# National Assessment of Long-Term Groundwater Response to Pesticide Regulation

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**ABSTRACT:** Quantitative assessments of long-term, national-scale responses of groundwater quality to pesticide applications are essential to evaluate the effectiveness of pesticide regulations. Retardation time in the unsaturated zone ($R_u$) was estimated for selected herbicides (atrazine, simazine, and bentazon) and degradation products (desethylatrazine (DEA), desisopropylatrazine (DIA), desethyldesisopropylatrazine (DEIA), and BAM) using a multidecadal time series of groundwater solute chemistry (~30 years) and herbicide sales (~60 years). The sampling year was converted to recharge year using groundwater age. Then, $R_u$ was estimated using a cross-correlation analysis of the sales and the frequencies of detection and exceedance of the drinking water standard (0.1 $\mu$g/L) of each selected compound. The results showed no retardation of the highly polar, thus mobile, parent compounds (i.e., bentazon), while $R_u$ of the moderately polar compounds (i.e., simazine) was about a decade, and their degradation products showed even longer $R_u$. The temporal trends of the degradation products did not mirror those of the sale data, which were attributed to the various sale periods of the parent compounds, sorption of the parent compounds, and complex degradation pathways. The longer $R_u$ in clayey/organic sediments than in sandy sediments further confirmed the role of soil-specific retardation as an important factor to consider in groundwater protection.



**KEYWORDS:** pesticides, groundwater, national assessment, lag time, retardation time, transport time
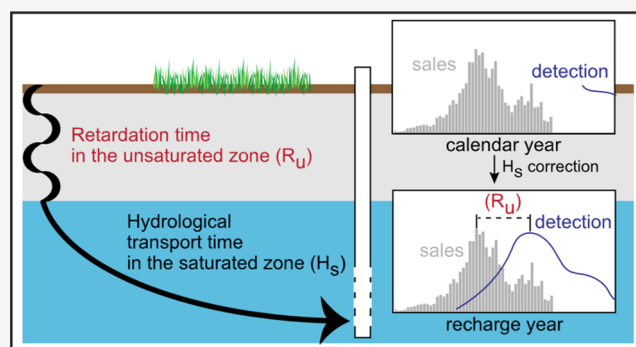
## 1. INTRODUCTION

Over the last two decades, regulations have been implemented in the European Union (EU) and at national levels in Europe to alleviate the contamination of groundwater resources caused by pesticide use.[1−3] However, a recent status assessment of EU water bodies showed that 6.5% of the area of groundwater bodies were failing the good chemical status as defined in the EU Water Framework Directive due to pesticides.[3] In Denmark, where groundwater is the sole source of drinking water, this was the case for 7.5% of the total 2050 groundwater bodies representing 17% of the total volume of the Danish groundwater bodies,[4] and pesticides and their degradation products are still found in drinking water.[5,6]

Long legacy effects of persistent pesticides and degradation products in groundwater after application bans are explained by a time delay caused by (1) hydrological transport from the topsoil to the underlying aquifers and (2) compound-specific retardation during the hydrological transport. After mobilization from the topsoil, the pesticides and their degradation products are transported to aquifers mainly as solutes via water. They may be adsorbed and/or degraded along the flow paths in the unsaturated and saturated zones but to a lesser extent than in the topsoil because of low organic carbon content, low density of active microbial communities, and often anoxic conditions.[7,8]

One of the puzzling findings of extensive research on pesticides is the discrepancy between experimental results of laboratories and short-term studies vs observations in natural conditions.[9] For instance, atrazine, which was one of the most widely used herbicides and was banned in 1994 in the EU, has a half-life shorter than a year.[9,10] However, more than 20 years after the ban, it is still found in soils,[11,12] groundwater,[13−15] and drinking water[6] around the world. This finding underscores the importance of long-term, large-scale studies to better understand the fate and distribution of pesticides and degradation products in groundwater. Such research will be critical to evaluating the effects of pesticide applications and regulations
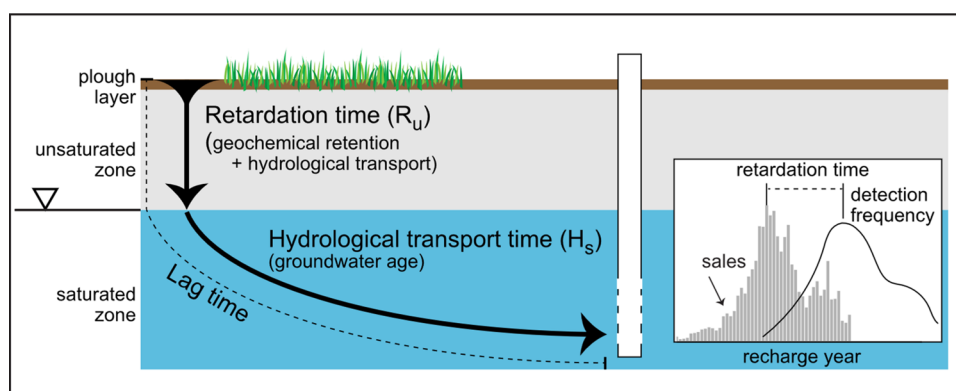
**Figure 1.** Conceptual model of the retardation time analysis of this study.

