draagt bij aan de risicobeoordeling volgens de Beslisboom Uitspoeling. Aanbevolen wordt om de uitkomst van de methodiek te evalueren in een aantal casussen van de beoordeling van een gewasbeschermingsmiddel op basis van een werkzame stof die reeds is toegelaten op de Nederlandse markt.

Trefwoorden: Gewasbeschermingsmiddel, bestrijdingsmiddel, biocide, pesticide, grondwater, monitoring, drinkwater, toelating, atlas

In the Netherlands, 60% of drinking water is abstracted from groundwater. Groundwater quality is monitored on a regular basis by the regional authorities and the water companies that use groundwater for the production of drinking water. The Groundwater Atlas for pesticides improves access to the pesticide monitoring results and a procedure is proposed for the use in registration. The aim of the procedure is to provide a plausible relationship between the presence of a substance in groundwater and the authorised use. It is recommended to evaluate the results obtained from the procedure in a number of risk assessment cases for a plant protection product based on an active ingredient which is already on the market.

Keywords: Pesticide, groundwater, monitoring, drinking water, registration, plant protection product, atlas

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Preface

In the registration procedure for plant protection products in the Netherlands, the leaching of active substances and relevant metabolites is assessed using models that describe the fate of these substances in the plant-soil system. The decision tree follows a tiered approach, where the lower tiers require less effort and information but are more conservative; higher tiers aim at being more realistic but require more effort and information. The lower tiers consist mainly of model calculations for the prediction of the potential for leaching to groundwater. If a safe use cannot be demonstrated based on these calculations, data from targeted groundwater monitoring studies can be used in the higher tiers of the decision tree. The aim of such targeted monitoring studies is to provide proof of the safe use of a plant protection product.

According to the Uniform Principles (EC 546/2011), Member States need to include monitoring data on the presence or absence of the active substance and relevant metabolites in groundwater in their evaluation of a plant protection product. In the Netherlands the groundwater quality has been monitored regularly by regional government authorities (Provinces of the Netherlands) and by drinking water companies for many years. These monitoring data are not generated for the purpose of authorisation of plant protection products, but to monitor the chemical status of the groundwater. Because these regular monitoring data could be used by the Board for the Authorisation of Plant Protection Products and Biocides (Ctgb) as a feedback on the results obtained in the other parts of the decision tree on leaching, the Dutch Ministry of Agriculture, Nature and Food Quality (LNV) and the Ministry of Infrastructure and Water Management (I&W) have commissioned Wageningen Environmental Research (WEnR) and the National Institute for Public Health and the Environment (RIVM) to improve access to these monitoring results and to propose a methodology for the use of monitoring results in the Groundwater Atlas in the assessment. The Working Group Groundwater Atlas was commissioned to develop a procedure for the use of regular groundwater monitoring results in the authorisation of plant protection products in the Netherlands.

This report and the Groundwater Atlas version 2022 were developed in the years 2017-2022 within the framework of the Research Theme BO-43-011.01-004. The Working Group Groundwater Atlas consisted of Roel Kruijne (WEnR), Erik van den Berg (WEnR), Mark Montforts (RIVM), Mathijs Meering (RIVM), Gijs Janssen (Deltares), Anton Poot (Ctgb) and Martin de Jonge (Vitens).

The authors want to thank the regional authorities and the drinking water companies that handed over their monitoring network data and measurement results to the Working Group Groundwater Atlas in order to make them available for use in the registration.

Wageningen, January 2023

Summary

In the Netherlands, approximately 60% of drinking water is abstracted from groundwater. The need to protect this source is described in the European and national guidance and covers all groundwater bodies which are suitable for drinking water production. In the registration procedure for plant protection products in the Netherlands, the leaching of active substances and relevant metabolites is normally assessed using models that describe the fate of these substances in the plant-soil system. Risk assessment of a plant protection product based on an active ingredient which is already on the market has to take into account all relevant groundwater monitoring results for this substance. The Dutch Ministry of Agriculture, Nature and Food Quality (LNV) and the Ministry of Infrastructure and Water Management (I&W) have commissioned Wageningen Environmental Research (WEnR) and the National Institute for Public Health and the Environment (RIVM) to improve access to these groundwater monitoring results and to propose a procedure for their use in the assessment by the Board for the Authorisation of Plant Protection Products and Biocides (Ctgb).

In the Netherlands the groundwater quality is monitored on a regular basis by the regional authorities (Provinces of the Netherlands) and by the water companies that use groundwater for the production of drinking water. The regional authorities select sampling points for their pesticide monitoring which belong to the national and regional groundwater quality monitoring networks. The drinking water companies select sampling points for pesticide monitoring which belong to the observation well fields surrounding their groundwater abstraction sites. The monitoring results show considerable variation in the sampling pattern regarding space, depth, time and frequency and also in the number and type of substances (active ingredients and relevant metabolites).

The Groundwater Atlas version 2022 contains measurement results from the regional authorities and the water companies originating from the last two and three decades, respectively. The major part of these measurement results originates from samples taken at 10 and 25 m depth and from sampling points with 2 m screen length. In most cases, the groundwater at these sampling points originates from soil moisture that has infiltrated at multiple fields and in subsequent years and there will be no direct relationship between the groundwater quality at this depth and a pesticide application at a single agricultural field. For this reason, the procedure presented in this report considers data from groups of sampling points rather than from individual sampling points.

The relevance of a groundwater sample for the risk assessment of a substance depends on the historical use of a pesticide in the area of influence of the sampling point. In lack of such historical use data, the period of authorized use of the substance is used to approximate the potential pesticide leaching. Combining this period with the historical land-use in the area of influence of the sampling point may provide insight in the relation between the authorised use and the measurement results. A steady-state version of the national hydrological model LHM was used to simulate the groundwater flow pattern in the vicinity of the sampling points from the regional monitoring networks and to indicate the expected travel time and the location and shape of the area of influence for these sampling points. Historical land-use in the area of influence of the sampling points was obtained from a series of land-use maps. Time-averaged land-use in the area of influence was aggregated into four categories with a breakdown of agricultural land-use into pasture, maize, arable crops, greenhouses, fruit orchards and flower bulbs.

A procedure is proposed to make a selection from the dataset for the substance of concern and to generate a report with a summary of the measurement results and the land-use statistics. The procedure proposed is described in four steps:

1. Make selections regarding the substance and evaluation period (default or user defined;
2. Make selections based on sampling depth (default or user defined);
3. Make a further selection based on metadata from the sampling points and specific quality issues related to sampling sites, sampling points and samples (implemented in the Groundwater Atlas application);

4. Generate a report with summary statistics of the selected measurement results from the regional authorities and from the drinking water companies in the target layer, and with the number of measurement values and the number of measurement results in the layers above and below the target layer (implemented in the Groundwater Atlas application).

In Step 1 and 2 the user has the choice either to use default settings for the evaluation period and the position of the target layer, or to use case-specific settings. By default, the evaluation period starts at the first authorisation date and ends at the current date or at the last expiration date according to the Groundwater Atlas substance list. Specific details about the history of authorised use may be reason for the user to choose alternative settings for the evaluation period. The default position of the target layer is proposed between 10 and 15 m depth. Alternative settings for the target layer boundaries can be used, for example when the percentage of measurement values in the layer above the target layer is relatively high.

The aim of the procedure is to provide a plausible relationship between the presence of a substance in groundwater and the authorised use. In lack of historical use data, and in view of uncertainties in the measurement results and the other data, the procedure can’t provide proof of such a relationship. In case there is no risk for leaching from the use of a plant protection product according to the assessment based on the decision tree leaching, but the results from the procedure proposed indicate that there might be a potential risk for leaching related to the (historical) use of the product, then the applicant can be asked to provide additional information to demonstrate the safe use of the product.

Conclusions
The need to protect groundwater as a source for drinking water production is described in the European and national guidance. The risk assessment of a plant protection product based on an active ingredient which is already on the market has to take into account all relevant groundwater monitoring results. The new Groundwater Atlas version 2022 improves access to the pesticide monitoring results available from the regional authorities and drinking water companies in the Netherlands.

The aim of the procedure proposed is to provide a plausible relationship between the presence of a substance in groundwater and the authorised use. It combines results from regular, non-targeted monitoring activities with information on the period of authorised use, the groundwater flow pattern according to a steady-state national hydrological model and historic land-use in the area of influence of the sampling point. The extent to which the outcome meets the aim of the procedure differs with the substance. This is explained by the lack of historical use data and by the variation in the sampling pattern regarding space, depth and frequency.

Recommendations
It is recommended to evaluate the results obtained from the procedure in a number of risk assessment cases for a plant protection product based on an active ingredient which is already on the market.

It is recommended to create a stable monitoring network for pesticides which represents the spatial extent of the protection goal. The sampling sites should be part of the existing groundwater quality monitoring networks from the regional authorities and from the drinking water companies, and sampling point depth should correspond with the depth considered in the decision tree on leaching.

The monitoring network data and measurement results from the regional authorities and drinking water companies were transferred from the owners to the developers of the Groundwater Atlas. Technical validation resulted in a few data quality issues related to some 5% of the total amount of measurement results. As soon as these issues are solved, it is recommended to add these measurement results to the Groundwater Atlas in the next regular update.

Anticipating the transfer of monitoring network data, sample data and measurement results owned by the regional authorities towards the National Key Registry of the Subsurface (BRO), the Society of the Provinces of the Netherlands (IPO) provided a dataset with monitoring network data and pesticide measurement results to the developers of the Groundwater Atlas. This dataset from the regional authorities may contain inaccurate screen depth values. It is recommended to replace the current screen depth values in the Groundwater Atlas database with the data values according to the BRO in the next regular update.

In January 2023 a new Groundwater Atlas database version 3.3.2 with additional measurement results from Brabant Water drinking water company was published. The Groundwater Atlas version 2022 user is advised to select this new database version 3.3.2.

The travel time of the groundwater towards the sampling points from the regional authorities was estimated with the national hydrological model LGM. In particular sampling points, the distribution of the calculated travel time may show a range in the order of 100 years. Inaccuracies in the input of the depth of the sampling point and the subsoil profile at the sampling point location may contribute to this wide range. It is recommended to improve the quality of these input data and to investigate the benefit from using more refined hydrological models for calculating the area of influence and the travel time distribution for relevant sampling points.

Water company Vitens provided a dataset with tritium-helium dating results of groundwater samples from the observation well field at two abstraction sites. The estimated travel time according to the national hydrological model LHM was compared with these tritium-helium dating results. Although the model results and the tritium-helium dating results show a similar increase in the age of the groundwater with depth, the absolute difference between the median travel time and the tritium-helium date at the sampling point ranges between 1 and 16 years. In view of these large differences and the limited spatial extent of this dataset, it is recommended to further investigate the plausibility of the travel times estimated with the national hydrological model LHM.

Samenvatting

In Nederland wordt ongeveer 60% van het drinkwater gemaakt uit grondwater. De bescherming van deze bron is vastgelegd in Europese en nationale richtlijnen en omvat al het grondwater dat potentieel geschikt is voor drinkwaterproductie. De Nederlandse beoordeling van het uitspoelingsrisico van werkzame stoffen en relevante metabolieten van gewasbeschermingsmiddelen is gebaseerd op modellen die het transport en de afbraak van deze stoffen in de bodem beschrijven. De beoordeling van een gewasbeschermingsmiddel op basis van een reeds toegelaten werkzame stof dient tevens gebruik te maken van alle relevante grondwater monitoringresultaten. Het Ministerie van Landbouw, Natuur en Voedselkwaliteit (LNV) en het Ministerie van Infrastructuur en Waterstaat (I&W) hebben Wageningen Environmental Research (WEnR) en het Rijksinstituut voor Volksgezondheid en Milieu (RIVM) opdracht gegeven om deze resultaten beter te ontsluiten en om een methode te ontwikkelen voor het gebruik in de beoordeling door het College voor de Toelating van Gewasbeschermingsmiddelen en Biociden (Ctgb).

In Nederland wordt de grondwaterkwaliteit al jaren regelmatig gecontroleerd door provincies en drinkwaterbedrijven. Deze monitoringactiviteiten worden niet uitgevoerd ten behoeve van de toelating van gewasbeschermingsmiddelen en biociden, maar om de chemische toestand van de grondwaterlichamen of de kwaliteit van het ruwwater voor drinkwaterproductie te bewaken. Het belangrijkste doel van de Grondwateratlas is om deze reguliere monitoringresultaten toegankelijk te maken voor gebruik in de toelatingsprocedure. Het doel van de voorgestelde methodiek voor het gebruik van deze monitoringresultaten van het diepe grondwater is om een verband te laten zien tussen de aanwezigheid van een stof in het diepe grondwater en het toegelaten gebruik. De uitkomst is bedoeld als bijdrage aan de risicobeoordeling zoals die is uitgewerkt in de Beslisboom Uitspoeling.

Voor deze monitoringactiviteiten selecteren de Provincies meetpunten die deel uitmaken van de Provinciale Meetnetten Grondwaterkwaliteit of van het Landelijk Meetnet Grondwaterkwaliteit. De waterbedrijven selecteren meetpunten die deel uitmaken van het puttenveld rondom hun winlocaties. De meetnetgegevens en meetresultaten zijn door de bronhouders overgedragen aan de ontwikkelaars van de Grondwateratlas. De dataset vertoont een grote variatie in ruimte, diepte, tijd en frequentie van bemonstering en in het aantal geanalyseerde stoffen.

De Grondwateratlas versie 2022 bevat meetresultaten van de provincies en van de waterbedrijven uit een periode van 2 tot 3 decennia. Het grootste deel van deze gegevens is afkomstig van monsters van het grondwater op 10 en 25 m diepte en van meetpunten met een filterlengte van 2 m. In veel gevallen is het grondwater ter hoogte van deze meetpunten afkomstig van water dat op meerdere percelen en in opeenvolgende jaren is geïnfiltreerd. De kwaliteit van het grondwater ter hoogte van deze meetpunten heeft geen directe relatie met een specifieke toediening op een specifiek perceel. Om deze reden is de methodiek uitgewerkt voor groepen van meetpunten, monsters en meetresultaten.

De relevantie van een grondwatermeetpunt voor de risicobeoordeling van een stof hangt samen met het historisch gebruik in het invloedsgebied. Over het algemeen zijn gegevens over het lokale gebruik niet beschikbaar en om deze reden is de periode van toelating van de werkzame stof gebruikt als benadering. Combinatie van de periode van toelating met het historisch landgebruik in het invloedsgebied van het meetpunt kan inzicht geven in de samenhang tussen het toegelaten gebruik en de meetresultaten. Een steady-state versie van het Landelijk Hydrologisch Model LHM is gebruikt om de grondwaterstroming naar de meetpunten van de provincies te simuleren en om de ligging en de omvang van het invloedsgebied van het meetpunt en de verdeling van de reistijd van het grondwater te bepalen. Het landgebruik in het invloedsgebied is verdeeld over vier categorieën met een onderverdeling van het agrarisch landgebruik in gras, mais, akkerbouw, kassen, fruit en bloembollen.

De methodiek omvat de selectie van de stof, de meetpunten, monsters en meetresultaten in de Grondwateratlas versie 2022 en is beschreven in vier stappen:

1. Selectie van de stof en de evaluatieperiode. Dit kan zowel een werkzame stof als een metaboliet zijn. De gebruiker heeft de optie om zelf het begin en het eind van de periode in te stellen.
2. Selectie van de bodemlaag van de evaluatie. De gebruiker heeft de optie om zelf de bovenrand en de onderrand van de bodemlaag van de evaluatie in te stellen.
3. Selectie op basis van het historisch landgebruik in het invloedsgebied en het kwaliteitslabel van de meetlocatie, het meetpunt en het monster. Deze stap is geïmplementeerd in de Grondwateratlas applicatie.
4. Genereer een rapport met een samenvatting en statistieken van de meetresultaten en de meetwaarden afkomstig van de bodemlaag van de evaluatie; van de provincies, de waterbedrijven, en van beide groepen meetnetbeheerders samen. Deze stap is geïmplementeerd in de Grondwateratlas applicatie.

In Stap 1 en 2 zijn default waarden voor de evaluatieperiode en de bodemlaag van de evaluatie beschikbaar. De evaluatieperiode begint op de datum van toelating van het eerste gewasbeschermingsmiddel op basis van de werkzame stof en eindigt op de laatste expiratiedatum of op de huidige datum. De default instelling voor de positie van de bodemlaag van de evaluatie is tussen 10 en 15 meter diepte. Het rapport bevat, naast de samenvatting van de meetresultaten in de bodemlaag van de evaluatie zelf, tevens de aantallen meetwaarden en meetresultaten in de boven- en onderliggende bodemlaag. Van de meetpunten in de bodemlaag van de evaluatie is de verdeling gegeven van het historisch landgebruik in het invloedsgebied; voor de groep meetpunten met een meetwaarde (concentratie) en voor de groep meetpunten met een meetresultaat (concentratie of limietwaarde).

De resultaten in het rapport op basis van de default instelling van de periode en de positie van de bodemlaag van de evaluatie kunnen aanleiding zijn om andere waarden te kiezen. Details over de historie van het toegelaten gebruik kunnen aanleiding zijn om andere waarden te kiezen voor het begin en het eind van de evaluatieperiode. Een relatief hoog percentage meetwaarden in de bovenste bodemlaag ten opzichte van de bodemlaag van de evaluatie zelf, kan aanleiding zijn om andere waarden te kiezen voor de grenzen van de bodemlaag van de evaluatie.

Conclusies
De bescherming van het grondwater dat potentieel geschikt is voor drinkwaterproductie is vastgelegd in Europese en nationale richtlijnen. De beoordeling van een gewasbeschermingsmiddel op basis van een reeds toegelaten werkzame stof dient gebruik te maken van alle relevante monitoringresultaten. De Grondwateratlas is uitgebreid met (nieuwe) meetnetgegevens en meetresultaten van provincies en waterbedrijven, en met gegevens over de periode van toelating van stoffen op de Nederlandse markt en over het landgebruik in het invloedsgebied van de meetpunten van provincies. Met de release van de nieuwe Grondwateratlas versie 2022 is de ontsluiting van de monitoringresultaten voor gebruik in de toelating verbeterd.

De voorgestelde methodiek heeft tot doel om een verband te laten zien tussen de aanwezigheid van een stof in het diepe grondwater en het toegelaten gebruik. De methodiek omvat de selectie van de stof, de meetpunten, monsters en meetresultaten. De uitkomst in de vorm van het rapport voor de toelating is bedoeld als aanvulling op de resultaten uit andere onderdelen van de beslisboom uitspoeling. De mate waarin de uitkomst van de methodiek voldoet aan de doelstelling verschilt met de stof. Dit wordt verklaard door het ontbreken van gegevens over het historisch gebruik en door de grote variatie van de dataset in ruimte, diepte, tijd en frequentie van bemonstering.

Aanbevelingen
Aanbevolen wordt om de methodiek te evalueren door een aantal casussen te doorlopen voor de werkzame stof van een gewasbeschermingsmiddel dat momenteel is toegelaten op de Nederlandse markt.

De variatie in de dataset voor wat betreft ruimtelijke spreiding, diepte, en tijdstip en frequentie van bemonstering, maakt dat de hoeveelheid beschikbare meetresultaten en daarmee ook de uitkomst van de methodiek per stof verschilt. Om de toepasbaarheid van de methodiek voor het gebruik van reguliere grondwater monitoringresultaten te verbeteren, wordt de opzet van een landelijk meetnet voor bestrijdingsmiddelen aanbevolen. Zo’n meetnet bestaat uit een selectie van de meetpunten van provincies en waterbedrijven en de opzet van het meetprogramma dient zo goed mogelijk aan te sluiten bij het beoogd gebruik in de beoordeling.

Technische validatie van de meetnetgegevens en meetresultaten van provincies heeft geleid tot een aantal vragen aan de bronhouders met betrekking tot zo'n 5% van het totale aantal meetresultaten. Aanbevolen wordt, zodra deze vragen zijn beantwoord, om de betreffende gegevens alsnog op te nemen in de eerstvolgende reguliere update van de Grondwateratlas.

De provincies zijn momenteel bezig met de overdracht van hun grondwater monitoringgegevens naar de Basisregistratie voor de Ondergrond (BRO). Mogelijk wordt de BRO de toekomstige bron van meetnetgegevens en meetresultaten van provincies in de Grondwateratlas. Aanbevolen wordt, zodra dit proces is afgerond, om te inventariseren welke gegevens in de Grondwateratlas verschillen van die in de BRO en of het wenselijk is om beide instrumenten op onderdelen te synchroniseren.

In Januari 2023 heeft WEnR in opdracht van Vewin een Grondwateratlas database versie 3.3.2 gepubliceerd met (nieuwe) meetresultaten van Brabant Water. De gebruiker van de Grondwateratlas versie 2022 wordt geadviseerd om deze nieuwe Grondwateratlas database versie 3.3.2 te selecteren.

De reistijd van het grondwater naar de meetpunten van de provincies is geschat op basis van berekeningen met het landelijk hydrologisch model LHM. In bepaalde meetpunten is de spreiding van de berekende reistijd in de orde van 100 jaar. Een deel van deze spreiding kan verklaard worden uit de invoer; te weten een verschil tussen de filterdiepte volgens de meetnetgegevens van de bronhouder en het profiel van de ondergrond volgens het model. Aanbevolen wordt om de kwaliteit van deze invoer te verbeteren en om de meerwaarde te onderzoeken van meer verfijnde versies van het hydrologisch model LHM.

Waterbedrijf Vitens heeft resultaten ter beschikking gesteld van de datering van grondwatermonsters afkomstig van waarnemingsputten rondom twee winlocaties. De mediane waarde van de reistijd volgens het LHM is vergeleken met de datering. Ofschoon de leeftijd van het grondwater volgens het LHM en volgens datering dezelfde toename met de diepte laat zien, bedraagt het absolute verschil tussen de mediane reistijd en de leeftijd volgens datering in een meetpunt 1 tot 16 jaar. Vanwege dit grote verschil en de beperkte ruimtelijke schaal van deze vergelijking, wordt aanbevolen om de plausibiliteit van de LHM resultaten in de meetpunten nader te onderzoeken en uit te breiden naar studies in andere regio's waarin een datering van grondwatermonsters is uitgevoerd.

1 Introduction

1.1 Protection groundwater

In the Netherlands, approximately 60% of drinking water is abstracted from groundwater. The need to protect this source is described in general terms in the Groundwater Directive 2006/118/EC of the European Union: *"Groundwater in bodies of water used for the abstraction of drinking water or intended for such future use must be protected in such a way that deterioration in the quality of such bodies of water is avoided in order to reduce the level of purification treatment required in the production of drinking water"*. The protection of both groundwater abstraction areas and possible future sources is also included in the Dutch Water Act and is also mentioned in the policy outlook of the Dutch Government "Structuurvisie voor de Ondergrond (STRONG)". This protection goal only describes in general terms to what extent the groundwater needs to be protected and was made more explicit in order to provide a basis for decision taking.
Van den Berg et al. (2017) briefly describe the specific protection goal based on the current regulation (Besluit gewasbeschermingsmiddelen en biociden, Article 8) and the protocol described in Van der Linden et al. (2004).

In the registration procedure for plant protection products in the Netherlands, the leaching of active substances and relevant metabolites is normally only assessed using models that describe the fate of these substances in the plant-soil system. If safe use cannot be demonstrated by these calculations, data from targeted monitoring studies could be used according to the decision tree on leaching (Van der Linden et al., 2004). For the interpretation of monitoring results obtained from a targeted monitoring study, Cornelese et al. (2003) provide guidance on handling of the results and wrote that the null hypothesis to be tested is whether the 90th percentile in space of the long-term average concentration in groundwater at 10 m depth is above 0.1 μg/L.

