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Mobility and persistence of pesticides and emerging contaminants in age-dated and redox-classified groundwater under a range of land use types

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- groundwater age and redox status vary substantially with monitoring depth.
- converting sampling date to recharge date supports the assessment of trends.
- recharge year relates contaminant concentrations to emission histories.
- Redox-age diagrams help interpret contaminant mobility and persistence.
- certain pesticides, metabolites and ECs are frequently found in Fe-reduced waters.



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Understanding groundwater contamination patterns is hampered by the heterogeneous groundwater age and redox status over the depth range typically sampled for identifying pesticides and emerging contaminants threats. This study explores depth patterns of groundwater age and redox status across various land use types, unraveling spatial and temporal trends of pesticides and emerging contaminants using data from groundwater quality monitoring in the south of the Netherlands. The Netherlands is an ideal testing ground due to its high population density and widespread groundwater contaminant concentrations were analyzed based on recharge year, land use type, and redox status. Redox-recharge year diagrams were developed to visually evaluate contaminant patterns in relation to these factors and to assess concentration patterns in relation to contaminants in agricultural areas. However, certain contaminants, including BAM, desphenyl-chloridazon, short-chain PFCAs, PFOA, and EDTA, were consistently found in older water and Fe- or SO₄-reduced conditions, indicating their mobility and persistence in the regional groundwater system. Comparing the presence of contaminants in specific redox classes and recharge periods with known

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application or leaching history provides insights into retardation (e.g., PFOS) and degradation (e.g., 2-hydroxyatrazine, benzotriazole), explaining lower detection frequencies in earlier recharge periods. Identifying recharge years from age-dated groundwater helps relate contaminants to farmland application or river water recharge periods, revealing leaching history and contamination origins. The presented framework has the potential to enhance the interpretation of large groundwater datasets from dedicated, short-screened observation wells, such as those from the Danish GRUMO network, the Dutch monitoring networks, and parts of the US National Water Quality Program.

1. Introduction

Groundwater is a vital resource in the Netherlands, supplying twothirds of the country's drinking water. However, it is under pressure from pollution due to high population density and intensive agriculture, leading to widespread contamination with nutrients, pesticides, and emerging contaminants (Van Grinsven et al., 2016; Kivits et al., 2018; Sjerps et al., 2019; Post et al., 2020). The effects of intensive livestock farming on groundwater have been studied since the 1980s using monitoring systems and modeling approaches (e.g., Fraters et al., 1998; Tiktak et al., 2002; Schipper et al., 2008; Broers et al., 2024a). A national groundwater quality monitoring network was established in 1984 and provincial authorities complemented this with denser networks monitored annually (Van Duijvenbooden et al., 1985; Broers, 2002). Initially, these campaigns focused on the effects of excessive manure and fertilizer applications, assessing reduction goals set by the Dutch Fertilizer Act (Koninkrijk der Nederlanden, 1986) and the EU Nitrates Directive (EU, 1991). As one of the largest producers of agricultural and veterinary products, the production of manure by poultry, cattle, and pigs has put significant agricultural pressure on groundwater since the 1970s. Manure production peaked in 1985, and the nitrogen excretion from farming peaked accordingly (Fig. 1).

Monitoring of pesticides and emerging contaminants (ECs) in national and provincial networks began much later and was never



Fig. 1. History of manure production and resulting nitrogen excess in Dutch agriculture between 1970 and 2021 and sales of herbicides, fungicides, insecticides, and other pesticides in the Netherlands between 1985 and 2018. Source: Manure production: CBS Statline (2023). Nitrogen excess in Dutch agriculture, Environmental Data Compendium (2023a), Pesticide sales: Environmental Data Compendium (2023b).

systematically conducted on a national scale, although modeling studies assessed groundwater pollution risks (Tiktak et al., 2002; Boesten et al., 2015; Kraalingen et al., 2022). According to the Netherlands Statistical Bureau (CBS), pesticide sales provide the most complete overview of trends in pesticide applications, with over 95 % of sales related to farmland applications (Fig. 1). A drop in pesticide sales occurred in 1993 when soil disinfectants like 1,3-dichloropropene were regulated due to excessive leaching of 1,2-DCP, affecting drinking water production (Fig. 1; Beugelink, 1989). The Water Framework Directive (WFD, EU, 2000) and Groundwater Directive (GWD, EU, 2006) led to renewed concerns and boosted monitoring of pesticides and emerging contaminants since around 2010 (e.g., Baran et al., 2022). Unlike pesticides, emissions of emerging contaminants such as PFAS have not been systematically registered, and production figures for these substances are often lacking (Stuart et al., 2012; Bunting et al., 2021).

Strict regulations on manure and fertilizers since 1985 have decreased nitrogen levels through measures like manure exports and processing (CBS, 2010; CBS Statline, 2023). Consequently, nitrate concentrations in the uppermost groundwater in the southern sand region of the Netherlands dropped from over 200 mg/l around 1990 to about 70 mg/l since 2010 (Van Grinsven et al., 2016). However, trends in groundwater contamination below 10 m depth were challenging to detect due to groundwater age and redox conditions heterogeneity (Broers and Van der Grift, 2004). Trend assessment in agriculturally polluted water improved in the early 2000s when Böhlke (2002) introduced the concept of "recharge year," which transforms the sampling date into a recharge date through age dating. This approach allows trends to be assessed over a longer period than the actual monitoring program and mitigates the masking effects of groundwater age heterogeneity, preventing trends from different recharge periods from being mixed. Tritium-helium age dating has enabled this concept by providing precise dating of young groundwater (Schlosser et al., 1988; Solomon and Cook, 2000; Kipfer et al., 2002). Using this technique, Wassenaar et al. (2006) assessed nitrate trends in Canada, and Visser et al. (2007a) demonstrated trend reversal of agricultural pollutants, including nitrate and sulfate, in the intensive livestock region in the south of the Netherlands, the focus of this study. Laier (2004) and Hansen et al. (2010) used chlorofluorocarbons (CFCs) as age tracers instead of tritium-helium, showing nitrate trend reversal in oxic Danish groundwater through the same recharge year approach. Further developments included incorporating hydrochemical processes into trend assessments based on the recharge year, including denitrification (Visser et al., 2009a; Tesoriero et al., 2007) and corrections for degassing introduced by subsurface denitrification (Visser et al., 2007b, 2009b). Tritiumhelium age dating has proven particularly useful for monitoring networks with short-screened (multi-level) observation wells, which exhibit narrow age distributions because they are sampled by laminar flow and are not pumped for water supply (Desens et al., 2023). These wells are typically used for monitoring in fluvial or marine unconsolidated deposits in deltaic or coastal aquifer settings, which are areas with intensive farming and associated agricultural pollution (e.g., Visser et al., 2007a; Hansen et al., 2010; Kim et al., 2022). Tritium-helium age dating has also been applied to domestic and public supply wells, though water from these wells shows mixed age distributions, requiring lumped parameter modeling and multiple tracers to assess broader age distributions (Jurgens et al., 2012, 2016, 2022). Monitoring networks in the US and Europe often rely on these pumped wells, so tritium-helium is frequently combined with tracers such as CFCs, sulfur hexafluoride (SF₆), and even ⁸⁵Kr, ³⁹Ar, ⁴He, and ¹⁴C (Corcho Alvarado et al., 2007; Visser et al., 2013; Visser et al., 2016; Broers et al., 2021). However, for mixed distributions, the recharge year approach is less useful because contaminant concentrations derive from various recharge periods which are mixed in the well.

The critical role of redox processes in evaluating agricultural pollution and groundwater quality trends, including nitrate, has long been recognized (McMahon and Chapelle, 2008; Jessen et al., 2017; Lindsey

et al., 2023). Since both transformation processes and travel time affect concentration-depth profiles and temporal trends, combining age dating with redox classifications is beneficial for understanding contaminant transport (e.g., Broers and van der Grift, 2004; Visser et al., 2009a; Tesoriero et al., 2007; Denver et al., 2010; Landon et al., 2011; Degnan et al., 2020). Assessing redox status is especially important in regions with high proportions of anoxic or mixed redox status, typically present in coastal plains and river deltas with abundant organic matter or pyrite in subsurface deposits that act as electron donors (e.g., Tesoriero et al., 2024; Koch et al., 2024). In these settings, redox transformations such as denitrification can lead to degassing and solute degradation, impacting both age tracers and target variables like nitrate and organic contaminants (e.g., Visser et al., 2009b; Zhang et al., 2009; Denver et al., 2010; Tesoriero and Puckett, 2011; Sültenfuß et al., 2011; Tesoriero et al., 2021). Massmann et al. (2008) were the first to apply tritium-helium age dating to study pesticides and pharmaceuticals in local riverbank filtration settings, exploring the relationships between groundwater age, subsurface redox processes, and degradation patterns for organic contaminants. Furthermore, tritium-helium apparent ages are increasingly used to calibrate and validate transport models for inorganic chemicals (e.g., Zhang et al., 2012) and pesticides (e.g., Åkesson et al., 2014; Frederiksen et al., 2023), although applications involving large monitoring datasets remain scarce.

We hypothesized that evaluating monitoring data on pesticides, their metabolites, and emerging contaminants is equally sensitive to groundwater age and redox variability across typical sampling depth ranges. Groundwater age dating is necessary to disentangle the effects of time-variable contaminant inputs, advective flow variability, and transformation processes. Thus, we explored groundwater age, redox status, and land use types within one consistent framework, applying it to monitoring data from Dutch networks. The application of the recharge year approach to pesticides and emerging contaminants using tritium-helium was explored by Katz et al. (2014) and recently by Buszka et al. (2023) for PFAS, using regional datasets from the US National Water Quality Program (NWQP), but has not been systematically applied to regional monitoring networks. Kim et al. (2022) were the first to use groundwater ages to correlate pesticide detections in Danish groundwater with pesticide sales, focusing mainly on oxic groundwaters, while pesticide occurrences in Dutch drinking water supply wells are mostly from anoxic waters. Our study aims to investigate a wide spectrum of pesticides and emerging contaminants across various redox conditions, groundwater ages, and land use types to better understand their temporal and spatial patterns.