**Table 1. Pesticides and Degradation Products Included in This Study**[a,b,c,d]

| compound (abbreviation) | parent compounds | CAS no. | sale period | $K_{fOC}$ (mL g$^{-1}$) | DT50 (days) | no. of well screens in the final data set (number of sample years) |
|---|---|---|---|---|---|---|
| atrazine (A) | | 1912-24-9 | 1960−1994 | 70−429 (174) | 6−150 (75) | 298 (9) |
| simazine (B) | | 122-34-9 | 1957−2004 | 124−1585 (750) | 27−102 (60) | 298 (9) |
| cyanazine (C) | | 21725-46-2 | 1973−1996 | 30−427[e] (190) | 12−25 (16) | |
| terbuthylazine (T) | | 5915-41-3 | 1972−1996 | 151−333 (231) | 6−167 (72) | |
| desethylatrazine (DEA) | A | 6190-65-4 | | 79−110 (110) | 45−170 (45) | 298 (9) |
| desisopropylatrazine (DIA) | A, S, C, T | 1007-28-9 | | 130 | | 298 (9) |
| desethyldesisopropylatrazine (DEIA) | A, S, C, T | 3397-62-4 | | | | 298 (9) |
| 2,6-dichlorobenzamide | dichlobenil, chlorthiamid | 2008-58-4 | dichlobenil (1969−1996); chlorthiamide (1965−1980) | 31−51 (41) | 73−1848 (138) | 298 (9) |
| bentazon | | 25057-89-0 | 1974 | 3−158 (60) | 3−35 (20) | 298 (9) |

[a]Degradation products are shown in italic. [b]$K_{fOC}$ is the Freundlich sorption isotherm normalized to soil organic carbon. [c]$DT_{50}$ is the half-life in topsoil. [d]$K_{fOC}$ and $DT_{50}$ are all from the Pesticide Properties Database (https://sitem.herts.ac.uk/aeru/ppdb/). [e]$K_{oc}$ instead of $K_{foc}$.

and developing more sustainable water resource management strategies.

Studies have reported that pesticide applications and groundwater recharge rates are important controls of the temporal trends of pesticides and degradation products.[13−15] Therefore, long-term monitoring data of both the pesticide input to the agricultural fields and pesticide concentrations as well as hydrogeological information are needed to quantitatively assess the groundwater quality responses to the pesticide input.[16] However, such comprehensive data sets are rarely available, and most studies of pesticides in groundwater are limited in time (i.e., snapshot observations[17−19]) and space (i.e., single watershed or aquifer[20,21]). A recent study has reported long-term trends of selected pesticides in groundwater on the national scale.[13] A drawback of their approach is the use of sample year that represents groundwater of different ages rather than recharge year that would account for the temporal variability in the pesticide input.

In Denmark, pesticide concentration data from the national groundwater monitoring program (GRUMO) and national pesticide sale data provide a rare opportunity to evaluate the long-term groundwater responses to pesticide regulations. GRUMO has been monitoring groundwater quality for over 30 years and is currently active at more than 1400 well screens across the country to cover the spatial heterogeneity of

Denmark. GRUMO provides a time series of pesticides in groundwater and groundwater age data. The groundwater age allows analyzing a longer time period than that of the actual monitoring program by estimating the recharge years.[21−23] In Denmark, detailed information on hydrogeology and surface geology is also available. In addition, the pesticide sale statistics on the national scale are available to indirectly estimate the pesticide input to the agricultural fields. Based on these data sets, our study focused on (1) assessing the long-term trends of the occurrence of selected pesticides and degradation products in the shallow groundwater and (2) quantifying the lag time from pesticide regulation to changes in the observed pesticide occurrence in the shallow groundwater on the national scale.

## 2. METHODS AND MATERIALS

**2.1. Definitions of Lag Time, Hydrological Transport Time, and Retardation Time.** We estimated the lag times ($L$) between the pesticide regulations or bans and changes in the observed pesticide occurrence and (or) concentrations in groundwater. The basic assumption was that the pesticide regulations become effective immediately after the implementation, resulting in changes in pesticide application and thus no lag time between the regulations and the pesticide input to the agricultural fields. Then, the lag time equals the water transit time from agricultural fields to the underlying aquifers plus the

compound-specific delay time due to sorption and other retardation processes along the pathways. We also assumed that retardation predominantly occurs in the unsaturated zone, particularly in the topsoil, and becomes relatively negligible in the saturated zone.[24−27] Retardation, i.e., sorption, is mediated mainly by soil organic matter,[26−28] which shows the highest content in the plow layer (i.e., typically 0.3 m below the land surface (m bls)) and decreases with depth. Therefore, the lag time ($L$) was defined as the sum of the retardation time in the unsaturated zone ($R_u$) and the hydrological transport time in the saturated zone ($H_s$; Figure 1)

$$L = R_u + H_s \qquad (1)$$

Here, we assumed that $H_s$ is equal to the groundwater age determined by environmental tracers, such as tritium/helium ($^3$H/$^3$He) and CFC because these tracer gasses in the unsaturated zone are usually in atmospheric equilibrium; hence, the "clock starts ticking" only when the water passes the groundwater table. By assuming so, $R_u$ in eq 1 effectively represents the transport times in the unsaturated zone, including both hydrological transport and geochemical retardation times. Retardation of the pesticide compounds is controlled by the intricate interplay between hydrological transport, i.e., diffusion advection, and geochemical retardation, i.e., sorption−desorption; therefore, they cannot be separated. In this study, the recharge year, which was calculated by subtracting the groundwater age ($H_s$) from the sampling year, was used to directly compare the temporal trend of pesticide occurrences in groundwater with that of the annual pesticide sales, thereby allowing the estimation of $R_u$.

### 2.2. Selection of Pesticides and Degradation Products.

We selected pesticides and degradation products that (1) are banned or have restricted use in Denmark, (2) are included in the list of mandatory compounds to monitor in Danish drinking water wells, and (3) are frequently detected as parent compounds or degradation products in Danish groundwater. Based on these criteria, our study focused on two triazine herbicides (atrazine (A) and simazine (S)), three of their degradation products, (desethylatrazine (DEA), desisopropyla-trazine (DIA), and desethyldesisopropylatrazine (DEIA)), the benzothiazinone herbicide bentazon (B), and the degradation product 2,6-dichlorobenzamide (BAM; Table 1) that originates from the benzonitrile herbicides diclobenil and chlorthiamid. Cyanazine and terbuthylazine, which are the triazine herbicides used until 1996, were rarely detected in groundwater (Table 1); therefore, these compounds were excluded.

