Ministry of Environment of Denmark
Environmental Protection Agency

Prioritisation strategy for use on the Danish EPA´s "List of Pesticides"

- Risk of leaching to groundwater

Environmental review no. 62

May 2023

Publisher: The Danish Environmental Protection Agency

Editors:
Signe B. Rasmussen (The Danish Environmental Protection Agency, DEPA)
Ulla E. Bollman (Geological Survey of Denmark and Greenland, GEUS)
Steen Marcher (The Danish Environmental Protection Agency, DEPA)
Anders R. Johnsen (Geological Survey of Denmark and Greenland, GEUS)

ISBN: 978-87-7038-514-5

Contents

1.	**Summary**	**4**
2.	**Danish summary / Dansk sammendrag**	**5**
3.	**Introduction**	**6**
4.	**Data sources**	**8**
4.1	EFSA data	8
4.2	The pesticide properties database – PPDB	9
4.3	EPI-suite	9
4.4	Uncertainty related to data sources	10
5.	**The prioritisation strategy**	**11**
5.1	Sales rates	12
5.2	Known groundwater risk	13
5.3	Predicted Environmental Concentrations in groundwater – PECgw > 0.1 µg/L	15
5.4	Hydrolysis < 100 days	16
5.5	GUS > 1.8	16
5.6	Hydrolysis > 100 days	18
6.	**Inspiration from the German "Recommendation list"**	**19**
6.1	Main conclusions	19
7.	**Validation**	**20**
7.1	Pesticides used for the validation	20
7.2	Validation of the GUS index	20
7.3	Validation of the EPI-suite model (with regards to the GUS index)	22
7.4	Validation of the prioritisation strategy	24

Appendix 1

1. Summary

The Danish Environmental Protection Agency (EPA) and the Geological Survey of Denmark and Greenland (GEUS) have developed a prioritisation strategy for use on the Danish EPA´s List of Pesticides. The pesticides (active substances and degradation products) included in the list are potentially relevant to include in groundwater monitoring. The strategy is based on information on historical sales data, known risk of leaching to groundwater, predicted/modelled concentrations in groundwater and physical/chemical parameters (aqueous hydrolysis, degradation half-lives in soil, and partitioning coefficients between water and soil organic carbon) relevant for evaluating the risk of leaching to groundwater.

The strategy works as a decision tree, with prioritised decision nodes placing the pesticides in different prioritisation groups. Within each group the pesticides are ranged according to their properties, resulting in a single list of pesticides individually prioritised depending on their estimated risk of leaching to groundwater.

The strategy was tested on 175 pesticides with known prevalence in Danish groundwater. The validation showed that the approach cannot be applied without generating a number of both false positives (estimated high risk of leaching but no findings in groundwater) and false negatives (estimated low risk of leaching but findings in groundwater). The methodology therefore includes uncertainties, which is expected and considered unavoidable and acceptable.

2. Danish summary / Dansk sammendrag

Miljøstyrelsen og GEUS har udviklet en prioriteringsstrategi til brug på Miljøstyrelsens liste over pesticider (også kaldet Bruttolisten). De pesticider (aktivstoffer og nedbrydningsprodukter), der er opført på listen, er potentielt relevante at medtage i grundvandsovervågningen. Strategien er baseret på oplysninger om historiske salgsdata, kendt risiko for udvaskning til grundvand, modellerede koncentrationer i grundvand og fysiske/kemiske parametre (vandig hydrolyse, halveringstider for nedbrydning i jord og fordelingskoefficienter mellem vand og organisk kulstof i jorden), der er relevante for vurderingen af risikoen for udvaskning til grundvand.

Strategien fungerer som et beslutningstræ med prioriterede beslutningsknuder, der placerer pesticiderne i forskellige grupper. Inden for hver gruppe er pesticiderne rangeret efter deres egenskaber, hvilket resulterer i én enkelt liste over pesticider, der er prioriteret individuelt afhængigt af deres anslåede risiko for udvaskning til grundvandet.

Strategien blev afprøvet på 175 pesticider med kendt forekomst i dansk grundvand. Valideringen viste, at strategien ikke kan anvendes uden at generere et antal både falsk positive (estimeret høj risiko for udvaskning, men ingen fund i grundvandet) og falsk negative (estimeret lav risiko for udvaskning, men fund i grundvandet). Metoden omfatter derfor usikkerheder, hvilket er forventeligt og anses for uundgåeligt og acceptabelt.

3. Introduction

In 2019, large pesticide screenings in groundwater were initiated in Denmark due to a supplementary agreement to the now former Danish Pesticide Strategy[1]. The screenings were carried out as part of the national groundwater monitoring program, GRUMO[2]. In this work, pesticides were defined as active substances that are a part of plant protection products, PPPs, and their degradation products. Some of these active substances have also been, or are used, in biocidal products. As part of the work with the screenings, the Danish Environmental Protection Agency (the Danish EPA) has developed a List of Pesticides (in Danish: Miljøstyrelsens Bruttoliste), which currently contains approximately 1.630 pesticides. The pesticides included in the list are potentially relevant to include in groundwater monitoring. The work with the list of pesticides at the Danish EPA is a continuation of the work with a list developed by the Danish Regions[3]. The Regions used their list in the work with identifying pesticide point sources[4].

The List of Pesticides at the Danish EPA is currently a dynamic list being updated regularly with new pesticides identified in the general work and activities conducted by the Danish EPA in relation to groundwater protection.

During three large screenings in 2019 - 2021 it was evident that the commercial market of high quality analysis´ offered by international laboratories was more or less depleted. This means that it is necessary to provide funding for the development of additional analytical methods if more pesticides are to be included in screenings/monitoring. It is not expected that all compounds on the List of Pesticides will occur on a large scale in the Danish groundwater, hence a prioritisation of the pesticides is needed to ensure a sensible use of resources.

This document presents a prioritisation strategy developed by GEUS and the Danish EPA, which is to be used to prioritise the pesticides on the Danish EPA´s List of Pesticides. The prioritisation strategy was developed for, and validated on, Danish conditions. However, the strategy is considered applicable for other lists of pesticides, if the relevance of each step is evaluated together with the arguments and criteria for the steps.

The prioritisation strategy is ready for use, and the Danish EPA is currently preparing the List of Pesticides for the actual prioritisation exercise to be carried out. The work with developing this prioritisation strategy was initiated in 2021, and consisted of three workshops with participants from GEUS and the Danish EPA alongside data gathering and processing of data. The prioritisation strategy was validated on 175 pesticides that are either currently included in the Danish national groundwater monitoring program, GRUMO, or analysed in the large screenings in 2019 and/or 2020.

---

[1] https://mim.dk/miljoe/tillaegsaftale-til-pesticidstrategien/

[2] https://www.geus.dk/vandressourcer/overvaagningsprogrammer/grundvandsovervaagning

[3] https://www.regioner.dk/regional-udvikling/miljoe-og-ressourcer/grundvandsforurening

[4] Christensen A. (2019): Redegørelse for projektet “Nye pesticidanalysepakker 2018”. Region Midtjylland. Marts 2019

Furthermore, it was recommended in an international review of the Danish groundwater protection activities[5] to look for inspiration in a similar work[6] carried out by the German EPA. This work was reviewed and discussed at one of the workshops, for the full discussion and conclusions see appendix 1.

[5] https://mim.dk/media/219355/endelig-rapport-international-review-of-danish-groundwater-protection.pdf

[6] https://www.umweltbundesamt.de/sites/default/files/medien/362/dokumente/uba_empfehlungsliste_psm-metaboliten_apr2019.pdf

4. Data sources

To enable all pesticides on the list to be prioritised and ranged individually, data from three different sources were gathered. The three sources are described below, and the specific parameters extracted from the sources are presented in table 1. A discussion of the arguments for including these specific parameters is presented in section 5.

4.1 EFSA data

To secure a high data quality and credibility, it was decided to use a primary source of specific pesticide data. The primary data source was the EU risk assessment of pesticides. These data were generated as part of the EU approval process of active substances, and the quality is therefore checked by experts across the EU, including experts from the Danish EPA. Additionally, these data are used in the national authorisation process of individual plant protection products containing the specific active substance(s).

More specifically, the necessary data were extracted from the EFSA conclusions. EFSA (European Food Safety Authority) is the EU body that, together with the member states, is responsible for the risk assessment of new active substances and active substances that are to be renewed. When a risk assessment of a given active substance has been finalised, EFSA publishes an EFSA conclusion, which summarises the scientific risk assessment, together with a list of endpoints to be used in the national risk assessments of plant protection products containing the active substance. Endpoints relevant for the environmental fate of the active substance and accompanying degradation products are for example degradation half-lives in soil (DT50) and partitioning coefficients between water and soil organic carbon (Kfoc).

The EFSA conclusion is sent to the European Commission, which has the mandate to decide (by vote) if a given active substance should be approved in the EU. The outcome of this vote is constituted in a review report, which among other things summarises the concerns regarding the use of the active substance. A concern relevant in the context of this work is related to the risk of leaching to groundwater, expressed as the groundwater sentence (for more details see section 5.2). The review reports for all active substances on the List of Pesticides have therefore been visited in order to identify active substances that have been assigned a groundwater sentence during the EU risk assessment process.