Risk assessment of a plant protection product based on an active ingredient which is already on the market has to take into account all relevant groundwater monitoring results for this substance. These results can be obtained from the regular monitoring activities conducted by the regional authorities and drinking water companies. Strictly from a registration point of view, these may be referred to as non-targeted monitoring programmes (Gimsing et al., 2019). However, in this report we refer to regular monitoring. The proposed method for the use of regular monitoring results from deep groundwater described in this report may contribute to the risk assessment by providing feedback on the results obtained in the other parts of the decision tree on leaching.

1.2 Decision tree on leaching

Since 2005 the decision tree on leaching is in effect in the Dutch authorisation procedure (Van der Linden et al., 2004). The generic protection goal of the decision tree on leaching is the drinking water function of the groundwater. The decision tree consists of three steps called tiers (Figure 1). If the outcome of a tier does not meet the criterion, safe use needs to be demonstrated in the next tier in order to make registration possible. The lower tiers require less effort and information but are more conservative; higher tiers aim at being more realistic but require more effort and information.

In Tier 1, calculations with the PEARL model for the FOCUS Kremsmünster scenario are used to determine the leaching potential of a substance at shallow depth (1 m below soil surface). No monitoring data can be used in this tier.

Tier 2 involves two parts:

- Calculations with GeoPEARL, a spatially distributed version of the PEARL model, for the potential area of use, and
- The option to use monitoring data from the uppermost groundwater.

Tier 3 evaluates the behaviour of the substance in the saturated part of the soil, up to a depth of 10 m below soil surface. This tier is divided into two parts:

- The option to consider behaviour studies with soil materials from the water-saturated zone, and
- The option to consider monitoring data obtained from a depth of 10 m or more below soil surface.

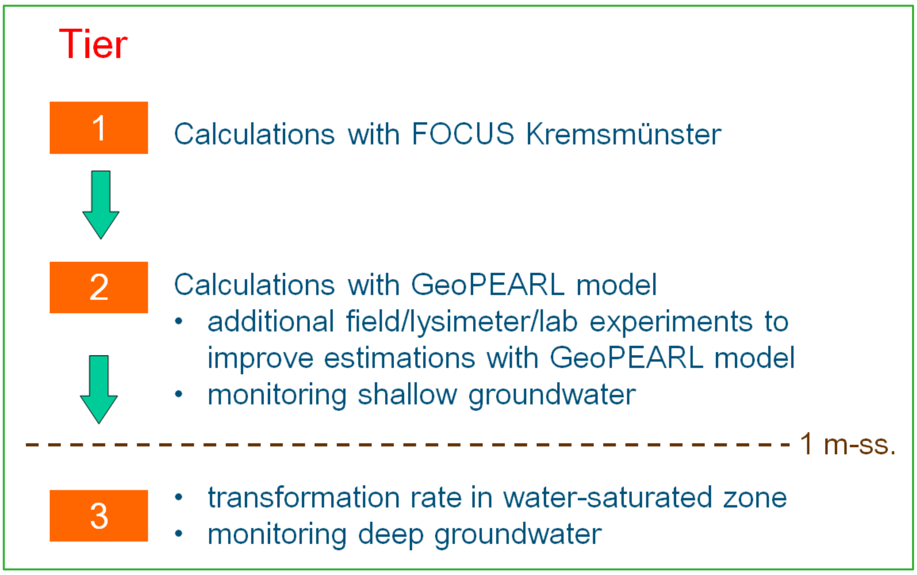


Figure 1 *The Dutch decision tree on leaching.*

A new GeoPEARL version with improved soil organic matter map and groundwater abstraction map was developed and tested for use within the decision tree on leaching (Van den Berg et al., 2017). The authors propose some modifications in the procedure for using the leaching models within the current framework of the decision tree on leaching, in order to warrant the internal consistency of the decision tree.

The use of monitoring data in Tier 2 refers to the uppermost groundwater (ranging from 0 to 1 m below groundwater level) beneath fields which are treated with the substance. It is evaluated whether the 90th percentile concentration in the uppermost groundwater is below the limit value. Provided that all requirements are fulfilled, these monitoring results for the upper groundwater can overrule results obtained from the model calculations.

The use of monitoring data in Tier 3 refers to the deeper groundwater (10 m or below). In most cases there is no direct relationship between a sampling point in deeper groundwater and a treated field (Cornelese et al., 2003). The authors mention the need of careful sampling point selection and propose a population of measurement results in the order of one hundred for the statistical testing of measurement results. With this population, the null-hypothesis needs to be tested whether the 90th percentile in space of the long-term average concentration in the groundwater at 10 m depth is above 0.1 µg/L.

1.3 Regular groundwater monitoring data

In the Netherlands the groundwater quality has been monitored regularly by regional government authorities (Provinces of The Netherlands) and by drinking water companies for many years. At present, groundwater samples are collected at thousands of sampling sites throughout the Netherlands (Figure 2). This monitoring data is not generated for the purpose of authorisation of plant protection products, but rather to monitor the chemical status of the groundwater bodies. Because these regular monitoring data could be used by the Board for the Authorisation of Plant Protection Products and Biocides (Ctgb), the Dutch Ministries of Agriculture, Nature and Food Quality (LNV) and Ministry of Infrastructure and Water Management (I&W) have commissioned Wageningen Environmental Research (WEnR) and the National Institute for Public Health and the Environment (RIVM) to develop the Groundwater Atlas for pesticides and to propose a methodology for the use of monitoring results in the assessment.

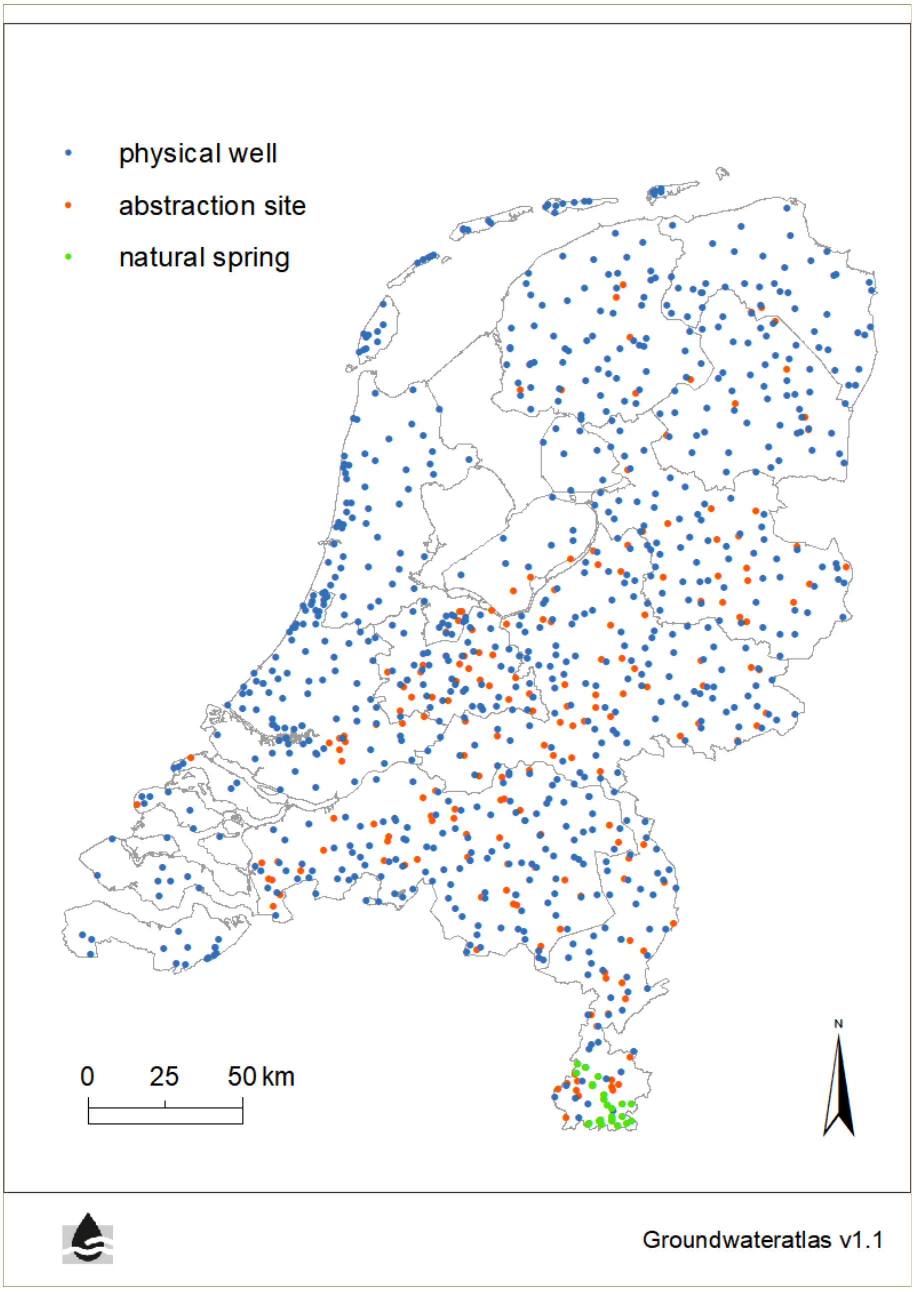


Figure 2 *Sampling sites monitored for pesticides on a regular basis: Physical wells owned by the regional authority (blue), abstraction sites for drinking water (red; with multiple observation wells at different locations shown as a single dot), and natural springs (green) in the Groundwater Atlas v1.1.*

The Groundwater Atlas may contain monitoring results from samples taken at any fixed sampling point and at any depth below the groundwater table. Since there are only few monitoring results available for the uppermost groundwater, the proposal described in this report addresses the use of monitoring results from deep groundwater (starting at 10 m below soil surface according to Tier 3 of the decision tree on leaching). A procedure for the use of monitoring results from the uppermost groundwater may be developed at a later stage.

1.4 Development of the Groundwater Atlas to be used in registration

In the year 2015, the Groundwater Atlas project team initiated a stakeholder group with representatives from Ctgb, the association of drinking water companies in The Netherlands (Vewin), drinking water company Vitens, Province of Drenthe, Province of Limburg, the Dutch crop protection association (Crop Life NL, before June 2022 Nefyto), the Institute of Environmental Science (CML) and the Ministry of I&W (Rijkswaterstaat WVL). In the year 2016, Vewin and eight drinking water companies funded an additional project to prepare the transfer of monitoring network data and a long time series of monitoring results to the project team. The major part of the data supplied in 2016 by the drinking water companies is available in the Groundwater Atlas version 1.1 (Kruijne et al., 2017). In a separate TKI-project, a tool was delivered to the drinking water companies who may want to transfer new monitoring results to the Groundwater Atlas in the future (Kruijne et al., 2018).

The aim of the Groundwater Atlas is to make relevant monitoring data accessible for use in the authorisation procedure. The Groundwater Atlas version 1.1 (available at www.pestidicemodels.eu/groundwateratlas) includes the major part of the relevant measurement results from samples taken at observation wells owned by drinking water companies (Kruijne et al., 2017). In a separate project funded by the Dutch Ministry of Infrastructure and Water Management (I&W), a dataset with monitoring network data and measurement results from samples taken on behalf of the regional authorities during the period 1994 – 2019 was prepared for the Groundwater Atlas. In the project conducted within the framework of Research Theme BO Agro 20-002, metadata from the regional monitoring network samplings sites and registration data were prepared. The 2022 version of the Groundwater Atlas contains the major part of the existing, relevant data on pesticides in groundwater.

1.5 Reading Guide

The next three chapters describe the preparation of the Groundwater Atlas database with internal version number 3.2.2: i.e. the monitoring network owned by the regional authorities and the drinking water companies; the sampling site metadata; and the substance identification and registration data and quality labels for specific data objects. The proposed procedure to use these groundwater monitoring results in registration is described in Chapter 5. The discussion is included in Chapter 6 and recommendations and conclusions in Chapter 0.

The annexes include a glossary for the Groundwater Atlas application and this report (A), details on substance identification and registration data in the Groundwater Atlas (B), maps with sampling points in the LHM input (C), a discussion on the accuracy and uncertainty of the LHM results (D) and land-use data in the area of influence at regional network sampling points (E), an inventory of possible dependency of samples from water company sampling points (F), the use of data quality labels (G) and a table with the age of groundwater at sampling points in two well fields (H).

The Groundwater Atlas User Manual is provided in a separate report (Kruijne et al., 2022). More details on the groundwater monitoring network data and the measurement results from the regional authorities are available in a technical report published at www.pesticidemodels.eu/groundwateratlas.

2 Monitoring groundwater

In the Netherlands the groundwater quality is monitored on a regular basis by regional government authorities (Provinces of the Netherlands) and by water companies that use groundwater for the production of drinking water. In Sections 2.1 and 2.2 the monitoring networks and the available results are briefly described. In Section 4.1 the substance identification and registration data are described. The data specifications of the monitoring network, groundwater samples and the measurement results in the Groundwater Atlas v1.1 are given in (Kruijne et al., 2018). Additional data are needed in order to make a selection of measurement results possible. These metadata of samplings sites are described in Section 3.

2.1 Monitoring networks

2.1.1 Regional authorities

The national groundwater quality monitoring network (LMG) was installed in the period 1979-1984. The LMG consists of approximately 350 permanent sampling sites which are evenly distributed among the Netherlands. Generally, these sampling sites are situated in an area with agricultural land-use. The well screens with 2 m length were installed in aquifers at about 10, 15 and 25 m below soil surface. These design depths were chosen assuming theoretical groundwater ages of 12-13 years at 10 m depth and 33-44 years at 25 m depth (Broers, 2002). The well screens at 15 m depth serve as a backup in case sampling is not possible at either of the other well screens. At sampling sites with disturbing layers in the subsoil or with a relatively deep phreatic groundwater table, the number of screens and screen depth may deviate from these design values. The aims of the LMG are to monitor the status and trends in groundwater quality at approximately 10-25 m depth, and to interpret the environmental risk and policies (Van Vliet et al., 2012).

After the installation of the LMG, the regional authorities established a groundwater quality monitoring network (PMG) by increasing the sampling site density. Each PMG network was composed of a selection from the existing LMG sampling sites within the region and a number of new sampling sites. The purpose and the design of the PMG may differ with the region. In the Provinces of Noord Brabant and Drenthe, the balance was improved in the number of sampling sites in distinct area types of similar land-use, soil and geohydrological conditions (Table 3.1 in Broers, 2002). In other regions, e.g. the Province of Noord-Holland, the expansion aimed at monitoring the groundwater quality in specific, vulnerable areas, or in urban area. The twelve PMG networks together contain approximately 580 sampling sites corresponding with an average density of 1,7 sampling sites per 100 km^2 (Table 1). This table was adapted from (Verhagen et al., 2010). Note that the number of sampling sites of the LMG and PMG networks may be subject to changes during the course of time (Van Vliet et al., 2012). The PMG networks are owned and maintained by the regional authorities. In general, PMG and LMG sampling sites have a similar design and the well screens are installed at approximately the same depth. Depending on the presence of aquitards, sampling sites in regions relatively close to the North Sea coast and the Waddenzee may have screens at depths which deviate from the design and/or have an additional screen at shallow depth (i.e. at 5 m-ss. approximately).

The European Water Framework Directive Monitoring Program Groundwater quality (KMG) was set up in order to reach compliance with the formal requirements of the European Water Framework Directive. A sampling round in the KMG monitoring program comprises of a selection of sampling sites and sampling points (screens) from the LMG and PMG monitoring networks. A KMG sampling round distinguishes sampling points by depth classes (physical wells) and natural springs. These natural springs are located in the southern part of the Province of Limburg (Figure 2). To enable selection of sampling points within a specific depth range, the Groundwater Atlas database contains the depth of the top and the bottom of the well screen (m below soil surface).

Table 1 *Sampling site density in the national (LMG) and regional (PMG) groundwater quality monitoring networks (adapted from Verhagen et al., 2010, Annex 1, Table A).*

regional authority		**LMG**		**PMG**		**LMG+PMG**	**screen depth**
	area (100 km²)	**number of sites**	**density (100 km⁻²)**	**number of sites**	**density (100 km⁻²)**	**number of sites**	**(m-ss.)**
Friesland	35	27	0.8	19	0.5	46	10, 25
Groningen	24	21	0.9	89	3.7	110	10, 15, 25
Drenthe	27	28	1.0	62	2.3	90	9, 15, 24
Overijssel	34	38	1.1	29	0.9	67	5, 10, 15, 25
Gelderland	51	60	1.2	60	1.2	120	Varies
Utrecht	14	12	0.8	39	2.7	51	5-15, >15
Flevoland	15	n.a.	n.a.	n.a.	n.a.	0	n.a.
Zeeland	18	13	0.7	55	3.1	68	4, 13, 20
Noord-Holland	28	25	0.9	58	2.0	83	<5, 5-15, >15
Zuid-Holland	31	39	1.3	47	1.5	86	3, 10, 15, 25
Noord-Brabant	50	60	1.2	66	1.3	126	<5, 5-15, >15
Limburg	22	21	0.9	55	2.5	76	Varies
totals	350	344	1.0	579	1.7	923	

Contrary to the monitoring network data in Table 1, the tables and figures in the remaining part of this chapter refer to the sampling sites and sampling points which are used for regular pesticide monitoring and the results from these activities.

These figures and tables are based on the Groundwater Atlas version 2022 with internal version number 3.2.2. January 2023 a new Groundwater Atlas database version 3.3.2 with additional results from Brabant Water drinking water company was published. The user is recommended to download this new database version, and to select this new database version in the Groundwater Atlas version 2022 software application.

Table 2 *The number of sampling sites and sampling points with measurement results in the Groundwater Atlas version 2022.*

regional authority	**sampling site**	**sampling point**
Drenthe	41	81
Flevoland	59	135
Friesland	69	133
Gelderland	116	212
Groningen	29	66
Limburg	40	75
Noord-Brabant	121	163
Noord-Holland	108	220
Overijssel	54	117
Utrecht	86	137
Zeeland	51	59
Zuid-Holland	54	164
Total (physical wells, screens)	828	1562
Limburg (natural springs)	25	
Total	853	

2.1.2 Drinking water companies

The drinking water monitoring networks are owned by the companies who use groundwater as a source for drinking water production; Brabant Water (BW), Evides, Oasen, Vitens, Waterbedrijf Groningen (WBG), Waterleidingmaatschappij Midden-Limburg (WML) and Waterleidingbedrijf Drenthe (WMD). Water companies monitor the groundwater quality in specific programmes and projects and they store the results in their own database, without systematic reference to the aim of these monitoring activities. The sampling sites owned by the water companies have different numbers of observation wells. Compared to the regional monitoring networks, these sampling points show a wide range in screen length and depth.

In the Groundwater Atlas, each sampling site owned by a water company is part of an observation well which belongs to a specific abstraction site. Compared to the sampling sites of the regional monitoring network, these observation wells are situated in clusters at relatively short distance from the pumping wells. Assuming that the total area of the groundwater protection zones covers 5% of The Netherlands, the density of observation wells within these groundwater protection zones is approximately 1 per km^2. The different order of magnitude of the density of both groups of groundwater quality monitoring networks is illustrated in Figure 3; for an arbitrary 250 km^2 area with four sampling sites of the regional monitoring network and with two clusters of sampling sites.

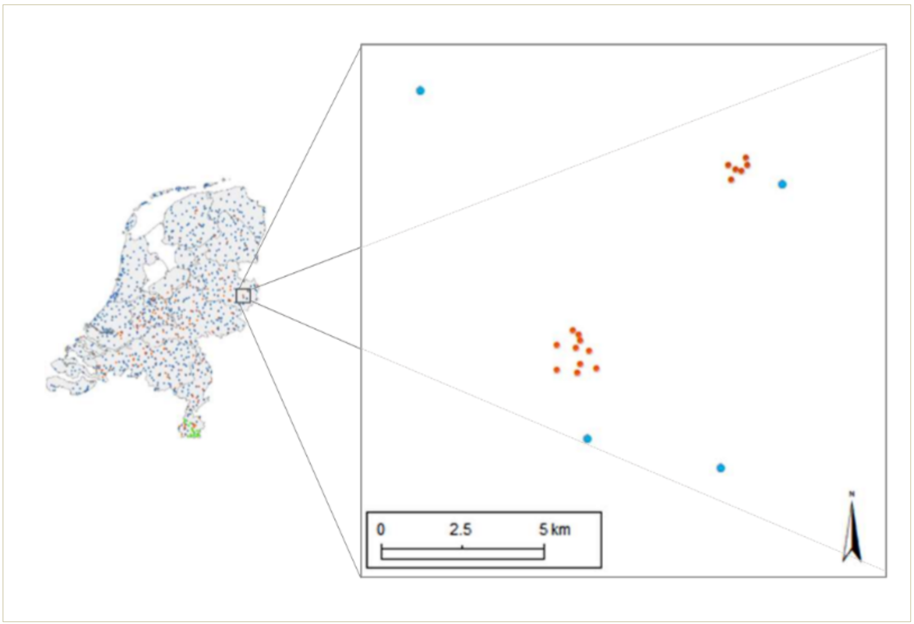


Figure 3 *Sampling site density in the regional groundwater quality monitoring network (blue; four sampling sites) and the water company network (red; two clusters of observation wells at relatively short distance from an abstraction site).*

As described, the groundwater abstraction sites show a wide range in sampling point density. The total number of groundwater abstraction sites, sampling sites (observation wells) and sampling points (well screens) with samples and measurement results in the Groundwater Atlas version 2022 is shown in Table 3.

Table 3 *The number of production sites, sampling sites and sampling points with measurement results per water company (Groundwater Atlas version 2022).*

water company	abstraction sites	sampling sites	sampling points
BW	28	227	548
Evides	2	7	17
OASEN	8	47	109
Vitens	96	1013	2752
WBG	4	56	98
WMD	10	54	271
WML	26	118	234
Total	174	1522	4029

2.2 Available monitoring results

2.2.1 Regional authorities

The regional groundwater quality monitoring network PMG is sampled for pesticides on a regular basis since the beginning of this century. Sampling years and frequency may differ with the region; the interval between two sampling rounds may be 3-4 years for well screens at 10 m depth, and 6 years for well screens at 25 m depth. The wells screens at 15 m depth are generally not sampled. Until 2012, sampling and laboratory analyses were conducted by different regional parties on behalf of the provinces. Starting with the sampling round in the year 2015, the analyses on the samples from all the regional networks are conducted by a single laboratory (KWR, 2018).

Although part of the national groundwater quality monitoring network sampling sites are included in the regional networks PMG, the LMG as a whole has not been used for pesticide monitoring on a regular basis. In addition, part of the PMG sampling points has not been included in the regular sampling rounds.

The Society of the Provinces of the Netherlands (IPO) provided a dataset with the measurement results for pesticides, other groups of chemicals and macro parameters obtained from samples collected in the regional groundwater monitoring networks during the period 1994-2019. Similar to the procedure that was followed with the datasets delivered by the water companies, the project group identified the substances in the regional dataset by the parameter name and CAS number and matched these with the active ingredients of plant protection products and biocide products and their metabolites in the Groundwater Atlas substance list (Section 4.1). New, relevant substances in the dataset were added to the Groundwater Atlas substance list. The total number of measurement results in the dataset from the regional authorities is shown in Table 4.