### 2.3. Data Sources.

*2.3.1. Groundwater Monitoring Data for Pesticides.* Pesticides and their degradation products are analytes included in GRUMO, and monitoring data are publicly available in the Danish National Well Database, Jupiter (www.geus.dk). GRUMO was established in 1989, and its structure and distribution of monitoring wells and analytical protocol of pesticides have evolved over time mainly to meet the requirements of the EU Water Framework and the Groundwater Directives[1,2] and to effectively monitor pesticides and their degradation products (details are given in the Supporting information).[29] Therefore, the list of mandatory compounds for monitoring, sampling frequency, and sampling locations has changed over different program periods. The selected compounds were mandatory for groundwater monitoring in the following periods: 1989−now (atrazine, simazine) and 1998−now (DEA, DEIA, DIA, bentazon, and BAM).[29]

In GRUMO, groundwater is generally sampled once a year following the technical guidelines of the Geological Survey of Denmark and Greenland (GEUS).[30] According to the guideline, the well screens are purged until continuous measurements of pH ($\pm$0.1 pH unit), oxygen ($\pm$0.3 mg/L), conductivity ($\pm$3%), temperature, and redox potential become stable, and then groundwater is sampled. Water samples for pesticides are not filtered and are stored in the dark and cold (1−5 °C) or in a freezer for up to 28 days (<−18 °C).

The pesticide analysis is performed by certified laboratories in Denmark, which must comply with the legal requirements and standards of both Denmark and EU[31,32] (details are given in the Supporting Information). The analytical method has been improved over the period of GRUMO, but state-of-the-art methods have always been used. Overall, pesticides are analyzed using liquid chromatography with tandem mass spectrometry (LC−MS/MS), and liquid chromatography−mass spectrome-try (LC−MS) and high-performance liquid chromatography−mass spectrometry (HPLC−MS) were also used in the past. The current minimum quality requirements for pesticides are that all analyses should be with a limit of detection (LOD) of 0.01 $\mu$g/L with an absolute uncertainty of 0.05 $\mu$g/L and a relative uncertainty of 30%.

*2.3.2. Groundwater Age.* Groundwater ages determined by dating techniques are also part of GRUMO, and the data are available in the Jupiter database. The CFC method[33] was used from 1997 to 2006 and the $^3$H/$^3$He method[34] from 2012−2021. All sampling was done by GEUS and the former Aarhus County in Denmark. CFC gases (CFC-12, CFC-11, CFC-113) were sampled in glass ampules and analyzed at GEUS.[35] Tritium and noble gases were sampled in polyethylene bottles and copper tubes, respectively, and analyzed at the Mass Spectrometry Facility at the University of Bremen, Germany.[36] Age estimations by the $^3$H/$^3$He method were corrected for excess air based on the concentration of neon. Samples containing both tritium and radiogenic $^4$He were excluded due to the high risk of mixing waters of different ages. For the ones estimated by the CFC method, anoxic groundwater samples (dissolved oxygen (DO) <1mg/L) were excluded because of the risk of CFC degradation under anoxic conditions.[37−39]

*2.3.3. Geological Information.* Surface geology, which represents the sediment type at 1 m bls, was retrieved from a digital map on a scale of 1:25,000.[40] The Danish georegion polygons, which delineate Denmark into 10 subregions and are based on geological formation conditions including the different stages of glacial advances, were retrieved as a shapefile.[41−43]

*2.3.4. Pesticide Sale Data.* National pesticide sale data were retrieved from sale statistics published by the Danish Environ-mental Protection Agency.[44]