EFSA has had the function described above since the year 2003, meaning that EFSA conclusions were not published before this time. This means that active substances only used before 2003 generally do not have a published EFSA conclusion. Such pesticides without an EFSA conclusion may have other early versions of an EU risk assessment, where fewer endpoints were published, for example together with the review report. If the review report contains usable endpoints, these are included as a source of data for the prioritisation.

Another issue is related to data quality and format. Over time, data requirements from the EU in the approval process have changed, including requirements to experimental study designs, data processing, and reporting format. In some cases, this results in data that are not of a comparable quality or format, meaning that although there are available EU data, it may not be usable for the work with prioritising. There are also examples of compounds where only some of the EU parameters are usable.

To sum up, all available EFSA conclusions have been visited with the purpose of extracting endpoints to be used in the prioritisation (table 1). It should also be mentioned that during the process of extracting data from the EFSA conclusions, all environmentally relevant degradation products included in the EU risk assessment were added to the Danish EPA´s List of Pesticides.

TABLE 1. List of parameters extracted or generated from the three different data sources.

	EFSA	PPDB	EPI-suite
DT_{50} (geometric mean, laboratory, normalised)	X		
K_{foc} (arithmetic/geometric mean, laboratory)	X		
Hydrolysis, DT_{50} (worst case in pH range 7-9, laboratory)	X		
PECgw (worst case, PELMO, Hamburg)	X		
GUS (based on experimental DT_{50} and K_{foc})	X		
GUS (origin may be unknown)		X	
GUS (estimated by models)			X
Groundwater sentence	X		

4.2 The pesticide properties database – PPDB

In the case of no available EFSA data, it was checked if data were available in the pesticide properties database, PPDB[7]. The data presented in this database generally originate from the EU evaluation of active substances, but additional sources of data have been cited in some cases, sources which origin is not clearly reported. The database furthermore contains errors with regard to compound identity for example CAS numbers, chemical structure and chemical names.

For these reasons, PPDB is not the primary source of data applied in this work, but is used if the database contains data for compounds with no usable EFSA data. PPDB data will be applied in such cases, since it is considered better than no data. PPDB does not contain information on predicted environmental concentrations in groundwater (PECgw), and only rarely information on hydrolysis, especially for pesticides with no EFSA data. Hence, it was decided to only extract the GUS value from PPDB, in the case of no available EFSA data (for information on the GUS index please refer to section 5.5).

4.3 EPI-suite

In the case of pesticides with no EFSA or PPDB data, it is not possible to assess the leaching potential, and thus not possible to prioritise/range them accordingly unless other types of data are retrieved. For these pesticides the US EPA Estimation Program Interface, EPI-suite[8], was used to estimate the data needed to calculate a GUS value, enabling a prioritisation of compounds with otherwise insufficient data. It must be stressed that the use of a GUS value estimated from EPI-suite predictions, is associated with very high uncertainty. For more details on the EPI-suite models see section 7.3.

[7] http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

[8] https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface

4.4 Uncertainty related to data sources

The three data sources described above include a range of uncertainties/risks associated with the parameters. It is estimated that the uncertainty associated with the sources increases in the following order: EFSA <PPDB <EPI-suite, as illustrated in figure 1 below. However, it is very important to keep in mind that all parameters, no matter the source, are associated with uncertainty. Although EFSA data is experimentally based and considered of the highest quality, it still only describes a moment in time, and is often based only on a minimum of four parallel experiments conducted on different soils. This accounts for degradation in soil (DT50) and sorption to soil (Kfoc) - two very important parameters used in the assessment of leachability to groundwater.

Another aspect of uncertainty related to data generation is the determination of possible degradation pathways and identification of possible degradation products (route of degradation). Historically, the focus has been on identifying the larger degradation products, and less attention has been given to the smaller degradation products, which are potentially more polar and persistent. This has resulted in examples of such degradation products not being identified and included in the EFSA conclusion and the following risk assessments.

The subsequent modelling exercises (for example predicted groundwater concentrations, PECgw) inherit the uncertainties related to the input data. Having a rather small and uncertain data foundation from the very beginning of the risk assessment therefore highly effects the credibility of the subsequent modelling, modelling results which are used directly to determine the fate of a plant protection product.

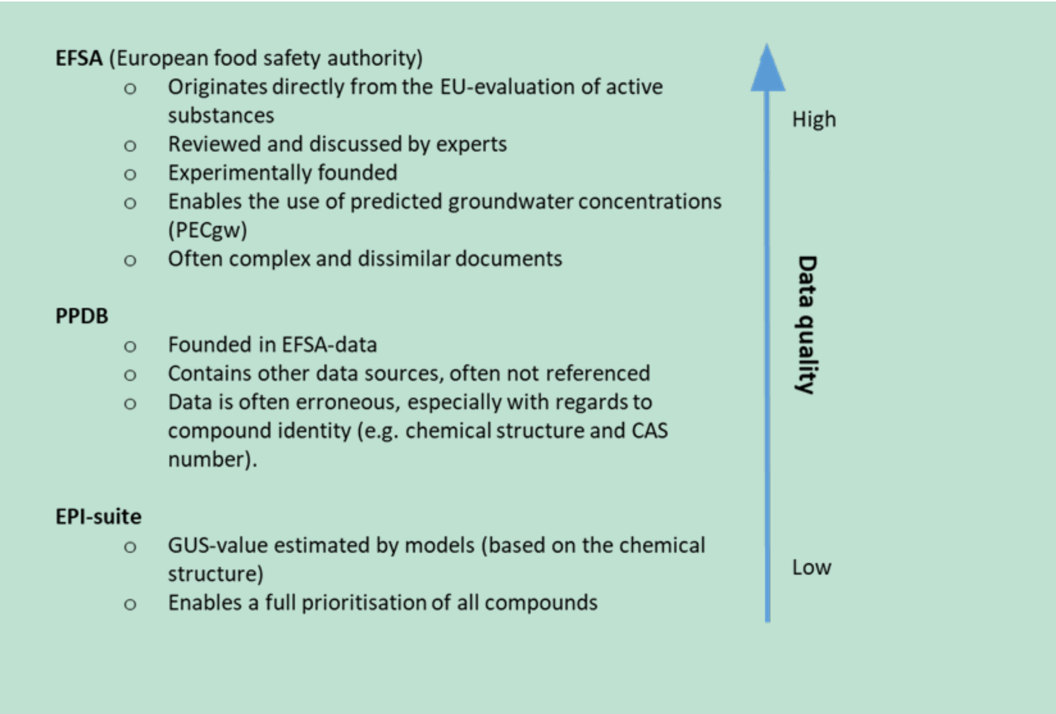

FIGURE 1. Data sources applied in the prioritisation and their estimated data quality.

5. The prioritisation strategy

As mentioned in section 3 the purpose of this work is to develop a prioritisation strategy to apply on an extensive list of pesticides (active substances and degradation products), which are to be individually ranged according to their risk of leaching to groundwater. The final strategy is illustrated in figure 2 below and followed by subsections describing the arguments for including the different steps/groups in the strategy. The strategy was also validated, which is presented in section 7.

The strategy consists of seven steps, where the first two steps ensure that pesticides, which are currently not considered relevant to include in groundwater monitoring activities are disregarded. The first step sorts out pesticides, which have already been included in previous monitoring in GRUMO. This includes both the ordinary monitoring program and the three large screenings conducted in the years 2019, 2020 and 2021. These compounds may be used for testing the validity of the strategy. The second step is related to the annual sales rates of the active substances and sorts out compounds which have not been sold in amounts high enough for the compounds to be considered as posing a risk in general to the Danish groundwater resource.

The five prioritisation steps arrange the remaining compounds into six groups, A to F, by use of the data mentioned in section 4. It is indicated (in italics) in each box to what level the specific parameter used for selection and ranging is considered reliable and provides a robust assessment.

Please recall that it is only the GUS value that is extracted from the PPDB database and the EPI-suite model, hence it is in the Groups A, C and E that other data than the EFSA data may be used.

In the following sections the different prioritisation steps are explained in detail.