For this purpose, we used results from surveillance monitoring in the provinces of Noord-Brabant and Limburg, age-dating all 146 multi-level monitoring wells and 277 corresponding well screens in the WFD Sand-Meuse groundwater body using tritium-helium, creating one of the largest ³H/³He datasets worldwide. The recharge year was determined by subtracting the ${}^{3}\text{H}/{}^{3}\text{He}$ apparent age from the sampling year. Subsequently, we classified concentrations of nutrients, pesticides, their metabolites, and emerging contaminants based on (1) recharge year derived from tritium-helium age dating, (2) land use type, and (3) redox conditions, thereby reducing uncertainty from the observed spatial and depth-dependent heterogeneity of both groundwater age and redox class under the studied land use types. This unique dataset was used to better understand the relationship between historical land use and application rates and to evaluate the mobility and persistence of anthropogenically derived solutes in groundwater, considering recharge periods and redox conditions. To our knowledge, this is the first study to combine information about redox status and tritium-helium ages for a large monitoring dataset of microcompounds in groundwater under various land use types within a consistent framework.

2. Material and methods

2.1. Study area and hydrogeological setting

Our study area comprises the province of Noord-Brabant and the middle and northern parts of the province of Limburg in the southern Netherlands (Fig. 2). The area covers about 6500 km^2 and is home to approximately 3 million inhabitants, 7 million pigs, 39 million poultry and 600,000 cattle. These figures show that the region is one of the areas in Europe with considerable environmental impacts from intensive livestock farming and urban living. As a result, leaching of diffuse pollutants to the shallow groundwater is common, although the increasing trend in leaching of agricultural solutes has been reversed due to national and Europe-wide legislation (Broers and Van der Grift, 2004; Visser et al., 2007a). The region is relatively flat, with altitudes ranging from mean sea level (MSL) in the north and west to approximately 40 m above MSL in the southeast (Fig. 2). Phreatic water tables are generally shallow, usually within 1–5 m below the surface. Geologically, the study area can be divided into three main zones, each with a different hydrogeological buildup: (I) the western part of Noord-Brabant, (II) the Roer Valley Graben in the center and (III) the uplifted Peel Block and associated Venlo Graben in the east (see roman numerals in Fig. 2). The multi-level wells sampled for the monitoring campaign abstract water from roughly the first 30 m of the shallow subsurface. In the western part of Noord-Brabant, the shallow aquifers consist of Late Pliocene and Early Pliocene sandy sediments of the fluvial and estuarine Waalre Formation and Early and Middle Pleistocene fluvial Stramproy Formation, overlain by Pleistocene eolian fine sands of the Boxtel Formation. In the Roer Valley Graben, most samples come from the Boxtel Formation which has a larger thickness in this region and consists of fluvio-periglacial and eolian deposits, and from the sands of the deeper Sterksel Formation, deposited by the Rhine-Meuse river system. At the Peel Block, the samples are mainly derived from the coarse sands and gravels of fluvial deposits from the Meuse River (Beegden Formation) and older Pliocene rivers (Kieseloolite Formation). The sandy sediments from all the mentioned formations are typically carbonate-free, favoring slightly acidic to near-neutral pH in most of the sampled waters. Several samples from the northern and northwestern areas were derived from parts of the

region where the shallowest sediments are either formed by fluvial clays from the Holocene age (Echteld Formation) or by marine clays from the Holocene Naaldwijk Formation. The monitoring wells from these fluvial and marine clay areas are classified as *clay areas* in the remainder of the paper.

2.2. Well selection, sampling and measurements

We analyzed a selection of 146 multi-level observation wells with corresponding 277 individual well screens, forming the WFD monitoring network for the Sand-Meuse groundwater body (Fig. 2; Broers et al., 2005). The groundwater wells discussed in this study are part of surveillance and operational monitoring programs in relation to the EU Water Framework Directive (EU, 2000) and Groundwater Directive (EU, 2006) for the Sand-Meuse groundwater body. The multi-level monitoring wells are equipped with 3 or 4 filter screens positioned at depths ranging from approximately 5 to 30 m below the surface. Clay borehole seals are installed between the screens to prevent short-circuiting within the well. Filter screens at depths of 10 and 25 m were sampled systematically with an annual frequency in the past and with varied frequencies in later years (e.g., Broers and Van der Grift, 2004). These main filter screens have a 2-inch internal diameter, enabling the use of positive displacement pumps for purging and sampling, which is necessary for sampling dissolved noble gases (see the next section). The design of the monitoring networks was based on homogeneous area types to ensure a representative selection of wells with comparable combinations of land use types, soil types and hydrologic situations (e.g., Broers, 2002; Broers and Van der Grift, 2004). The homogeneous area types include farmland on dry soils, farmland on wet soils, urban areas, nature areas, marine and fluvial clay areas and discharge areas. Here, the discharge areas are well-drained regional outlets of the groundwater systems, where converging flow of younger and older groundwater may mix during drainage to surface water systems (Broers, 2004). Wet farmland areas typically have a dense artificial drainage network to enable farming under wet conditions. In the remainder of the paper, we refer to these area types as land use types, without distinguishing between wet and dry farmland because age dating results sufficiently explain the differences between the two area types (see the next section).



Fig. 2. Map of the study area showing the location of the multi-level monitoring wells of the WFD surveillance networks within the Dutch provinces of Noord-Brabant and Limburg.

This paper evaluates measurements of pesticides, their metabolites, and emerging contaminants from sampling campaigns in 2012, 2016, 2019, and 2022, which were cooperatively organized by the provincial authorities of Noord-Brabant and Limburg, the two southernmost provinces of the Netherlands. The data was used to gain insight into a broad selection of contaminants as required for the EU-WFD and GWD surveillance monitoring. As such, the data were also used as Dutch input to the EU Watch List for groundwater, which is meant to support EU member states under the WFD Common Implementation Framework (Lapworth et al., 2019). Details about the sampling strategy, techniques, and analysis of microchemistry, pesticides, and emerging contaminants is presented in the Supplementary Information, Section S1, Tables S1 and S2.

2.3. ${}^{3}H/{}^{3}He$ age dating

We accomplished tritium-helium age dating on a set of 146 monitoring wells, covering 277 age-dated well screens. Fifty-one of these were sampled in campaigns in 2001, 2005, and 2008, and the remaining ones in 2017 and 2018. SI: Appendix I summarizes the metadata, tritium and noble gas measurements of the dataset. The ${}^{3}\text{H}/{}^{3}\text{He}$ data was used to establish the apparent age of the groundwater, which is defined as the time that has passed since the infiltrating water reached the groundwater surface and its sampling (Suckow, 2014; Desens et al., 2023). Tritium is naturally present in atmospheric water in low background concentrations, but the concentration peaked in the 1950s and 1960s due to above-ground nuclear weapons testing. Since the ban on aboveground testing in the mid-1960s, concentrations in rainwater have stabilized slightly above natural background levels. Tritium decays into tritiogenic helium $({}^{3}He_{trit})$ with a half-life of 12.3 years. By measuring both ${}^{3}H$ and ${}^{3}He_{trit}$, the apparent groundwater age can be determined using the following equation (Tolstikhin and Kamensky, 1969; Poreda et al., 1988):

$$au = \lambda^{-1} ln \left(rac{{}^3He_{trit}}{{}^3H} + 1
ight)$$

where τ is the groundwater age in years, λ is the decay rate constant of tritium (0.05626 yr⁻¹) and ³*H* and ³*He*_{trit} are the concentrations of tritium and tritiogenic helium. Tritium and tritiogenic helium are reported in Tritium Units (TU), where 1 TU is equal to 1 atom of tritium per 10¹⁸ atoms of hydrogen, and 1 TU of ³*H* decays to 1 TU of ³*He*_{trit}. Our groundwater samples were analyzed at the oceanographic lab of the University of Bremen (Sültenfuß et al., 2009), and apparent groundwater ages were determined, correcting for excess air components and degassing following Visser et al. (2007b) (SI: Section S2).

Subsequently, the apparent ³H/³He groundwater age was used to derive the *recharge year* of a groundwater sample, which is calculated as the sampling year minus the groundwater apparent age for the monitoring screen at hand. Here, we assume that the apparent tritium-helium age is a time-constant variable as it is a function of long-term groundwater recharge rates, and of the dimensions and porosity of the sampled aquifers which are unlikely to change over time. As our sampling points consist of short screens in non-pumped observation wells, we also assume that the apparent ages do not represent a broad range of travel times, but rather situations close to piston flow conditions, especially in recharge situations where converging flow lines are unlikely (e.g., Broers, 2004; Desens et al., 2023). Desens et al. (2023) demonstrate that this condition is likely met for observation wells in a nearby region with short screen intervals that are not pumped. Their study shows that dispersion appears to be limited for ages up to 40 years, in contrast to wells with longer-screened intervals in the same area.