### 2.4. Data Processing.

Figure 2 describes all of the steps of the data processing. The raw data of the selected compounds were extracted on the May 31, 2021 from Jupiter along with corresponding groundwater ages; inorganic chemistry such as the concentrations of nitrate, sulfate, and DO; and meta data of the well screen (Figure 2). This raw data set was first processed to remove replicates and obviously erroneous data points. Most pesticide analyses had an LOD of 0.01 $\mu$g/L, and analyses with LOD >0.02 $\mu$g/L were excluded to ensure data quality. Analytical results below the LOD were substituted with 0. The cleaned pesticide data set was then linked with the information on the surface geology and the georegions of the sampling locations using QGIS v 3.10 (Figure 2).
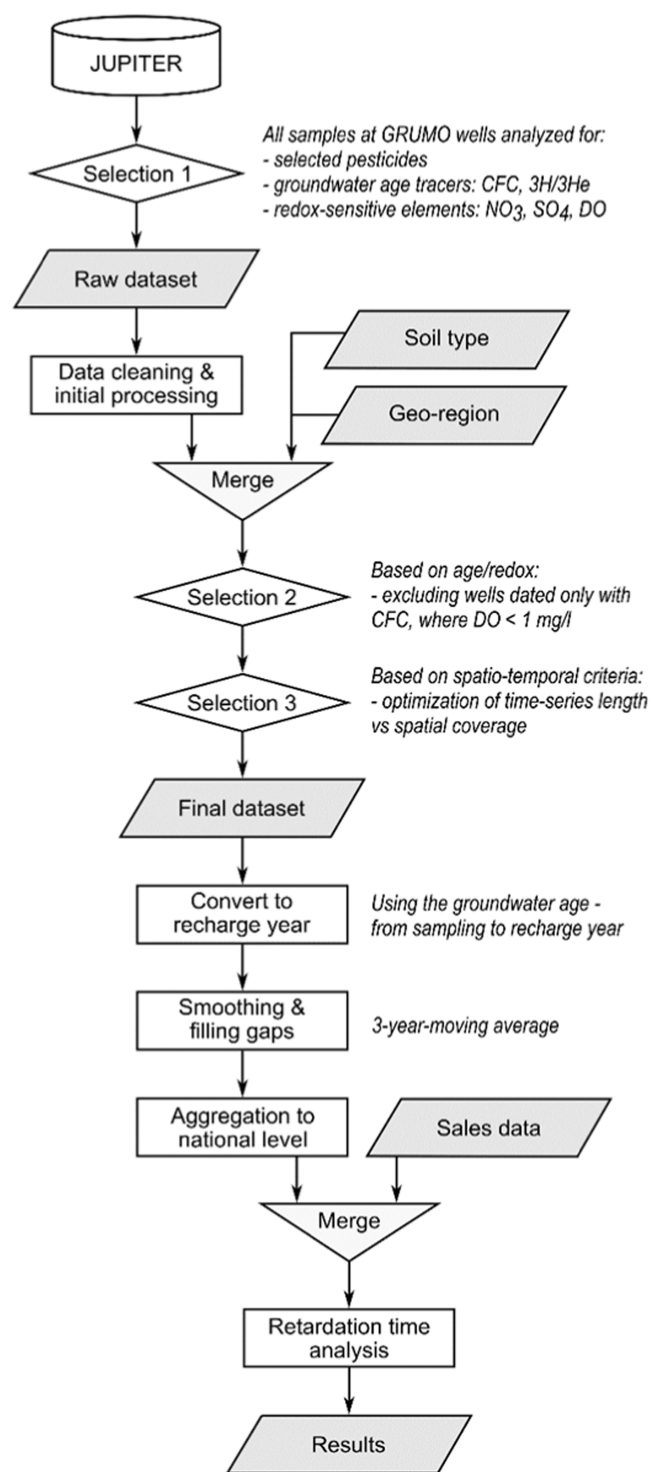
**Figure 2.** Flow chart of the data processing protocol.

m length for most of the well screens (Figure S2). Each pesticide at the individual well screen was averaged over a 3 year window (±1 year of the sampling year). Among them, 229 (mean depth = 16.9 m bls) and 69 (mean depth = 24.2 m bls) well screens were dated using the CFC and $^3$H/$^3$He methods, respectively. The CFC-dated wells were all with oxic conditions, while among those of $^3$H/$^3$He-dated wells, 39 were oxic, 9 were anoxic, 16 were reduced, and 5 were with unidentified redox conditions. A summary of the final data set used in the further analysis is available in Table 1 and Figure 3. The sampling years of the final
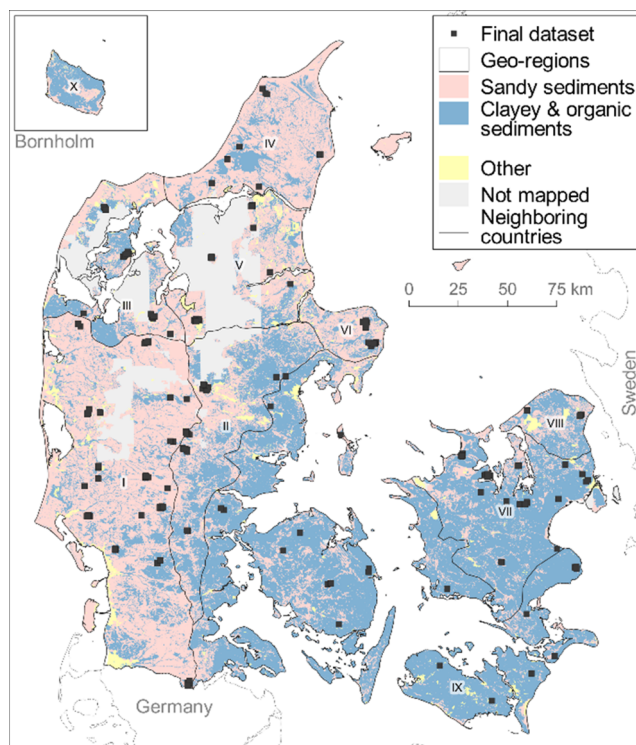


**Figure 3.** Location of the sampling points (well screens) of the final data sets as distributed among the 10 Danish georegions, which is indicated with roman numerals. The surface geology/sediment type at a 1 m depth is shown in the background.

data set were converted to recharge years using the groundwater age data (Figure S3), and then the annual frequencies of pesticide detection and exceedance of 0.1 $\mu$g/L at the national level were calculated.

**2.5. Cross-Correlation Analysis for Retardation Time.** To calculate the retardation time in the unsaturated zone ($R_u$), a cross-correlation analysis was carried out between the pesticide sales (calendar year) and the frequencies of detection and exceedance of 0.1 $\mu$g/L (recharge year) at the national level using Matlab. For the degradation products, the sum of sold amounts of all of the parent compounds was used. The cross-correlation analysis was done only for the period where (1) the pair of pesticide monitoring data and sale data was 10 years or longer and (2) at least eight georegions except for the island of Bornholm were covered (Figure 3). Bornholm was excluded because it is hydrogeologically different and much smaller than the rest of the country. $R_u$ was estimated by averaging lag years of the three highest, statistically significant positive correlations (i.e., Person correlation coefficient) between −5 and 40 lag years. The negative lag years were included to account for the uncertainties of groundwater age measurements.