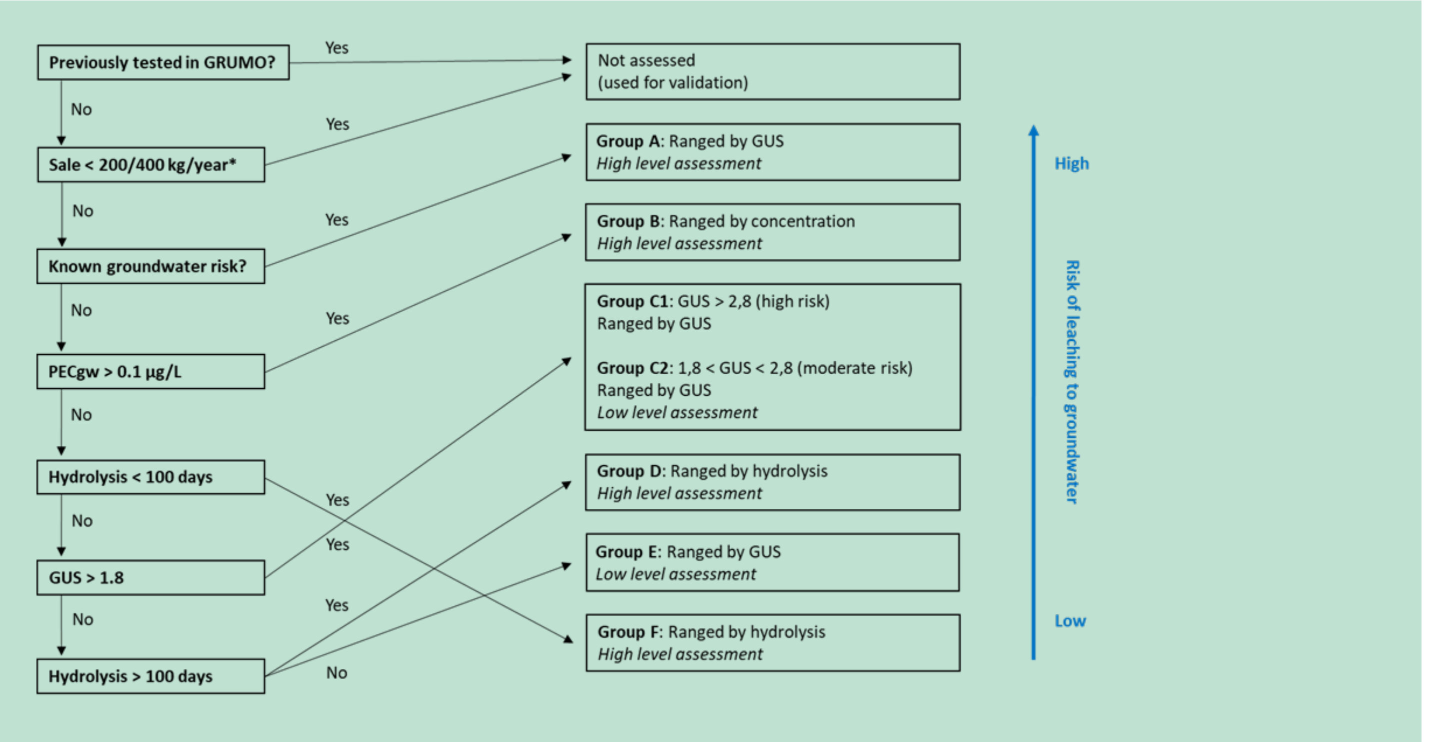

FIGURE 2. Prioritisation strategy developed to prioritise the Danish Environmental Protection Agency´s "List of pesticides" according to risk of leaching to groundwater. The level of uncertainty for each of the parameters applied in the strategy is indicated in italics in each of the boxes to the right. For more information on data sources and the connected uncertainty see section 4.
*Active substances, and degradation products there from, are not included in the prioritisation if they have an average annual sales rate less than 400 kg/year for the period from 1956 to 2000 and an average annual sales rate less than 200 kg/year for the period from 2001 to 2020. Thus, the sales rate have to be below the cut off value for both periods, for the active substance to be excluded from the prioritisation.

5.1 Sales rates

The risk of a pesticide causing a widespread diffuse contamination of groundwater is likely dependent on the magnitude of its use. If a pesticide has only been used in very small amounts and/or over a short period of time, the risk of the pesticide being transported to several groundwater bodies is small. It was therefore decided to make use of the annually published sales statistics of pesticide active substances[9] to set a minimum limit for sold amount of the active substances.

Since 1987 the Danish EPA has published the national sales rates (kg/year) of pesticide and biocide active substances together. Before 1987 and back to 1956 there were also conducted a registration of sold compounds, but these data was not published as specific sales statistics as it has been done since 1987. The annual sales statistics back to 1956 are published by the Danish Regions, and can be downloaded from their homepage[10]. Up until 2010 the annual sales rates of active substances were made collectively for pesticides and biocides, whereas

[9] https://www2.mst.dk/Udgiv/publikationer/2022/01/978-87-7038-369-1.pdf

[10] https://www.miljoeogressourcer.dk/udgivelser.php?lixId=5046

from 2010 and onward a distinction was made between active substance sold as plant protection products and biocidal products. This means, that the data from the period 1956 - 2009 may contain an unknown amount of active substance sold as biocidal products.

The Danish Regions carried out a similar exercise in 2018[11] in order to identify pesticides likely to be found in groundwater at point source contaminations. The approach with regard to sales rates applied by the Danish Regions was used as inspiration, but with minor changes.

As done by the Danish Regions, it was decided to set two different minimum limits for the amount of sold active substance for two time periods. For the period 1956 – 2000 an average of 400 kg/year, and for the period 2001 – 2020 an average of 200 kg/year. Practically, it means that the sales rate of a given active substance has to comply with either of the two limits in order to continue in the prioritisation. If an active substance is sold less than 400 kg/year in the period from 1956 to 2000, and less than 200 kg/year in the period from 2001 to 2020, it will be sorted out.

The cut-off limits were based on sales- and prevalence data for the herbicide rimsulfuron and its' degradation products. Rimsulfuron is the pesticide sold in smallest amounts where the degradation product PPU still triggers an evaluation of a potential inclusion on the list of pesticides that Danish drinking water suppliers are obliged to monitor (detected in 1 % or more of the samples, and/or detected in 0.2 % or more of the samples with a concentration above 0.10 µg/L). Rimsulfuron was sold from 2001 to 2019 with a mean annual sale of 209 kg/year, hence the 200 kg/year cut-off. The longer pesticides are present in the groundwater, the higher the chance of dilution and degradation, hence the increased sales cut-off before 2000.

The List of Pesticides contains many degradation products, which are not sold on the market, but produced in the environment as the active substance degrades. It was decided in this work that the degradation products should inherit the sales rates from the active substance(s), directly transferring the importance of an active substance to the degradation product. This is considered a conservative approach, as most degradation products are not formed 1:1 when an active substance degrades. Furthermore, degradation products being formed from more than one active substance (e.g. 1,2,4-triazole), will obtain a summed sales rate from all documented mother compounds. Another reason for letting the degradation products inherit the sales rate from the mother compound(s) is to avoid the uncertainties that comes if formation fractions are applied on the sales rates.

It is part of the prioritisation strategy to conduct an expert judgement of the final prioritised list, but also of the compounds being sorted out. This expert judgement will be carried out by the Danish EPA and GEUS to avoid that known problematic compounds are sorted out, and thereby not considered for monitoring. Compounds never registered as sold in Denmark are especially important in this regard, as they would automatically be sorted out. An example is metazachlor, which has never been authorised for use in Denmark, while a selection of its degradation products, often found in German groundwater[12], were found in Danish groundwater in the 2019 screening.

5.2 Known groundwater risk

During the EU evaluation of an active substance, specific concerns are identified, concerns that may not support a non-approval of the active substance, but are considered important for

---

[11] Christensen A. (2019): Redegørelse for projektet "Nye pesticidanalysepakker 2018". Region Midtjylland. Marts 2019.

[12] https://www.schleswig-holstein.de/DE/fachinhalte/G/grundwasser/Downloads/berichtGrundwasser-beschaffenheit.pdf?__blob=publicationFile&v=2

the member states to consider for product authorisations. The member states are obliged to consider the need for setting risk mitigation measures or conditions for the specific uses in that member state. The groundwater sentence mentioned in section 4 is used in the prioritisation strategy as it indicates a potential risk to groundwater.

When a groundwater sentence is stated in a review report during the EU approval process of an active substance, it means that the work carried out by scientific experts from a range of member states indicate that the use of this active substance may pose a risk to groundwater resources, under certain conditions. There are though, few examples where a groundwater sentence is assigned to an active substance due to lack of documentation or studies (e.g. for degradation products) relevant for the risk assessment of groundwater. This is termed as a data gap.

A groundwater sentence may have different wording in different review reports, but it has a basic structure in line with the example illustrated in figure 3 below. The groundwater sentence is added to the review report of an active substance, meaning that the sentence is related to a specific active substance, but is often related to its degradation products. However, it is rarely specified which compound(s) is causing the concern. It could for example be two out of seven degradation products causing the concern for groundwater, but it could also be the active substance alone, or the active substance and three degradation products. In a few cases, the groundwater sentence specifies which compounds are causing the sentence.

When evaluating the risk of groundwater contamination by several pesticides, which have not previously been monitored in Danish groundwater, the groundwater sentence is considered an informative parameter to include in the work. Therefore, a “known groundwater risk” is currently determined by the presence of a groundwater sentence in the review report. Furthermore, if known monitoring data from other EU member states shows that a given pesticide is found in more than 1 % of the analysed samples, the pesticide will also be placed in Group A. However, monitoring data from other member states will not be searched in parallel to the other parameters in the prioritisation strategy, but will only be used if the Danish EPA is made familiar with such data.