Table 4 *The number of measurement results per regional authority and decade in Groundwater Atlas version 2022.*

region name	**1994 - 1999**	**2000 - 2009**	**2010 - 2019**	**total**
Drenthe		2361	10398	12759
Flevoland	2271	4156	20089	26516
Friesland	44	6614	22976	29634
Gelderland		15800	55017	70817
Groningen		3118	14818	17936
Limburg		672	13976	14648
Noord-Brabant	1889	16950	71408	90247
Noord-Holland	24	5061	49962	55047
Overijssel		6372	14936	21308
Utrecht		4380	25977	30357
Zeeland		2644	8388	11032
Zuid-Holland		4324	53260	57584
Total (physical wells)	4228	72452	361205	437885
Limburg (natural springs)		746	3143	3889
Total	4228	73198	364348	441774

The distribution of the measurement results from the regional authorities with sampling depth in Figure 4 is based on the midpoint between the upper and lower end of the screen. As can be seen in the figure, 18% of the total amount of measurement results were obtained at 9 m sampling depth and 12% was obtained at 24 m sampling depth.

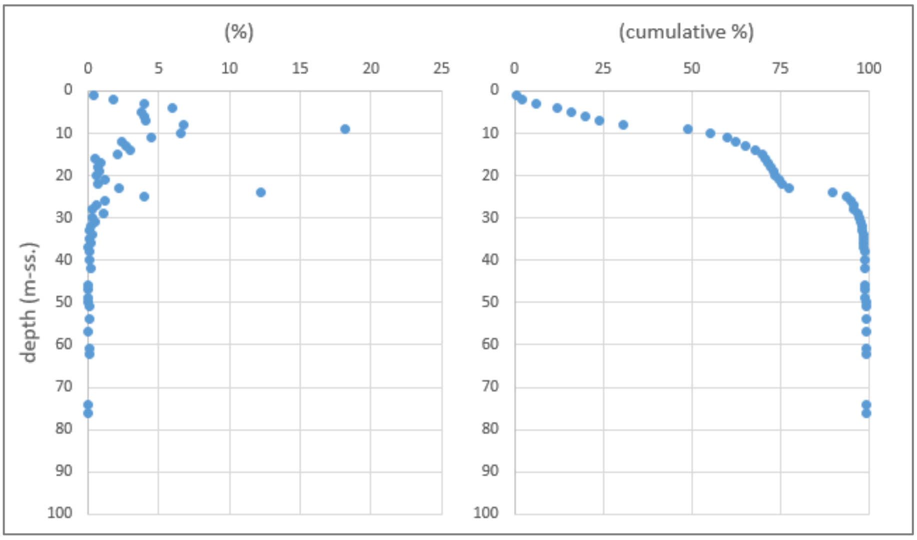


Figure 4 *Depth-distribution of the measurement results from the regional authorities in Groundwater Atlas version 2022.*

The measurement results from the regional authorities originate from samples taken at sampling points with 2 m (72%) or 1 m (26%) screen length. In addition to the numbers reported in this section, the measurement results from particular sampling points with missing screen depth values were not included in the Groundwater Atlas. More details on the groundwater monitoring network data and the measurement results from the regional authorities are available in a technical report published at www.pesticidemodels.eu/groundwateratlas (in Dutch). If the owner can provide these screen depth values, these sampling points and measurement results could be added to the next Groundwater Atlas database version.

2.2.2 Drinking water companies

The sampling frequency and the number of measurement results may vary with the drinking water company and the abstraction site. The total number of groundwater samples, substances, measurement results (either a reporting limit or a measured concentration) and measurement values (measured concentration) per company is shown in Table 5.

Table 5 *The number of samples, substances, measurement results and measurement values per drinking water company in Groundwater Atlas version 2022.*

water company	samples	substances	measurement results	measurement values
BW	1838	158	45579	296
Evides	2373	429	2373	9
OASEN	989	154	8132	785
Vitens	12999	306	251306	8635
WBG	209	274	23520	136
WMD	2255	265	79357	1602
WML	2745	171	34582	352
Total	23408	1757	444849	11815

The total number of measurements in the Groundwater Atlas version 2022 per drinking water company and decade is shown in Table 6.

Table 6 *The number of measurement results per decade and drinking water company in Groundwater Atlas version 2022.*

water company	`60	`70	`80	`90	`00	`10	2020-2021	total
Brabant Water					14588	30991	0	45579
Evides					130	2168	75	2373
OASEN				581	2906	4645	0	8132
Vitens	15		222	67381	96413	79633	7642	251306
WBG					7166	13817	2537	23520
WMD					13601	64674	1082	79357
WML				7451	16443	10688	0	34582
Total	15		222	75413	151247	206616	11336	444849

The distribution with sampling depth of the measurement results from the drinking water companies is shown in Figure 5. Compared to the distribution of the measurement results from the regional authorities shown in Figure 4, a wide range in sampling depth is visible in Figure 5.

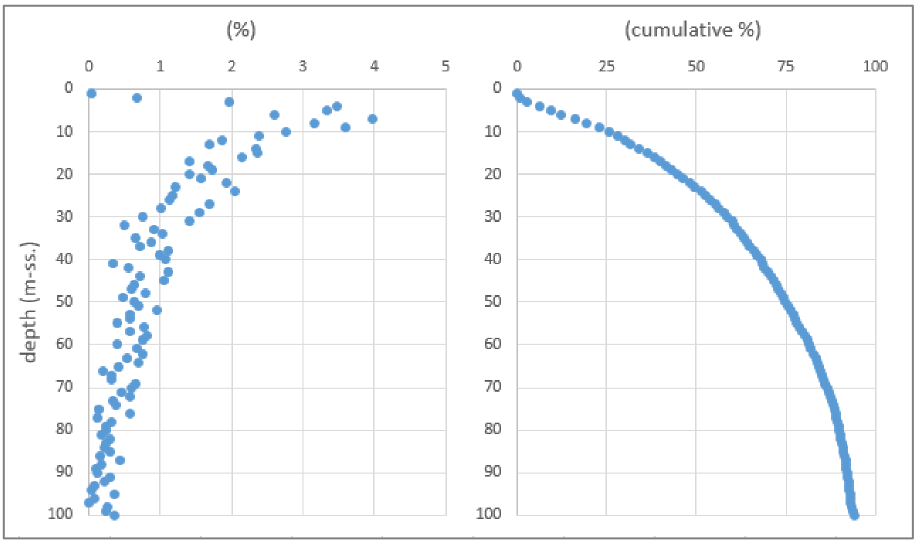


Figure 5 *Depth-distribution of the measurement results from the water companies in Groundwater Atlas version 2022.*

The measurement results from the drinking water companies originate from samples taken at sampling points with 2 m (54%) or 1 m (37%) screen length.

In addition to the numbers reported in this section, new measurement results were recently provided by the water company Brabant Water. These results could be added to the next Groundwater Atlas version 2022 and may be included as part of a regular update of the Groundwater Atlas database in the near future.

2.2.3 Regional authorities and drinking water companies together

The total number of measurement results from groundwater observation wells per sampling year is shown in Figure 6.

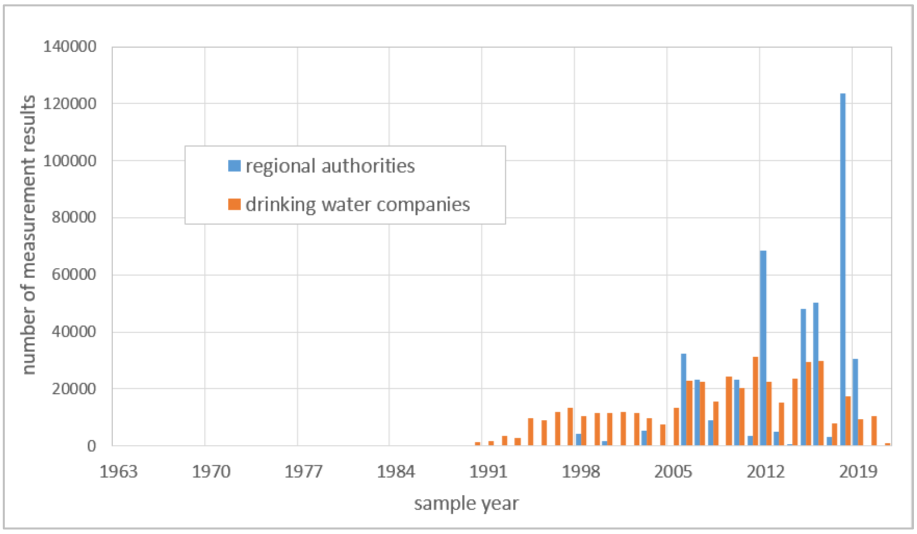


Figure 6 *The number of measurement results from the regional authorities and from the drinking water companies per sampling year in Groundwater Atlas version 2022.*

For the regional authorities and drinking water companies together, the measurement results originate from samples taken at sampling points with 2 m (63%) or with 1 m (32%) screen length.

3 Sampling site metadata

3.1 Introduction

As described in the previous chapter, the major part of the measurement results was obtained from samples taken at approximately 10 m depth from sampling points with 2 m screen length. In most cases, there will be no direct relationship between the groundwater at this depth and a pesticide application at a single agricultural field (Cornelese et al., 2003). Instead, the groundwater at this sampling depth may originate from soil moisture that has infiltrated at multiple fields and in subsequent years. In this report and in the Groundwater Atlas application, the area of influence of a sampling point is considered as the surface area which is connected with the groundwater in the sampling point; via downward soil moisture flow in the unsaturated zone and groundwater flow in the saturated zone. Depending on the annual precipitation and the groundwater flow pattern, the shape and the location of the area of influence may differ with the year.

The relevance of a groundwater sample for the risk assessment of a substance further depends on the historical use of a pesticide in the area of influence of the sampling point. In lack of such historical use data, which are generally not available in the Netherlands, the period of authorized use of the active ingredients was incorporated in the Groundwater Atlas. When combined with the historical land-use within the area of influence of the sampling points, the period of authorized use may provide insight in the relation between the authorised use and the measurement results.

3.2 Groundwater flow pattern

Generally, groundwater infiltration conditions prevail in the higher Pleistocene part of the Netherlands, with forest and arable land, and sandy soils. Regions with upward seepage conditions, i.e. where the groundwater is discharged towards the surface water system, are abundant in the lower Holocene regions of the Netherlands, with grassland, and peat and clay soils. Regions with intermediate conditions are more or less characterised by local interactions between the groundwater and surface water (drainage) systems. These type of regions (Figure 7) were considered in the design of the national groundwater quality monitoring network and part of the regional groundwater quality monitoring networks. Within these 'homogeneous areas' with generally similar land-use, soil and geohydrological conditions, local differences in the pathway and the dynamics of groundwater flow occur. The age of the groundwater at the sampling points within regions with upward seepage conditions shows more variability (i.e. a wider range), compared to the age of the groundwater at the sampling points within regions with groundwater infiltration conditions (Broers, 2002).

The Groundwater Atlas contains measurement results from sampling points at a large number of abstraction sites (Table 3). The volume pumped may vary in time and the abstraction may have influence on the groundwater flow in the (phreatic) aquifer. The Groundwater Atlas does not contain data on pumped volumes of groundwater, but the abstraction may affect the age and origin of the groundwater at the sampling points. In general, the relation between the measurement results and the land-use in the area of influence of the sampling points in the water company network may be more complex compared to a regional groundwater quality monitoring network. For this reason, the working group decided to collect metadata for the sampling points of the regional monitoring network only. In the next phase, the working group may evaluate the usefulness and relevance of these metadata for the procedure proposed in this report and may recommend to extend the current set of metadata to a selection of sampling points owned by the drinking water companies.

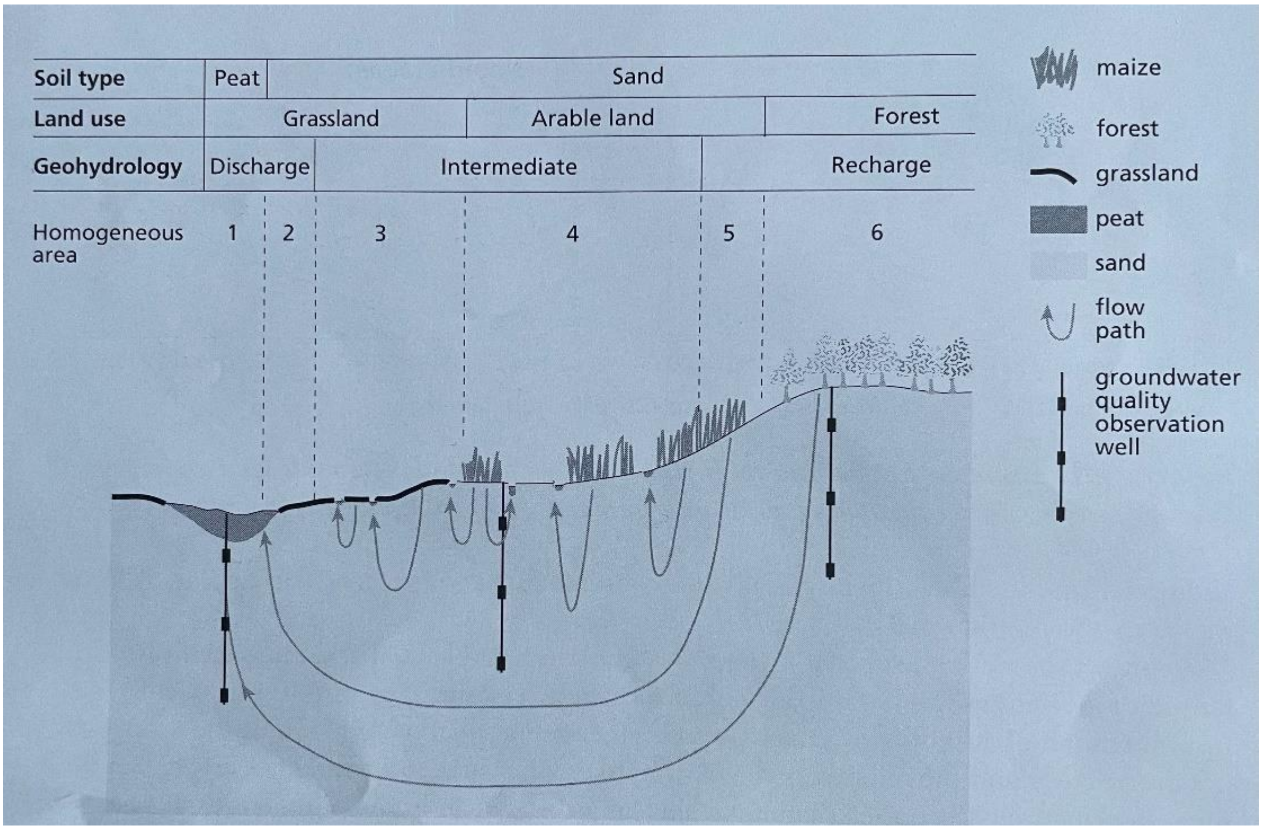


Figure 7 *Simplified schematisation of groundwater flow in area types with homogeneous land-use, soil and geohydrological conditions (copy of Figure 3.6; Broers, 2002).*

3.3 Area of influence and age of the groundwater sample

The national geohydrological model LHM was run in steady state to calculate the location and size of the area of influence and the age distribution of the groundwater at the sampling points of the regional groundwater monitoring networks (Ball and Janssen, 2019). Technical documentation of the model run is provided in Annex C and a discussion on the accuracy and uncertainty is provided in Annex D.

All sampling points in the regional network with the bottom depth of the screen ≤ 30 m-ss. were selected. In order to prepare the input for the LHM model, the top - and bottom screen depths (m-ss.) were converted into screen levels (m+NAP). The dataset was checked for inconsistencies and was combined with the elevation and subsoil profile data in the LHM. Sampling points at the Waddeneilanden were removed because this region is not present in the LHM version used. In addition, a few sampling points were removed because the screen depth reaches below the bottom of the model. The remaining dataset contains 2522 sampling points from the regional monitoring network. A set of 32 sampling points was added to the LHM input in order to compare the LHM results with measurements at two abstraction sites owned by the Vitens water company (Section 3.5).

The LHM version fresh-salt is based on the LHM (Dutch acronym for *National Hydrological Model*) version 4.0 (Hunink et al., 2019). LHM 4.0 is a groundwater flow model, the LHM version fresh-salt is a groundwater flow and solute transport model. To enable solute transport calculations, the vertical resolution of the LHM-fresh-salt is much higher than that of the LHM itself, however the geohydrological schematisation is the same. The vertical schematisation in the LHM 4.0 model consists of eight model layers, representing the phreatic system and the aquifers. Each model layer is represented by a parameter that represents the conductivity for water flow in the horizontal direction (through the aquifer), and a resistance to water flow in the vertical direction (i.e. the exchange with other model layers, with high resistance values representing aquitards). The presence and properties of these subsoil layers are defined at 250 m spatial resolution (based on REGIS 2.2; Hummelman et al., 2019). In the LHM-fresh-salt, the model layers of the LHM are further subdivided into thinner layers for accurate solute transport calculations. This resulted in 39 model layers. For the current purpose, even a higher vertical resolution is applied to the upper groundwater system, resulting in 54 model layers in total. Again, the geological schematisation (i.e. the distinction in aquifers and aquitards and their properties) in all three model versions is exactly the same.

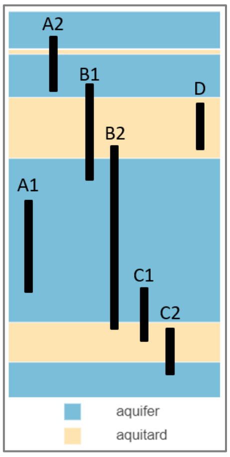
Monitoring wells are generally installed with the screen position in the aquifer. However, in the model some sampling points have (part of) the well screen located in an aquitard. This may be explained by:
1. The coarseness of the model and the uncertainties involved in the geohydrological schematisation.
2. Inaccurate values for the top end and bottom end of the well screen in the Groundwater Atlas.

As for the 2nd source of inaccuracies; the maximum deviation in these screen depth values is estimated at 0,5 m. This estimation is based on the approximate vertical distance between the surface elevation at the sampling site and the upper end of the well pipe. According to the contact person representing the regional authorities, a field survey was conducted recently in order to validate these values for use in the National Key Registry of the Subsurface (BRO - the Dutch acronym for *BasisRegistratie voor de Ondergrond*). In a next phase, these validated data could replace the current data in the Groundwater Atlas version 2022.

To understand the placement of the well screens in the model (entirely in aquifer, partially in aquifer, entirely in aquitard), the following labels were assigned to each sampling point (Table 7):
- A1: entire well screen located in 1 aquifer.
- A2: well screen located in 2 aquifers with no confining layer or a very thin confining layer (aquitard) in between the aquifers (difference between bottom of upper layer and top of lower layer less than 0.01 m).
- B1: well screen located in 2 aquifers with a confining layer in between the aquifers.
- B2: well screen located in 2 aquitards with an aquifer in between the aquitards.
- C1: top of well screen located in an aquifer, bottom of well screen located in an aquitard.
- C2: top of well screen located in an aquitard, bottom of well screen located in an aquifer.
- D: entire well screen located in 1 aquitard; and
- E: Partially below model: entire well screen located in one or many aquifers and/or aquitards, with part of the well screen located below the model (bottom of layer 8).

When the entire screen is located below the bottom of the model, no simulations can be done. This situation occurs at a few sampling points in the Eastern part of The Netherlands. These sampling points were removed from the input file.

Table 7 *The number of sampling points (screens) in the LHM input per case (see text).*



Case	number of sampling points (screens)
A1	1681
A2	173
B1	10
B2	3
C1	72
C2	89
D	491
E *	3
Total	2522

-* Partially below model.

Annex C contains maps with the location of these sampling points. Part of the sampling points in the LHM input apparently were no part in the pesticide monitoring activities conducted by the regional authorities. The number of measurement results and the number of sampling points included in these monitoring activities is given in Table 8. It can be seen in the table that the major part of the measurement results were obtained at samples from sampling points with screen position Case A1.

Table 8 *The number of measurement results and number of sampling points per case in Groundwater Atlas version 2022 (see text).*

Case	measurement results	(%)	sampling points	results per sampling point
A1	262076	66	894	293
A2	31380	8	92	341
B1	1211	< 1	4	303
B2	0	0	0	-
C1	9003	2	35	257
C2	14075	4	46	306
D	76121	19	263	289
E *	282	< 1	2	141
total	394148	100	1336	295

-* Partially below model.

A script was written to post-process and print the results to output files, for collecting land-use data and for further analysis. This output includes:

- The travel times of the groundwater particles; summarized by the range (max, min) and the 5, 50 and 95-percentiles.
- The location and shape of the capture zone; described by a list of grid cells at two resolutions (25 m and 250 m).
- The sampling point / screen position relative to the aquifers and aquitard of the subsoil profile (label A-E; as described above).
- The travel time and path for each individual groundwater particle.

The distribution of the calculated travel time of the particles ending at a sampling point (well screen) may show a considerable range; in case the well screen is positioned partially in an aquitard (Cases B, C, D; Figure 8) or when the flow path passes through an aquitard this age range may reach the order of 100 years. The usefulness of these results for the procedure proposed in this report needs to be further evaluated in a next phase.

In Figure 8 the LHM results are shown for the example sampling site B52G0211 (location name Grubbenvorst). The site has three sampling points (well screens) at different depth. The map shows the starting point of the groundwater particles at the flowpath towards these sampling points (the map at the background is not used in the Groundwater Atlas). The cluster of these starting points represents the area of influence of the sampling point. The land-use in the area of influence is derived from the 250 m cells (the symbol + denotes the edge of the cell) covering these groundwater particles. The 250 m resolution and the location of these cells with land-use data match with the 250 m cells in the LHM model.

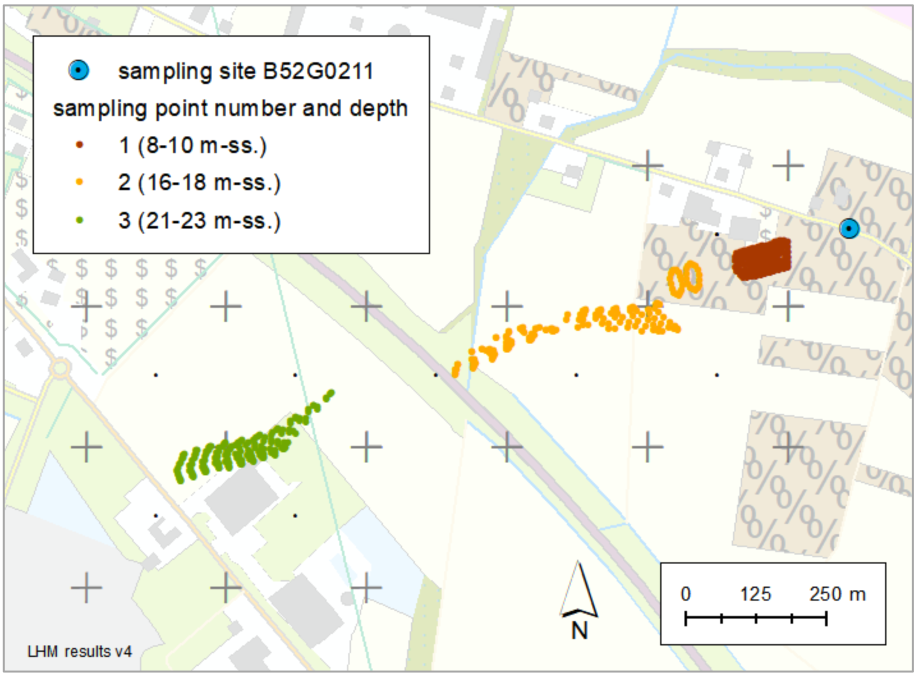


Figure 8 *Example sampling site B52G0211 with the starting point of the groundwater particles flowpath towards the sampling point. The flowpath was simulated with the steady-state LHM version fresh-salt using the subsoil schematisation Regis 2.2 at 250m resolution.*

3.4 Historical land-use

A set of historical land-use data was prepared from a series of rural land-use maps (nine LGN versions, with the production year covering the period 1985–2016. LGN is the Dutch acronym for *Landelijk Grondgebruiksbestand Nederland*). Considering the age of groundwater samples at 10 m depth, more recent land-use data are less relevant at this moment. The period can be extended with more recent land-use data in the future.