Due to the revisions of GRUMO, the monitoring locations and sampling frequencies changed over time; therefore, the number of well screens commonly monitored over time decreases with increasing the number of monitoring years (Figure S1). To minimize artifacts due to these changes and also to ensure spatial and temporal representativeness, only 298 well screens monitored for 9 years (2010−2013 and 2016−2020; Figure S1) were selected. These well screens belong to 261 individual wells (89% with a single screen, 11% with two to four screens), providing separate discrete sampling intervals with ≤1
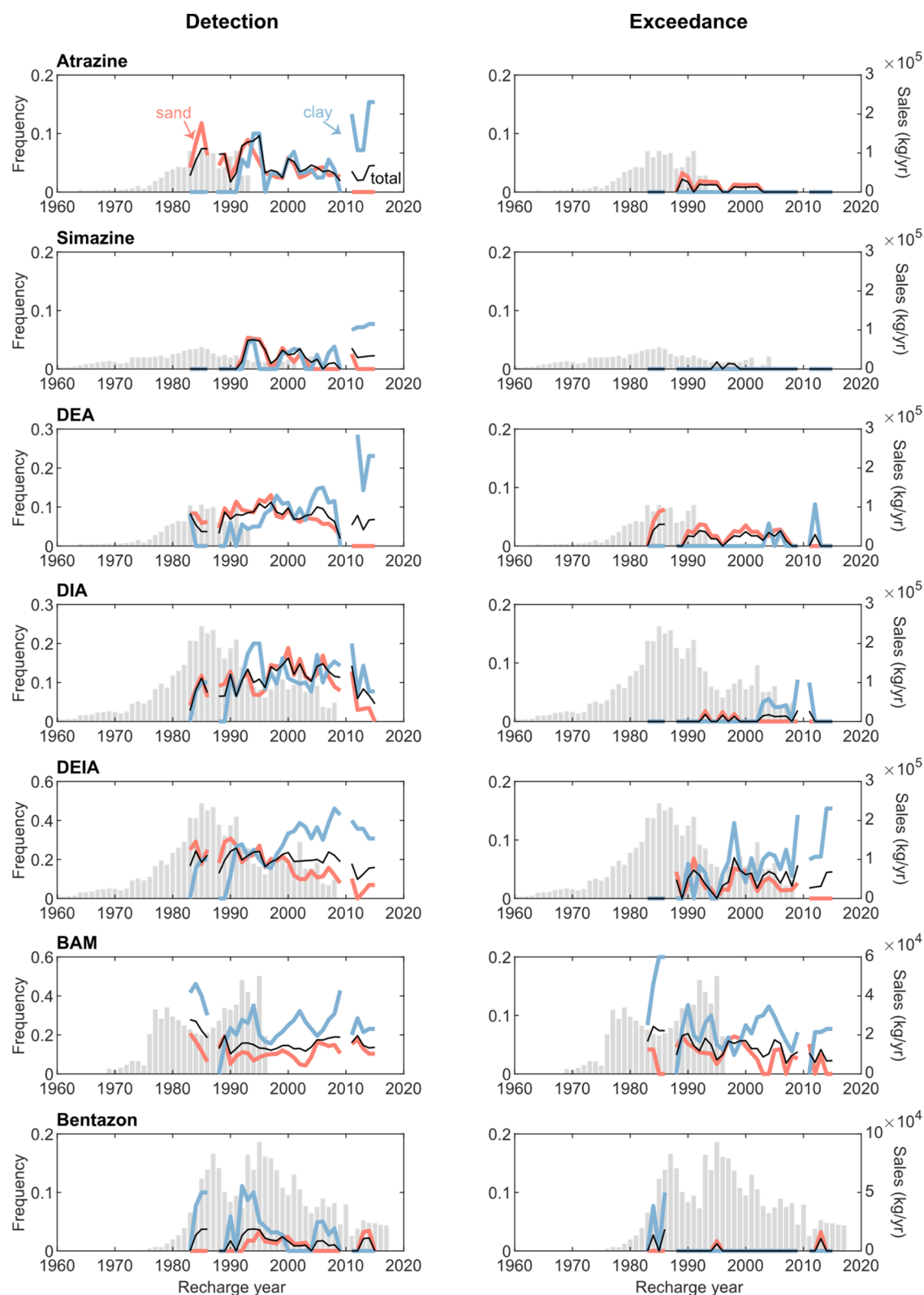
**Figure 4.** Time series of frequencies of detection and exceedance of 0.1 $\mu$g/L of atrazine, simazine, DEA, DIA, DEIA, BAM, and bentazon across all wells (black) and divided into sandy sediments (red) and clayey + organic sediments (blue). Sale data (kg/year) of parent compounds are shown in gray bars.

## 3. RESULTS AND DISCUSSION

In this study, we investigated the retardation times in the unsaturated zone of pesticides and their degradation products by analyzing the correlation between the annual pesticide sales in Denmark and the pesticides detected in the groundwater. The underlying assumption is that changes in the sales of specific compounds reflect the compounds being applied, resulting in changes in the pesticide occurrence in groundwater. When the

**Table 2. Means and Standard Deviations of the Retardation Time Estimated Using the Pesticide Detection and Exceedance Frequencies[a]**

| | detection (year) | | | exceedance (year) | | |
|---|---|---|---|---|---|---|
| | total | sand | clay | total | sand | clay |
| A | 3 ± 1 (0.58) | 2 ± 1 (0.67) | 34 ± 3 (0.74) | 9 ± 1 (0.63) | 9 ± 1 (0.62) | |
| S | 13 ± 2 (0.41) | 11 ± 1 (0.61) | 35 ± 3 (0.74) | 12 ± 1 (0.52) | | |
| DEA | 14 ± 1 (0.62) | 10 ± 1 (0.71) | 33 ± 5 (0.77) | | 1 ± 1 (0.44) | 24 ± 3 (0.44) |
| DIA | 15 ± 1 (0.66) | 12 ± 1 (0.55) | 9 ± 1 (0.40) | 19 ± 1 (0.53) | 9 ± 1 (0.44) | 21 ± 3 (0.61) |
| DEIA | 7 ± 1 (0.47) | 1 ± 2 (0.76) | 22 ± 1 (0.78) | 14 ± 1 (0.53) | 11 ± 3 (0.47) | 33 ± 3 (0.73) |
| BAM | | | | 3 ± 4 (0.51) | 5 ± 1 (0.46) | |
| B | −1 ± 1 (0.65) | | −2 ± 1 (0.68) | | | |