The ${}^{3}H$ and ${}^{3}He_{trit}$ concentrations can be checked against the initial inputs of tritium by precipitation summing the measured concentrations in the samples. In shallow groundwater where no mantle-derived ${}^{3}He$ is present, the only source of ${}^{3}He$ is the decay of ${}^{3}H$. After corrections for

excess air, the sum of the ${}^{3}H$ and ${}^{3}He_{trit}$ concentrations, or so-called "initial ³H", should reflect the initial concentrations of tritium in the infiltrating rainwater at the derived recharge date (e.g., Desens et al., 2023). Fig. 3 shows the evaluation of the *initial* ${}^{3}H$ in relation to the derived recharge year of the groundwater. Most of the data plot near the initial tritium in precipitation (solid line and monthly measurements of the Dutch GNIP stations Gilze-Rijen, Emmerich, De Bilt and Groningen as grey dots). A discrete apparent ${}^{3}H/{}^{3}He$ age could be determined for these 180 well screens, which likely indicates unhindered recharge of groundwater by precipitation (dark blue dots on Fig. 3). Samples from other well screens clearly plot below the precipitation input line or have lowered Ne/He ratios, which point to mixing between modern groundwater and pre-1950 groundwater. Thus, the turquoise points in Fig. 3 represent samples with tritium concentrations indicating a component of post-1950 water but with initial tritium (³H plus ³He_{trit}) below precipitation inputs due to mixing with old, almost tritium-free pre-1950 waters. Clearly, the derived recharge year for those samples is affected by the mixing process and does not reflect a single moment in time which characterizes the sample sensibly; therefore, these samples were classified as having mixed age, and the recharge year was not used in further interpretations. The light-green measurement points represent samples that are either very low in tritium (<0.10 or even <0.02 TU) or have Ne/He ratios <1.0, indicating ⁴He-accumulation, both suggesting a predominant contribution of water originating from recharge before 1950 (SI: Section S2 for details). Subsurface radiogenic ⁴He production is known to affect deeper aquifers in the region (e.g., Broers et al., 2021; Walraevens et al., 2020) and apparently determines the Ne/He ratio in several measurement points in regional discharge areas in our study as well. This green group of samples in Fig. 3 was classified pre-1950 and used as such in further interpretations.

A specific number of measurements plot above the precipitation input line (orange dots in Fig. 3). These samples show an excess of initial tritium relative to recharge as rainwater. We relate these measurements to the recharge of water from the Meuse River. Two nuclear power plants at Chooz (France) and Tihange (Belgium) are known to discharge tritium into the Meuse River. This has apparently led to elevated tritium concentrations in the water from the Meuse River reaching over 750 TU at the border crossing near Eijsden (data from RIWA-Maas, 2022, orange dashed line in Fig. 3). Water from the Meuse River is used in the research area for irrigation of agricultural areas through a network of streams and ditches and may infiltrate into the groundwater. All of the wells showing elevated *initial* ³H concentrations relative to precipitation were located near a stream or ditch fed with water from the Meuse River, or along the riverbanks themselves, such as observation well 138. The Meuseinfluenced waters were distinguished as a separate land use type in the remainder of the paper.

We translated the recharge year derived from the samples with discrete ages (dark blue and orange dots in Fig. 3) into classes of their recharge periods: 1965–1980, 1980–1990, 1990–2000, 2000–2010 and 2010–2020. The class pre-1950 was added as a presumed reference unaffected by recent contamination and included all samples with very low ³H and/or characterized by ⁴He accumulation (see above). Because of the unknown proportion of pre-1950 and post-1950 water in the mixed waters of Fig. 3, these samples from the mixed class were considered uninformative for our purpose of understanding contamination patterns in relation to application or usage history. Consequently, these well screens were not included in the evaluation of inorganic chemistry and microcompounds in Section 3.

2.4. Redox classification

The redox status of the groundwater was assessed to improve understanding of the patterns of pesticides and emerging contaminants and to evaluate the persistence and mobility of individual solutes. For this purpose, we applied a redox classification scheme developed for the national and regional monitoring networks in the Netherlands (Graf-



Fig. 3. Initial tritium (log scale) versus recharge year, showing the age classes derived for each of the samples and the tritium concentrations in infiltrating rainwater and recharge water from the Meuse River.

Pannatier et al., 2000), which was evaluated and updated for redox assessment on a regional scale (Pinson et al., 2020) and in a European setting (Pinson et al., 2021). The classification scheme evaluates individual samples based on concentrations of nitrate, iron, chloride, sulfate, and manganese and treats brackish and freshwater samples in separate decision trees (SI: Section S3). Except for a few samples, groundwater in our dataset is evaluated using the fresh groundwater tree with Cl < 200 mg/l, which main decision level is based on a 2 mg/l threshold for nitrate. Samples with concentrations above this threshold are classified as oxic, suboxic, Mn-reduced, or mixed. Mixed waters have ≥ 0.5 mg/l Fe, and Mn-reduced waters have Fe <0.5 mg/l and Mn ≥0.5 mg/l. Oxic and suboxic waters were not further distinguished because reliable dissolved oxygen field measurements were not available for all wells. Therefore, we combined the oxic and suboxic classes throughout the paper, where $NO_3 > 2 \text{ mg/l}$ and both Fe and Mn are below the 0.5 mg/l threshold. Samples with concentrations below the nitrate 2 mg/l threshold are classified as Mn-reduced, Fe-reduced, or SO4-reduced, depending on their sulfate, iron, and manganese concentrations. Low-sulfate samples (<5 mg/l) and brackish waters with a low SO₄/Cl ratio relative to seawater were classified as SO4-reduced (SI: Section S3). Nitrate-poor groundwater with sulfate above 5 mg/l is either classified as Mn-reduced or Fereduced; Mn-reduced samples have low Fe (<0.5 mg/l) and substantial Mn (≥0.5 mg/l). All other samples were classified as Fe-reduced, because the sulfate concentrations indicate that potential sulfate reduction is incomplete.

2.5. Redox-age diagrams

For our analysis, we explored the groundwater age versus depth and redox status versus depth for each land use type. Although the redox sequence from oxic to sulfate-reduced water generally shows a trend with depth, the depths of the redox transformations vary spatially between different monitoring locations, resulting in heterogeneity of redox status at specific monitoring depths. The same is true for groundwater age, which, on average, increases with increasing depth, but varies at different monitoring locations (e.g., Broers, 2004). Therefore, we developed redox-recharge year diagrams (referred to as redox-age diagrams) that combine information about redox classes and groundwater age for the studied contaminants, supporting the evaluation of the mobility and persistence of contaminants in relation to land use, redox status, and contamination history. These diagrams are more effective than traditional visualizations based on concentration-depth patterns, which are limited by unknown age and redox status at individual monitoring depths, thus hindering interpretation. Instead, the diagrams provide a visual representation of the transport from young, oxic waters in the upper left corner towards older, anoxic waters in the lower right corner. Mobile and conservative solutes with a long application history may be represented across a broad area of the diagram, reflecting their widespread presence and mobility. In contrast, solutes that experience retardation due to sorption processes in both the unsaturated and saturated zones may be concentrated in the left part of the diagram, indicating limited mobility. Solutes that degrade under denitrifying conditions may be predominantly found in the upper row of the diagram, corresponding to areas with Oxic/suboxic water conditions. Fig. 4 shows an example redox-age diagram for BAM (2,6-dichlorobenzamide), a herbicide and fungicide metabolite frequently found in groundwater and drinking water in the Netherlands (Swartjes et al., 2016; Sjerps et al., 2019). The redox-age diagrams summarize concentrations using color and size, with individual measurements randomly located within the grid blocks. Samples with concentrations below the Level of Quantification (LOQ) are represented by the smallest symbols. The diagrams support interpretations about the mobility and persistence



Fig. 4. Redox-age diagram for BAM for the specified redox classes and recharge periods for *farmland- sandy soils*. The X-axis describes the 6 recharge periods derived from ${}^{3}\text{H}/{}^{3}\text{H}e$ age dating.

of substances. Mobile substances will show higher concentrations over a larger set of recharge periods (x-axis), but interpretations should consider the contaminant application history, as changing usage over time results in varying concentrations over the recharge years. A trend in concentrations from recent to older recharge periods may suggest that a substance is being retarded or degraded, and trends in concentrations from Oxic/suboxic to more reduced conditions (y-axis) suggest degradation. The BAM example diagram suggests substantial mobility over a range of recharge periods since 1965 and limited degradation along the redox gradient between Oxic/suboxic and Fe-reduced conditions.

By comparing the redox-age diagrams with data on contaminant emission history, further inferences can be made about the mobility and persistence of the solutes. For pesticide application history, we utilized national data from the Dutch Environmental Data Compendium (2023b), CTGB (2023), and data from Kruijne and Ickenroth (2020) for the 16 most common pesticides in the studied region. We summarized the indicative application history for each pesticide in the redox-age diagrams for each recharge period (represented by grey horizontal bars), expressed as percentage classes relative to the registered maximum emissions (see Fig. 4). The indicative emissions were derived from pesticide admission history and estimated emissions to groundwater for the years 1998, 2004, 2008, 2012, and 2016 (Kruijne et al., 2011; Kruijne and Ickenroth, 2020). We assumed that the emissions during the recharge period 1980-1990 are comparable to those in 1990-2000, which seems reasonable given the recorded sales of herbicides and fungicides between 1985 and 2000 (Environmental Data Compendium, 2023b). For emerging contaminants, production, usage, and emission history are generally less well-known, and thus, grey bars have not been included in the redox-age diagrams.

2.6. Percentage of detections

We used the percentage of detections across different recharge periods, redox classes, and land use types to provide an overview of the contaminants' mobility and persistence, as presented in overview tables and redox-age diagrams. Detections are defined as observations with a concentration above the highest observed Limit of Quantification (LOQ) for the specific contaminant in our complete dataset. We refer to all observations, whether below or above this LOO, as measurements (detections + non-detects). The percentage of detection is calculated as the ratio of detections to total measurements, multiplied by 100 (in %). We computed these percentages for the entire dataset and separately for each recharge period, redox class, and land use type, including a detailed breakdown for recharge periods and redox classes within the farmland-sandy soils land use type. In the redox-age diagrams for pesticides (e.g., Fig. 4), the detection percentages are shown for recharge periods (columns) and redox classes (rows) within the farmland-sandy soils category. Detailed information is provided in Tables S3 and S4 for all area types combined, and in Tables S5 and S6 for recharge periods and redox classes within farmland-sandy soils.