The LGN legend contains nine classes of agricultural land-use (Annex E). The design of the regional groundwater monitoring networks in Noord-Brabant and Drenthe considers the land-use classes grassland, arable land and forest (Broers, 2002). In a regional study for five provinces in the Northern part of the Netherlands, land-use was aggregated into the classes agriculture, nature, and urban (Van der Linden et al., 2016). Part of the agricultural land-use classes in the LGN legend, such as fruit orchard, flower bulbs, have a relatively small national acreage. However, in a few particular sampling points the contribution of these minor land-use classes may be significant.

It was decided to incorporate four classes of land-use with a breakdown of agricultural land-use:

- AGRI agriculture.
  - PAST pasture.
  - MAIZ maize.
  - ARCR arable crops.
  - GRHO greenhouses.
  - ORCH fruit orchard.
  - FBLB flower bulbs.
- URBA non-agricultural land-use in urban area.
- NATU non-agricultural land-use and fallow in rural area.
- SWAT surface water.

The area of influence of a sampling point is considered as a homogeneous surface area consisting of 250 m grid cells. For each year (LGN version) the land-use distribution in this homogeneous area of influence is calculated using the number of groundwater particles per 250 m grid cell as a weighting factor.

Depending on the region, the land-use distribution in the area of influence may be more or less constant during the evaluation period. This may be different in regions with typically dominant agricultural land-use pasture and scattered parcels grown with maize. However, the procedure proposed in this report uses the temporal average land-use in the area of influence. The annual land-use distribution for these sampling points may become available at www.pesticidemodels.eu/groundwateratlas.

3.5 Comparing age of groundwater samples

Comparing the simulated age of the groundwater at these sampling points may provide information about the quality of the results. Meinardi (1994) constructed time series of the weighted average tritium concentration in precipitation in the Netherlands. Until the year 1990 these data were collected at a sufficient number of weather stations to derive a regional gradient. The author combined these results with tritium measurements in groundwater samples to estimate the year of infiltration of the water sampled. This resulted in estimations of the age of the groundwater in 688 sampling points of the national and regional groundwater quality monitoring networks within the sandy soil regions of the Netherlands (Meinardi, 2003). However, a comparison of the sampling point data according to Meinardi (2003) and the LMG - and PMG monitoring network data used in the Groundwater Atlas resulted in 79 instances of ambiguous screen number and depths. These data quality issues could not be solved.

For a part of the sampling points in the groundwater quality monitoring networks in the Provinces of Noord-Brabant and Limburg, the age of the groundwater sample was determined based on tritium-helium measurements (Kivits et al, 2019ab; Van Vliet et al., 2019). The result for a particular sampling point can be either a discrete value (age in years), a classification (the sample is a mixture of water of different age classes), or the qualification ‘Meuse’ (i.e. the origin of the groundwater sample is influenced by surface water from the river Meuse that is brought into the region via water supply channels). Although these groundwater age data in sampling points owned by the two regional authorities were not provided to the Groundwater Atlas Working Group, it is believed that these measurement results may be useful to interpret and validate the LHM results in a next step.

As described in the previous sections, the age and area of influence of the groundwater was calculated with the LHM model for the sampling points of the regional networks. In 2010, on behalf of the drinking water company Vitens, the age of the groundwater was determined by $^3H/^3He$ dating in a well field within range of two abstraction sites located in the eastern part of the Province of Overijssel (Broers et al., 2012). These sampling points were added to the LHM input in order to be able the compare the LHM results with these $^3H/^3He$ dating results. A table with the results is included in Annex H.

The samples were taken from 38 observation wells at 12 sampling sites. The age according to the $^3H/^3He$ dating method increases with depth below soil surface (Figure 9; left hand side); which is normal for groundwater infiltration conditions in the higher Pleistocene part of the Netherlands (Broers et al., 2012). In these sampling points, at 10 m depth below soil surface, the age ranges between 10 and 15 years approximately. At the right hand side, the age according to the $^3H/^3He$ dating method is plotted against depth below groundwater level. A similar increase in age with depth below groundwater level (Annex H) can be seen but with a slightly smaller range at a particular depth compared to the plot against depth below surface level. Note that the age according to the $^3H/^3He$ method is included in the residence time in the unsaturated zone. The residence time in the unsaturated zone can be estimated in the order of years. This is generally short compared to the residence time in the groundwater body.

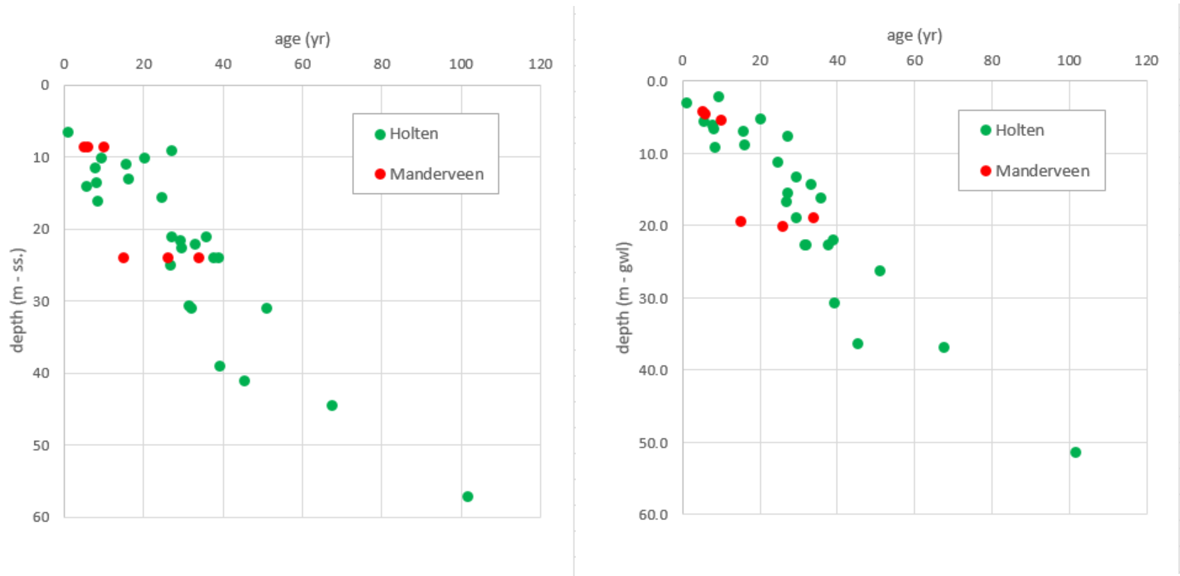


Figure 9 *Age of groundwater at sampling points within range of two abstraction sites owned by drinking water company Vitens; determined by $^{3}H/^{3}He$ dating method (Broers et al., 2012). Left: depth in m below soil surface. Right: depth in m below groundwater table.*

The median travel time in the groundwater body according the LHM model is shown in Figure 10 (left hand side at depth in m-ss.; right hand side at depth below groundwater table). Note that the median travel time in the groundwater body according to the LHM model does not include the residence time in the unsaturated zone.

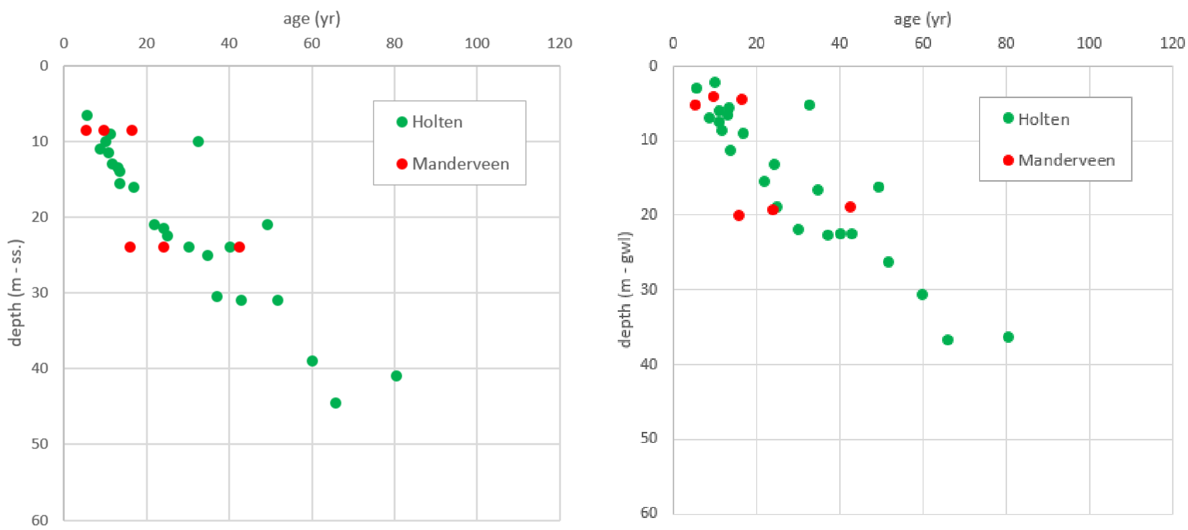


Figure 10 *Median travel time in the groundwater at sampling points within range of two abstraction sites owned by drinking water company Vitens (calculated with the LHM model. Left: depth in m below soil surface (data point 147,57 is not shown). Right: depth in m below groundwater table (data point 147,51 is not shown).*

The scatter plot in Figure 11 shows datapairs with the median travel time in the groundwater body (vertical axis) and the age of the groundwater determined by $^{3}H/^{3}He$ dating method (horizontal axis). The absolute difference between the median travel time in the groundwater body and the age of the groundwater determined by $^{3}H/^{3}He$ dating method ranges between 1 and 16 years (24 sampling points with screen depth < 30 m-ss.).

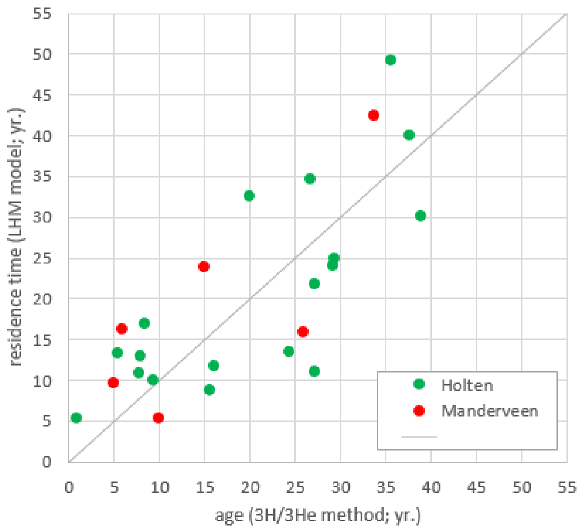


Figure 11 *The median travel time in the groundwater body (vertical axis) compared with the age of the groundwater (determined by $^{3}H/^{3}He$ dating method; horizontal axis) at the sampling points < 30 m depth-ss.*

3.6 Summary

In particular cases, the distribution of the calculated travel time of groundwater particles towards a sampling point (well screen) show a range in the order of 100 years. Inaccurate values for the depth of the top and the bottom of the well screen and the coarseness of the subsoil schematisation at the sampling point contribute to the magnitude of this range. The usefulness of these results for the procedure proposed in this report needs to be further evaluated in a next phase.

The median travel time according to the model was compared with the age determined by tritium-helium dating in the well field within range of two abstraction sites owned by water company Vitens. Starting at 10 m depth approximately, the results obtained from two methods ($^{3}H/^{3}He$ dating and model calculation) show a similar increase in age of the groundwater with depth. At particular depth below soil surface, the results from both methods show a considerable range in the age of groundwater. When these results are plotted against depth below groundwater level, a similar increase in the age of the groundwater with depth can be seen.

At a particular sampling point the difference in age according to $^{3}H/^{3}He$ dating and the median travel time in the saturated zone according to the LHM model ranges between 1 and 16 years (n = 24).

4 Other data components

4.1 Substance identification and registration data

The Groundwater Atlas contains a substance list with active ingredients (and a few other components) of plant protection products and biocide products and their metabolites. The substance identification in the Groundwater Atlas is in line with the authorisation database (www.ctgb.nl). For active ingredients, the date of market introduction of the 1st authorized product and the end of the last authorisation (or the future expiration date) are provided, as well as the registration types (plant protection product, biocide product) and the product group. Using the Ctgb registration databases, the major part of the data gaps present in the first version of the substance list (Kruijne et al., 2017; Annex 4) were filled. Both the substance list and the attached list of synonyms are part of the Groundwater Atlas version documentation. The project group proposed to start a Groundwater Atlas version control group which may provide recommendations concerning the regular updates of the measurement results (Kruijne et al., 2018, Chapter 4). The formal version number of the Groundwater Atlas described in this report is 3.2.2; i.e. software application version number 3, database structure version number 2, and substance list version number 2.

Two types of relation between substances can be stored in the Groundwater Atlas. For 72 metabolites the relation with the parent substance(s) is specified. The other type of relation between substances applies to isomers which are both reported with separate measurement results for the substance and with measurement results for the mixture. This applies to the four specific cases mentioned in Annex B. By default, only one single substance can be selected during a session in the Groundwater Atlas. The substance list within the Groundwater Atlas version 2022 is prepared for the user option to combine the measurement results for substances having this type of relationship in a session. This option may be implemented for use in a future version of the Groundwater Atlas.

4.2 Data quality labels

The Groundwater Atlas database contains quality labels for the data items sampling site, sampling point, and groundwater sample. The intended use of these quality labels is to improve the selection of measurement results; by incorporating information about the current status of these objects. The domain and the meaning of these quality labels are described in this section. Details are provided in Annex G.

Sampling site

0. Default. Sampling site data as provided by the owner.
1. Issue / question concerning the sampling site data addressed to the owner.
2. Issue / question concerning the sampling site metadata addressed to the Groundwater Atlas developer or to the owner.
3. No issue or question.

Sampling point

0. Default. Sampling point data as provided by the owner.
1. Issue / question concerning the sampling point data addressed to the owner.
2. Issue / question concerning the sampling point metadata addressed to the Groundwater Atlas developer or to the owner.
3. No issue or question.

Groundwater sample

0. Default. Sample data and measurement results as provided by the owner.
1. Issue / question concerning the sample identification to the owner.
2. Issue / question concerning one or more measurement results from the sample to the owner.
3. No issue or question.

New information, which in most of the cases mentioned here can be provided by the owner, may lead to a change in the status (the value) of quality labels in the Groundwater Atlas. Such an update could be part of the preparations for the release of a new Groundwater Atlas database version.

4.3 Use of the Groundwater Atlas Input Validator tool

With a grant from the '*TKI-Deltatechnologie*' research programme, The Groundwater Atlas Input Validator was developed in order to facilitate the technical validation of monitoring network data and measurement results. The tool is used by drinking water companies who want to transfer new monitoring results to the Groundwater Atlas; comprising of monitoring network data, sample data and measurement results. The data owner sends the spreadsheets with validated data to the Groundwater Atlas developers. The developers upload these files from the participating drinking water companies and from the regional authorities into one Groundwater Atlas master database. The features of the tool, the proposed work flow and principles of the Groundwater Atlas version control are described in (Kruijne et al., 2018). The procedure is meant to support the transfer of new monitoring results and to maintain consistency with the data between different owners and with the data already present in the Groundwater Atlas.

5 Proposed procedure to use monitoring data in registration

The proposed procedure to use monitoring data in combination with the decision tree on leaching has to combine the relevant measurement results both from the regional authorities and the drinking water companies in the Groundwater Atlas. The aim is to provide a plausible relationship between the presence of a substance in groundwater and the authorised use. The metadata and measurement results used in the procedure come from different sources and monitoring activities. None of these monitoring activities is dedicated to the risk assessment of a plant protection product. In view of the uncertainties in the (meta)data and the results which are combined in the procedure, it is foreseen that the procedure can't provide proof of a relationship between the presence of a substance in groundwater and the authorised use. A plausible relationship between the presence of a substance in groundwater and the authorised use obtained from the procedure may contribute to the assessment within the tiered approach of the decision tree. The procedure can be used to feedback monitoring results in the leaching assessment according to the decision tree leaching. In case there is no risk for leaching from the use of a product according to the assessment based on other parts of the decision tree, but the results from the procedure for the use of groundwater monitoring results indicate that there might be a potential risk for leaching related to the (historical) use of the product, then Ctgb can ask the applicant to provide additional information to demonstrate the safe use of the product.

The procedure is described in the following steps:
1. Make selections regarding the registration dossier (substance and evaluation period).
2. Make selections based on sampling depth.
3. Make a further selection based on metadata from the sampling points and/or groundwater samples.
4. Generate a report with a summary of the selected measurement results from drinking water companies and from provinces.

5.1 Selections regarding the registration

In the Groundwater Atlas, the user can browse a substance list with substance and authorisation features and the number of monitoring results available. For active ingredients, the year of first authorisation and the year of last authorisation (or the year of expiration) are shown. For registration purposes, these are the recommended values for the start and the end of the evaluation period. The user has the option to choose alternative years. When applicable, the metabolite related to the active ingredient is shown in the report. In case the selected substance is a metabolite, the active ingredient is shown in the report. Note that a metabolite can have a parent relation with multiple active ingredients with measurement results in the Groundwater Atlas, and that an active ingredient can have a relation with (degrades into) multiple metabolites with measurement results in the Groundwater Atlas.

The authorisation types are stored in the substance list: the plant protection product type and the biocide type. The information in the substance list and the (internal) substance relationships may help the user to select the appropriate substance and to choose the start and the end date of the evaluation period. The procedure does reflect on the authorised agricultural use of a plant protection product within the evaluation period of the assessment. Other uses (e.g. industry, public authorities, private) and sources (infiltrating surface water) may contribute to the presence of a substance in groundwater samples, but are not considered in the procedure.

At this 1st step, the substance measurement results within the evaluation period are selected. The substance measurement results from samples taken before the start date or after the end date of the evaluation period will not be considered in the next steps.

5.2 Selection based on sampling depth

The target depth for Tier 3 assessment according to the decision tree on leaching is 10 m below the soil surface. In the Groundwater Atlas, a sampling point is defined by the depth of the top and the bottom end of the well screen. The maximum screen length in the Groundwater Atlas is 5 m.

For registration purposes, it is proposed to set the upper boundary of the target layer equal to 10 m-ss. The target layer begins at this upper boundary. Considering the maximum value of the screen length in the Groundwater Atlas, it is further proposed for registration purposes to set the lower boundary of the target layer equal to 15 m-ss. The target layer ends at this lower boundary depth. The position of the target layer is now set at $10 \leq d \leq 15$ m-ss. Note that the user has the option to choose other depth values for the target layer.

At this 2nd step, the measurement results within the target layer are selected. The substance measurement results from sampling points having both the upper end and the lower end of the screen within the target layer are selected. The measurement results and the measurement values from sampling points reaching above the target layer are not selected. These are counted and the totals in this layer will be included in the report (Section 5.4). In a similar way, the measurement results and the measurement values from sampling points reaching below the target layer are counted and the totals will be included in the report as well.

In the example shown in Figure 12, Screen 3 is located within the target layer. Screen 1, 2 and 4 are counted in the layer above the target layer. Screen 5 and 6 are counted in the layer below the target layer.

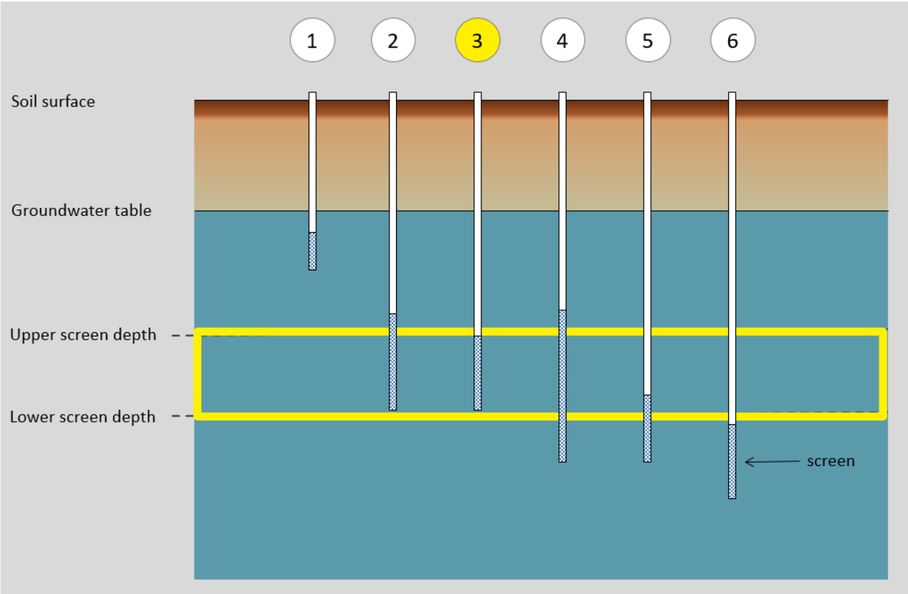


Figure 12 *Sampling points with the screen at different positions relative to the (highlighted) target layer.*

5.3 Further selection based on metadata from the sampling points

Further selection aims at removing false positive and false negative measurement results from the selection as much as possible. These false positive and false negative measurement results have no relation with the authorised agricultural use and/or with the protection goal and they provide no information on the behaviour of the substance in the environment. A false positive measurement result is a measurement value which is considered as non-plausible or not representative for the authorised use. False positive measurement values may be caused e.g. by a damaged sampling site, contamination of a well screen, contamination of a sample.

A false negative measurement result is a reporting limit obtained at a groundwater sample which is considered non-relevant. Examples of false negative measurement results are: a groundwater sample originating from an area where the product has never been used; a groundwater sample originating from water infiltrated in a year prior to the first year of authorisation.

The user options to further reduce the number of false negative measurement results in the selection are to choose alternative values for the start and the end of the evaluation period, considering parent-metabolite relationships and the amount of measurement results available. A few data quality issues regarding sampling sites, sampling points and groundwater samples were labeled in the Groundwater Atlas database. The removal from the selection of these data objects is incorporated in the procedure. Historical land-use in the area of influence is available for the major part of the sampling points owned by the regional authorities. Processing these land-use data is also incorporated in the procedure.

At this 3rd step, information about the quality of the data and the infiltration area of the sampling point is taken into account. Some instances of false positive measurement results are stored in the Groundwater Atlas database. As part of the implemented procedure, these data objects are removed from the selection (target layer) and from the counted measurement values and the counted measurement results in the layer above the target layer and in the layer below the target layer (details are provided in Annex G):

a. The measurement results from samples with quality label = 1: i.e. the measurement results from six sampling points in one regional authority with a reported risk for contamination via surface runoff or by spray drift.
b. The measurement results from samples with quality label = 2: i.e. the measurement results from two regional authorities and specific sampling years.