[a]The means of the correlation coefficients between the pesticide sales and frequencies are shown in the parenthesis.

sales of the pesticide change, the groundwater response will be delayed because of (1) hydrological transport in the saturated zone ($H_s$), which was assumed to be equal to groundwater age; and (2) retardation in the unsaturated zone ($R_u$), which is the effect we attempted to estimate.

Our results should be interpreted with caution. First, $R_u$ can be sensitive to the selection criteria of the number of well screens and the length of the monitoring period (Table S1). This is particularly true for the compounds with low frequencies, such as atrazine and simazine. However, the overall temporal trends of the different data sets were similar (Figure 4 vs S4). Thus, this study focused on the relative differences of $R_u$ among the selected compounds rather than the absolute values. In addition, the standard deviations of the retardation times should be interpreted as the indication of the similarity between the pesticide sales and groundwater pesticide time series, which is the assumption of the cross-correlation analysis, rather than the accuracy of retardation time. Second, the assumption of no retardation in the saturated zone may also introduce uncertainty. The organic matter in the saturated zone may indeed be negligible, but some pesticides like the triazines may adsorb to inorganic constituents like some clay minerals, resulting in delayed responses due to retardation in the saturated zone.[26,45] In such cases, $R_u$ may be slightly overestimated. Third, we presumed that changes in the sale of a specific pesticide correspond directly to the changes in the application. In some cases, however, it may only be a coarse estimate if agricultural practices have changed over time. Fourth, the groundwater age measurements also have limitations.[46−48] Groundwater is a mixture of water of different ages from different sources;[47,48] thus, the measurements should be considered as a probabilistic distribution rather than a single deterministic year.[46] GRUMO uses only one age tracer for each well screen, so it is not possible to model the age distribution. Because most wells are used only for monitoring (i.e., sampled by laminar flow only) and have a short screen length (i.e., 68% well screens with a <1 m screen interval; Figure S2), it was concluded that the effect of mixing may be insignificant. Another factor of the uncertainty of the groundwater age measurement is that the CFC gasses may not be in perfect atmospheric equilibrium throughout the unsaturated zone, which means that retardation times of the CFC-dated cases can be slightly underestimated. This effect is negligible for tritium/helium.

Despite these uncertainties, our results still provide new insights into the groundwater responses to pesticide regulations compared to the sampling year-based approach. In the case of the sampling year time series, it is not possible to separate the actual signals caused by the pesticide regulations from the ones caused by lumping up different ages of groundwaters. Our study

significantly minimized the effects of the latter by correcting for the groundwater ages. Conversion from sample year to recharge year can also greatly expand the temporal period of a limited monitoring program (Figure S3).

Long-term monitoring programs often undergo multiple revisions over time to align with the changes in legislation and political priorities. As a result, the groundwater chemistry data may show a false temporal trend if the effects of revisions are not accounted for. These artifacts were minimized by selecting only the well screens that were consistently monitored over the period and using 3 years averages. Altogether, we concluded that the comparison between the pesticide sales and groundwater chemistry time series of our study reveals the groundwater responses to the pesticide regulations.

**3.1. Long-Term Trends of Pesticide Concentrations in Danish Groundwater.** Atrazine (cumulative total sales: 1313 tons from 1960 to 1994) was one of the most frequently detected parent compounds of the triazine group (Figure 4) and was found every year in 2−10% of the well screens of the final data set (Figure 4) from the recharge year 1983 and onward. The atrazine sales peaked twice (years 1985 and 1991) before it was banned (year 1994), and its detection frequency in groundwater also showed two peaks (recharge years 1986 and 1995; Figure 4). This temporal similarity resulted in 3 ± 1 years of retardation time (Table 2). The atrazine concentrations, however, rarely exceeded the EU drinking water quality criterion of 0.1 μg/L. The short retardation time implies that atrazine leaching from the unsaturated zone responded rapidly to regulations.

Simazine (cumulative total sale: 1167 tons from 1957 to 2004), which is another parent compound from the triazine group, was detected at a much lower frequency (0−5%) compared to atrazine, and no concentrations of simazine exceeded 0.1 μg/L except for 3 recharge years in the late 90s (Figure 4). The low simazine frequencies may be due to its higher $K_{foc}$ of 750 mL/g compared to 174 mL/g for atrazine (Table 1). Simazine may, therefore, adsorb more strongly to soil organic matter in the topsoil. Simazine's retardation time in the unsaturated zone was 13 ± 2 years (Table 2).

DEA is a degradation product of atrazine. Although its detection frequency displayed much muted and more delayed responses compared to atrazine, it showed two peaks (recharge years 1997 and 2016; Figure 4), resulting in 14 ± 1 year of retardation time (Table 2). The exceedance frequency was always low without a clear temporal trend (∼2%); thus, retardation time was not estimated. DIA is also an atrazine degradation product but is also derived from the triazine herbicides simazine, cyanazine (cumulative total sale: 850 tons from 1976 to 1996), and terbuthylazine (cumulative total sale: 1109 tons from 1972 to 1996). DIA showed a smooth temporal

trend at a higher detection frequency compared to DEA, which may be attributed to its multiple sources. The retardation time of DIA was 15 ± 1 years (Table 2). DEIA is also derived from the four triazine herbicides and is the most frequently detected compound (up to 26%) among the triazine compounds. In addition, DEIA's annual exceedance frequency was also the highest among the triazine group (up to 7%; Figure 4). DEIA's retardation time with the detection frequency was 7 ± 1 years (Table 2).