6. Particular conditions to be taken into account on short term basis by Member States in relation to the granting of authorisations of plant protection products containing fluopicolide.

On the basis of the proposed and supported uses (as listed in Appendix II), the following particular issues have been identified as requiring particular and short term attention from all Member States, in the framework of any authorisations to be granted, varied or withdrawn, as appropriate:

In this overall assessment, Member States must pay particular attention to:

- the protection of aquatic organisms;.
- the protection of groundwater when the active substance is applied in regions with vulnerable soil and/or climatic conditions;
- the risk to operators during application;
- the potential for long range transport via air.

Conditions of authorisation shall include risk mitigation measures and monitoring programmes shall be initiated to verify potential accumulation and exposure in vulnerable areas, where appropriate.

FIGURE 3. An example of a groundwater sentence (marked with a red circle around it) from the review report of fluopicolide.

The goal of this prioritisation is to range all pesticides on the list, one by one. The unspecified information in the groundwater sentence challenges this exercise, as it is often not clear which compound is causing the presence of the sentence. It was decided to work around this challenge by identifying all compounds (active substance and degradation products) having predicted groundwater concentrations (PECgw) over the quality criteria of 0.1 µg/L in the EU assessments. This information can be found in the EFSA conclusions. More specifically, an EFSA conclusion contains a table in chapter 6 providing an overview of selected parameters relevant for ground- and drinking water risk assessments, including the active substances and degradation products exceeding the threshold value of 0.1 µg/L by modelling. The compounds having a PECgw > 0.1 µg/L were noted as having a groundwater sentence.

The groundwater sentence was applied in the review report some time before EFSA was established. therefore a few pesticides have a review report containing an unspecified groundwater sentence, but no EFSA conclusion. These pesticides are no longer approved in the EU and were only approved before the time of EFSA, or the compounds are currently under re-evaluation in the EU (first evaluation by EFSA). The above-mentioned approach to identify the affiliation of the groundwater sentence to specific compounds can therefore not be used in these specific cases. It was therefore decided to assign a groundwater sentence to the active substance and all degradation products mentioned in the review reports. This is a conservative approach overestimating the number of compounds affiliated to a groundwater sentence, but it is considered relevant due to lack of data.

The GUS index (see section 5.5) was used to individually range the pesticides within Group A, but for the few active substances (and associated degradation products) not having an EFSA-conclusion, a GUS value was determined by use of PPDB-data or EPI-suite. This also accounts for compounds not having EFSA data of the right format or quality.

5.3 Predicted Environmental Concentrations in groundwater – PECgw > 0.1 µg/L

As part of the EU evaluation, an assessment of the potential of the active substance and degradation products to be transported to groundwater must be conducted. This assessment includes experimental studies that determine the potential of the compounds to be biologically degraded in soil (the parameter DT50), and studies that determine the mobility (the parameter Kfoc) of the compounds. These experimentally determined parameters can be used for the simple estimation of a GUS value (see section 5.5), but they can also be used as input values to relatively complicated methods such as numerical dynamic models that estimate pesticide transport to deeper soil layers.

One of the primary advantages of using numerical models, is that the models can combine parameters controlling and affecting leaching of pesticides to groundwater: parameters describing the use (application dates, dosages, type of crop), parameters describing the physical/chemical properties (e.g. DT50 and Kfoc), and climate (e.g. precipitation, temperature, solar radiation, humidity and windspeed). This combination of parameters makes numerical model predictions much more precise than simple indices such as the GUS value.

The parameter PECgw is a high quality data parameter. The quality criteria for pesticides and their degradation products (both relevant and non-relevant) in ground- and drinking water in Denmark is 0.10 µg/L, and it is therefore the obvious choice of threshold.

EFSA applies different models for assessing the risk to groundwater, but in relation to product authorisations, Denmark currently only accepts the use of the PELMO model[13] with the Hamburg scenario, and the MACRO model[14] with the two specially developed national scenarios Karup and Langvad. But in practise very few product applications use the MACRO model.

For the work presented here, it was decided to extract predicted groundwater concentrations only of relevance to Danish conditions, hence the PELMO model with the Hamburg scenario. There are though examples of active substances that have been assessed in the EU, but the assessments were not made by use of the PELMO model. This means that some (although few) compounds have got an EFSA conclusion, but no PECgw for use in this work.

The use of the approach to affiliate an unspecified groundwater sentence to pesticides (see section 5.2 above) creates a rather large overlap with the prioritisation step based on predicted groundwater concentrations. Both steps apply the PECgw, meaning that this step assures a high ranking of pesticides with a PECgw > 0.1 µg/L, but not having a groundwater sentence. The number of pesticides placed in Group B is therefore expected to be relatively low, but the prioritisation step is none the less considered important and relevant.

5.4 Hydrolysis < 100 days

As part of the EU evaluation, abiotic degradation in water must be determined, also termed hydrolysis and expressed by a DT50 (days). This parameter describes the potential of a chemical to spontaneously disintegrate in aquatic environments without help from microorganisms. The hydrolysis half-life thereby indicates the persistence in water when there are no specific degradation mechanisms.

The hydrolysis half-life is considered a high-quality parameter with little uncertainty, because it is a relatively simple and trustworthy laboratory experiment to perform. More importantly, the parameter is also considered to be of higher quality than the inherently imprecise GUS values (see section 5.5 below). It has less uncertainty, which is why it is prioritised over GUS.

The threshold of 100 days is considered to be a conservative approach. The hydrolysis is often determined at 20°C, whereas the Danish groundwater temperature is usually around 10°C. This is not expected to have a noticeable effect on this application of hydrolysis data, as the speed of reactions are commonly known to be reduced by 2.0-2.5 times when the temperature is lowered 10°C. A hydrolysis DT50 of 100 days under standard conditions therefore corresponds to around 250 days under groundwater conditions. Assuming a DT50 of 225 days, the pesticide concentration in groundwater after 10 years (14.6 half-lives) will be reduced to 4.02*10-5 of the original concentration. In other words, the concentration that escapes the upper soil layers (input to groundwater) must be 250 µg/L in order for the pesticide to be detected in groundwater (assuming a detection limit of 0.01 µg/L), and 2500 µg/L for the quality criteria of 0.10 µg/L to be exceeded. Such high concentrations are only found at the most severe point source contaminations.

5.5 GUS > 1.8

The GUS index[15] is a simple mathematical description providing estimated information on the risk of leaching to groundwater. The index relies on a correlation between sorption (K_{oc} or K_{foc}) and degradation (DT_{50}) in soil, according to the equation below:

---

[13] https://esdac.jrc.ec.europa.eu/projects/pelmo

[14] https://esdac.jrc.ec.europa.eu/projects/macro

[15] Gustafson, D. (1989): Groundwater ubiquity score: A simple method for assessing pesticide leachability. Environmental toxicology and chemistry. April 1989.

$GUS = \log(DT_{50}) * (4-(\log K_{oc}))$

Where DT_{50} is the half-life in soil, and K_{oc} (alternatively K_{foc}) is the partition coefficient between soil organic carbon and water. The higher the K_{oc}, the higher affinity to bind to soil organic matter.

A high GUS value indicates a high theoretical risk of leaching to groundwater. As proposed by Gustafson and generally accepted, the GUS values can be arranged according to risk of leaching as follows:

GUS value	Risk of leaching
> 2.8	High risk
1.8 – 2.8	Moderate risk
< 1.8	Low risk

A prerequisite for applying the GUS index in a meaningful way is that an A-horizon (high organic carbon content) is present, as the Koc, and for that matter also the half-life in soil (DT50) is determined in such soils. This soil horizon has proven specifically important for degradation to occur and for sorption of chemical compounds. In the case of pesticides and areas where pesticides are used, an A-horizon is often present (agricultural areas), but the Danish Regions which are responsible for handling point source contamination have expressed concern that this might not be the case in relation to pesticide point sources[16]. Under such conditions the pesticides are not subjected to the same level of sorption and degradation as expected when applying the GUS index, and leaching may occur although a compound has a low GUS value.

Furthermore, pesticides having low affinity towards organic carbon, but high affinity to other soil constituents (e.g. iron oxides and clay) do not comply with the GUS index. Glyphosate is a good example of such a compound. Furthermore, compounds having other uses than as pesticides, may also not comply with the GUS index, as the loading may be disproportionately high compared to a typical pesticide use on the field. The GUS index is furthermore a crude simplification compared to numerical modelling, as the GUS index does not take into account pesticide dose, climate and geology etc. The GUS index therefore has some disadvantages and is only to be used as an indication of the potential for leaching to groundwater in the absence of better descriptors, and should be considered as a very uncertain "method".

It should also be kept in mind that the GUS values responsible for the ranking of pesticides in Group A, C and E may be of different quality, because the GUS value may originate from a lower quality source than the experimentally based EFSA data (see figure 1 in section 4). It is therefore also unavoidable that some pesticides will be ranked either too high or too low on the final prioritised list. A certain amount of "false positives" (high GUS value, but not leaching to groundwater) are more acceptable than "false negatives" (low GUS value, but leaching to groundwater).