At this 3rd step, the measurement results from samplings points with less than 5% agricultural land-use within the area of influence (the sum of the agricultural land-use classes; details in Annex E) are removed from the selection (target layer) and from the counted measurement values and the counted measurement results in the layer above the target layer and in the layer below the target layer. For the sampling points within the selection and with no land-use data available, it is assumed that agricultural land-use is present.

5.4 Summarizing the selected measurement results

Measurement results from drinking water companies originate from sampling sites arranged in well fields within short distance from the abstraction sites (pumping wells). Sampling activities may differ with the water company and the abstraction site. In general, sampling density within these clusters of sampling points is high compared to the sampling density of the regional monitoring networks. For these reasons, is was decided to summarize in the Groundwater Atlas report two subsets of the selected measurement results in the target layer; from the regional authorities and from the water companies. The 90-percentile and the maximum of the measurement values are given for each subset and for the combination of both. Counts of the measurement results and the measurement values from sampling points in the layer above target layer and from the layer below are part of the context and included in the report (Figure 13). The average land-use distribution in the sampling points from the regional authorities within the target layer is included in the Groundwater Atlas report: both for the sampling points with a measurement value and for the sampling points with a measurement result (6 resp. 59 sampling points according to the example shown in Figure 13). Note that each sampling point has a weighting factor equal to 1 in these average figures, irrespective of the number of samples.

The percentage of measurement values in the three layers gives information on the depth distribution in the presence of the substance in the groundwater. A relatively high percentage outside the target layer may be explored by generating reports with alternative positions of the target layer.

	A	B	C	D	E	F	G
1	Report for registration						
2							
3	Substance	BAM (CASNr 2008-58-4)					
4	This substance has no metabolites						
5	This substance has no parents						
6							
7	Date of first authorization	27-6-1980					
8	Expiration date	1-10-2008					
9	Productgroup	None specified					
10	Selection of period						
11	Begin date	27-6-1980					
12	End date	1-10-2008					
13							
14	Depth of target layer (m-ss.)						
15	Top	10					
16	Bottom	15					
17							
18	Target layer	regional	water	both			
19		authorities	companies	groups			
20	Number of measurement values	10	85	95			
21	Number of measurement results	97	183	280			
22	Number of measurement values / results (%)	10.3	46.4	33.9			
23	Maximum measurement value (ug/L)	0.68	8.8	8.8			
24	P90 of measurement values (ug/L)	0.6	1.1	0.89			
25							
26	Layer above the target layer						
27	Number of measurement values/number of measurement results	170/860 (19.8%)					
28							
29	Layer below the target layer						
30	Number of measurement values/number of measurement results	626/2274 (27.5%)					
31							
32	Land-use in sampling points from the regional authorities						
33							
34	Sampling points with land-use data	AGRI	URBA	NATU	SWAT		
35	Land-use for the sampling points with measurement values (%, n=6)	72	22	3	3		
36	Land-use for the sampling points with measurement results (%, n=59)	74	12	12	2		
37							
38	Agricultural land-use (AGRI) break down	PAST	MAIZ	ARCR	GRHO	ORCH	FBLB
39	Land-use for the sampling points with measurement values (%, n=6)	16	6	48	0	0	1
40	Land-use for the sampling points with measurement results (%, n=59)	38	4	28	1	3	1
41							
42	Land-use explanation:						
43	AGRI=agriculture						
44	URBA=non-agricultural land-use in urban area						
45	NATU=non-agricultural land-use and fallow in rural area						
46	SWAT=surface water						
47	PAST=pasture						
48	MAIZ=maize						
49	ARCR=arable crops						
50	GRHO=greenhouses						
51	ORCH=fruit orchard						
52	FBLB=flower bulbs						
53							
54	Groundwater Atlas for pesticides in The Netherlands, Version 3.2.2						

Figure 13 *Example Groundwater Atlas report for metabolite BAM.*

In addition to the summary provided in the Groundwater Atlas report, the individual measurement results remain available for interpretation within the Groundwater Atlas by means of tables, graphs and maps, and can be exported.

5.5 Remarks

The procedure applies to the measurement results obtained from physical wells and not to the measurement results obtained from natural springs. A sample from a natural spring is regarded by the regional authority as a groundwater sample and from this point of view the measurement results are within scope of the Groundwater Atlas. However, a sample from a natural spring is a mixture of water with a wide variety in age and origin (Van Vliet et al., 2019) which is different from samples taken at a groundwater observation well. The user chooses via the Groundwater Atlas user interface whether the session applies to the data obtained from physical wells or from natural springs. Combining results from both types of sampling sites is not possible.

The procedure does not apply to substances which have a registration as a biocide product and have (had) no registration as a plant protection product. Information on the use of biocides is too limited compared to plant protection products and the scope of the land-use data is at the rural area. Note that all features in the Groundwater Atlas except the report function are available for any substance with measurement results.

A measurement value from a groundwater sample taken at a sampling point with indications for surface water infiltration can be regarded as a mixture of water from different sources. From a registration point of view, the measurement results from that sample may be regarded as a false positive measurement. However, the available datasets indicating surface water as an origin of groundwater at the sampling points is limited (in spatial extent) and therefore it was decided not to incorporate these in the procedure proposed.

A few plant protection products consist of a mixture of isomer active ingredients with different biological activity. Registration dossiers of these products may apply to the mixture and/or to the most active isomer only. The substance list contains different data rows for the isomer and mixture; these are identified by substance name and CAS number. The Groundwater Atlas version 1.1 contains two instances with measurement results for both the mixture and the active isomer (Annex B). The new substance list in the Groundwater Atlas version 2022 was prepared for the user option to combine the measurement results for the mixture and the isomer. This is the exception to the general rule that a session in the Groundwater Atlas applies to a single substance. The user option to combine a particular mixture and isomer may be implemented in a future version of the Groundwater Atlas.

The (maximum) deviation of the screen depth values for the sampling points in the regional groundwater monitoring networks is estimated at 0.5 m (Section 3.3). Although this deviation may have an effect on the selections made, a different outcome of the procedure proposed is not expected. So, the procedure is implemented with the screen depth values currently available in Groundwater Atlas version 2022. When the transfer of the groundwater quality monitoring network data and measurement results owned by the regional authorities towards the National Key Registry of the Subsurface (BRO) is completed, it is recommended to make an inventory of these differences and to replace the current screen depth values in the Groundwater Atlas.

6 Discussion

The Groundwater Atlas for pesticides includes several options to generate for a single substance a summary of measurement results in different categories, and to explore the distribution of these results in space, depth and time by means of maps, graphs or tables. The Groundwater Atlas version 2022 is extended with the option to generate a report with a summary of selected measurement results. The procedure can be applied either with the settings for the evaluation period and depth of target layer as proposed for the use in registration, or with alternative, user-defined settings. There are no default settings for the evaluation period and depth of target layer available regardless of the substance.

The procedure considers the substance, the evaluation period, the depth and thickness of the target layer, metadata from sampling points, and the quality of sampling sites, sampling points, and groundwater samples. The report contains a summary for the target layer with subsets of the selected measurement results from the regional authorities and from the drinking water companies. Land-use statistics in the infiltration area of sampling points from the regional authorities are summarized; for the group of sampling points with measurement values and for the group of samplings points with measurement results. The measurement results from sampling points above the target layer and from sampling points below the target layer are part of the context and these are summarized in the report as well. Individual measurement results may be important in a specific case and can be exported for further processing.

In the Netherlands, results from groundwater monitoring programmes targeted for registration are not available. The results in the Groundwater Atlas were obtained from the regional authorities and drinking water companies who conduct regular monitoring activities for different purposes. The major part of these measurement results originates from samples at observation wells at approximately 10 m depth and with 2 m screen length. In most cases, at this depth there will be no direct relationship between the groundwater quality and a pesticide application at a single agricultural field. The groundwater at these sampling points may originate from soil moisture that has infiltrated at multiple fields and in subsequent years.

The relevance of a groundwater sample for the risk assessment of a substance further depends on the historical use of a pesticide in the area of influence of the sampling point. In lack of historical use data, which are generally not available at local scale, the period of authorized use of the active ingredient was made available in the Groundwater Atlas. Combined with the historical land-use in the area of influence of sampling points owned by the regional authorities, these data may provide insight in the relation between the authorised use and the measurement results. Relevant historical use may cover the registration period of multiple plant protection products with different authorised use. Major changes in the area of permitted use, the maximum application rate and/or label-specific restrictions may be reason to choose alternative settings for the evaluation period and depth of the target layer.

The proposed procedure for the use of these regular groundwater monitoring results contributes to the risk assessment by providing feedback on the results obtained in the other parts of the decision tree on leaching. The spatial and temporal distribution pattern of the measurement results differs with the substance and specific data components may be incomplete (e.g. land-use in the area of influence is only available for the sampling points owned by regional authorities). There is no generic procedure which can be applied beforehand in order to demonstrate the outcome. Because the measurement results in the Groundwater Atlas were obtained from regular monitoring activities, statistical testing of a hypothesis which can be either accepted or rejected is no part of the procedure proposed. In this aspect the procedure proposed differs from the one described in Cornelese et al. (2003) for the use of the results from targeted groundwater monitoring studies at 10 meter depth as considered in the decision tree leaching.

The proposed method for the use of regular groundwater monitoring results in the authorisation of plant protection products combines datasets from different sources and owners:

- A list of active ingredients and metabolites with substance attributes and basic registration data such as the registration type and the period of authorised use of the active ingredient, delivered by Ctgb;
- The groundwater flow pattern and the distribution of travel time within the saturated zone from the area of influence towards the location and depth of sampling points of the national and regional groundwater quality monitoring networks. These results were calculated with the steady state version of the National Hydrological Model LHM-fresh-salt and based on REGIS 2.2 subsoil schematisation;
- The historical land-use in the area of influence, retrieved from LGN land-use maps covering the period 1985-2016;
- Monitoring network data and measurement results handed over by the regional authorities and drinking water companies. These data were technically validated and stored into the Groundwater Atlas database by Wageningen Environmental Research.

These data sources contain some degree of missing data values and the geographical data may show differences in spatial coverage. Combining these sources inevitably leads to an increase in uncertainty and reduction in the amount of data that remains available for interpretation. For example: according to the monitoring network data provided by the regional authorities and drinking water companies and the subsoil schematisation in the LHM model, a considerable amount of sampling points have the top and/or the bottom of the well screen located within an aquitard. Groundwater quality monitoring wells are generally installed with the well screen located in the aquifer and therefore the quality of these input data needs to be further investigated. Although the actual shape and the location of the area of influence of a sampling point may differ with the year, it was decided to use a single, steady state hydrological model with national coverage rather than dynamic, more refined regional models. The benefits of using more refined hydrological model for calculating the area of influence and the travel time distribution for a selection of sampling points may be explored in a next phase.

In view of these uncertainties and data gaps, it was decided to incorporate the time-average land-use based on a series of land-use maps with basically the same map legend; irrespective of the sampling point and the settings for the evaluation period. In the report for registration, the time-average land-use in the sampling points from the regional authorities is summarized for the group of sampling points with measurement values and for the group of sampling points with measurement results.

In addition to the emission by pesticide leaching from the rootzone at the agricultural field treated, infiltrating surface water is known as another source of pesticides in groundwater. However, the available information about the spatial extent and magnitude of this source and its contribution to pesticide concentrations in groundwater samples is incomplete. For this reason it was decided not to consider infiltrating surface water in the procedure proposed.

The procedure in the new Groundwater Atlas version 2022 applies to measurement results from sampling points in deeper groundwater according to the decision tree on leaching (> 10 meter). Measurement results obtained from new groundwater monitoring networks for pesticides can be incorporated in the current version of the Groundwater Atlas. Measurement results from an early warning system consisting of relatively shallow, permanent observation wells in the upper groundwater may have a direct relation with a single treatment at a particular agricultural field (e.g. Van Loon et al., 2022). A procedure to use the measurement results from such a monitoring network in the registration is not available in the Groundwater Atlas version 2022.

The first version of the Groundwater Atlas database was built in 2016 using a concept version of the data catalogue for the relevant registration objects in the National Key Registry of the Subsurface (BRO). When preparing the data from the regional authorities and/or water companies for the Groundwater Atlas, data quality issues were addressed concerning completeness, missing sampling rounds, nodata values, and truncated data records. More specific quality issues were related to the substance identification, sampling point ID (e.g. in case of a replaced sampling point), plausible screen depth values, monitoring network names, abstraction sites, sampling rounds, sample ID, the distinction between sampling date and date of analysis, the distinction between reporting limits and measurement values, and macro parameters obtained from the samples taken for pesticide monitoring. The major part of these issues was solved during the technical validation conducted in co-operation between the Groundwater Atlas developers and the data owners. The technical validation does not include the verification of individual measurement results.

7 Conclusions and recommendations

7.1 Conclusions

The need to protect groundwater as a source for drinking water production is described in the European and national guidance. The risk assessment of a plant protection product based on an active ingredient which is already on the market has to take into account all relevant groundwater monitoring results. The new Groundwater Atlas version 2022 improves access to the pesticide monitoring results available from regional authorities and drinking water companies in the Netherlands.

The aim of the procedure proposed in this report is to provide a plausible relationship between the presence of a substance in groundwater and the authorised use. It combines the results from regular, non-targeted monitoring activities with information on the period of authorised use, groundwater flow according to a steady-state national hydrological model and historic land-use in the area of influence of the sampling point. The extent to which the outcome meets the aim of the procedure differs with the substance. This is explained by the lack of historical use data and by the variation in the sampling pattern regarding space, depth and frequency.

7.2 Recommendations

It is recommended to evaluate the results obtained from the procedure in a number of risk assessment cases for a plant protection product based on an active ingredient which is already on the market.

It is recommended to extend the group of sampling points with available metadata with a selection of sampling points from the drinking water companies and to create a stable monitoring network for pesticides with sampling sites which are part of the existing groundwater quality monitoring networks and with sampling points at the depth considered in the decision tree on leaching.

The monitoring network data and measurement results from the regional authorities and drinking water companies were transferred from the owners to the developers of the Groundwater Atlas. Technical validation resulted in a few data quality issues related to some 5% of the total amount of measurement results. These data quality issues were reported to the contact person on behalf of the regional authorities. As soon as these issues are solved, it is recommended to add these measurement results to the Groundwater Atlas in the next regular update.

Anticipating the transfer of monitoring network data, sample data and measurement results owned by the regional authorities towards the National Key Registry of the Subsurface (BRO), the Society of the Provinces of the Netherlands (IPO) provided a dataset with monitoring network data and pesticide measurement results to the developers of the Groundwater Atlas version 2022. This dataset from the regional authorities may contain inaccurate screen depth values for sampling points. Although a different outcome is not expected, such deviations do have an effect on the selection in the procedure. It is recommended to replace the current screen depth values in the Groundwater Atlas database with the data values in the (BRO) in the next regular update.

In January 2023 a new Groundwater Atlas database version 3.3.2 with additional measurement results from Brabant Water drinking water company was published. The Groundwater Atlas version 2022 user is advised to select this new database version 3.3.2 in the application.

The travel time of the groundwater towards the sampling points from the regional authorities was calculated with the national hydrological model LGM. In particular sampling points, the distribution of the travel time may show a range in the order of 100 years. Inaccuracies in the input data about the depth of the sampling point and the subsoil profile at the sampling point location may contribute to this wide range. It is recommended to improve the quality of these input data and to investigate the benefit from using more refined hydrological models for calculating the area of influence and the travel time distribution for a selection of sampling points from the regional authorities and from the drinking water companies.

Water company Vitens provided a dataset with tritium-helium dating results at groundwater samples from observation wells at two abstraction sites. The estimated travel time according to the national hydrological model LHM was compared with these tritium-helium dating results. Although the model results and the tritium-helium dating results show a similar increase in the age of the groundwater with depth, the absolute difference between the median travel time and the tritium-helium date ranges between 1 and 16 years at a particular sampling point. In view of these large differences and the limited spatial extent of this dataset, it is recommended to further investigate the plausibility of the travel times estimated with the national hydrological model LHM.

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Annex A Glossary

Data regarding the substances in groundwater are referred to as **measurement results**. A measurement result is expressed as an upper limit value (<LOD, <LOQ, <LOR) or as a real concentration value.

A measurement result expressed as a real concentration is referred to as **measurement value**.

A **monitoring network** consists of a group of permanent sampling sites. The monitoring network name refers to a company, a regional authority (province), or a national network.

A **sampling site** is a permanent location which belongs to at least one monitoring network. A sampling site can be either a physical well or a spring. The geographic location of a sampling site is defined by a coordinate pair.

A **physical well** consists of one or more screens.

A **screen** is part of a physical well. The screen has a number according to the construction of the physical well, and an upper depth and a lower depth (m below soil surface).

A **spring** is a location where groundwater emerges at surface level. By definition, a spring has no screen.

A **sampling point** refers to a combination of sampling site (physical well) and screen number or to a spring.

There are four categories of **substances**; Active substance, Metabolite, Other, and Both. The category Other is used for a few substances only, e.g. a contamination or a non-active isomer. The category Both is used for a few substances which have (or had) a registration as an active substance and which are also known as a metabolite. For substances from the category Metabolite, Other, Both, the relation with the active substance(s) is available in the list of substances.

The **area of influence** of a sampling point is the surface area connected with the groundwater at the sampling point; via downward soil moisture flow in the unsaturated zone (through the root zone towards the groundwater table) and groundwater flow in the saturated zone.

Annex B Substance identification and registration data

This annex contains a description of the Groundwater Atlas substance list and describes the handling of substances with an isomer relationship.

Substance list

The Groundwater Atlas version 2022 was developed using a list of 859 substances. The Groundwater Atlas database contains only those 555 substances with measurement results available. The substance list is organised in a table with a data row for each substance. The table contains data fields with the substance identification, the number of measurement results, the substance type, the relationship between substances, the start and end of the period of registration and two types of product registration (Table B.1).

The fields with the type of product registration (either plant protection product, biocide, or both) in the new Groundwater Atlas version 2022 replace the fields with registration for agricultural use and non-agricultural use in the Groundwater Atlas version 1.1 (Kruijne et al., 2017; Annex 4). For the major part of the substances with measurement results, information on the period and type of product registration is available in the databases maintained at the Ctgb.

Table B.1 *Substance identification and registration data in de Groundwater Atlas substance list.*

header	description, domain	blank allowed?
substance ID	Internal identification number (not printed)	N
CAS_nr	CAS registry number	N
Stof	Common name of the substance in Dutch	N
substance name	Common name of the substance in English	N
measurement results	Number of measurement results (≥ 0)	N
aquocode	Abbreviation code of the substance, often used in the Netherlands. For reference only.	Y
substance type ID [a]	Type of substance. Domain: A active ingredient, M metabolite, B both active ingredient and metabolite, V contamination, NAP not applicable	N
product group ID [a]	Type of active ingredient. Domain: F fungicide, G soil disinfectant, H herbicide, I insecticide, O other, nap: not applicable, nodata: not available	N
substance relation ID	Indicates relation to other substance: Domain: M-<substance ID> metabolite-parent, I-x isomers ($1 \leq x \leq 4$). V = contaminant in the formulated product.	Y
remark (Dutch)	remark, mostly refers to related substances	Y
remark (English)	remark, mostly refers to related substances	Y
first authorisation date [a, b]	year of appearance on the market in NL as a plant protection product. nodata: not available	Y
expiration date [a, b, c]	last year of permitted use as a plant protection product. nodata: not available	Y
authorised plant protection product [a]	Indicates whether the active ingredient is (was) authorised as a plant protection product	N
authorised biocide product [a]	Indicates whether the active ingredient is (was) authorised as a biocide product	N

a) for active ingredients only; b) for active ingredients in authorised plant protection products only; c) either the expiration date of current authorised products, or the date expired.

Isomers
A limited number of plant protection products consist of a mixture of isomer active ingredients with different biological activity. Registration dossiers of these products may apply to the mixture and/or to the most active isomer only. When monitoring results are reported by the owner we assume that the measurement result and the substance identification do correspond with each other. The substance list contains different data rows for the isomer and mixture; these are identified by substance name and CAS nr.

The Groundwater Atlas version 2022 contains 4 instances of the (possible) combination of measurement results for the mixture and for the active isomer, respectively (number of measurement between brackets):
- dimethenamid / dimethenamid-P (2444/774).
- fluazifop-butyl / fluazifop-P-butyl (1045/1368).
- mecoprop / mecoprop-P (8385/0).
- metolachlor / S-metolachlor (6650/0).

In addition, for these metabolites both the racemic mixture and the S-isomer are included in the substance list of the Groundwater Atlas version 2022:
- dimethenamid-ESA / dimethenamid-P-ESA (398/0).
- dimethenamid-OA / dimethenamid-P-OA (368/0).
- metolachlor-ESA / S-metolachlor-ESA (773/0).
- metolachlor-OA / S-metolachlor-OA (988/0).
- fluazifop / fluazifop-P (646/0).

Interpretation of monitoring data for these active substances and metabolites is complicated, because in all four cases plant protection products based on the racemic mixture and products based on the active isomer have been authorised in the past. Currently only products based on the active isomer are still authorised. Only for S-metolachlor there was no overlap with the period for authorisation of products based on the racemic mixture. Note that the racemic mixture and the active isomer can have different substance properties (Table B.2) and preferential enantiomeric transformation or racemisation can occur in different environmental compartments. Table B.2 is for information only - the Groundwater Atlas does not contain substance properties.

Table B.2 *Properties determining the behaviour in the environment (Pesticide Properties Database (https://sitem.herts.ac.uk/aeru/ppdb/en/index.htm; per 20-8-2019; for illustration).*

Substance name	**CAS-nr.**	**Substance name**	**CAS-nr.**	**Sorption coefficient K_{oc} / Kf_{oc}[A]**		**Degradation half-life DT50 in soil (d) (Typical, Field, Lab)**	
mixture	mixture	isomer	isomer	mixture	isomer	mixture	isomer
dimethenamid	87674-68-8	dimethenamid-P	163515-14-8	69[A]	227[A]	F: 13	F: 7
fluazifop-butyl	69806-50-4	fluazifop-P-butyl	79241-46-6	3000	3394	T: 21, L: 15	T: 1, F: 8.2
mecoprop	7085-19-0	mecoprop-P	16484-77-8	31[A]	59.8[A]	TL: 8.2	TL: 5.2
metolachlor	51218-45-2	S-metolachlor	87392-12-9	163[A]	226.1[A]	T: 90, L: 15, F: 21	T: 15, L: 14.5, F: 21

[A] Value for Kf_{oc} instead of K_{oc}.

The new Groundwater Atlas version 2022 application was prepared for the optional feature to combine the available monitoring results for these instances of two isomers (either active ingredients or metabolites) and to evaluate them in one session. This option might be implemented in a future version of the Groundwater Atlas.

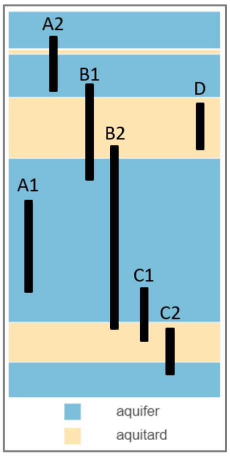
Annex C Maps with sampling points in the LHM input

The procedure to calculate the age and the area of influence of the groundwater at sampling points from the national – and regional groundwater quality monitoring networks is described in Chapter 3. This includes the preparation of input, the LHM-fresh-salt version, and the post-processing of the results. This annex contains a map showing the location of sampling points in each case in the placement of the well screen relative to the subsoil schematisation.