The triazine degradation products showed longer retardation times than the parent compounds, which was unexpected since triazine degradation products usually are more hydrophilic than their parent compounds (Table 1). In addition, the detection frequency of the degradation products, particularly ones that are from multiple parent compounds (i.e., DIA and DEIA), does not closely follow the sale data of the parent compounds (i.e., the second sales peak in the 2000s). The longer retardation time of the degradation products may be attributed to (1) the different sale periods and trends of multiple parent compounds, (2) high persistency and sorption of the parent compounds that may slowly produce degradation products from the topsoil over many years, and (3) conversion from one degradation product to another during transport under various redox conditions in both the unsaturated and saturated zone. The results further imply that for the triazine degradation products, pesticide sales may not be the primary control of their occurrence in the shallow groundwater.

BAM is a polar, mobile degradation product of dichlobenil (sold from 1969 to 1996) and chlorthiamid (sold from 1965 to 1980) and was detected throughout the monitoring period at a high frequency (∼20%) even two decades after the ban of the parent compounds (Figure 4). The exceedance frequency was around 10% (Figure 4). Indeed, BAM has been the most problematic pesticide contaminant in the Danish drinking water supply for many years because of BAM's high detection frequency across the country.[49] The detection frequency of BAM decreased during the recharge year of the 1980s and then became relatively invariant (Figure 4), while its exceedance frequency showed a weak decreasing trend over the period (Figure 4). The temporal trends of BAM, however, did not show a statistically significant correlation with the sold amount of the parent compounds; therefore, $R_u$ was not estimated for BAM (Table 2). This lack of correlation may be because the parent compounds (dichlobenil and chlorthiamid) sorb to the topsoil and slowly degrade to BAM over many years.[25,49] In addition, BAM shows very little degradation.[25,49] Like the triazine degradation products, this result further suggests that for degradation products that continuously "bleed" from a pool of sorbed parent compound in the topsoil, the retardation time cannot be calculated by comparing it with the parent sale data.

Bentazon is a polar and mobile herbicide that is still in use in Denmark, though with a restriction in dose and time of application from 1997 and onward. Bentazon was found in 0−4% of the well screens throughout the period (Figure 4). The detection frequency mirrored the sale data closely without any delay (Figure 4). Bentazon shows low sorption ($K_{foc}$: 3−158 mL g$^{-1}$; Table 1), and laboratory experiments have reported extremely slow degradation and confirmed negligible sorption of bentazon in the subsoil and the saturated zone.[27,28] Bentazon's retardation time was −1 ± 1 year, which may be attributed to the uncertainty of the groundwater age measurements (Table 2). This result indicates that polar, mobile, parent pesticides may show immediate response at the groundwater

table when applied amounts change at the land surface in response to factors such as changes in legislation.

**3.2. Retardation Time by Surface Sediment Types.** The retardation times were further analyzed for two different types of surface geology: sandy vs clayey plus organic sediments. For the triazine group compounds except for DIA, the retardation times were much longer in the clayey/organic sediments compared to those in the sandy sediments (Figure 4 and Table 2). For instance, the retardation times of atrazine and DEA in the sandy sediments were 2 ± 1 and 10 ± 1 years, respectively, while those in the clayey/organic sediments were 34 ± 3 and 33 ± 5 years, respectively (Figure 4 and Table 2). The high standard deviations of the retardation times of A, S, and DEA could also be interpreted as the important role of other factors such as climate in the leaching of these compounds rather than the input history of pesticides. The temporal trends of DEIA showed a clear contrast between the sandy and clayey/organic sediments (Figure 4). The highest detection frequency of DEIA in sandy sediments occurred close to the sales peak of its parent compounds (atrazine, simazine, cyanazine, and terbutylazine), resulting in a short retardation time of 1 ± 2 year, while the frequency peaked in 2008 for clayey/organic sediments, which was 22 ± 1 years after the sale peak.

By separating the sediment types, the effects of retardation, particularly by sorption, become more evident. Sorption of atrazine has been the target of numerous studies, as reviewed by Mudhoo and Garg (2011).[26] At near-neutral pH, atrazine is an uncharged and relatively hydrophobic pesticide, and soil organic matter is a strong sorbent for atrazine in topsoil. Below the organic-rich topsoil, where the soil organic content is much lower, atrazine also sorbs some types of minerals.[26,28] Clay minerals are a significant adsorbent for atrazine, but sorption to clay minerals varies depending on clay types, pH, cation exchange capacity, and types of cations attached to the clay.[26,50,51] Hence, not all clayey sediments will show the same retardation of atrazine, but the overall difference in sorption between the two sediment types as observed in our study was most likely caused by different sorptions.

In the case of BAM, there was no temporal trend in either type of sediments. However, the detection and exceedance frequencies in clayey/organic sediments were nearly double those in sandy sediments throughout the period (Figure 4). The higher frequencies could be due to preferential leaching through clay till macropores as a major pathway for pesticide contamination,[52] but may also be attributed to a larger pool of the parent compounds in the clayey/organic sediments than in the sandy sediments. For instance, the solid matrix−water distribution coefficient ($K_d$) of the parent pesticide dichlobenil is 1−2 orders of magnitude higher for clayey till than that for sand.[25] The aquifers under clayey/organic sediments, therefore, may be more vulnerable to BAM contamination for a longer period than those under sandy sediments.