This prioritising step arranges compounds having a GUS value above 1.8 in Group C, resulting in a relatively high rank. Hence, pesticides predicted to only leach at moderate levels are located in the same group as those with a high leaching potential, but recall that the compounds will be individually ranged according to their GUS value, naturally assuring a higher ranking of pesticides with a high GUS value within the group.

[16] Christensen A. (2019): Redegørelse for projektet "Nye pesticidanalysepakker 2018". Region Midtjylland. Marts 2019.

5.6 Hydrolysis > 100 days

As mentioned earlier, the half-life (DT50) by hydrolysis is not providing information on the risk of leaching to groundwater, but is instead providing information on the potential persistence of a compound if it was to reach the groundwater. This prioritisation step is therefore the final step, and splits the compounds in two groups: Group D with compounds having a hydrolysis DT50 above 100 days (compounds with hydrolysis DT50 equal to or below 100 days are placed in group F), and the remaining compounds having no hydrolysis data and a GUS value below 1.8.

6. Inspiration from the German "Recommendation list"

In 2020, an international review of the groundwater monitoring framework in Denmark was performed[17]. In the review, the Danish activities were compared to those of other EU member states. This review recommended the Danish EPA to look for inspiration in a similar prioritisation exercise carried out by the German EPA, resulting in the so called Recommendation List[18]. The Recommendation List contains a range of degradation products from currently approved active substances in Germany, which are recommended for the water authorities in the 16 federal states (Bundesländer) and the drinking water companies to be additionally monitored in relation to the standard pesticide parameter lists. More importantly, the document also describes how and why the degradation products were selected from a much larger group of degradation products.

The Danish EPA and GEUS reviewed the German approach and discussed to what extent the different prioritisation steps in the German approach is useable in the Danish prioritisation strategy. The details of this work can be found in appendix 1, thus only the main conclusions are reported in this section.

6.1 Main conclusions

Overall, there is a great overlap between the two approaches, where general themes are applied in both approaches, e.g. the use of sales rates and modelled groundwater concentrations followed by an expert judgement. However, there are a few differences primarily caused by differences in the focus of and conditions for the exercise. For example, it is important to notice that the German recommendation list is acting as a supplement to the already existing monitoring program. Additionally, the Danish approach also focus on the importance of compound specific properties, which enables a fully ranged List of Pesticides, as opposed to a separation into three groups depending on agricultural importance.

The main conclusion on the review of the German approach is that the two approaches already overlap as far as possible and the scientific discussions do not lead to further changes to the Danish approach, since differences are mainly due to the difference in purpose of the lists.

---

[17] https://mim.dk/media/219355/endelig-rapport-international-review-of-danish-groundwater-protection.pdf

[18] https://www.umweltbundesamt.de/sites/default/files/medien/3521/dokumente/2022_07_29_uba_recommendation_list_update2022_eng.pdf

7. Validation

The Danish prioritisation strategy presented in figure 2 was validated in order to test its applicability and performance. This section describes the validation of the strategy itself, together with an evaluation of the GUS index and the use of EPI-suite to calculate GUS values based on chemical structures.

7.1 Pesticides used for the validation

The prioritisation strategy was tested on 175 pesticides (both active substances and degradation products) previously analysed in Danish groundwater samples from the national groundwater monitoring program, GRUMO. Monitoring data from the ordinary program was used to represent pesticides detected, and data on non-detections originated from the large screenings carried out in 2019 and 2020.

The pesticides detected in groundwater were identified by use of the annual groundwater report[19], where pesticides detected in GRUMO during the past 10 years are reported with total detection rates and rate of detections above the quality criteria of 0.10 µg/L. The non-detected pesticides were randomly selected since data was not yet included for all non-detected pesticides in the two screenings from 2019 and 2020.

A total of 175 pesticides were included in the validation, where 72 were with detections, and 103 were without detections. The pesticides with detections were arranged in two categories according to the extent of findings (see table 2), where Category 1 is pesticides detected in 1 % or more of the samples, and/or pesticides detected in 0.2 % or more of the samples with a concentration above 0.10 µg/L. Category 2 is pesticides detected less than those placed in Category 1, and the non-detections were placed in Category 3. The criteria defining Category 1 is used by the Danish EPA to identify pesticides subject to a potential inclusion in the list of pesticides that Danish drinking water suppliers are obliged to monitor.

TABLE 2. The three categories containing the 175 pesticides included in the validation of the Danish prioritisation strategy, with an indication of origin of the monitoring data.

Category	Definition	Number of pesticides	Origin of monitoring data
1	Pesticides detected ≥ 1% of the samples Pesticides detected ≥ 0.2 % in concentrations above 0.10 µg/L	44	Groundwater report 2011-2020 Large screening 2019 + 2020
2	Pesticides detected, but detected less than those in Category 1	28	Groundwater report 2011-2020 Large screening 2019 + 2020
3	Pesticides not detected	103	Large screening 2019 + 2020

7.2 Validation of the GUS index

As described in section 5, the GUS index is an important factor in ranging each of the pesticides one by one. It is therefore also relevant to have a look at how well this specific parameter is performing, especially in relation to pesticides previously detected in groundwater samples. As also mentioned in section 4, the EPI-suite model will be used to estimate a GUS value for pesticides that do not have useable EFSA or PPDB data. The model has therefore been

[19] https://www.geus.dk/Media/637753300019725848/Grundvand%201989-2020_a.pdf

used to estimate a GUS value for the pesticides used for validation that do not have EFSA or PPDB data. The performance of the EPI-suite model is evaluated in section 7.3 below.

The GUS index is presented and briefly described in section 5.5, but as mentioned it is a relatively simple approach based on the two parameters: degradation half-life in soil (DT50) and sorption (Kfoc). It is generally agreed that a GUS value above 2.8 indicates a high risk of leaching, a GUS value between 1.8 and 2.8 a moderate risk of leaching, and a value below 1.8 a low risk of leaching. Evaluating the performance of the GUS index in this context, can be done by looking at the number of "false negatives" (pesticides with a low GUS value, but frequently detected in groundwater) and "false positives" (pesticides with a high GUS value, but not detected in groundwater).

The 126 pesticides used for validation are illustrated in figure 4, where they are sorted according to their detection rates (by categories) and compared to the predicted GUS value calculated or estimated from one of the three sources: EFSA, PPDB or EPI-suite. In this comparison, pesticides with low or no sales rates in Denmark, are excluded, as they might bias the dataset.

If looking at the pesticides most frequently detected (Category 1), it is seen that 64 % have a GUS value above 2.8, correctly indicating a high risk of leaching. A moderate risk of leaching is estimated by GUS for 18 % of the Category 1 pesticides, and 18 % are estimated to pose a low leaching risk. In this relation the 18 % estimated to have a low risk of leaching represents false negatives, and are highly undesired as they represent pesticides not expected to leach, but have been found to leach.

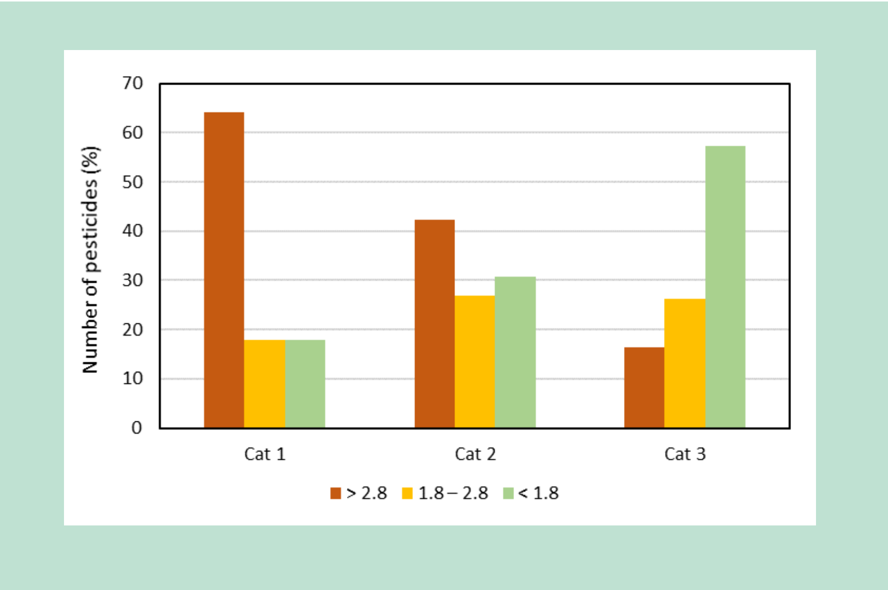

FIGURE 4. The 175 validation pesticides sorted according to their level of detections in Danish groundwater (Cat. 1: detected in 1 % or more of the samples, and/or pesticides detected in 0.2 % or more of the samples with a concentration above 0.10 µg/L. Cat. 2: detected less than those placed in Cat. 1. Cat. 3: non-detections), and their corresponding GUS values (based on either EFSA data, PPDB or EPI-suite).