3. Results and discussion

3.1. Heterogeneity of groundwater age and redox patterns with depth

The interpretation of pesticide and emerging contaminant measurements has been complicated by variations arising from differences in groundwater age and subsurface redox conditions, factors often overlooked in routine data analysis. To address this issue, we systematically analyzed groundwater age and redox conditions across the depth range of the monitoring networks within the Sand-Meuse groundwater body, differentiating between various land use types. Fig. 5 presents the observed variations in groundwater age and redox conditions in relation to monitoring depths for each area type. The maps show the spatial distribution of the land use types and the locations of the associated monitoring wells, while the graphs summarize the corresponding age-depth and redox-depth patterns. The age-depth relation for the *farmland-sandy soils* area type (Fig. 5, upper row, center panel) indicates that the groundwater is generally <50 years old and ages with depth, roughly in line with the theoretical age distribution for homogeneous aquifers with thicknesses between 50 and 80 m, recharge rates of 250–320 mm/year, and 35 % porosity (Vogel, 1967; Raats, 1981; dashed lines in Fig. 5). The blue line represents a linear regression with the intercept constrained to pass through the origin (0,0) and serves as a rough indicator of the general trend between apparent age and depth for the specific land use type analyzed. In the *farmland-sandy soils* area, some wells yield water where young water is mixed with older water or



Fig. 5. Age-depth relation and redox-depth patterns for different area types. The maps show the extent of each area type and the associated monitoring locations. The age-depth relations are based on ${}^{3}\text{H}/{}^{3}\text{H}$ e age dating and differentiate between discrete ages, mixed ages, and pre-1950 ages (see Fig. 3 for explanation). The redox classes are based on the classification described in Section 2.4.

even water dated as pre-1950 or pre-1920. The large variations in groundwater age with depth makes monitoring depth a suboptimal variable for interpreting hydrochemical patterns or contamination history (Visser et al., 2007a). Redox classes also show a heterogeneous pattern with depth (right panel of Fig. 5). Under farmlands, the probability of encountering Oxic/suboxic water, which contains nitrate and/ or oxygen, decreases with depth, while the proportion of Fe-reduced and SO₄-reduced water increases (Fig. 5, upper row, right panel). Again, a wide range of redox classes is present at specific monitoring depths, making monitoring depth an inadequate proxy for redox class as well. In conclusion, the observed variations in groundwater age and redox classes at specific depths complicate the interpretation of hydrochemical patterns and agricultural contamination history when using depth as a primary parameter (see also Broers and Van der Grift, 2004; Visser et al., 2009a).

Natural areas exhibit a more straightforward age-depth relationship with a relatively steep age-depth gradient, but redox conditions vary at specific depths as well (Fig. 5, second row). For example, groundwater at depths between 5 and 15 m depth shows approximately 30 % Oxic/ suboxic and 70 % Fe-reduced water. The patterns for urban waters (third row) are roughly comparable with those under farmlands, though with more limited data available.

Distinct age-depth and redox-depth patterns are present under discharge areas, which are dominated by upward seepage of older groundwater, and under marine and fluvial clay areas, where clay aquitards at the top of the profile hinder the recharge of underlying aquifers (see Sections 2.1 and 2.2). As a result, a substantial portion of the monitored water in these area types infiltrated before 1920 (pre-1920). These areas are typically dominated by Fe-reduced or SO₄-reduced water. In contrast, monitoring wells influenced by recharge from the Meuse River show a steep age-depth relation, indicating relatively fast recharge. However, only a small portion of Meuse-influenced waters comprises Oxic/suboxic water, with large variations present at shallow depths.

Based on the observed age-depth patterns, one might expect a high probability of detecting recent contaminants in the area types of *farmland-sandy soils, natural areas, urban areas,* and areas with *Meuse River recharge.* However, even in these hydrologically more vulnerable areas, patterns of pesticides and emerging contaminants are likely obscured by the large variability in groundwater ages and redox conditions over the depth profile, as illustrated in Fig. 5. Therefore, we chose to focus on the combination of land use type, groundwater age, and redox class as our primary variables in the analysis, presenting the results in redox-age diagrams and summarizing tables.

3.2. Redox-age patterns of pesticides and metabolites

Fig. 6 provides an overview of pesticide detections (numbers) and the percentage of detections relative to measurements (color classes) across all recharge periods, redox classes, and land use types. Detailed information about the measurements and detections for each recharge period, redox class, and land use type is presented in Tables S3 and S4. The figure reveals that most pesticide detections are from observation wells in farmland-sandy soils, urban areas, and waters showing signs of Meuse River recharge. Pesticides and metabolites are typically present in waters originating from recharge periods of 1980-1990 and younger, with incidental detections of BAM, dimethylsulfamide (DMS), bentazon, mecoprop (MCPP), diethyltoluamide (DEET), and aclonifen in older waters. The ample presence of post-1980 water in the mentioned land use types (see Fig. 5) and the known pesticide pressures (Fig. 1) explain the detections in these areas. Nature reserves, clay areas and discharge areas show fewer detections, due to lower emissions and smaller contributions of young water, respectively (see the previous section).

Fig. 6 demonstrates that the five most frequently detected pesticides and metabolites are persistent across the full range of redox conditions from Oxic/suboxic to Fe-reduced. The two chloridazon metabolites, along with BAM, DMS, and bentazon were detected in 21–35 % of all collected samples, 17–47 % of all Oxic/suboxic samples, and 13–28 % of all Fe-reduced samples (see Table S4). The high percentage of detections combined with their redox insensitivity confirms the mobility and persistence of these pesticides and metabolites in the shallow subsurface, which have affected Dutch waterworks for decades, exceeding the drinking water standard of 0.1 μ g/l in abstracted water (Boesten et al., 2015). Our dataset, however, lacks sufficient data from SO₄-reduced conditions, which makes conclusions about degradation under these methanogenic conditions impossible (SI: Section S3 and Fig. S6 for gas measurements validating the redox classification and methanogenic conditions).

Tritium-helium age dating also supported the identification of the origin of Meuse River-recharged water, characterized by high initial tritium in the river (see Section 2.3). For several pesticides and metabolites, this method pinpointed their relatively high contributions from river recharge, including the chloridazon metabolites, bentazon, MCPP, 2-hydroxy-atrazine, carbendazim, glufosinate and diuron (Fig. 6). The latter two are found only in recently river-recharged groundwater, emphasizing the role of groundwater-surface water interaction in contamination patterns. Urban areas detections are less common, with the exceptions of DMS, desphenyl-chloridazon, bromacil and especially BAM (see Fig. 6). Dichlobenil, the parent herbicide, was frequently used in urban settings, accounting for about 30 % of total sales in the Netherlands (Van der Linden et al., 2007), which explains the high percentage of detections in urban areas (Fig. 6).

We explored the detections of the six most frequently detected pesticides and metabolites in more detail through the redox-age diagrams in Fig. 7, focusing solely on measurements and detections in the *farmlandsandy soils* land use type (see Tables S5 and S6 for a detailed breakdown of detections, measurements, and detection percentages for each recharge period and redox class within this category). We first discuss the redox-age diagrams of nitrate and sulfate as they can be used as proxies for identifying recharge periods and redox conditions where agricultural pollution in groundwater is most evident. Understanding the extent of agricultural pollution aids the interpretation of the redoxage diagrams for agriculturally derived microcompounds, such as pesticides and emerging contaminants (see following sections).

3.2.1. Nitrate and sulfate; indicators of inorganic agricultural pollution

Agricultural contamination of groundwater by nitrate has been a focus of the monitoring networks in the Sand-Meuse groundwater body. Previous studies in the region have shown that nitrate contamination is confined to the shallow subsurface due to the reactive nature of deltaic sediments, which promote denitrification (e.g., Broers and Van der Grift, 2004; Zhang et al., 2009; Visser et al., 2009a). This is confirmed by the shallow presence of Oxic/suboxic water in Fig. 5 and by the redox-age diagram of farmland-sandy soils (Fig. 7; upper left panel). Fig. 7 shows that nitrate is mainly found in water from recharge periods 2000-2010 and 2010-2020 and is (by definition) limited to waters with Oxic/suboxic or Mn-reduced conditions. Thus, the peak in nitrogen leaching from manure and fertilizers during 1980-1990 (Fig. 1) is not reflected in nitrate concentrations due to denitrification coupled with pyrite oxidation in the shallow subsurface (Zhang et al., 2009; Visser et al., 2007a; Zhang et al., 2012). Instead, the 1980-1990 peak is revealed by elevated sulfate (and iron) concentrations in groundwater from this recharge period (Fig. 7, upper right panel), resulting from pyrite consumption. This led to higher sulfate in Fe-reduced waters infiltrating between 1965 and 1990 compared to younger groundwater (e.g., Zhang et al., 2009; Zhang et al., 2012; Jessen et al., 2017). In younger Oxic/suboxic water, sulfate levels result from a combination of manure leaching and atmospheric deposition (e.g., De Vries et al., 2003, 2014). Atmospheric sulfur sources have decreased due to measures like reducing coal-fired power plants, catalytic converters, and farming innovations, including manure injection and air scrubbers (Melse et al., 2009). However, concentrations in the most recent groundwater remain elevated relative to natural