To understand the placement of the well screens (entirely in aquifer, partially in aquifer, entirely in aquitard), the following labels were assigned to each location:

- A1: entire well screen located in 1 aquifer.
- A2: well screen located in 2 aquifers with no confining layer or a very thin confining layer (aquitard) in between the aquifers (difference between bottom of upper layer and top of lower layer less than 0.01 m).
- B1: well screen located in 2 aquifers with a confining layer in between the aquifers.
- B2: well screen located in 2 aquitards with an aquifer in between the aquitards.
- C1: top of well screen located in an aquifer, bottom of well screen located in an aquitard.
- C2: top of well screen located in an aquitard, bottom of well screen located in an aquifer.
- D: entire well screen located in 1 aquitard.
- E: Partially below model: entire well screen located in one or many aquifers and/or aquitards, with part of the well screen located below the model (bottom of layer 8).

Table C.1 *The number of sampling points (screens) in the LHM input per case (see text).*



Case	number of sampling points (screens)
A1	1681
A2	173
B1	10
B2	3
C1	72
C2	89
D	491
E *	3
Total	2522

-* Partially below model.

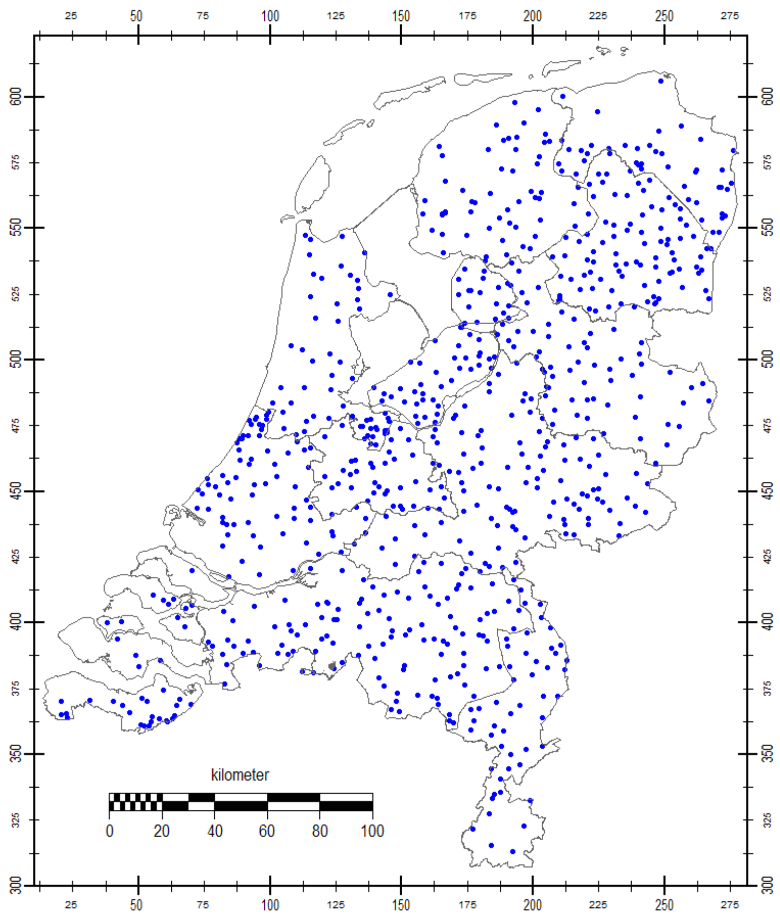


Figure C.1 *Locations of well screens in case A1.*

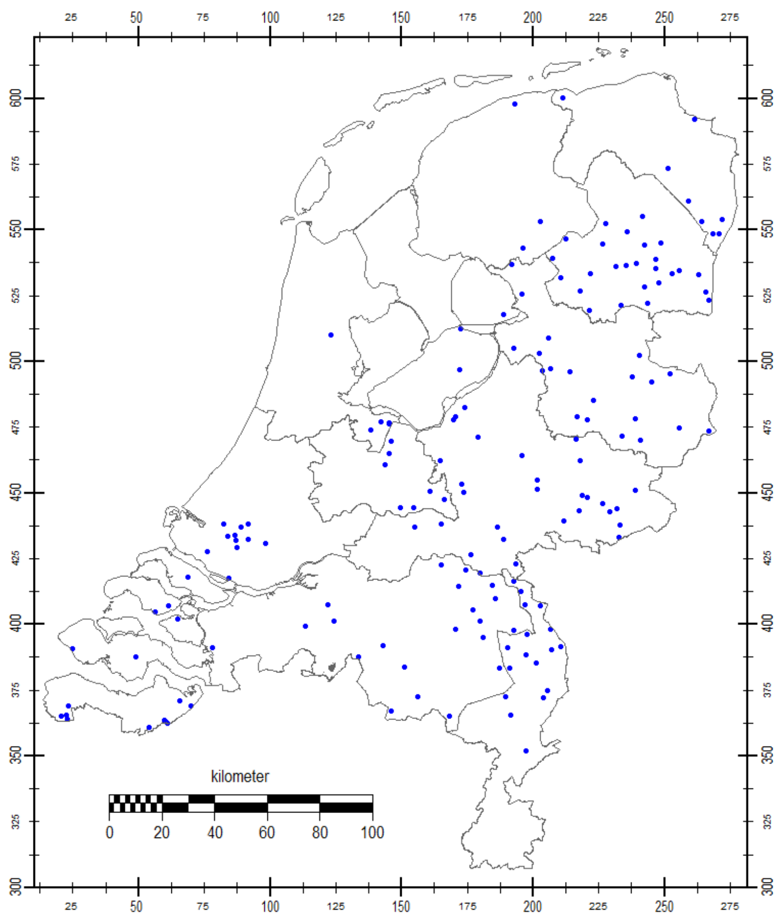


Figure C.2 *Locations of well screens in case A2.*

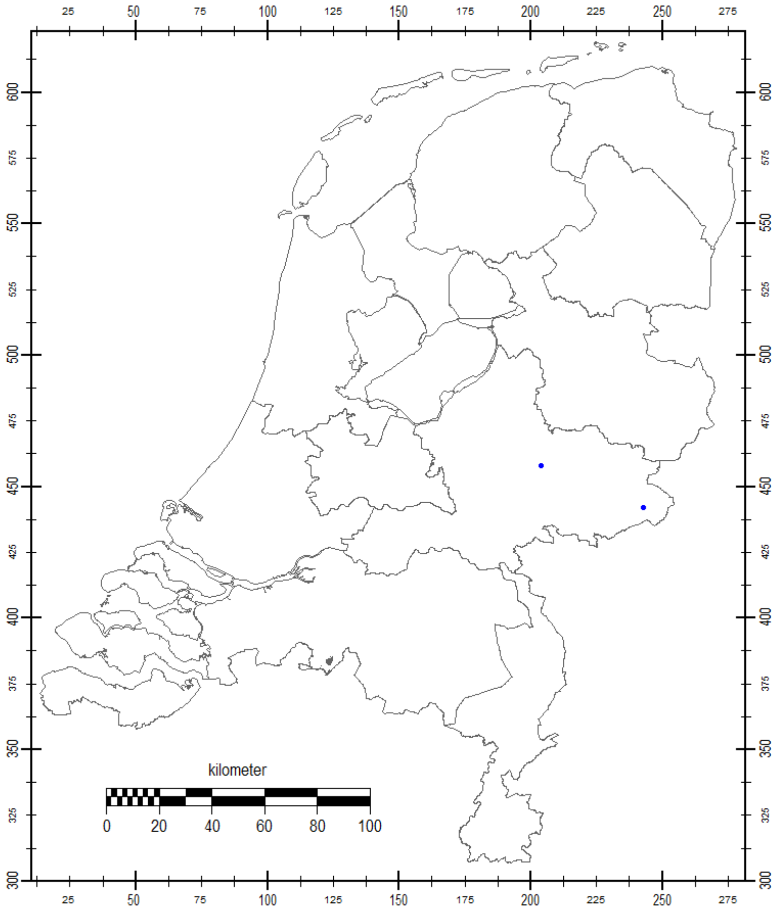


Figure C.3 *Locations of well screens in case B1.*

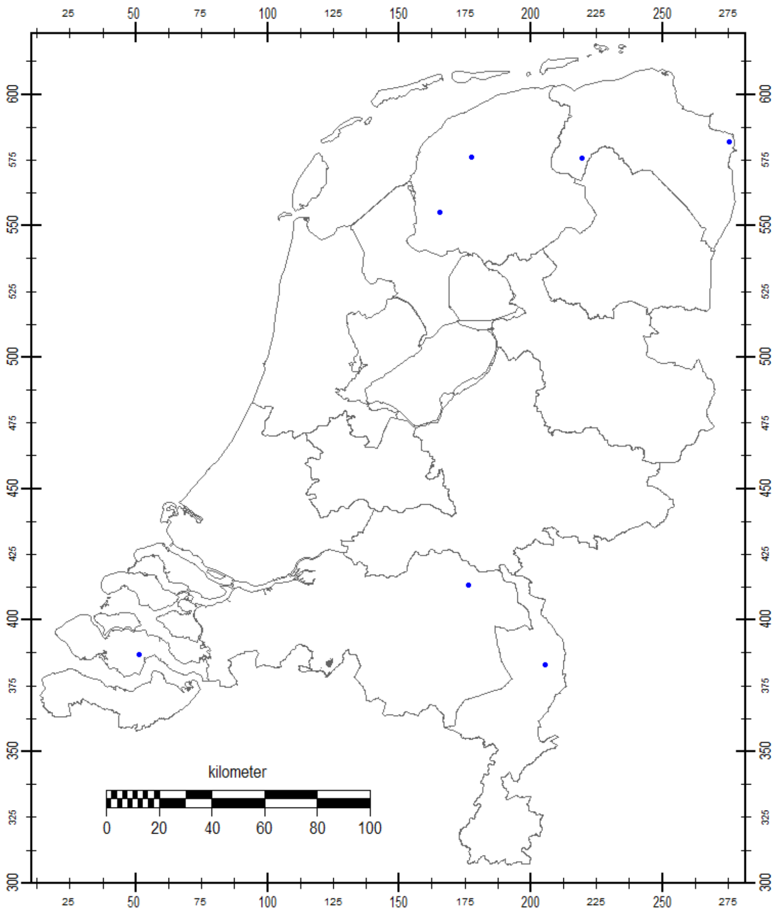


Figure C.4 *Locations of well screens in case B2.*

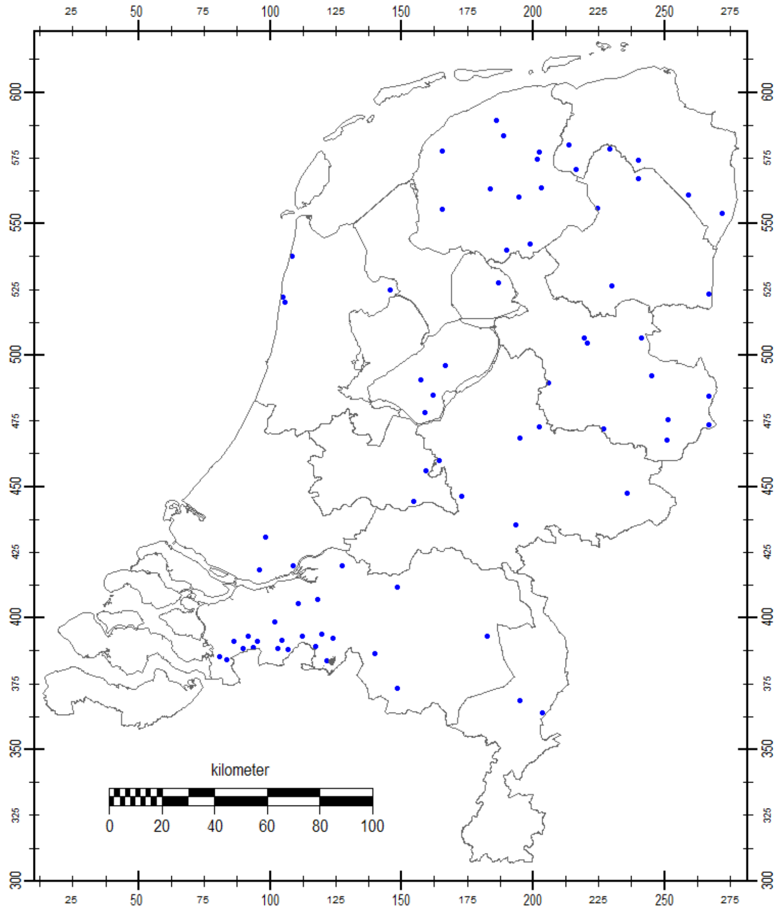


Figure C.5 *Locations of well screens in case C1.*

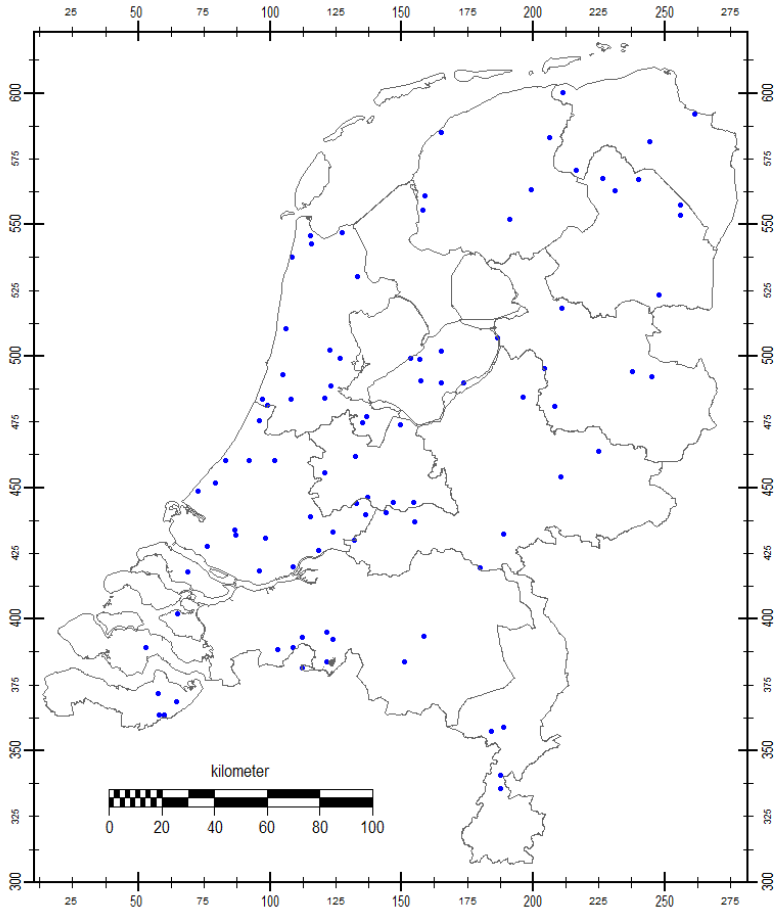


Figure C.6 *Locations of well screens in case C2.*

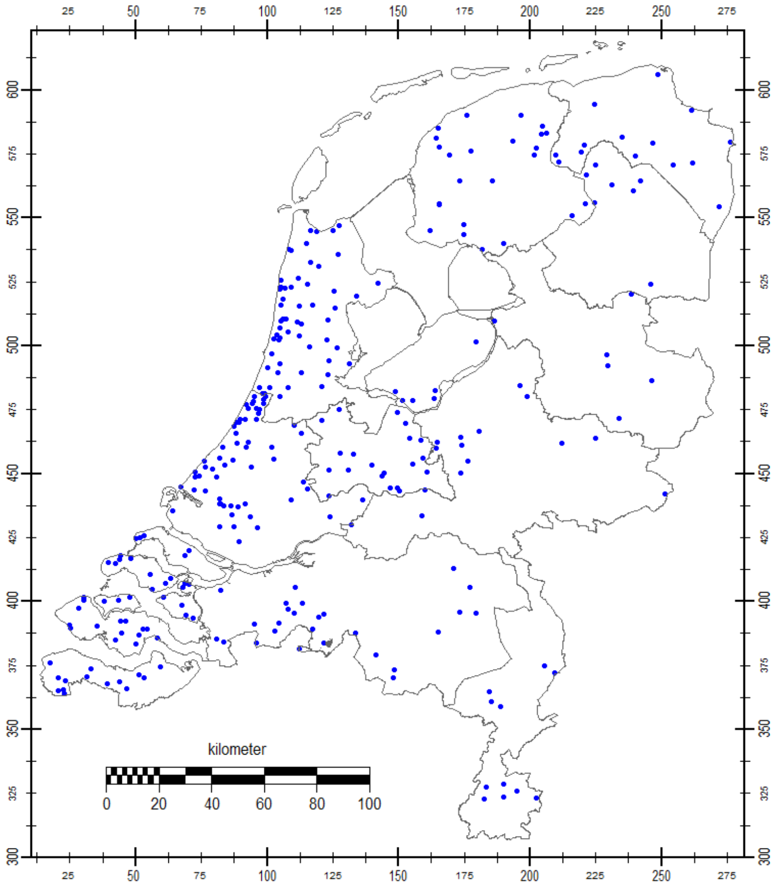


Figure C.7 *Locations of well screens in case D.*

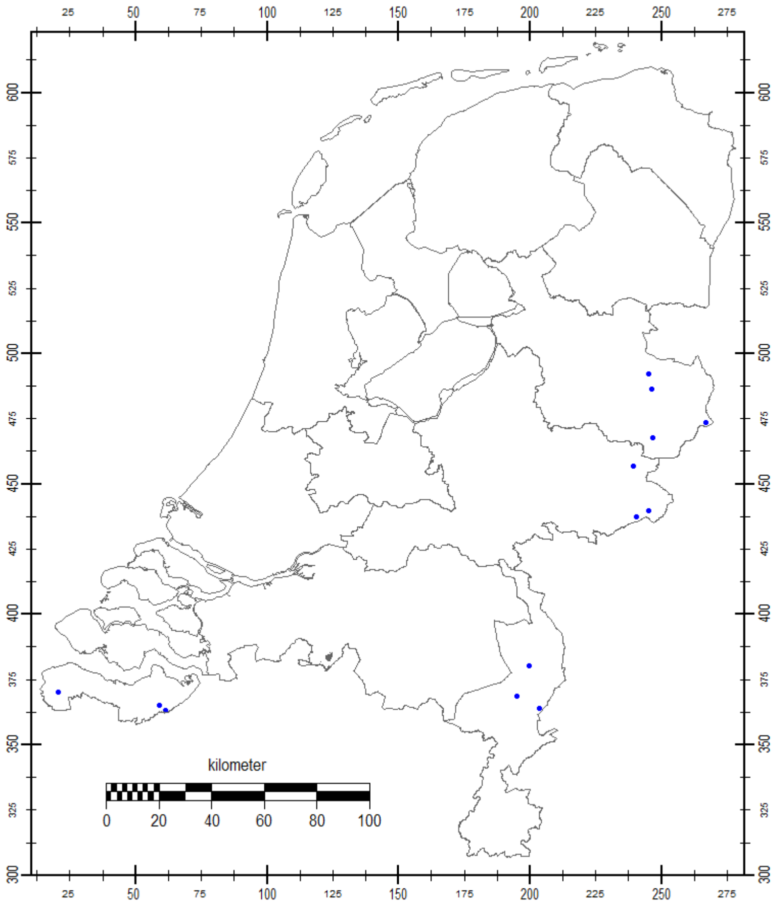


Figure C.8 *Locations of well screens that are located partially below the bottom of the model (bottom of layer 7).*

Annex D Discussion on accuracy and uncertainty of the LHM results

Gijs Janssen, 6 sep 2019

Contents

1. Model uncertainty.
2. Model resolution.
3. Assumption of stationarity.

Introduction

The particle tracking is an analytical postprocessing step performed on a numerically derived flow field. The analytical nature of the postprocessing step makes that results can be produced at any resolution in time and space. The reliability, however, of a calculated flow path, and with that of the end points, depends on the accuracy of the numerical flow field. The numerical flow field suffers from various sources of uncertainty. The most important ones are given below.

1. Model uncertainty

Like any model, the LHM is a simplification of reality. It uses conceptualizations and uncertain parameterizations. The geohydrological layer schematisation of the model is basically an interpolation between point observations, aggregated to a (computationally) feasible number of model layers. As shown in Section 3.3, these interpolation result in mismatches with the positions of the filters, demonstrating the inaccuracy at the local level. Furthermore, the layer model only represents heterogeneity of the subsurface build-up on a macroscopic scale. Heterogeneity, however, exists at all scales. Parameters like hydraulic conductivities and porosities are estimates. Groundwater recharge is obtained from another hydrological model (Meta)SWAP which has its own uncertainties and deviations from reality.

2. Model resolution

The LHM model has a (lateral) grid resolution of 250x250m. Everything that happens within a 250x250m grid, is aggregated and upscaled to that scale. The flow solution produced by the model consists of fluxes/velocities over all the interfaces of all cells (e.g. v_{x1}, v_{x2}, v_{y1} and v_{y2} in Figure 1). In the lateral direction, these interfaces are 250m apart. These fluxes/velocities are the only information available for the particle tracking algorithm to determine the direction and speed of the particles. The particle tracking algorithm basically simply creates an internal flow field by interpolating the velocities at the cell interfaces. Between the cell interfaces, no further information is available about the pattern of the flow field[1]. In reality, the flow field is influenced by (among other things) the position of sinks and sources within the flow field. Because the placing of these sinks and sources can't be represented in the model at a higher resolution than 250x250m, much detail is lost[2], which negatively influences the accuracy with which the flow field can be represented and particles can be tracked.

An illustration of this is given in Figure D.1. The top figure shows two monitoring wells in a flow field that is influenced by a draining ditch. The left monitoring filter receives older water than the right one, because of the more lateral directed groundwater flow at the left filter. The model, however, can't distinguish between the two situations, as it does not "know" the internal flow field in the cell as depicted in the top figure. Instead, it constructs an interpolated flow field based on the fluxes/velocities at the cell interfaces, as this is the only information it has. The result is that particles tracked from the monitoring well will show travel times and arrival locations that differ from both situations in the top figure.

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[1] At any point in space, a particle's speed and direction is calculated as a vector which is the resultant of the velocities at the cell's interfaces.

[2] Numerically, a grid cell is nothing more than a computation node (point), to which flow properties and sink and source terms are applied. All groundwater recharge, rivers, drains, lateral and vertical flows, wells etc., that are present within the cell, act on that single node in the center of that cell. In other words, they lose their location. The model does not know where in the cell exactly these fluxes are.