As the level of detections decreases when moving from Category 1 pesticides down to Category 3 pesticides, it is seen that the percentage of pesticides estimated to have a high risk of leaching is also decreasing (the red bar in figure 4). However, the GUS index still predicts a high risk of leaching for 16 % of the pesticides not detected in groundwater (Category 3), which then represents the false positives, which are also undesired.

Overall, it is seen in figure 4, that the GUS index correctly predicts the general leaching pattern of the validation pesticides, with the highest estimate of leaching risk (red bars) located to the left in the figure, and decreases while moving to the right. Correspondingly, it is seen that the pesticides with the lowest estimate of leaching risk (green bars) are located to the right in the figure, and decreases when moving to the left. However, the presence of the false positives and especially the false negatives supports the previous statement that the GUS index is a simplified approach that is not appropriate for use on all pesticides and in all situations.

Although it is recognised that the GUS index has its limitations, and does not include information on agricultural practice (e.g. dosage, crops, and time of application), it is still concerning that 18 % of the pesticides detected in a rather high frequency and/or concentration are estimated by the GUS index to have a low risk of leaching to groundwater. Assuming that the 18 % underestimation is transferable to the pesticides that are to be prioritised according to the developed strategy, it means that a relatively high proportion of the pesticides that may have leached to the groundwater already will be ranged low on the list (false negatives). Historically, Denmark (compared to other countries) has a solid tradition of being extra protective of the groundwater, which is calling for extra concern about the 18 %.

It has to be stressed that the GUS index is a very simple approach with high uncertainty. The prioritisation strategy will therefore estimate an incorrect risk of leaching for some of the pesticides on the list. None the less, it is found applicable and relevant (fit for purpose) for the current work with prioritisation of a list of pesticides for compounds where no other data is available, as the rather uncertain prioritisation based on the GUS index is better than no prioritisation. Furthermore, the GUS index may be used to prioritise compounds within a group, where ranking is less important than between groups.

7.3 Validation of the EPI-suite model (with regards to the GUS index)

EPI-suite[20] is a collection of physical/chemical property and environmental fate estimation programs developed by the US EPA and Syracuse Research Corp. (SRC). For the estimation of the GUS index the results of KOCWIN™ and BIOWIN™ are used. Based on the chemical structure KOCWIN™ estimates the organic carbon-normalised sorption coefficient for soil and sediment (K_{oc}) using two different models: the Sabljic molecular connectivity method with improved correction factors and the traditional method based on log K_{ow} (estimated using KOWWIN™).

BIOWIN™ estimates the aerobic and anaerobic biodegradability of organic chemicals using seven different models. The output of BIOWIN3 was transferred to half-lives (days) using the suggested default half-lives by Aronson et al.[21] (table 3). For the following calculation of the GUS index the results of BIOWIN3 were used, while both model results for the K_{oc} were tested during validation.

[20] US EPA, 2022. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. United States Environmental Protection Agency, Washington, DC, USA. https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface.

[21] Aronson D, Boethling R, Howard P & Stiteler W. Estimating biodegradation half-lives for use in chemical screening. Chemosphere 63 (2006) 1953–1960.

TABLE 3. Transfer of the results from BIOWIN3 to half-lives using the conversion scheme suggested by Aronson et al., 2006.

BIOWIN3 category		Default half-lives (days) suggested by Aronson et al., 2006
Descriptor	**Model output**	
Hours	> 4.75	0.17
Hours-Days	4.25 – 4.75	1.25
Days	3.75 – 4.25	2.33
Days-Weeks	3.25 – 3.75	8.67
Weeks	2.75 – 3.25	15.0
Weeks-months	2.25 – 2.75	37.5
Months	1.75 – 2.25	120
Recalcitrant	1.25 – 1.75	240
	< 1.25	720

To validate the estimation of the EPI-suite model, the GUS value for the most frequently detected pesticides in Danish groundwater (GRUMO-report 2019, table 13 & 14) as well as randomly selected pesticides analysed in the large groundwater screenings in 2019, was estimated using EPI-suite 4.1 (in total 52 compounds, experimental GUS ranging from -2.3 to 8.5).

The estimated GUS values using EPI-suite were compared to the GUS index found in PPDB. Using the K_{oc} based on the estimated KOW (based on the KOWWIN™ model) shows a better correlation than when using the Sabljic molecular connectivity method. Furthermore, the correlation between PPDB and EPI-suite GUS values (Figure 5a) were considered good, and was therefore used in the further validation of the prioritisation strategy, as well as in the described generation of GUS values for pesticides not having EFSA-data or PPDB data (section 4.3).

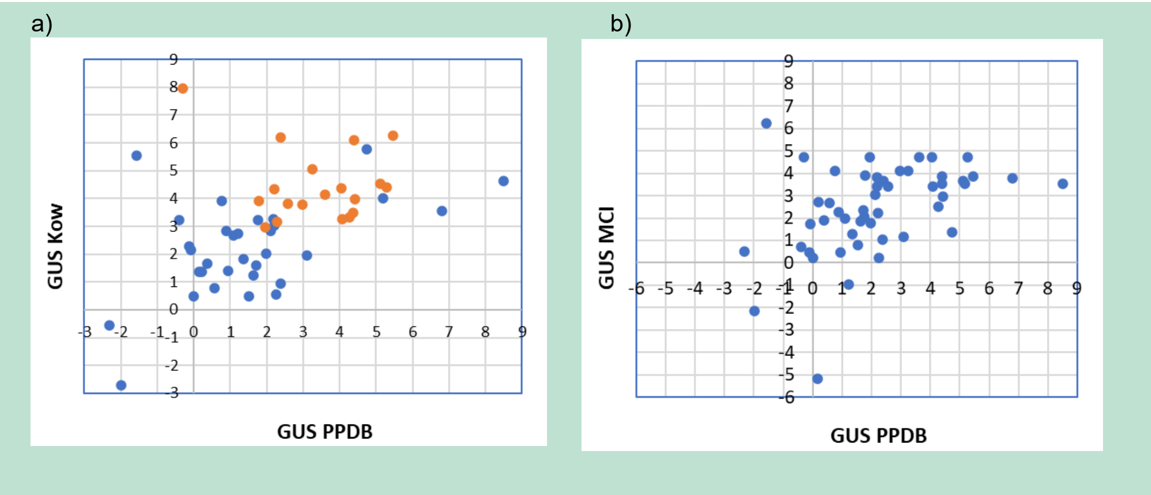

FIGURE 5. Correlation between GUS values listed in PPDB (GUS PPDB) and GUS estimated using EPI-suite: (a) K_{oc} estimation based on log KOW and (b) K_{oc} estimation based on Sabljic molecular connectivity method (MCI). Compounds detected in >1% of the analysed groundwater samples between 2011-2020 are marked with orange (Cat. 1).

From figure 5a it is clear that all Category 1 compounds (table 2), included in the validation of the EPI-suite model have an estimated GUS value >2.8. Only a few compounds with fewer/no detection in groundwater have an estimated GUS index >2.8 (false positives). These are terbutylazine-hydroxy, azamethiphos, aldicarb, dimethoat, carfentrazon-ethyl, carbendazim, metazachlor and its metabolites metazachlor-OA and metazachlor-ESA. This is considered an acceptable number of false positives.

7.4 Validation of the prioritisation strategy

As mentioned above, the strategy was tested against 175 pesticides, which all have been previously analysed in Danish groundwater samples. These pesticides are a part of the group of pesticides not being assessed as indicated in the first step in the prioritisation strategy (figure 2). Another parameter contributing to pesticides not relevant for assessment is active substance sales rates, which is the second step in the strategy. Of the 175 pesticides included in the validation, 49 are discarded due to low sales rates, leaving 126 pesticides to pass through the remaining strategy and be individually ranged. When the strategy is to be applied on the List of Pesticides, the discarded pesticides will be subject to an expert judgement. This expert judgement will include information (if available) such as use and findings in other countries.

Figure 6 below illustrates the partitioning of the 126 pesticides between the six groups (A to F) in the prioritisation strategy. Recall that the three categories describe the level of detections, where Category 1 (red bars) illustrates a high level of detections, Category 2 (yellow) a low level of detections, and Category 3 (green) no findings above the detection limit. It is seen that the Category 1 pesticides are generally placed in Group A and C, with a smaller number placed in Group D and E. The ideal pattern is for Category 1, and to a lesser extent Category 2, pesticides to be located in the groups further to the left in the figure, indicating a high ranking, and pesticides with no detections located in the groups further to the right, indicating a low ranking.

The primary focus is on a correct ranking of the Category 1 pesticides, which the validation appears to support. Recall that there is an overlap between the criteria for being placed in Group A and B, as both are more or less based on predicted groundwater concentrations (PECgw). Group B can therefore be considered as a sort of “buffer” supplementing Group A, and catching any pesticide with a high modelled risk of leaching, but not having a groundwater sentence assigned to it during the EU approval process. It is seen that only one of the validation pesticides is placed in Group B, which indicates that applying the groundwater sentence as a parameter for “known groundwater risk” is an important and effective tool in the strategy. Although it currently appears of less importance to include the predicted groundwater concentration (PECgw) in the strategy, it is decided to maintain it for the above mentioned reason.