	hest LOQ (µg/l)	measurements	ections	etections	0-2020	0-2010	0-2000	0-1990	5-1980	-1950		c-Suboxic	-reduced		educed	h-reduced		mland-sandy soils	ure	an	ase		charge
Solute	hig	Nr-	Det	%	201	200	199	198	196	Pre		Oxi	Mn	kiM	Fe-I	SQ		Far	Nat	Urb	Me	Cla	Dise
Pesticides and metabolites																							
Desphenyl chloradizon	0.125	234	83	36	24	36	15	8	0	0		35	11	4	32	1		61	0	5	7	6	4
Methyl desphenyl chloridazon	0.05	204	49	24	14	25	8	2	0	0		25	2	3	19	0		39	0	0	5	5	0
Dimethyl sulfamide	0.1	404	85	21	14	40	18	12	1	0		29	11	5	38	2		58	14	8	4	0	1
BAM	0.06	404	84	21	29	32	12	11	4	0		45	8	2	20	3		54	2	1	4	7	10
MCPP	0.03	404	26	6	4	13	5	3	1	0		4	0	2	20	2		21	0	0	5	0	0
2-Hydroxyatrazine	0.05	359	9	2.5	6	3	0	0	0	0		4	0	0	5	0		4	0	0	5	0	0
1,2 Dichloropropane	0.1	117	2	1.7	0	0	1	1	0	0		0	1	1	0	0		2	0	0	0	0	0
Diethyltoluamide	0.06	404	6	1.5	0	2	0	2	1	1		1	1	1	2	1		3	1	0	0	1	1
Metalaxyl	0.03	404	6	1.5	2	4	0	0	0	0		5	0	0	1	0		6	0	0	0	0	0
Glufosinate	0.1	184	2	1.1	1	1	0	0	0	0		0	0	0	1	1		0	0	0	2	0	0
Bromacil	0.03	287	3	1	0	1	2	0	0	0		3	0	0	0	0		0	0	3	0	0	0
Diuron	0.03	287	3	1	3	0	0	0	0	0		1	0	0	2	0		0	0	0	3	0	0
Aclonifen	0.05	234	2	0.9	1	1	0	1	1	0		1	0	0	2	0		2	0	0	0	0	0
Carbendazim	0.00	404	3	0.7	2	0	0	1	0	0		1	0	0	2	0		1	0	0	2	0	0
Lenaci	0.03	404	3	0.7	1	2	0	0	0	0		0	0	0	3	0		3	0	0	0	0	0
Simazine	0.03	287	2	0.7	1	1	0	0	0	0		2	0	0	0	0		2	0	0	0	0	0
Fenitrothion	0.05	359	2	0.6	0	0	0	0	0	2		0	0	0	2	0		2	0	0	0	0	0
Ethofumesate	0.05	404	2	0.5	2	0	0	0	0	0		1	0	0	1	0		0	0	0	1	0	1
Methiocarb	0.03	404	2	0.5	0	0	1	1	0	0		1	0	0	1	0		2	0	0	0	0	0
Tebuconazole	0.03	404	2	0.5	0	1	0	1	0	0		0	0	0	2	0		1	1	0	0	0	0
Chloridazon	0.05	384	1	0.3	0	0	0	1	0	0		0	0	0	1	0		1	0	0	0	0	0
Glyphosate	0.5	400	1	0.2	0	0	0	0	0	1		0	0	0	0	1		0	0	0	0	0	1
AMPA	0.5	400	0	0	0	0	0	0	0	0		0	0	0	0	0		0	0	0	0	0	0
Metolachlor	0.03	401	0	0	0	0	0	0	0	0		0	0	0	0	0		0	0	0	0	0	0
Emergine and and and a			-				-	-	-					-					-	-			-
Emerging contaminants	0.001	86	70	91	22	10	7	0	1	2		27	0	1	22	2		15	7	0	6	1	3
PEOA	0.001	86	59	69	27		5		1	2						2		37	5			1	3
PFBA	0.004	86	51	59	24				1	0	1	19				2		33	4			1	3
PFBS	0.001	86	50	58	25		4	4	0	0		23			19	2		32	2			0	3
PFHxA	0.001	86	43	50	21		5	3	0	0					17	2		27	3			1	2
PFHpA	0.011	86	35	41	16	- 13	- 4	2	0	0		12	4		16	2		23	2	5	3	0	2
PFHxS	0.001	86	27	31	15	11	1	0	0	0		13	2	1	9	2		17	2	4	2	0	2
EDTA	0.005	288	79	27	24	34	17	3	1	0		29	6	2	40	2		47	0	13	16	0	3
Bisphenol-A	0.006	112	16	14	5	6	2	0	2	1		6	2	1	6	1		6	2	1	4	0	3
DEDA	0.05	18	2	11	2	2	0	0	0	0		1	1	0	2	1		7	0	1	2	0	0
PEOS	0.004	86	5	6	3	2	0	0	0	0		2	1	0	2	0		2	0	1	2	0	0
тсрр	0.05	77	4	5	3	0	0	0	0	1		2	1	0	0	1		1	0	0	2	1	0
Carbamazepine	0.01	112	5	4.5	5	0	0	0	0	0	1	2	3	0	0	0		0	0	0	5	0	0
Paracetamol	0.02	112	5	4.5	2	2	0	0	0	1		1	0	0	2	2		2	0	2	0	0	1
MTBE	0.2	117	5	4.3	1	2	1	1	0	0		0	2	1	1	1		0	1	4	0	0	0
Benzotriazole	0.05	77	3	3.9	3	0	0	0	0	0		2	1	0	0	0		1	0	0	2	0	0
FRD-903	0.001	27	1	3.7	1	0	0	0	0	0		1	0	0	0	0		0	0	0	1		0
loxitalamic acid	0.02	112	4	3.6	1	1	1	0	0	1		2	0	0	2	0		4	0	0	0	0	0
Primidon Distrizois scid	0.01	66 100	2	3	0	2	0	0	0	0		0	0	0	2	0		0	0	1	1	0	0
Ibunrofen	0.02	112	2	1.0	2	0	1	1	0	0		0	0	0	2	0		1	0	0	0	1	0
lopamidol	0.02	112	2	1.8	0	1	1	0	0	0		0	0	0	2	0		0	0	0	2	0	0
PFDA	0.005	86	0	0	0	0	0	0	0	0		0	0	0	0	0		0	0	0	0	0	0
PFNA	0.001	86	0	0	0	0	0	0	0	0		0	0	0	0	0		0	0	0	0	0	0
PFudA	0.005	86	0	0	0	0	0	0	0	0	ΙL	0	0	0	0	0	ll	0	0	0	0	0	0
					Legend 0	no det	tection	IS		30-50	0%												

Fig. 6. Overview of the number of detections (numbers) and the percentage of detections (detections/measurements in %, presented through color classes) for 27 pesticides and metabolites and 26 emerging contaminants, including the sum of PFAS, across all recharge periods, redox classes and land use types. Underlying data are provided in Tables S3 and S4.

50-70%

70-100%

0-10%

10-30%



Pesticide application history - 75-100% of max - 50-75% - 25-50% - 1-25% 0%

Fig. 7. Redox-age diagrams of nitrate, sulfate and six commonly found pesticides in relation to recharge years and redox class for *farmland-sandy soils*. X-axis describes the 6 recharge periods that were derived from 3 H/ 3 He age dating.

conditions, given the intensive farming and urban and industrial activities in the Netherlands. Thus, the combined redox-age diagrams of nitrate and sulfate in Fig. 7 identify the recharge periods and redox conditions where agricultural pollution in groundwater is most evident, specifically in Oxic/suboxic and Fe-reduced environments since 1965. Given the resemblance between the peak in nitrogen and pesticide emissions (Fig. 1), these are the recharge periods during which pesticide detections can be anticipated. Indeed, detections of desphenylchloridazon, BAM, DMS, and bentazon correspond with the redox conditions and recharge periods where nitrate and sulfate indicate the presence of agriculturally polluted groundwater.

3.2.2. Chloridazon metabolites

Detections of desphenyl-chloridazon are observed throughout the entire recharge period from 1980 to 2020, with the highest percentage of detections occurring during 2000–2010 (60 %, Fig. 7), representing 31 detections out of 52 measurements under farmland-sandy soils for this period (see Tables S5 and S6). Desphenyl-chloridazon exhibits the highest concentration (often $>5~\mu\text{g/l})$ and the greatest abundance (62 %) under Oxic/suboxic conditions but is also amply present in Fereduced waters (34 %). The herbicide chloridazon, introduced in 1979, has metabolites detected in water from the early recharge period (1980-1990), indicating high mobility and persistence. The use of chloridazon in agriculture has decreased by half between 1980 and 2016, with its approval ending in 2020 (Table S7, Kruijne and Ickenroth, 2020). The frequent detections of chloridazon metabolites in all groundwater recharged since the earliest application suggest very limited retardation of the metabolites during groundwater transport. The ample presence of chloridazon metabolites in Fe-reduced waters and deeper groundwater (Sjerps et al., 2019) further confirms the general lack of degradation in the saturated zone. The parent herbicide chloridazon was not detected in the dataset, suggesting either complete degradation to its metabolites or substantial sorption in the soil or shallow subsurface (e.g., Schuhmann et al., 2016).

3.2.3. BAM, DMS and bentazon

BAM (2,6-dichlorobenzamide) detections are most frequent in samples from farmland recharge during 2010-2020 (48 %, or 19 detections out of 40 measurements; see Tables S5 and S6) and in Oxic/suboxic water (38 %). BAM is found in all agriculturally polluted water from the recharge period 1965-1980 onward and across the entire redox gradient: Oxic/suboxic (38 %), Mn-reduced (25 %), and Fe-reduced conditions (14 %) (Fig. 7). BAM is a metabolite of the herbicide dichlobenil and the fungicide fluopicolide, and it is one of the most frequently detected chemicals in groundwater in the study area, including in water from several drinking water supplies (e.g., Swartjes et al., 2016). Although the approved use of dichlobenil ended in 2008 (Table S7), the high detection percentage of BAM in recent groundwater (48 %, 2010–2020) may be linked to the increased use of fluopicolide, particularly in potato cultivation, since its approval in 2007 (Fig. 7; Kruijne and Ickenroth, 2020). Alternatively, the persistence could be due to slow degradation of the parent compounds in the topsoil and ongoing leaching into groundwater, as suggested by Kim et al. (2022). The decrease in detection percentage from Oxic/suboxic to Fe-reduced groundwater indicates some degree of BAM degradation along the redox gradient. The presence of BAM in water from the earliest application periods suggests limited retardation.