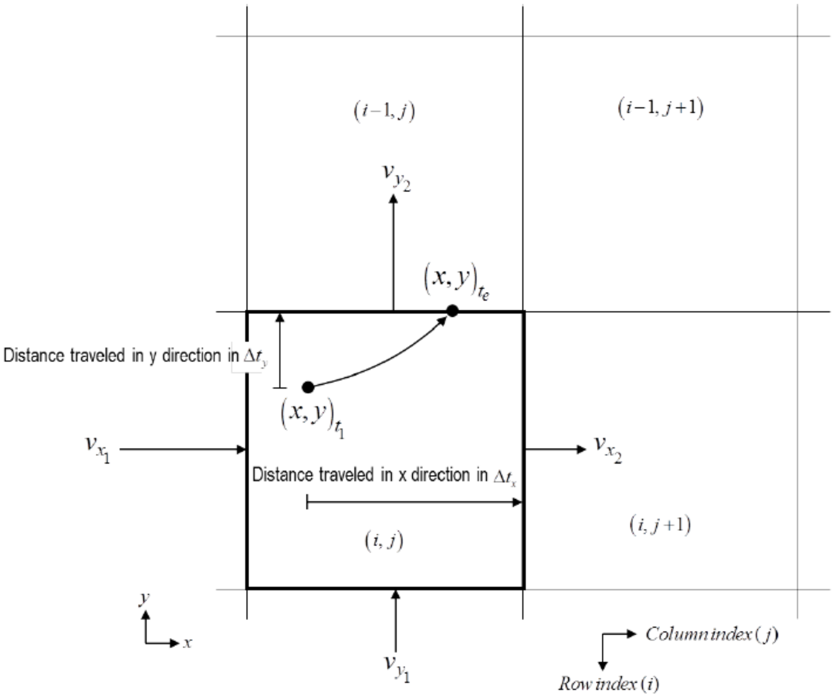

Figure D.1 *Schematic showing the computation of the exit point and travel time for the case of two-dimensional flow in the x-y plane. From Pollock (2012).*

It is clear that the methodology would greatly benefit from a higher resolution groundwater model. Currently, however, a nationwide groundwater flow model of the Netherlands is only available at 250x250m resolution.

Figure D.2 nicely combines the two sources of uncertainty mentioned so far in this and previous section. Basically, the red arrows are uncertain because of the model uncertainty. The flow lines are uncertain because of the course model resolution; they are merely based on the red arrows, disregarding everything that influences the flow field within the cell.

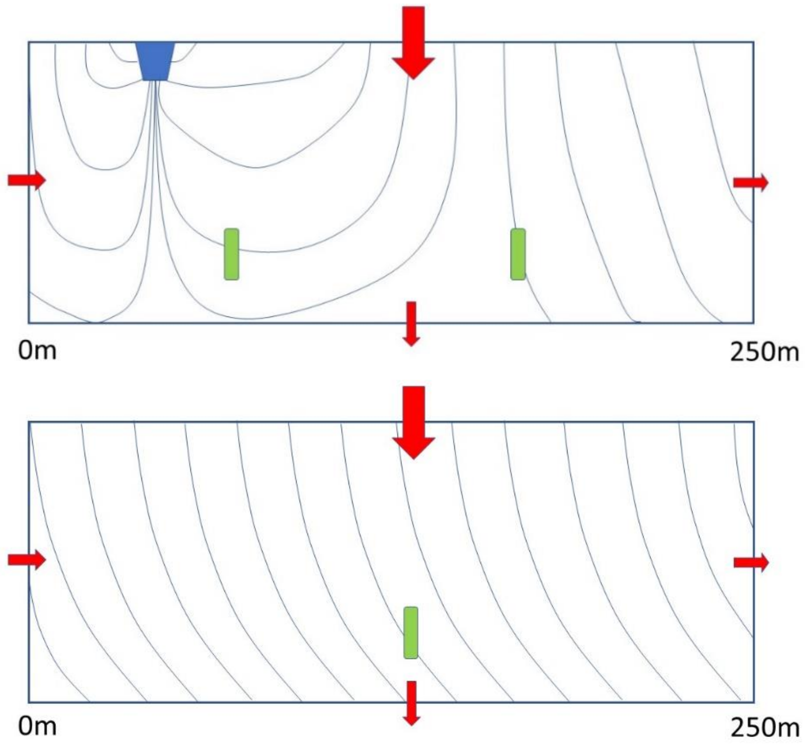

Figure D.2 *Illustration of the loss of detail in the representation of the "true" flow field in the model. Above: example of a "true" (not necessarily realistic) flow field within a LHM cell (2D cross section view). Below: representation of the flow field by the model. Blue flipped trapezium represents a draining ditch. Red arrows represent fluxes/velocities at the cell interfaces, as calculated by the model. Blue lines represent flow lines. Green bar represents a monitoring filter. Nothing to scale.*

3. Assumption of stationarity

This study has been conceived to use a steady-state version of the LHM model. As such, results represent streamlines derived from a "time-averaged" flow field. In reality, of course, the system is dynamic, and the position of a particle at a certain moment depends on the history of these dynamics since the release moment of the particle.

The various sources of uncertainty raise the question at which scale/resolution it is feasible to produce, visualize and process the results. So far, we have been producing plots showing the influence zones at 25x25m resolution. It seems better, however, to scale this up to (at least) the resolution of the model (250x250m).

Annex E Land-use in the area of influence of regional network sampling points

Considering the age of groundwater at 10 m depth and the date of the groundwater samples, it was decided to combine the land-use data covering the period 1985 – 2016 (Table E.1) into one dataset. Since the release of the 1st version in 1985, the number of modifications to the LGN legend was limited. Based on expert knowledge, specific mixed (ambiguous) classes in LGN version 2 were assigned to the main classes of agricultural crops. The general quality of the satellite images and the resulting accuracy of the main classes of agricultural land-use in LGN versions 1 and 2 is less compared to the other versions.

Table E.1 *Production year and agricultural land-use classes in the Landgebruikskaart Nederland (LGN-version 1 - 8; www.lgn.nl).*

Description / LGN version	**1985**	**1992**	**1996**	**1998**	**1999**	**2003**	**2007**	**2012**	**2016**
	1 [a]	**2 [a,b]**	**3**	**3+**	**4**	**5**	**6**	**7**	**8**
Pasture	x	x	x	x	x	x	x	x	x
Maize	x	x	x	x	x	x	x	x	x
Potato	x	x	x	x	x	x	x	x	x
sugar beet	x	x	x	x	x	x	x	x	x
Cereal	x	x	x	x	x	x	x	x	x
other agricultural crops	x	x	x	x	x	x	x	x	x
Greenhouse	x	x	x	x	x	x	x	x	x
fruit orchard	x	x	x	x	x	x	x	x	x
flower bulb		x	x	x	x	x	x	x	x
tree nursery [c]							x	x	x
fruit nursery [d]							x	x	x
urban area [e]	x	x	x	x	x	x	x	x	x
fallow, forest, nature [f]	x	x	x	x	x	x	x	x	x
surface water [g]	x	x	x	x	x	x	x	x	x

Notes:

a the accuracy of LGN versions 1 and 2 is relatively low compared to the other LGN versions.

b includes mixed classes of agricultural land-use; these were assigned to the land-use classes maize, potato, sugar beet, cereal, other agricultural crops, and fruit nursery.

c In version 1 to 5 included in land-use class other agricultural crops.

d In version 1 to 5 included in land-use class fruit orchard.

e composed of several classes in the LGN legend (mixture of infrastructure, buildings and other non-agricultural use in urban area).

f composed of several classes in the LGN legend (fallow land, forest and other non-agricultural land in rural area).

g composed of salt and sweet water in the LGN legend.

The land-use in the area of influence of the sampling point is calculated from the land-use statistics in the 250 m cells covering the groundwater particles, using a weighting factor based on the amount of particles with the simulated flowpath starting within the 250 m cell (Figure D1.1; see also Figure 8).

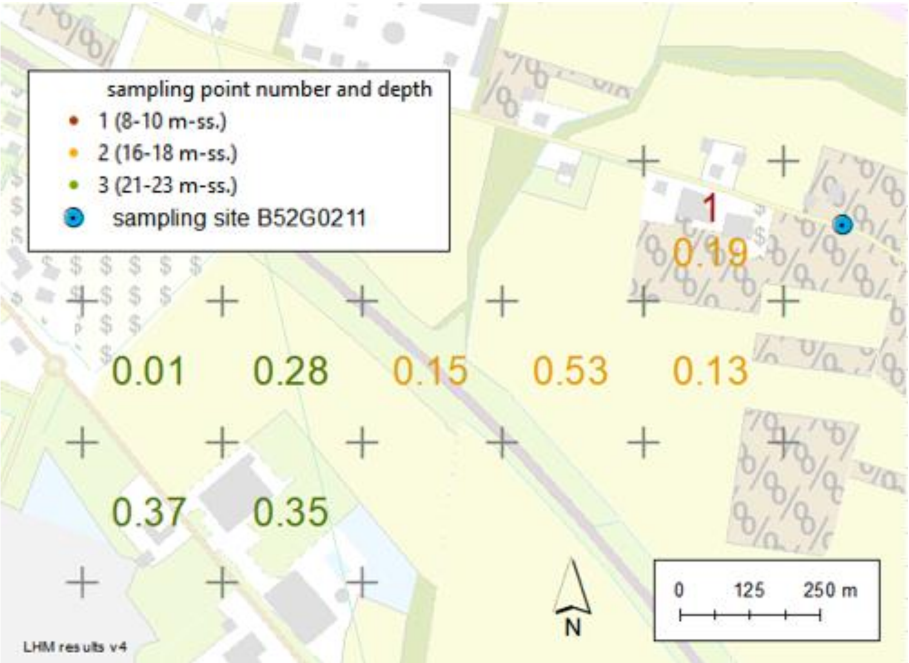

Figure E.1 *The weighting factor in the 250 m cells contributing to the area of influence of sampling points 1, 2, and 3 at the example sampling site B52G0211 (the map in the background map is not used in the Groundwater Atlas).*

The land-use classes were aggregated to obtain a single classification for the entire period 1985 – 2016 for use in the Groundwater Atlas (Table E.2). The historic land-use and the average land-use in the area of influence of the example sampling site is shown in Figure E.2.

sampling point ID	measurement values	measurement results
B52G0211.1	7	361
B52G0211.3	10	274

Table E.2 *The land-use classification used to describe the area of influence of sampling points in the Groundwater Atlas and the national acreage in 1998 (according to the LGN version 3).*

Code	description	(km^2)
PAST	pasture	12500
MAIZ	maize	2750
ACRO	arable crops	6630
GRHO	greenhouses	135
ORCH	fruit orchard	280
FBLB	flower bulbs	230
URBA	non-agricultural land-use in urban area	6470
NATU	non-agricultural land-use and fallow in rural area	4740
	total area	35095

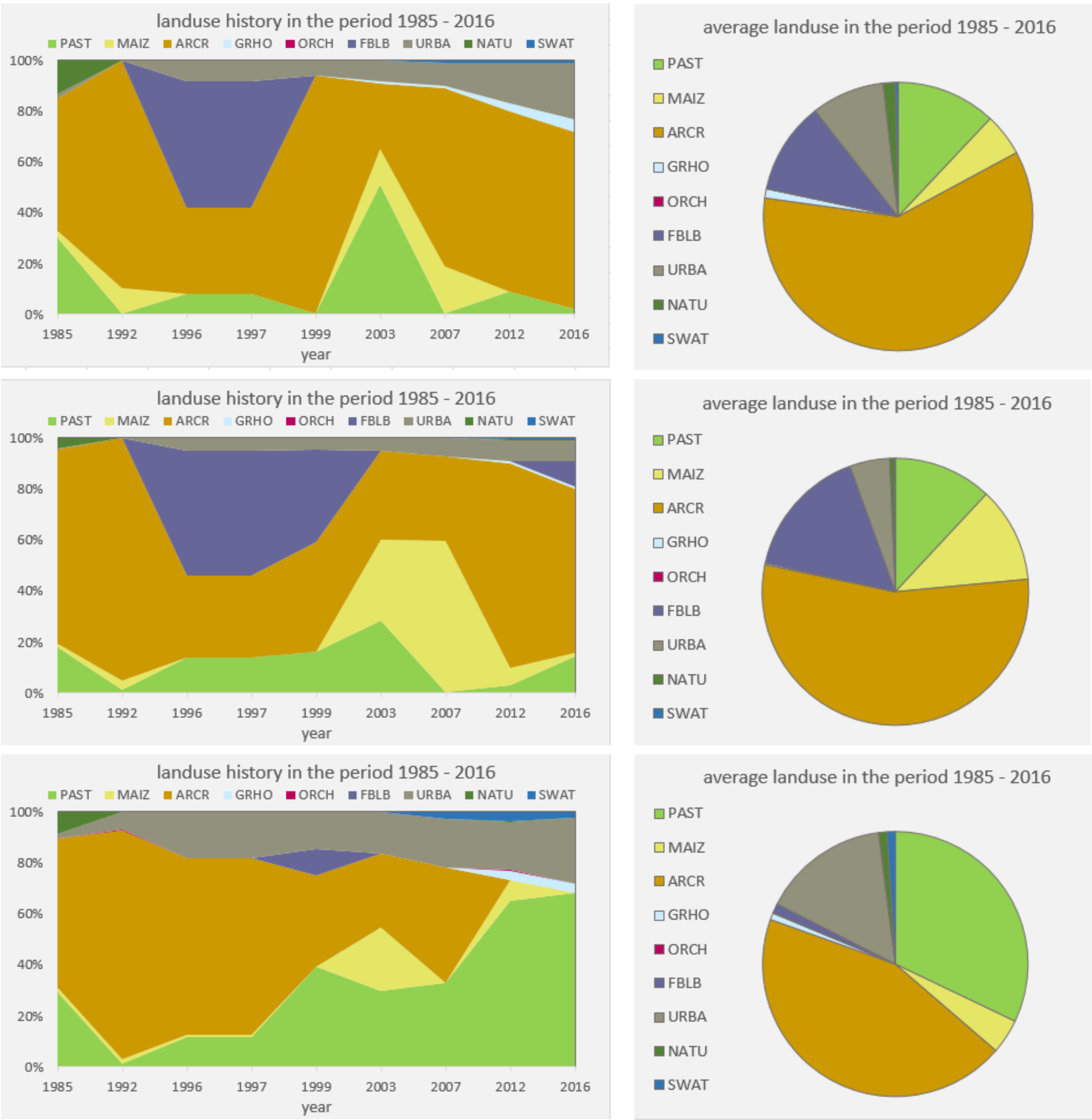

Figure E.2 *The land-use history (left) and the temporal average land-use (right) in the period 1985-2016 in the area of influence of sampling points 1 (up), 2 (middle) and 3 (below) at the example sampling site B52G0211.*

Annex F Dependency of samples from the water companies network

Mathijs Meering & Mark Montfoorts, RIVM

This annex covers the potential dependency of samples from the water companies. The reason behind this annex is the difference in source of the measurement results within the Groundwater Atlas. The Groundwater Atlas contains sampling points and measurement results of provinces and water companies. The density of the monitoring network of the provinces is around 2-3 sampling sites per 100 km^2. The density of water company sampling sites is around 1 sampling site per km^2, based on the assumption that the total of groundwater protection areas comprises 5% of the surface of the Netherlands. The differences in (abundance of) measurement data of the water companies (sampling site location, sampling depth and sampling frequency) as compared to the measurement data of the provinces could lead to a bias when combining the measurement results of both data sources into a single dataset for decision taking. A combined dataset in which the 'variation' in measurement data of the water companies is aligned with the measurement data of the provinces, was deemed desirable. This in order to avoid overrepresentation of measured substances, and to explore the presence of dependent measurement results. The annex explores options to deal with this signalled bias. The data used for the analyses performed in this annex are measurement results of the water companies that were present in the Groundwater Atlas v1.1.

Dependency

Questions that arise are: When are measurement results considered as dependent? What defines an overrepresentation? In other words, when do measurement results represent the same? In this annex, dependency between measurement results is defined as: temporally and/or spatially separate measurements that represent the same matter (e.g. the quality of a groundwater body, or the impact of application/area of influence on this groundwater body).

Furthermore, it is important to think about what could be the considerations behind labelling measurement results as dependent. In other words, what will the data be used for and how does the method of usage affect overrepresentation? For example, do you want to examine the measurement results of all extraction sites altogether, or do you want to examine the measurement results of each extraction site separately?

The next question is: how do you get from dependent measurements to a replacement, representative value? Which meta information of the sampling point is relevant in case of different measured concentrations? Is the mutual distance in space and/or time "too small"?

Spatial

If sampling points around a extraction site measure in the same groundwater, then it indeed represents the same matter, but mutual distance is not an *a priori* criterion. A mutual distance between measurement results of 5 km can relate to the same land use or the same groundwater body, while elsewhere a distance of 1 km can separate different groundwater bodies or areas of influence.

For example: Extraction site 51 in Figure F.1 gives an impression of the spatial mutual distance between measurement results. The mutual distance between the red-outlined measurement results is the greatest lateral distance between measurement results within an extraction site (across all extraction sites). This distance is 6364 m. Now, there is another extraction site adjacent to this extraction site: extraction site 95. The measurement results of extraction site 95 are at considerably shorter distances from the measurement results of extraction site 51 than these 6364 meters. In other words, measurement results of different extraction sites can be closer to each other than measurement results within an extraction site.

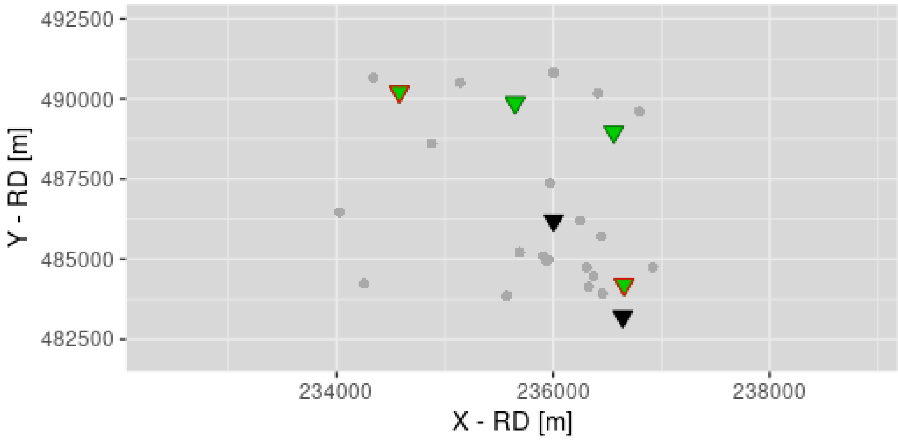

Figure F.1 *Measurement results of extraction site 51 (green triangles). Sampling site 28DP0080 and 28BA3168 within extraction site 51 are outlined in red. The black triangles are nearby measurement results of extraction site 95. In gray, the measurement results of the drinking water companies measured at depths other than 10-15 m below the surface.*

Temporal
Patterns over time (e.g. a measurement result for a particular substance is available every year for a 10 year period) are not necessarily a repetition of the same problem, but rather information you may need together with temporal and spatial patterns in land use, and groundwater flow rates. A total of 347 bentazone measurement results, measured by the drinking water companies in the layer between 10 and 15 m below soil surface, are present in the Groundwater Atlas. At several sampling points only 1 measurement result of bentazone is available. At these sampling points there is no difference in time to other measurement results. This leaves 274 measurement results that are potentially temporally dependent.

Figure F.2 shows a frequency distribution of the temporal distance between the measurement results of bentazone. The temporal distance is always the difference in time to the next measurement of bentazone at the relevant sampling point. The largest time difference between two consecutive measurement results is 11.92 years. In other words, assuming a dependency distance of t = 12 years, for each sampling point the entire series of measurement results will be clustered.

Figure F.2 *Temporal distance between consecutive measurement results (per sampling point) for a case of bentazone (n = 274).*

It is unlikely that measurement results from samples taken 12 years (or more) apart come from the same point load of bentazone, but they could come from the same type of land use. However, a time difference between measurement results in which the same matter / event is represented cannot be clearly defined. Groundwater flow velocities are highly variable across the Netherlands from a spatial perspective. Differences in groundwater travel times in combination with the groundwater bodies (flow directions) and the uncertainty within the area of influence prevent us from defining a 'temporal dependence distance'.

Clustering dependent data
From this spatial and temporal dependence the following question arises: what happens if you decide to cluster data based on this information? What does it mean if you cluster the measurement results (per sampling point) within an extraction site? To study this, for two substances, the average concentration per extraction site was taken and the distribution of concentrations was investigated. The sampling points by definition represent the same point locations and by taking the average per extraction site you get a long-term average. It is not a true spatial percentile, it is a substitute spatial distribution. This is because we cannot assign an area of influence, or a specific "surface of groundwater", to the extraction locations.

The concentration distribution of 1) the non-clustered measurement results and 2) the clustered measurement results per extraction location are compared:
- If the distributions do not differ, we conclude that the clustering of measurement results does not matter. If there is such a thing as dependence, it doesn't matter. Or you have to screen your data in a different way to find a dependency between measurement results.
- If the distributions do show differences: what do we learn from that?

For dikegulac (Case 1; this annex), we see little difference between the concentration distribution of the non-clustered measurement results (Figure F.3, F.4) and the concentration distribution of the average concentrations per extraction location (Figure F.5).

For bentazone (Case 2; this annex), averaging the concentrations per extraction location (Figure F.9) appears to filter out a group of frequent and high concentrations compared to the non-clustered measurement results (Figure F.7, F.8). We don't want to lose this information in a clustering, we want to understand it. And when you have understood it, or in order to understand it, a tailor-made data manipulation follows.

Conclusion
Looking back on the original problem definition: *"The density of the monitoring network of provinces is approximately 2-3 sampling sites per 100 km^2. The density of sampling sites of water companies is approximately 1 per km^2 (assuming that the groundwater protection areas as a whole comprise 5% of the surface of the Netherlands). This leads to a bias in a dataset with measurement results from both groups together."*

In this statement, assumptions are made: a spatial weight is assigned to sampling points by dividing the number of points on the total surface area (provinces or groundwater protection area). Then it follows that the observations within the extraction sites represent a much smaller area than those of the provinces. The bias that is detected would arise due to not weighing observations to this surface area. Filtering out potential dependent results is also not the same as assigning a weight to the measurement results, but it can reduce this bias: the number of sampling points is reduced - and probably more at water extraction sites than elsewhere. But even then it remains that all observations (all sampling points) should have their own weight in terms of area of influence or volume of groundwater body, if the information is to be understood in terms of exceeding a limit value in a certain percentile in space and/or time (e.g. 90th percentile of the area based on long-term average).

In short, a decision about dependence cannot be determined from the measurement results themselves. When analyzing the data, clarity is needed about the selected data: what time interval, what depth range of measurements, or what age of the groundwater is selected? How do you use the time series of measurements? How do you deal with different measurement frequencies in the time interval? How do you weigh the difference in sampling points within a extraction site (at times 1 sampling point, at times 2 or more sampling points)? How do you decide per extraction site whether the multiple sampling points over-represent the same information? And what do you do if sampling points from different extraction locations provide the same information (cf. extraction sites 51 and 95, see Figure F.1)?

These are some questions regarding how information should be used across all extraction sites. These questions should also be asked when analyzing the provincial data.

Case 1: Substance with limited amount of measurement results - dikegulac (65)
The 65 measurement results of dikegulac have been measured across 16 extraction sites.