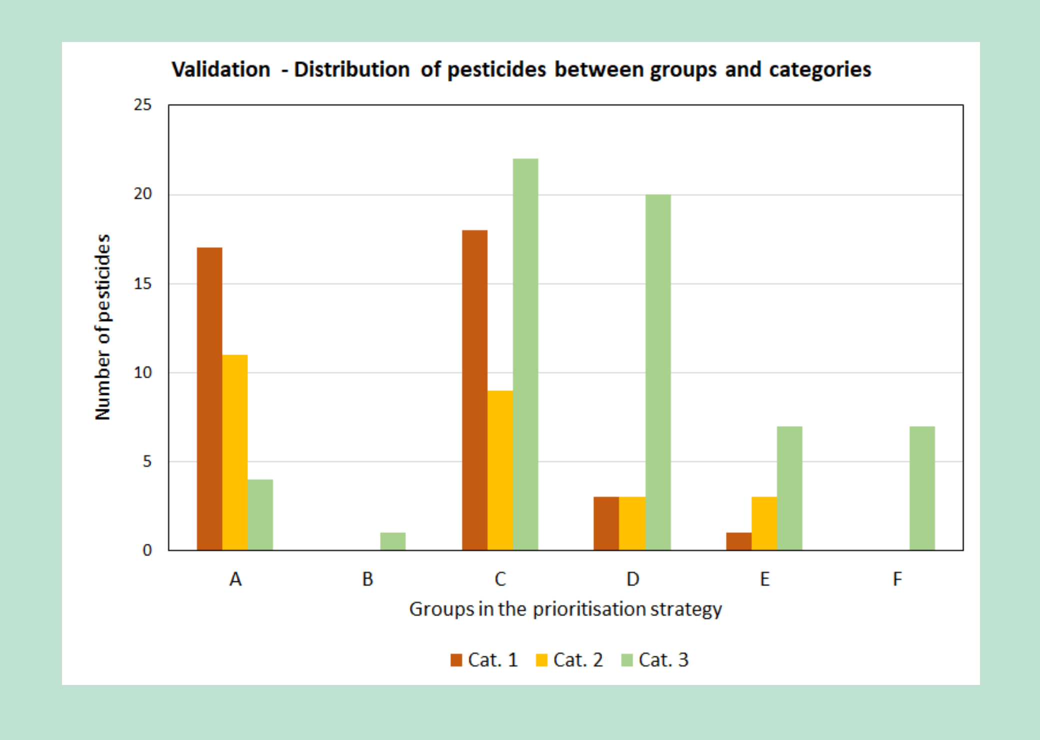

FIGURE 6. Distribution of the 126 validation pesticides between the 6 Groups defined according to the strategy, and the three categories defined by extent of detections in Danish groundwater. Pesticides excluded due to low or no sales rate are not a part of this illustration.
Category 1: Pesticides detected in GRUMO ≥ 1% of the samples and/or detected ≥ 0.2 % in for concentrations above 0.10 µg/L within the period 2011-2020; Category 2: Pesticides in GRUMO detected less than those in Category 1 within the period 2011-2020; Category 3: Pesticides not detected in the large screenings of 2019 and 2020.
Group A: Known groundwater risk; Group B: Modelled groundwater concentration above 0.1 µg/L; Group C: GUS value above 1.8; Group D: Abiotic hydrolysis above 100 days; Group E: No data on abiotic hydrolysis and a GUS value below 1.8; Group F: Abiotic hydrolysis below 100 days.

The pesticides with no detections (Category 3) are seen to be primarily distributed between the last 4 Groups, C to F, with approximately one third placed in each of the Groups C and D, and the last third divided more or less evenly between the Groups E and F. As mentioned earlier, it is preferred to have as few “false positives” as possible, meaning that the Category 3 pesticides should be placed further to the right in figure 6. From the validation it appears difficult to completely avoid a number of false positives in especially Group C, which mainly is caused by including pesticides predicted to have a moderate risk of leaching according to the GUS index (GUS values in the range of 1.8 – 2.8).

Appendix 1. Inspiration from the German "Recommendation list"

In 2020, an international review of the groundwater monitoring framework in Denmark was performed[22]. In the review, the Danish activities were compared to those of other EU member states. This review recommended the Danish EPA to look for inspiration in a similar prioritisation exercise carried out by the German EPA, resultning in the so called Recommendation List. The Recommendation List contains a range of degradation products from currently approved active substances in Germany, which are recommended for the water authorities in the 16 federal states (Bundesländer) and the drinking water companies to be additionally monitored in relation to the standard pesticide parameter lists. More importantly, the document also describes how and why the degradation products were selected from a much larger group of degradation products.

Degradation products from active substances in products currently not authorised for use in Germany are not included, because they are usually already included in the standard monitoring programme of the Bundesländer (if they are frequently found). The recommendation list was made on a request from the German federal states, which are responsible for the monitoring of pesticides, as they needed input on which additional degradation products to monitor in groundwater besides the ones already included in the standard monitoring program. The German list is only a recommendation, not a legally binding document, because the German EPA does not have the legal rights in a federal system to decide which pesticides the federal states are to monitor. Furthermore, active substances are not included in the Recommendation List, because they are already included in the Bundesländer monitoring program.

The current German prioritisation strategy and Recommendation List[23] replaced the former version of the Recommendation List from 2019 (in German). The difference between the two versions is mainly the specific degradation products on the final list, and some supplementary text. The German prioritisation strategy has not been changed from the first version to the next, but the input data used in the different evaluation steps have been updated.

The Danish EPA together with GEUS reviewed and discussed the prioritisation approach applied in the German Recommendation List. The applicability of the German approach was discussed, step by step, and the main conclusions are described below.

The German prioritisation strategy is illustrated in the decision tree presented in figure A1. The strategy applies a preselection prior to the use of three different types of information, which is transferred into three main prioritisation steps:

---

[22] https://mim.dk/media/219355/endelig-rapport-international-review-of-danish-groundwater-protection.pdf

[23] https://www.umweltbundesamt.de/sites/default/files/medien/3521/dokumente/2022_07_29_uba_recommendation_list_update2022_eng.pdf

- Data on sales rates for the active substances and treated area
- Groundwater concentration (from modelling and lysimeter studies) and toxicological relevance (from the EU assessment)
- Expert judgements

The degradation products are not individually ranged, as is the case in the Danish approach, but are by prioritisation divided into three groups depending on their importance in relation to groundwater monitoring. Furthermore, the selection strategy does not include all, but two or three degradation products with the highest expected concentration in groundwater for each active substance.