DMS and bentazon exhibit a broader distribution, with no strong preference for Oxic/suboxic or recently recharged water. These substances are present throughout the recharge period 1980–2020 and across Oxic/suboxic and Fe-reduced conditions. DMS, used as a fungicide in fruit cultivation and arboriculture, was approved for agricultural use from 1980 to 2008 (Table S7). The highest concentrations under farmland are from the periods 2000–2010 and 1990–2000, aligning with its usage history (Fig. 7). The detection of DMS in all recharge years during which application was permitted suggests limited retardation. Consistent findings of DMS in Fe-reduced conditions indicate high persistence and mobility, with limited degradation and sorption in both Oxic/suboxic and Fe-reduced environments, consistent with findings in Denmark (Frederiksen et al., 2023).

For bentazon, the highest concentrations and detection percentages occur in water from the recharge periods 1990–2000 and 2000–2010 (27 % and 29 % detections, respectively; see Tables S5 and S6). Bentazon, used in agriculture since 1972, occasionally appears in water from the 1965–1980 recharge period, indicating high mobility and persistence. Its use significantly declined after 2016, following the end of its approval for maize (Table S7), which explains the lower concentrations in the most recent recharge period. The widespread presence of bentazon in Fe-reduced waters and its problematic occurrence in deeper drinking water sources (e.g., Mendizabal and Stuyfzand, 2011) suggest limited degradation and low sorption during groundwater transport, as also observed in Danish groundwater (Kim et al., 2022).

3.2.4. Mecoprop, 2-hydroxy-atrazine and 1,2 dichloropropane

Mecoprop (MCPP) detections are less common in farmlands compared with the previously mentioned chemicals and predominantly occur in Fe-reduced waters (14 %), with a notable peak during the recharge years 1980–2010 (11–12 %, Fig. 7). However, MCPP has been frequently detected in waterworks abstracting deeper groundwater (Mendizabal and Stuyfzand, 2011; Boesten et al., 2015). MCPP was detected in both Oxic/suboxic and Fe-reduced waters, suggesting incomplete degradation under both conditions (Fig. 7). The lower detection percentage in the most recent recharge period (2 %) aligns with the known reduction in agricultural applications and the ban on its use in grassland in 2013 (Grey bars in Fig. 7 and Table S7).

In contrast, detections for 2-hydroxy-atrazine are few and result from more recent recharge (2–5 % over 2000–2020), occurring only in Oxic/ suboxic water (5 % detections in *farmland-sandy soils*, Fig. 7). Remarkably, these detections are from recharge years during which the use of the parent substance atrazine in maize was banned (Table S7 and grey bars in Fig. 7), which could indicate substantial sorption of the metabolite 2-hydroxy-atrazine in the soil and/or illegal use of the herbicide. The absence of 2-hydroxy-atrazine in samples from recharge years 1980–2000 suggests complete anoxic degradation of atrazine applied during these years. The four detections under Oxic/suboxic conditions in farmlands point to incomplete degradation of 2-hydroxy-atrazine under these conditions, consistent with findings from other studies in oxic waters (e.g. Jablonowski et al., 2009; Vonberg et al., 2014).

Apart from the six aforementioned pesticides, only 1,2-DCP and metalaxyl have detection percentages above 2 % in farmland-sandy soils (Table S6). 1,2-DCP was a notorious contaminant in many waterworks before 2010 due to its presence as an impurity in the widely used soil fumigant 1,3-dichloropropene (Beugelink, 1987, 1989; Boland et al., 1994; Kovar et al., 1998), which was regulated in 1993 (Koninkrijk der Nederlanden, 1993). In our dataset, 1,2-DCP was only detected twice, in groundwater from the recharge periods 1980–1990 and 1990–2000. Its absence in more recent recharge periods demonstrates the effectiveness of regulations for these disinfectants (see Fig. 1 and Table S7). Metalaxyl was detected only in recently recharged water in farmland-sandy soils (Table S6: 4 % and 5 % in the 2000-2010 and 2010-2020 recharge periods, respectively) and exclusively in Oxic/suboxic water. Since the peak in metalaxyl usage occurred before 2000 (Kruijne and Ickenroth, 2020), this pattern suggests substantial sorption in the soil and shallow Oxic/suboxic zones and/or degradation under more anoxic conditions, resulting in low overall mobility in the conditions found in the south of the Netherlands.

In summary, only eight pesticides were detected in >2 % of the measurements under the vulnerable land use type *farmland-sandy soils*, including four metabolites (Table S6), despite high levels of agricultural production and pesticide usage in the Netherlands (Fig. 1). The parent compounds chloridazon, dichlobenil, and atrazine were seldom or never observed in our dataset, and this absence also applies to other widely

used pesticides, including glyphosate, its metabolite AMPA, and dinoterb. For some substances, including glyphosate and AMPA, the apparent lack of detections may be due to the relatively high maximum LOQs of 0.5 μ g/l in our dataset. However, the general absence of these substances suggests substantial attenuation, possibly through degradation and sorption in the shallow groundwater's relatively high oxidation state. SI: Section S4 and Table S7 provide information on pesticides detected in <2 % of the cases, for which there is substantial uncertainty due to their incidental occurrence and low detection percentages.

3.3. Redox-age patterns of emerging contaminants

The distribution of emerging contaminants (ECs) in European surface and groundwater has come under recent scrutiny as the EU defines Watch Lists to support member states in focusing their groundwater monitoring efforts (Lapworth et al., 2012; Lapworth et al., 2019; Bunting et al., 2021). We evaluated the occurrence of ECs in the monitoring program of the Dutch southern provinces, as summarized in Fig. 6. Over the monitoring years 2012 to 2022, laboratory methods for some ECs, particularly per- and polyfluoroalkyl substances (PFAS), were substantially refined. For PFAS, we present the most recent data from the 2019 VU-series and 2022 EO-series (Table S2), analyzed with lower LOOs in preparation for the more stringent standards required by the European Drinking Water Directive and EFSA target values of 4.4 ng/kg body weight (EFSA, 2020; Van der Aa et al., 2022). Fig. 6 also includes the PFAS indicator sum, based on all measured PFAS, which is a required indicator for the EU Drinking Water Directive that comes into effect in 2026 (EU, 2020).

Detections and detection percentages for emerging contaminants are shown in Fig. 6, with detailed age-redox diagrams for eight prominent solutes in Fig. 8. Unlike pesticides, trends over the recharge years cannot be evaluated for most ECs in relation to admission or usage regulations due to the absence of such regulations at present. However, Table S8 summarizes usage, emission sources, and application history. The detection percentages in Fig. 8 cover all area types combined (see Tables S3 and S4 for a detailed breakdown). Fig. 6 reveals that most detections of ECs occur in farmland-sandy soils and urban areas, as well as in wells influenced by Meuse River recharge. The higher detection percentage in urban areas sets these contaminants apart from the pesticides and metabolites discussed in the previous section. ECs are predominantly found in waters from recharge periods 1980-1990 and later, although EDTA, Bisphenol-A (BPA), PFOA, and PFBA have shown occasional detections in older groundwater (see Tables S3 and S4 for a detailed breakdown). Additionally, unexpected incidental detections of BPA, TCPP, paracetamol, and ioxitalamic acid in pre-1950 waters were evaluated separately (see Section 3.4.1).

3.3.1. PFAS

PFAS are among the most frequently detected ECs in the study region (Fig. 6). PFOA, the most widely produced PFAS, was found in 79 % of samples from the most recent recharge period (2010-2020), representing 27 detections out of 34 measurements (Fig. 8 and Tables S3 and S4), and in 74 % from the 2000-2010 period. PFOA was also frequently detected in Fe-reduced waters from earlier recharge periods, although at lower concentrations (Fig. 8). Many PFOA detections exceeded the proposed US-EPA national primary drinking water regulation of 4.0 ng/l (US-EPA, 2023), but only two exceeded the former 2016 US-EPA threshold of 70 ng/l (US-EPA, 2016; US-EPA, 2022), both in samples recharged after 2000. High detection percentages were also observed for PFBA (57-71 % detections since 2000) and PFBS (74 % since 1980, Fig. 8). Concentrations rarely exceeded the 70 ng/l threshold, and this only occurred in the most recent recharge period. PFOA, PFBA, and PFBS were detected under all redox conditions, with equal proportions for Oxic/suboxic and Fe-reduced water for PFOA and PFBA, and slightly lower proportions for PFBS (72 % and 50 %, respectively).

The "sum of PFAS," representing the uncorrected total of all

measured PFAS in our samples, showed a pattern similar to PFOA, with high frequencies of occurrence in recent groundwater and significant presence in Fe-reduced groundwater recharged since 1980. With four exceptions, all concentrations remained below the 100 ng/l threshold for the sum of PFAS, as per the EU Drinking Water Directive (EU, 2020), which takes effect in 2026. However, concentrations above 10 ng/l for the sum of PFAS were common, which is concerning given recent stringent EFSA and US-EPA standards based on new toxicological evaluations (e.g., Van der Aa et al., 2022) and the apparent mobility of multiple PFAS under all redox conditions.