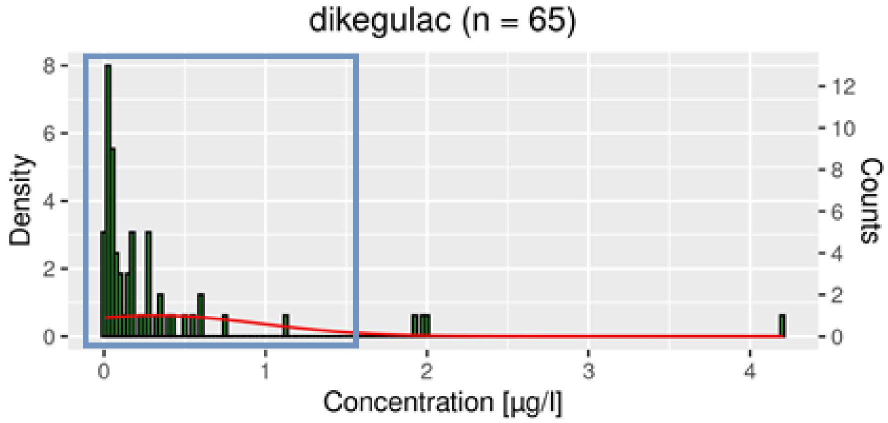

Figure F.3 *Density plot of all measured concentrations of dikegulac. Selected data: measurement results of the water companies measured at 10-15 m below the surface.*

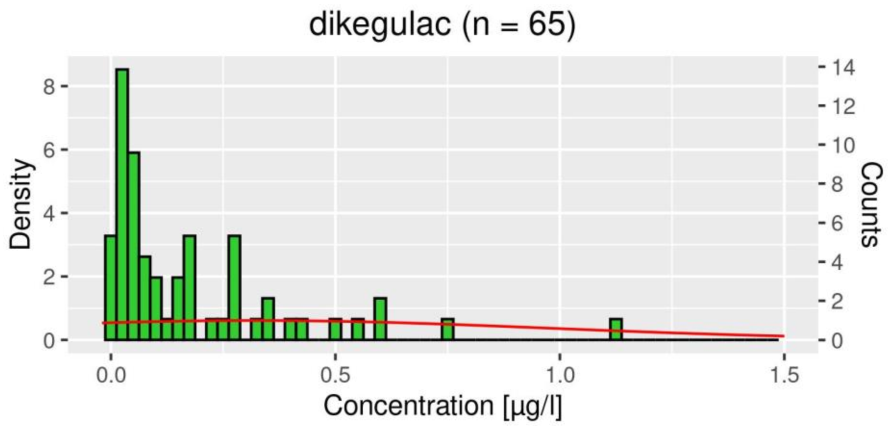

Figure F.1 *Zoomed in on Figure F.3.*

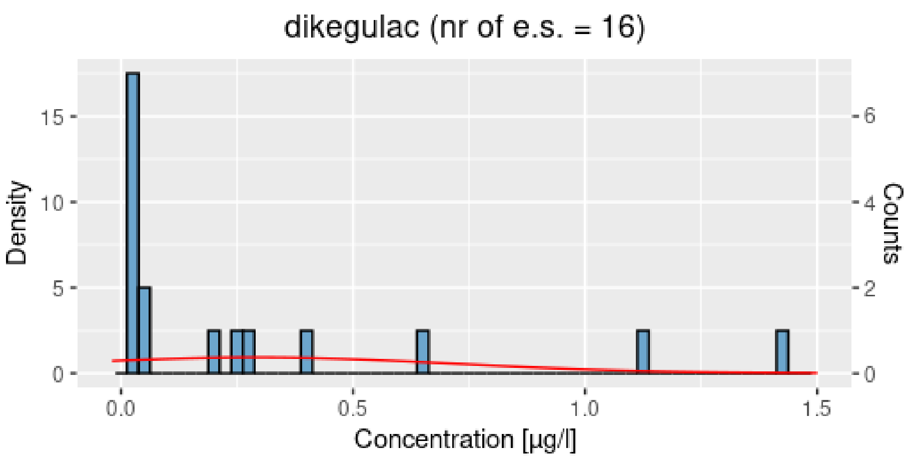

Figure F.5 *Density plot of the average measured concentrations of dikegulac (per extraction site). Data selection is the same as the selection in Figure F.3: only the data of the water companies measured between 10-15 m-mv.*

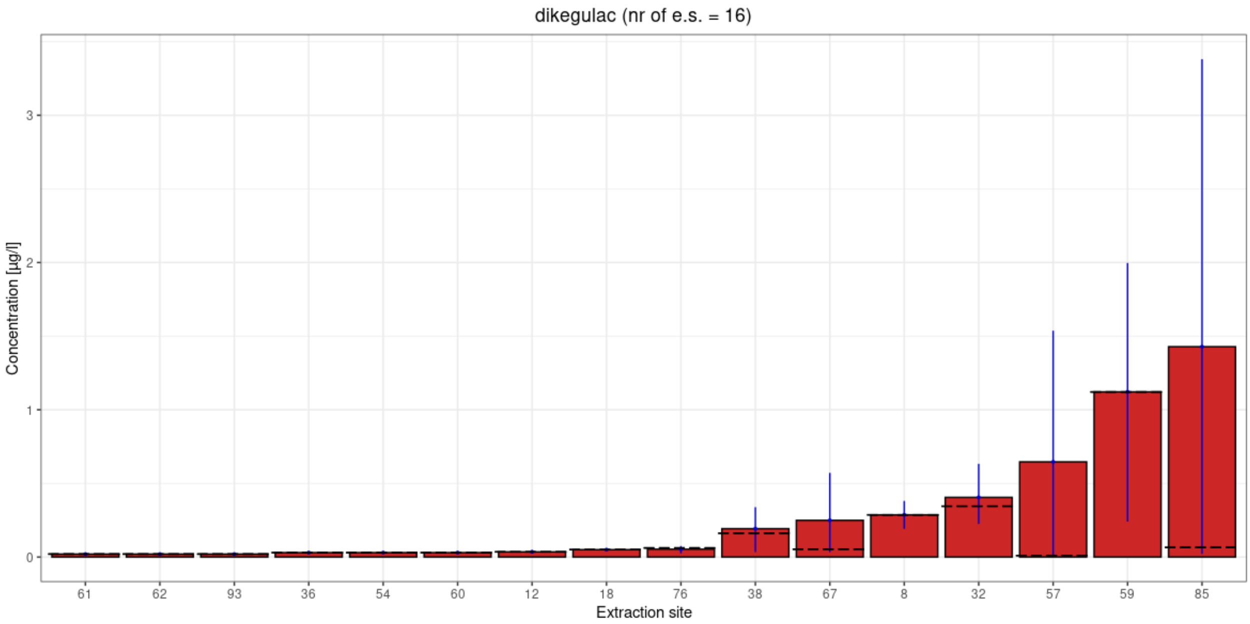

Figure F.6 *Average concentration of dikegulac per extraction site. The whiskers (blue) represent the 10th and 90th percentiles. The black dotted line indicates the median (often corresponds to the average, these are generally extraction sites with only 1 measurement result or extraction sites with only measurement results below the LOQ.*

Table F.9 *Number of measurement results and percentiles (in µg/l) across each extraction site with an averaged concentration of dikegulac.*

Extraction Site	nr of measurement results	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile
8	2	0.1917	0.22725	0.2865	0.34575	0.3813
12	2	0.023	0.0275	0.035	0.0425	0.047
18	3	0.05	0.05	0.05	0.05	0.05
32	4	0.225	0.2925	0.345	0.4575	0.633
36	2	0.03	0.03	0.03	0.03	0.03
38	23	0.034	0.0995	0.162	0.2715	0.3388
54	1	0.03	0.03	0.03	0.03	0.03
57	3	0.01	0.01	0.01	0.9645	1.5372
59	5	0.2416	0.283	1.121	1.987	1.9966
60	1	0.03	0.03	0.03	0.03	0.03
61	2	0.02	0.02	0.02	0.02	0.02
62	1	0.02	0.02	0.02	0.02	0.02
67	7	0.034	0.05	0.053	0.487	0.5718
76	4	0.025	0.0475	0.062	0.06775	0.0745
85	3	0.021	0.0375	0.065	2.1375	3.381
93	2	0.02	0.02	0.02	0.02	0.02

Case 2: Substance with a substantial amount of measurement results - bentazone (347)
The 347 measurement results of bentazone have been measured across 49 extraction sites.

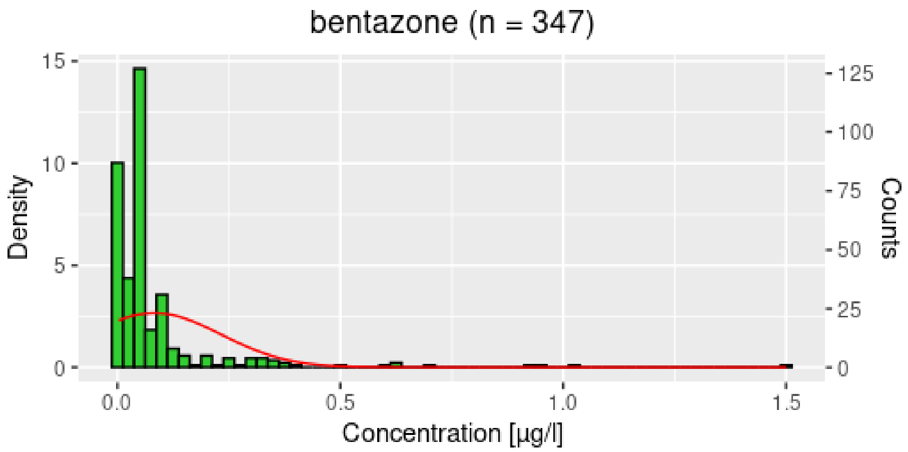

Figure F.2 *Density plot of all measured concentrations of bentazone. Selected data: measurement results of the water companies measured at 10-15 m below the surface.*

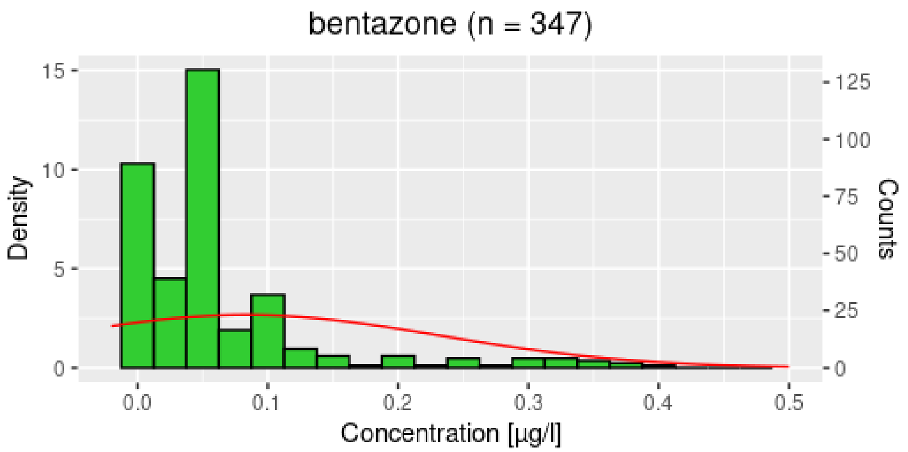

Figure F.3 *Zoomed in on Figure F.7.*

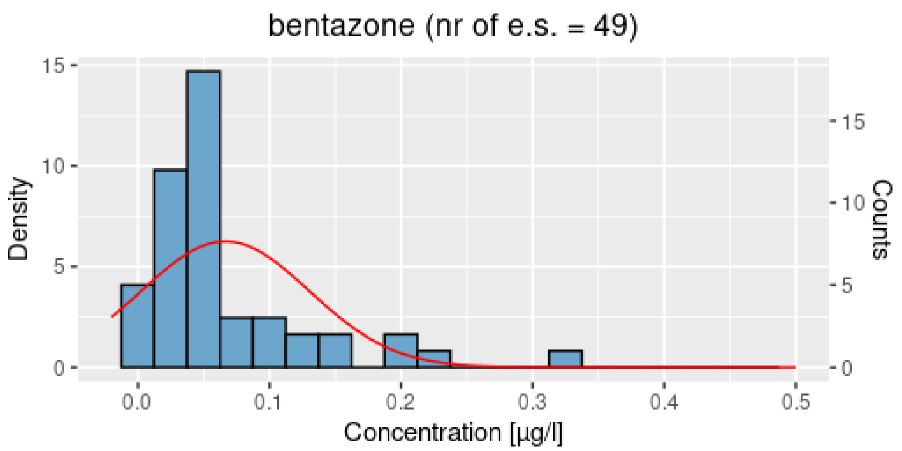

Figure F.4 *Density plot of the average measured concentrations of bentazone (per extraction site). Data selection is the same as the selection in Figure F.7: only the data of the water companies measured between 10-15 m-mv.*

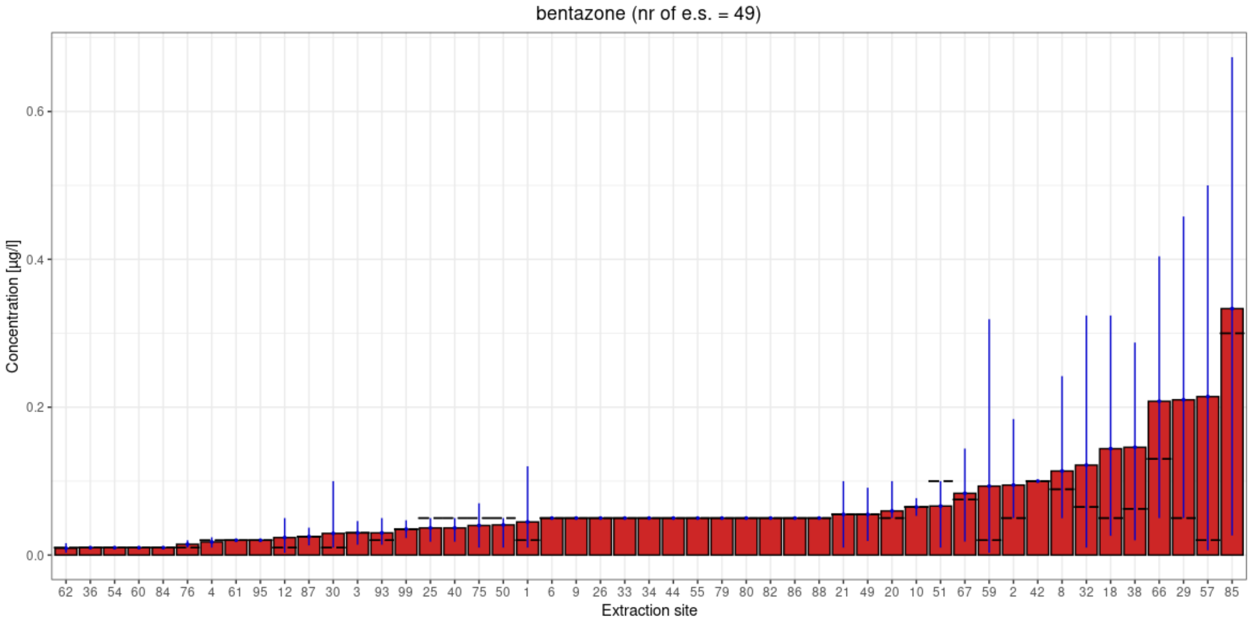

Figure F.5 *Average concentration of bentazone per extraction site. The whiskers (blue) represent the 10th and 90th percentiles. The black dotted line indicates the median (often corresponds to the average, these are generally extraction sites with only 1 measurement result or extraction sites with only measurement results below the LOQ.*

Table F.10 *Number of measurement results and percentiles (in µg/l) across each extraction site with an averaged concentration of bentazone.*

Extraction Site	nr of measurement results	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile
1	21	0.01	0.01	0.02	0.05	0.12
2	15	0.05	0.05	0.05	0.145	0.184
3	2	0.014	0.02	0.03	0.04	0.046
4	13	0.01	0.01	0.02	0.02	0.024
6	2	0.05	0.05	0.05	0.05	0.05
8	9	0.0498	0.05	0.089	0.111	0.242
9	1	0.05	0.05	0.05	0.05	0.05
10	2	0.053	0.0575	0.065	0.0725	0.077
12	19	0.003	0.01	0.01	0.05	0.05
18	28	0.026	0.05	0.05	0.12	0.324
20	26	0.05	0.05	0.05	0.05	0.1
21	6	0.01	0.01	0.055	0.1	0.1
25	3	0.018	0.03	0.05	0.05	0.05
26	1	0.05	0.05	0.05	0.05	0.05
29	9	0.05	0.05	0.05	0.32	0.458
30	14	0.01	0.01	0.01	0.01	0.1
32	12	0.01	0.01	0.065	0.2475	0.324
33	1	0.05	0.05	0.05	0.05	0.05
34	4	0.05	0.05	0.05	0.05	0.05
36	2	0.01	0.01	0.01	0.01	0.01
38	34	0.02	0.05	0.0625	0.08525	0.2874
40	3	0.018	0.03	0.05	0.05	0.05
42	1	0.1	0.1	0.1	0.1	0.1
44	2	0.05	0.05	0.05	0.05	0.05
49	2	0.019	0.0325	0.055	0.0775	0.091
50	13	0.01	0.05	0.05	0.05	0.05
51	8	0.01	0.01	0.1	0.1	0.1
54	1	0.01	0.01	0.01	0.01	0.01
55	1	0.05	0.05	0.05	0.05	0.05
57	3	0.0064	0.0115	0.02	0.32	0.5
59	8	0.003	0.01575	0.02	0.1	0.319
60	2	0.01	0.01	0.01	0.01	0.01
61	2	0.02	0.02	0.02	0.02	0.02
62	5	0.003	0.003	0.01	0.01	0.016
66	10	0.05	0.0925	0.13	0.2975	0.404
67	8	0.0182	0.0425	0.075	0.1155	0.144
75	7	0.01	0.01	0.05	0.05	0.07
76	13	0.01	0.01	0.01	0.02	0.02
79	1	0.05	0.05	0.05	0.05	0.05
80	5	0.05	0.05	0.05	0.05	0.05
82	2	0.05	0.05	0.05	0.05	0.05
84	3	0.01	0.01	0.01	0.01	0.01
85	6	0.0265	0.1	0.3	0.38525	0.6735
86	1	0.05	0.05	0.05	0.05	0.05
87	2	0.013	0.0175	0.025	0.0325	0.037
88	6	0.05	0.05	0.05	0.05	0.05
93	5	0.014	0.02	0.02	0.05	0.05
95	1	0.02	0.02	0.02	0.02	0.02
99	2	0.023	0.0275	0.035	0.0425	0.047

Annex G Use of quality labels

The Groundwater Atlas database contains quality labels for the data items sampling site, sampling point, and groundwater sample. The domain and meaning of the quality labels are:

Sampling site

0. Default. Sampling site data as provided by the owner.
1. Issue / question concerning the sampling site data addressed to the owner.
2. Issue / question concerning the sampling site metadata addressed to the Groundwater Atlas developer or to the owner.
3. No issue or question.

Sampling point

0. Default. Sampling point data as provided by the owner.
1. Issue / question concerning the sampling point data addressed to the owner.
2. Issue / question concerning the sampling point metadata addressed to the Groundwater Atlas developer or to the owner.
3. No issue or question.

Groundwater sample

0. Default. Sample data and measurement results as provided by the owner.
1. Issue / question concerning the sample identification to the owner.
2. Issue / question concerning one or more measurement results from the sample to the owner.
3. No issue or question.

The intended use of these quality labels is to improve the selection of measurement results; by removing non-relevant measurement results from the selection. All quality labels in the Groundwater Atlas 2022 master database have the value = 3 except the cases described here:

Drinking water companies

- Oasen, sampling site: Request to provide the surface elevation at the location of the sampling site (value = 1).
- Oasen, sampling point: Request to provide the surface elevation at the location of the sampling site (value = 1).
- WBG, sampling site: Request to provide the abstraction site ID for a sampling site (value = 1).
- WMD, sampling site: Request to provide the abstraction site ID for a sampling site (value = 1).
- Vitens, sampling site: Request to provide the abstraction site ID for sampling site 28DP0080 (value = 1).

Regional authorities

- All sampling sites (physical well): Request to provide the correct sampling site data - waits for the release of the BRO with the validated regional groundwater quality monitoring network data (value = 1).
- All sampling points (screens): Request to provide the correct sampling point data - waits for the release of the BRO with the validated regional groundwater quality monitoring network data (value = 1).
- Samples Province Limburg: Request to provide information about the condition of the sampling sites B58D0667, B52E0253, B46D0373 (two sampling points each) since publication in Franke et al. (2010). All samples from these six sampling points have the quality value = 1.
- Samples Province Zeeland: Request to explain the high number of measurement values (up to 100% of the number of measurement results) from samples taken in the years 2009, 2010, 2011, 2012 and 2013. These samples have the quality label value = 2 (the sampling sites and sampling points from this regional authority have the quality value = 1).
- Samples Province Groningen: Request to explain the high number of measurement values (up to 100% of the number of measurement results) from samples taken in the years 2015 and 2016. These samples have the quality label value = 2 (the sampling sites and sampling points from this regional authority have the quality value = 1).

Annex H Age of groundwater at sampling points in two well fields

The results in this table are used for comparing the median travel time in the saturated zone (according to the LHM model) with the age of the groundwater sample according to tritium-helium measurements (Section 3.5).

ID	**site**	**screen depth (m-ss.)**	**Screen length (m)**	**gwl (m-ss.)**	**screen depth (m-gwl.)**	**age (yr)**	**P50 travel time (yr)**
28CA3309_3	Holten	13.5	1	7.0	6.5	7.8	13.1
28CA3309_4	Holten	16	1	7.0	9.0	8.3	16.9
28CA3336_3	Holten	13	1	4.3	8.7	15.9	11.8
28CA3336_4	Holten	15.5	1	4.3	11.2	24.3	13.6
28CP0168_2	Holten	22	5	7.9	14.1	32.9	-
28CP0196_1	Holten	10	2	7.9	2.1	9.3	10.0
28CP0196_3	Holten	24	2	2.1	21.9	38.8	30.2
28CP0207_1	Holten	9	2	1.5	7.5	27.0	11.1
28CP0207_3	Holten	24	2	1.5	22.5	37.6	40.1
28CP0245_1	Holten	11.5	1	5.6	5.9	7.6	10.9
28CP0245_2	Holten	21	2	5.6	15.4	27.0	21.9
28CP0245_3	Holten	57	2	5.6	51.4	101.6	146.7
28CP0248_1	Holten	6.5	1	3.6	2.9	0.8	5.5
28CP0248_2	Holten	11	1	4.1	6.9	15.5	8.8
28CP0248_3	Holten	22.5	1	3.7	18.9	29.3	25.0
28CP0250_1	Holten	21.5	1	8.3	13.2	29.1	24.2
28CP0250_2	Holten	30.5	1	7.9	22.7	31.3	37.1
28CP0250_3	Holten	44.5	1	7.8	36.7	67.4	65.8
28CP0267_1	Holten	14	2	8.5	5.5	5.3	13.5
28CP0267_2	Holten	25	2	8.5	16.5	26.6	34.7
28CP0267_3	Holten	31	2	8.5	22.6	31.7	42.9
28CP0267_4	Holten	39	2	8.4	30.6	39.0	60.0
28CP0268_1	Holten	10	2	4.9	5.1	19.9	32.6
28CP0268_2	Holten	21	2	4.9	16.1	35.5	49.2
28CP0268_3	Holten	31	2	4.8	26.2	50.8	51.7
28CP0268_4	Holten	41	2	4.7	36.3	45.2	80.5
28FP0097_1	Manderveen	8.5	1	3.3	5.2	9.8	5.4
28FP0097_2	Manderveen	24	2	3.9	20.1	25.8	15.9
28FP0102_1	Manderveen	8.5	1	4.5	4.0	4.9	9.8
28FP0102_2	Manderveen	24	2	5.1	18.9	33.7	42.5
28FP0105_1	Manderveen	8.5	1	4.1	4.4	5.8	16.4
28FP0105_2	Manderveen	24	2	4.8	19.3	14.9	24.0

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