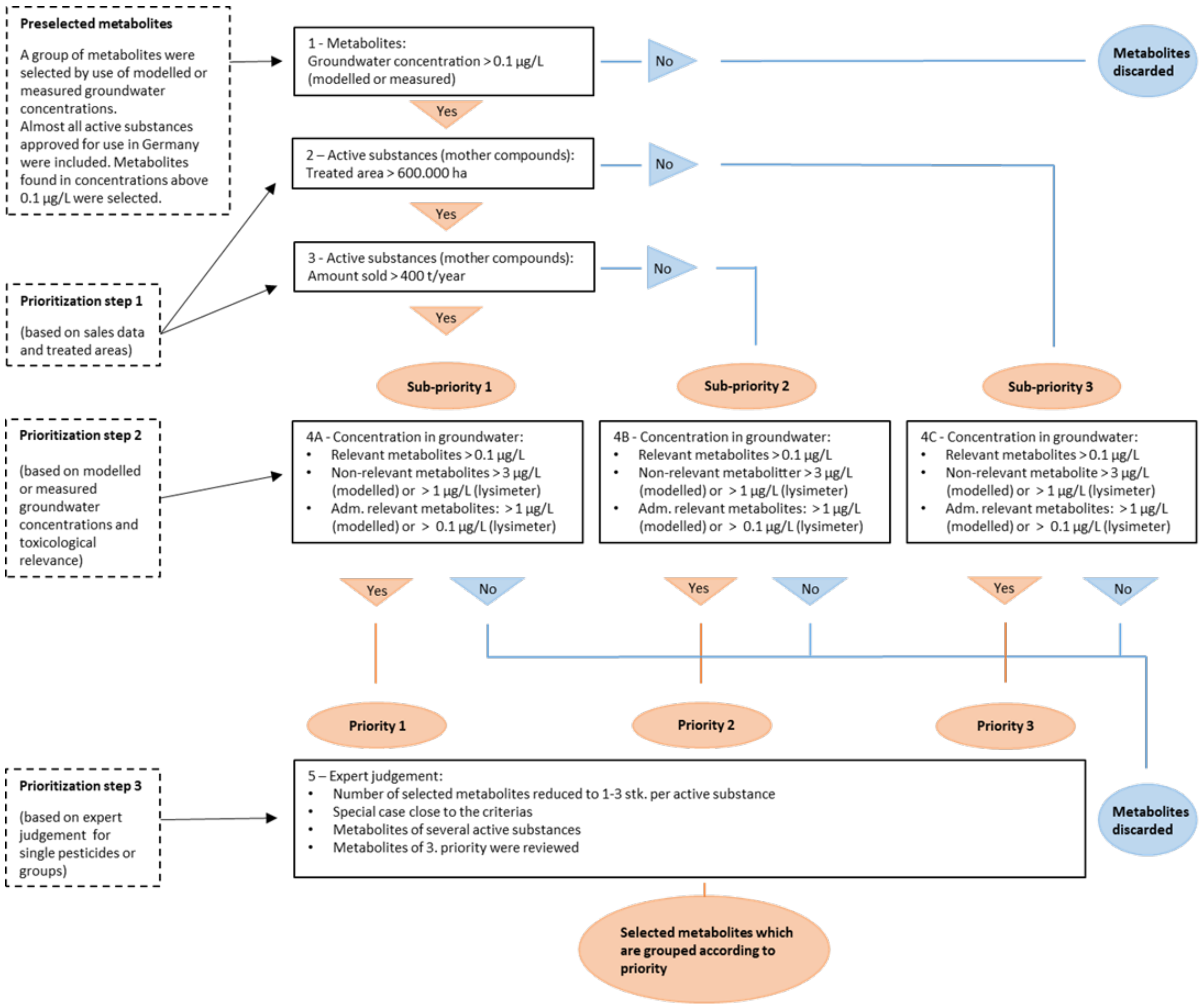

FIGURE A1. Prioritisation strategy used to select and group degradation products (metabolites) presented in the “Recommendation list”. The water authorities in the Federal states (Bundesländer) and the German drinking water companies are recommended to include these degradation products in their monitoring.

1.1 Discussion of the German approach

General considerations

The purpose of the German approach is not directly comparable to the purpose of the work in Denmark. The German approach identifies and selects a number of pesticides (degradation products) from a larger group of pesticides, and discards the pesticides not selected. The purpose of the Danish approach is to individually range a group of already selected pesticides. The framework of the two approaches are therefore different, which means that the implementation of the prioritisation steps are different.

The German approach includes information on the active substances to select relevant degradation products, but the active substances themselves are not included in the final Recommendation List. This is a result of the conditions set for the German approach, and not a result of scientific considerations. None the less, it highly influences the selection and use of different data sources. For example is the term “toxicological relevance” used in the German approach, a term only related to degradation products and not the active substances. This would pose a challenge to the Danish approach since the List of Pesticides contains both active substances and degradation products. Furthermore, in Denmark the limit value for the pollution of groundwater of 0.10 µg/L is set for both relevant and non-relevant degradation products and therefore no differentiation is made in the Danish approach based on this information.

Additionally, the German approach only includes degradation products (which are not already included in existing monitoring programs) from active substances currently authorised for use in Germany. This is directly in contradiction with the purpose of the Danish work, because it is also considered important to have focus on previously authorised pesticides. In addition, pesticides which have never been authorised for use in Denmark, but with at potential illegal use can also be included in the Danish approach after an expert evaluation. Here information about use and findings in groundwater in e.g. Germany and Sweden can be included.

The German EPA has gathered information on the degradation products from EFSA conclusions, which corresponds fully with the Danish approach. The information collected is a modelled or measured (lysimeter studies) groundwater concentration and toxicological relevance of the degradation products. However, the Danish approach also includes information on compound specific properties collected from EFSA conclusions.

Pre-selection
The German EPA produced a list of degradation products from active substances authorised for use in Germany. A preselection was carried out where all degradation products with a modelled or measured groundwater concentration below 0.1 µg/L were discarded. This ensured that results from the leaching estimate at EU level was involved in the selection procedure. The number of remaining degradation products (approximately 300) were still too large in relation to German groundwater monitoring, hence further refinement was requested (by the Bundesländer).

Since the Danish List of Pesticides also contains pesticides no longer approved for use in the EU, it contains a number of pesticides without an EFSA conclusion, which challenges an adoption of this preselection as a prioritisation step in the Danish approach. If there are no EFSA data, there are no available modelled or measured (lysimeter) groundwater concentrations. Additionally, there are examples on degradation products which, according to the EFSA conclusion, are not expected to leach in concentrations above the quality criteria of 0.10 µg/L, but are detected in groundwater significantly above 0.10 µg/L. Such an example is CGA62826 (N-(2, 6-dimethylphenyl)-N-(Methoxyacetyl)alanin), which is a degradation product from metalaxyl.

Sales data and treated area
Information on agricultural use and treated area were included in the German approach for the same reasons as those for incorporating the sales rates in the Danish approach. The German EPA has included sales rates, but also information on “treated area” for the active substances that leads to the degradation products on the list. Information on treated area comes from a

limited number of farms in Germany, which collaborates with authorities on this matter. The treated areas reported in the Recommendation List are extrapolated from these farms to a national scale, and is therefore considered to be uncertain. The purpose of this prioritisation step is not to discard any degradation products, but to separate them into three subgroups according to their agricultural importance.

Applying information on treated area enables a more detailed analysis on the use of the individual pesticides. But this approach is not transferable to the Danish List of Pesticides, because the list contains a number of relatively old pesticides, where such information is not available. Furthermore, it is the opinion of GEUS and the Danish EPA that compound-specific properties and specific use conditions (e.g. crops and date of application) are affecting the leaching potential to a higher extent than historical sales rates. For example two pesticides with very high sales rates in Denmark, isoproturon and glyphosate, are rarely found in groundwater.

Groundwater concentration and toxicological relevance
This prioritisation step in the German approach combines knowledge on toxicity with modelled or measured groundwater concentrations, and discards degradation products not complying with the criteria illustrated in figure A1. Degradation products that do comply with the criteria remain in the group assigned (subpriority 1, 2 and 3 in figure A1) depending on agricultural importance. Hence, a number of degradation products (non-relevant degradation products according to the EU assessment) with a modelled or measured groundwater concentration above 0.1 µg/L is discarded, and not included in the Recommendation List.

For example, during prioritisation step 1 active substance X is estimated to be applied in an area larger than 600.000 ha, but is sold in amounts less than 400 t/year. This results in a placing of the toxicologically non-relevant (nrM) degradation product Y (active substance X degrades to degradation product Y) to sub-priority 2. During prioritisation step 2, degradation product Y, is found to leach to groundwater at a concentration of 2.5 µg/L by modelling (PECgw), which is below the threshold of 3 µg/L (see figure 1). Hence, the none-relevant degradation product is discarded and will not be part of the German recommendation list.

The Danish risk assessment of plant protection products includes a special focus on the protection of groundwater resources. For example, all degradation products (with a few exceptions) no matter whether they are considered “toxicologically relevant” or not have to comply with the quality criteria of 0.10 µg/L. The Danish approach would therefore not accept degradation products with a modelled or measured groundwater concentration above 0.10 µg/L to be discarded.

Furthermore, the use of toxicological information is not relevant for the Danish approach, because the main purpose is to range all pesticides on the list only according to their risk of leaching to groundwater, without taking into account potential human hazards.

Use of expert judgements
There was a request to further reduce the number of pesticides on the German Recommendation List, which is why it was decided to reduce the number of degradation products per active substance. This evaluation was done manually by the use of expert judgements considering modelled and measured groundwater concentrations accompanied by other information e.g. national monitoring data and availability of analytical methods.

GEUS and the Danish EPA agrees with the use of expert judgements, mainly to prevent pesticides being falsely discarded (as a result of sales rates) or ranged low on the fully prioritised List of Pesticides. However, the Danish approach includes all degradation products per active substance if they are a part of the environmental risk assessment conducted at EU level, and thereby also mentioned in the EFSA conclusion.

1.2 Overall applicability of the German approach

In the above sections, it is discussed to what extent the different prioritisation steps in the German approach is useable in the Danish prioritisation strategy. Overall, there is a large overlap between the two approaches, where general themes are applied in both approaches, e.g. the use of sales rates and modelled groundwater concentrations followed by an expert judgement. However, there are a few differences primarily caused by differences in the focus of and conditions for the exercise. For example it is important to notice, that the German recommendation list is acting as a supplement to the already existing monitoring program.

The main difference between the two methods is the inclusion of previously approved pesticides in the Danish approach, as opposed to only including pesticides which are currently approved for use. Furthermore, the Danish approach makes directly use of compound specific properties, which enables a fully ranged List of Pesticides, as opposed to a separation into three groups depending on agricultural importance. Compound specific properties are indirectly included in the German approach through the modelled groundwater concentrations.

Hence, the main conclusion on the review of the German approach is that the two approaches already overlap as far as possible. The scientific discussions do not lead to further changes to the Danish approach, since differences are mainly due to the difference in purpose of the list

Prioritisation strategy for use on the Danish EPA´s "List of Pesticides" – Risk of leaching to groundwater

This strategy individually range a group of pesticides according to their risk of leaching to groundwater. The strategy is based on information on historical sales data, known risk of leaching to groundwater, modelled concentrations in groundwater and physical/chemical parameters relevant for evaluating the risk of leaching to groundwater.

The Danish Environmental
Protection Agency
Tolderlundsvej 5
DK - 5000 Odense C

www.mst.dk