PFOA has been produced industrially since the mid-1950s (Table S8) and is known to spread atmospherically and through industrial discharges into rivers (e.g., Dauchy et al., 2012; Wong et al., 2018; Calore et al., 2023). The use of pesticides might have contributed additional PFAS, as sales of EU-authorized pesticides containing PFAS as an active ingredient have increased in the EU and the Netherlands (e.g., PAN-Europe, 2023), potentially leading to the leaching of unknown amounts of PFAS metabolites into groundwater, separate from atmospheric inputs. PFBA, PFBS, PFHxA, PFHpA, and PFHxS are considered more mobile PFASs due to their relatively small molecular size and associated low sorption affinities in the vadose zone (Brusseau, 2019). Although PFBA, PFBS, PFHxA, and PFHxS are expected to experience less retardation in both the vadose and saturated zones compared to PFOA, the relatively high number of PFOA detections likely results from its more extensive use and environmental releases, including atmospheric emissions (Wong et al., 2018). Notably, PFBA, known for its lack of retardation in the saturated zone, has been routinely used as a conservative tracer in field and laboratory studies (e.g., Nelson et al., 2003). The widespread presence of PFBA in many groundwater wells sampled for this study indicates its high mobility and frequent environmental emissions in the densely populated southern Netherlands, likely originating from atmospheric sources. In contrast, PFOS was only incidentally detected in recently recharged waters influenced by the Meuse River (Fig. 6), suggesting greater sorption in the subsurface, as predicted by Brusseau (2019) and Eschauzier et al. (2013), or possibly indicating less atmospheric transport. High detection percentages of PFBS have been observed since the 2000-2010 recharge period, corresponding with the replacement of PFOS in flame retardants and stain repellents since 2002. Earlier detections may indicate PFOS emissions that included PFBS as an impurity (e.g., Buszka et al., 2023). Other highmolar-volume substances, such as PFDA, PFNA, and PFuDA, were not detected in any samples, confirming their predicted higher sorption capacities in soils and unsaturated zones (Brusseau, 2019). The frequent occurrence of PFOA, PFBA, PFBS, PFHxA, and PFHxS in Fe-reduced waters across all recharge periods since 1980 underscores the high persistence and low degradability of PFAS, even in deeper anoxic groundwater.

3.3.2. EDTA and BPA

EDTA was frequently present in groundwater recharged after 1990, with relative frequencies of 29-35 % for these recharge years (Fig. 8). High EDTA concentrations above 25 µg/l were observed in Oxic/suboxic, Mn-reduced, and Fe-reduced waters (31 %, 30 %, and 29 % of all measurements, respectively; see Fig. 8). Many of these detections originated from waters influenced by the Meuse River, with a frequency of 80 % in our samples, and from urban settings with 52 % detections (Table S4). Unlike PFAS, EDTA has long been known to influence drinking water sources based on bank filtration (Van Dijk-Looyaard et al., 1990). However, its listing as an 'emerging' contaminant is somewhat surprising given its long history of use, particularly since 1980 as a substitute for phosphate in cleaning agents (Table S8). The high percentage of EDTA detections in waters influenced by Meuse River recharge can be attributed to the ineffective removal of EDTA during sewage treatment, consistent with its known presence in many European river systems (Oviedo and Rodríguez, 2003). A study by Henzler et al. (2014) confirms the almost conservative, non-sorptive behavior of EDTA



Fig. 8. Patterns of eight commonly found emerging contaminants in relation to recharge years and redox classes for all area types combined. The x-axis describes the six recharge periods derived from ${}^{3}H/{}^{3}He$ age dating.

during riverbank filtration at a Berlin field site under various redox conditions, corroborating the redox insensitivity of EDTA observed in this study's groundwater samples. The common occurrence of EDTA in urban settings is likely due to its widespread industrial and household applications and could be related to leaking sewage systems. Its presence under farmlands is probably related to its use as a chelating agent to dissolve micronutrients in liquid fertilizers (Table S8). Detections of BPA were much less frequent than for EDTA and were more scattered across recharge periods and redox classes, with concentrations above $0.02 \,\mu g/l$ occurring only since the recharge year 1990 (Fig. 8). The emission sources for BPA are relatively unclear. Its presence in surface water and sewage (e.g., Arnold et al., 2013) likely contributes to the 31 % detection rate in waters recharged from the Meuse River (Table S4). However, its presence under farmlands and natural reserves is not well understood. Contamination during sampling from PVC lining of the wells is possible and may also explain the incidental presence in pre-1950 water (see Section 3.4.1).

3.3.3. Pharmaceuticals

The pharmaceutical carbamazepine was found exclusively in recently recharged, Oxic/suboxic, or Mn-reduced water influenced by the Meuse River, a pattern not observed for any other contaminants in this study. The presence of carbamazepine in river water and its recharge into young groundwater aligns with findings from Henzler et al. (2014), who investigated riverbank filtration at Berlin waterworks. They reported moderate retardation (R = 1.7) and substantial degradation (t1/2 = 66 days) for carbamazepine, which may explain why it was not detected in deeper, partially Fe-reduced water from older recharge periods in our dataset (Fig. 8). However, Hamann et al. (2016) suggest that while sorption of carbamazepine plays a role, degradation is limited under both oxic and anoxic conditions. Our dataset is too small to draw definitive conclusions, but it suggests that carbamazepine is much less mobile than other substances influenced by river recharge, such as EDTA and low-molar-volume PFAS.

Several other pharmaceuticals, including paracetamol, ibuprofen, and primidone, as well as the contrast agents ioxitalamic acid, diatrizoic acid, and iopamidol, were detected in low percentages. These were mostly found in urban or river recharge settings and under a range of redox conditions, although detection percentages are uncertain given the limited sample size (Fig. 6 and Tables S3 and S4). The likely transport route involves emissions from sewage systems to surface water and subsequent recharge into groundwater (e.g., Hass et al., 2012; Müller et al., 2012; Lapworth et al., 2012). The presence of diatrizoic acid and iopamidol in Meuse River recharged water is credible, given their known presence in Meuse River water (Wolf et al., 2012; RIWA-Maas, 2022).

3.3.4. MTBE, triazoles and TCPP

MTBE, a fuel additive introduced in 1979, was incidentally detected in urban water recharged after 1980 (Fig. 8 and Table S8). Notably, MTBE was found across all redox classes except the Oxic/suboxic class, a pattern not observed for any other investigated substances. Previous field studies in riverbank recharge settings confirm MTBE's persistence under both oxic and anoxic conditions (Hamann et al., 2016). However, other studies have reported differences in MTBE degradation rates between oxic conditions ($t_{1/2} = 21$ days, Achten et al., 2002) and anoxic conditions ($t_{1/2} = 578$ days, Schirmer et al., 1999). Therefore, the lower detection frequency in our study might be attributed to more efficient degradation under oxic conditions.

Detections of benzotriazole and tolyltriazole were incidentally observed in groundwater recharged from the Meuse River. This finding aligns with expectations, as these substances are known to be only partially removed by wastewater treatment plants, allowing substantial amounts to enter rivers and lakes (e.g., Olds et al., 2022; Zhou et al., 2023). Their presence in the most recent Meuse River recharge water and occurrence only under Oxic/suboxic conditions suggest that biodegradation under more reduced conditions may limit their mobility. The flame retardant TCPP was incidentally detected in recently recharged water from the Meuse River, likely linked to wastewater sources (Regnery et al., 2011). However, the small sample size and potential false positives in pre-1950 water samples introduce uncertainty into these results (see Section 3.4.1).

3.4. Use of redox and groundwater age in surveillance monitoring

3.4.1. Identification of false positives

Fig. 6 highlights instances where pesticides or emerging contaminants were detected in water classified as pre-1950 based on a measured tritium concentration of 0.01 \pm 0.02 TU. Given the precise tritium determinations, which strongly suggest the total absence of water from the last 70 years in the sampled groundwater at these locations, these detections must be considered artefacts from sampling and/or laboratory procedures. A detailed examination of these samples reveals that none of the detections could be reproduced in other measurement years, thus confirming the artificial nature of these incidental detections for BPA, DEET, glyphosate, paracetamol, and ioxitalamic acid (SI: Section S5). Tritium-helium age dating is particularly valuable in identifying false positives when analyzing large datasets. This is especially true for datasets collected from multiple laboratories and regional authorities, where detection limits and sampling procedures may vary and change over time. Such variability in detection limits and procedures has been recognized as a potential source of error and confusion in previous national assessments of pesticide monitoring (e.g., Schipper et al., 2008; Bexfield et al., 2020). Evaluating test samples from waters that are clearly pre-1950 supports quality assurance and control of our datasets, particularly for contaminants that can be easily introduced during sampling, such as PFASs, DEET, and BPA (e.g., Pulster et al., 2024). High-precision tritium data with low detection levels (< 0.02 TU) are crucial for thorough validation for this purpose, although lower precision data can still aid in the evaluation of national and regional scale pesticide data by distinguishing between modern and pre-modern waters (e.g., Bexfield et al., 2020).

In evaluating the data on pesticides and emerging contaminants, we focused on detections above the highest observed LOQ in our dataset to limit the number of false positives, acknowledging variations in LOQs across the three sampling campaigns and the different laboratories involved. While we recognize the risk of underestimating the number of detections with this approach, our priority was to minimize the occurrence of false positives, taking a conservative approach in reporting groundwater contamination. Given the relatively few detections in pre-1950 waters (SI: Section S5 and Table S9), we believe we have found a justifiable balance.

3.4.2. Age dating and recharge periods

Age dating, particularly using the tritium-helium $({}^{3}H/{}^{3}He)$ method, has proven effective for determining water recharge periods, especially in short-screened, non-pumped observation wells, which sample from a narrow age distribution (Visser et al., 2007a; Massmann et al., 2008; Kim et al., 2022; Desens et al., 2023). Uncertainties for non-degassed samples are estimated around ± 1 year (Desens et al., 2023), while degassed samples may have uncertainties up to five times larger after correction (Visser et al., 2007b). In our study, degassing mainly occurred in samples from farmland-sandy soils due to high nitrate loads and subsurface denitrification, leading to N2 gas buildup. Corrections were based on measured Total Dissolved Gas pressures (SI: Section S2). Given the uncertainty ranges of the apparent ages, potential misclassifications due to aggregation over 10-year recharge periods are limited to one period and could occur in either direction (younger or older). Such misclassifications might increase uncertainty in detection percentages or concentrations within these periods or result in detections in periods with no historical emissions, such as 1965-1980 and pre-1950. However, these instances are rare (see Section 3.4.1).

Alternative tracers like CFCs, SF₆, or ⁸⁵Kr are sensitive to subsurface

degradation (CFCs) or degassing (SF₆, 85Kr), affecting derived ages, particularly in the partly anoxic conditions of our study area (Visser et al., 2009b). Danish researchers responsible for regional monitoring of agricultural pollutants have shifted to tritium-helium age dating since 2012 due to the stabilization of atmospheric CFC concentrations around 2000 and the degradation of CFCs in anoxic waters hindering their applicability (Thorling et al., 2019; Kim et al., 2022).