Bentazon, which is the parent compound least affected by sorption and transformation, also showed different patterns between clayey/organic and sandy sediments: the detection frequency in clayey sediments mimicked the sale data closely with a retardation time of − 2 ± 1 years, which implies immediate response at the groundwater table in clayey sediments but less so in sandy sediments. The fast response may be caused by rapid transport via preferential pathways such as macropores and fractures in clay tills for compounds that do not sorb, such as bentazon.

**3.3. Lag Times of Pesticide Regulations.** The total time lags between pesticide regulations and groundwater responses at any given screen can be estimated by adding the retardation time in the unsaturated zone and the hydrological transport time in the saturated zone (i.e., groundwater age). For instance, at the national level, the detection frequency of atrazine in groundwater may peak nearly two decades after the peak of atrazine sales (1985) in areas under sandy sediments (2 years of $R_u$ (Table 1) +16 years, mean of the groundwater age ($H_s$); Figure 5), while it might take much longer under clayey/organic sediments, i.e., (52 years; 34 years of $R_u$ (Table 1) +18 years of
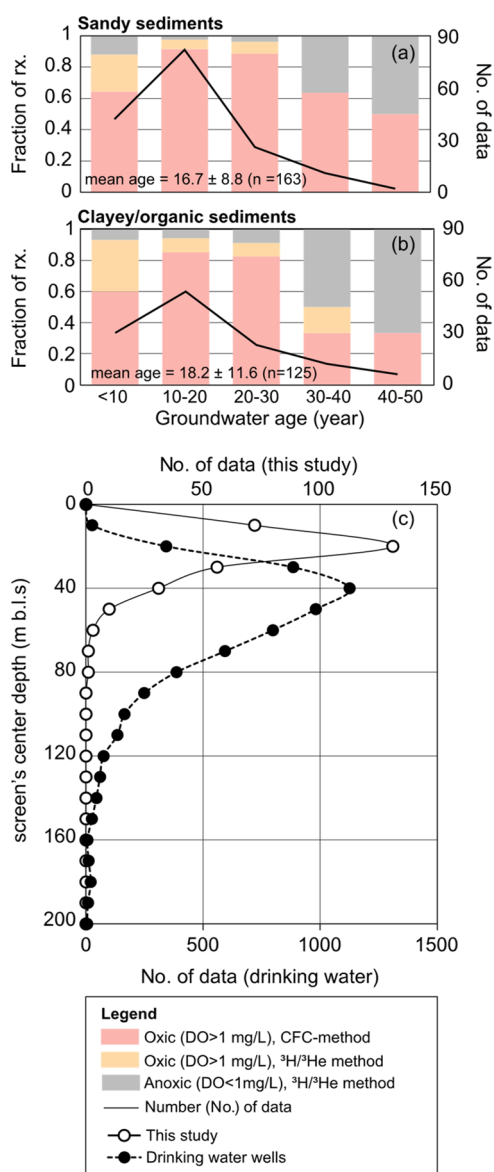


**Figure 5.** Histogram of groundwater age under sandy sediments (a) and clayey/organic sediments (b) by redox conditions of groundwater (left y-axis). The mean ages and standard deviations are shown in each panel. The number of groundwater age measurements is shown in parenthesis as well as a solid black line in each panel (right y-axis). The results of the 10 well screens underlain by other types of sediments are not shown here. DO: dissolved oxygen. The depth distributions of this study's well screens and the drinking water abstraction wells in Denmark are shown in (c) as depth to the center of the screen as meter below the land surface (m bls).

$H_s$ (Figure 5)). Indeed, over the last 12 years (2009–2020), the detection frequency of atrazine in groundwater under the sandy sediments decreased and remained low during the recent 5 years, while that in the clayey/organic sediments was still fluctuating (Figure S5). DIA, which showed about 10 years of retardation times in both types of sediments, also showing strong decreasing trends.

Regarding pesticide contamination of drinking water, it is likely that the response to regulations will be further delayed because Danish drinking water is abstracted from deeper wells (mean depth = 52.5 ± 29 m bls) than those of our study (mean depth = 18.5 ± 12 m bls) (Figure 5c). This bias is partly due to monitoring well screens being placed at a shallower depth than those used for drinking water abstraction. In addition, the exclusion of well screens with anoxic groundwater that was dated with CFCs from the study resulted in an underrepresentation of older, anoxic groundwater, likely causing a low bias in total lag times.

Altogether, our study clearly demonstrates that it may take several decades to see the effect of pesticide regulations on groundwater quality. The retardation times are much longer for nonpolar parent compounds (i.e., triazine herbicides) compared to polar compounds (i.e., bentazon) due to sorption. For triazines, the degradation products generally showed longer lag times compared to their parent compounds, and the temporal trends of degradation products from sorbing parent compounds were decoupled from the pesticide input (i.e., sales). The long lag times underscore the importance of long-term, consistent monitoring programs for pesticides in groundwater and drinking water.

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c02261.

Results of the retardation time analysis of two different data selection criteria (Table S1); number of well screens vs. number of years of the data sets (Figure S1); cumulative fraction of the well screen length of the final data set (Figure S2); time series of pesticide concentration in groundwater based on the sampling year and recharge year (Figure S3); time series of detection and exceedance frequencies of pesticides in groundwater using the 201 well screens, 15-year-long data set (Figure S4); time series of the detection and exceedance frequencies of pesticides in groundwater based on the sampling year (Figure S5), and description of the national monitoring program for groundwater quality in Denmark (GRUMO) including the history of the monitoring program, sampling protocol, and analytical methods (Pages S9–S12) (PDF)

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## Notes

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