Converting sampling years to recharge years extends the temporal scope of monitoring programs, which is particularly useful for detecting various pesticides, metabolites, and emerging contaminants from early recharge periods. For example, chloridazon metabolites, bentazon, and BAM were frequently detected during the 1980-1990 and 1990-2000 recharge periods, aligning with findings in Denmark for similar recharge years (Kim et al., 2022). Kim et al. excluded well screens with anoxic groundwater due to issues with CFC degradation, potentially introducing a bias towards oxic waters. This bias is likely, given our study's high detection rates of BAM and bentazon in Fe-reduced water using tritium-helium dating, which is not affected by tracer degradation. Similarly, PFOA and PFBA were frequently detected during the 1980-1990 and 1990-2000 periods, with PFBS detection since 2000, consistent with findings by Buszka et al. (2023) using tritium-helium age dating in the US NWOP. Buszka et al. also confirmed the lack of associations between redox categories and PFAS, including PFBS and PFHxS. These results highlight the potential of the proposed framework for use in short-screened observation wells in regional monitoring programs, such as the GRUMO network in Denmark, Dutch regional and national monitoring networks, and parts of the US NWQP (Lindsey et al., 2023).

The proposed methodology, which combines redox classification with recharge periods, overcomes issues arising from the interannual variability of pesticide and emerging contaminants concentrations over the monitoring periods 2012-2019 (most compounds) and 2019-2022 (PFAS). Such variability can result from seasonal changes in contaminant loads or differences in sampling and laboratory practices, which affect LOQs. Long-term monitoring programs often undergo revisions, potentially creating artificial trends due to changes in LOQs over time. To manage variability caused by changing LOQs, all measured values below the highest LOQ in the dataset were set to the LOQ, categorizing these values as non-detects. By analyzing temporal patterns based on recharge years instead of sampling years, data from successive sampling campaigns can be integrated, allowing for the assessment of detection percentages for recharge periods and redox classes in redox-age diagrams. Although this approach may increase variability in concentrations and detection percentages within redox classes or recharge periods, thus adding to the overall noise, it still enables the assessment of long-term trends related to recharge periods (e.g., Kim et al., 2022; Visser et al., 2007a). In conclusion, we support the assertion by Kim et al. (2022) that the recharge year approach effectively distinguishes between actual signals caused by changing contaminant inputs, such as those resulting from nutrient and pesticide regulations, and artificial signals arising from the aggregation of different ages of groundwater.

3.4.3. Redox classification

Fig. 5 illustrates the heterogeneous nature of redox conditions in the first 25 m of the subsurface in our study area, which includes a significant proportion of Fe-reduced and SO₄-reduced groundwater. This heterogeneity creates diverse conditions for processes such as microbial degradation (Lyngkilde and Christensen, 1992; Lyngkilde et al., 2013; Kivits et al., 2018; Christensen et al., 2000). Compared to other groundwater settings studied in the Horizon-2020 GeoERA HOVER project (Pinson et al., 2020, 2021) and in the United States by the USGS (McMahon and Chapelle, 2008; McMahon, 2012; Tesoriero et al., 2024), our study area shows relatively high proportions of anoxic groundwater. The abundance of anoxic groundwater, comprising our Fe-reduced and SO₄-reduced waters, is attributed to the reactive subsurface, rich in organic matter and Fe-sulfides, which serve as electron donors for reduction reactions (Zhang et al., 2009; Hartog et al., 2002).

The redox classification boundaries were established to provide a robust classification for samples collected in regional monitoring networks (SI: Section S3), resulting in relatively high thresholds of 5, 2, and 0.5 mg/l for nitrate, sulfate, iron, and manganese, respectively, compared with the Danish and US studies mentioned. Oxygen and methane measurements were not included in our classification due to quality control issues with oxygen measurements and the lack of routine methane measurements in our regional monitoring program. However, we validated the classification using methane and sulfide measurements in a subset of our data (SI: Section S3 and Figs. S5 and S6). These data confirm the classification, with Fe-reduced samples sometimes containing H₂S, indicating ongoing sulfate reduction, and SO₄-reduced samples showing elevated methane levels, suggesting ongoing methanogenesis in this redox class. A small number of samples containing both nitrate and iron, a combination not thermodynamically stable, were classified as mixed. This mixed class comprises only a limited number of samples, likely representing depth transects near the Fe/NO3 redox boundary (Postma et al., 1991), due to the short well intervals sampled in observation wells, which are not pumped for water production and therefore display a narrow range of groundwater ages (see also Desens et al., 2023).

The diversity of redox conditions in our study area was beneficial for understanding the mobility and degradation potential of the studied pesticides and emerging contaminants, as samples from all redox classes were present for most land use types and recharge periods. However, the number of SO₄-reduced samples was relatively low, especially in more vulnerable conditions such as farmland-sandy soils. Although large proportions of anoxic conditions may not be representative of other parts of Europe, they are indicative of other river deltas and coastal regions worldwide, including the Red River delta in Vietnam, the Ganges delta in Bangladesh, the Mississippi delta and coastal regions in the eastern US, and areas dominated by impermeable glacial tills like large parts of Denmark (Koch et al., 2019; Pinson et al., 2021; Buszka et al., 2023). The substantial nitrate loads in shallow groundwater, resulting from intensive livestock farming in this part of the Netherlands, have significantly impacted groundwater quality but have not generally led to nitrate breakthrough in deeper drinking water production wells. This is due to the reactive subsurface and denitrification reactions, which limit the extent and depth of nitrate contamination (Zhang et al., 2012). Interestingly, our study indicates that many pesticides and emerging contaminants, including PFAS, are not confined to the Oxic/suboxic groundwater zone where nitrate is present but can migrate to greater depths without substantial degradation or sorption. As a result, contamination of drinking water production wells by these substances is more widespread than by nitrate (Sjerps et al., 2019).

4. Conclusions

In our study, ³H/³He apparent groundwater age and redox status showed large heterogeneity over depth within and between the studied land use types, making explicit redox classification and age dating approaches vital for understanding patterns of groundwater quality parameters. The heterogeneity in groundwater age with depth exceeded initial expectations based on straightforward age models and theoretical concepts, complicating the interpretation of contaminant patterns and trends, particularly since the redox status and groundwater age appeared to be decoupled. We, therefore, adopted a classification and visualization approach that mitigates the uncertainties arising from spatial and depth-dependent variations in both groundwater age and redox status, using a large dataset of ³H/³He apparent ages to determine recharge periods for the classification process. Establishing the initial concentration of tritium $({}^{3}H_{initial})$ from measured ${}^{3}H$ and ${}^{3}He_{trit}$ aided in differentiating between water recharged by precipitation and water recharged from the Meuse River. It also facilitated the identification of waters with mixed ages and those predating 1950.

Applying this classification and visualizing the data in redox-age

diagrams, we demonstrated that most of the detections of pesticides, metabolites, and emerging contaminants were observed in the youngest recharge periods (2000-2010 and 2010-2020) and in agricultural areas. However, several contaminants were systematically detected in older water, such as the metabolites BAM and desphenyl-chloridazon, and the short-chain PFCAs, PFOA, and EDTA; these substances are clearly mobile and persistent in the regional groundwater system and under redox conditions ranging between oxic and sulfate-reduced. By comparing the presence of contaminants in specific recharge periods and redox classes with the known application or leaching history, deductions could be made about retardation (e.g. PFOS) and degradation (e.g. 2-hydroxyatrazine, benzotriazole), which explain the lower detection frequencies in water from earlier recharge periods. Utilizing age dating to identify recharge periods also aided in detecting trends in pesticide leaching over time in relation to government regulations and admission bans. Specifically, it revealed that newer recharge periods, post-ban implementation, exhibited lower concentrations and/or reduced abundance of DMS, bentazon, MCPP, and 1,2-DCP detections. Still, the ample presence of many pesticides and emerging contaminants in Fe-reduced water and in water from earlier recharge periods (1980-1990 for example) implies that these contaminants pass through the NO₃-Fe redox cline and may migrate to the larger depths of drinking water production sites, without substantial degradation or sorption. As such, these microcompounds pose a larger threat to the contamination of Dutch fresh groundwater resources than nitrate. Especially for shortchain PFASs (PFBA, PFBS, PFHxA PFHpA, PFHxS) and PFOA, the undegraded transport to deeper groundwater poses a potential threat for waterworks that partially abstract water from the last 40 recharge years.

Overall, the study enhanced the understanding of the fate of a wide spectrum of pesticides and emerging contaminants across various redox conditions, groundwater ages, and land use types, which collectively influence their temporal and spatial patterns in relation to contaminant pressures. Identifying the recharge year from age-dated groundwater helps to correlate the presence of pesticides and emerging contaminants with specific periods of farmland application or river water recharge, thereby elucidating the leaching history and sources of contamination. The framework presented has the potential to improve the interpretation of large groundwater datasets collected from dedicated, short-screened observation wells, focusing on detecting trends and trend reversals of pesticides and emerging contaminants in relation to their emission histories. This includes networks such as the Danish GRUMO network (Thorling et al., 2019; Kim et al., 2022), the Dutch national and regional monitoring networks, and portions of the US NWOP program that sample shallow observation wells (e.g., Buszka et al., 2023).

CRediT authorship contribution statement

Hans Peter Broers: Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. Tano Kivits: Writing – review & editing, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. Jürgen Sültenfuß: Writing – review & editing, Validation, Methodology, Formal analysis, Data curation. Matthijs ten Harkel: Writing – review & editing, Resources, Funding acquisition, Data curation, Conceptualization. Mariëlle van Vliet: Writing – review & editing, Visualization, Validation, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments & data policy

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Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT 3.5 in order to improve readability and language. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Appendix A. Supplementary data

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