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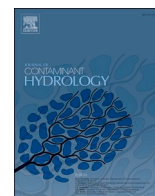
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Degradation of seven pesticides and two metabolites before and during aquifer storage transfer and recovery operation

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ABSTRACT

Degradation of 7 common pesticides (bentazon, boscalid, chloridazon, fluopyram, flutolanil, imidacloprid, and methoxyfenozide) and 2 metabolites of chloridazon (desphenyl-chloridazon, and methyl-desphenyl-chloridazon) was studied in an anoxic and brackish sandy aquifer before and during Aquifer Storage Transfer and Recovery (ASTR) operation. Fresh tile drainage water was injected and stored for later re-use as irrigation water. We hypothesized that electron acceptors (O_2 , NO_3), dissolved organic carbon (~ 24.7 mg/L), nutrients (NO_3^- : ~ 14.1 mg/L, NH_4^+ : ~ 0.13 mg/L, PO_4^{3-} : ~ 5.2 mg/L), and biodegrading bacteria in tile drainage water could stimulate degradation of the pesticides and metabolites (ranging between 0.013 and 10.8 $\mu\text{g/L}$) introduced in the aquifer. Pesticide degradation was studied at 6 depths in the aquifer using push-pull tests lasting ± 18 days before the onset of ASTR operation. Degradation was too limited to quantify and/or could not be assessed because of the potential occurrence of pesticide retardation. Utilizing push-pull tests to obtain degradation constants should only be considered in future studies for non-retarding pesticides with relative low half-lives (here < 20 days). During ASTR operation, pesticide degradation was studied at the same depths during 3 storage periods equally spread over 1.5 years of ASTR operation. Overall, trends of degradation were observed, although with relatively high half-lives of at least 53 days. Microbial adaptation of the aquifer and/or bioaugmentation by the injected biodegrading bacteria did not result in enhanced degradation during consecutive storage periods. Operational monitoring data over longer periods and distances yielded half-lives of at least 141 days. The slow degradation mostly agrees with previous studies. The injected tile drainage water composition did therefore not notably stimulate pesticide degradation. The relatively persistent behavior of the studied pesticides/metabolites implies that ASTR abstracted water will have generally high pesticide concentrations, and non-abstracted water may form a contamination risk for the surrounding native brackish groundwater.

1. Introduction

Managed Aquifer Recharge (MAR) is a quickly growing technique to intentionally replenish groundwater for later re-use (Dillon et al., 2019; Sprenger et al., 2017). MAR application has been initially focused on natural waters from streams, lakes, and aquifers (Dillon et al., 2019), but nowadays injected water is increasingly originating from more polluted waters, such as treated wastewater (e.g., Sheng, 2005; Vanderzalm et al., 2020), surface water (Jones and Pichler, 2007), or, as in the current study, tile drainage water from agricultural lands (Kruisdijk and van Breukelen, 2021). Tile drainage water originates from an agricultural

drainage system, which is designed to remove excess water in agricultural fields via subsurface pipes. This system optimizes crop growth and prevents rotting and crop death. Residence and transport of infiltrated water in aquifers is known to often improve water quality during MAR (e.g., Bekele et al., 2018; Dillon et al., 2003). In the current study, we assessed the degradation rates of pesticides and metabolites as introduced with tile drainage water during MAR operation, in order to better assess the risks for groundwater contamination.

Pesticide degradation depends on the physicochemical characteristics of the pesticide (Arias-Estevéz et al., 2008; Fenner et al., 2013), its initial concentration (Baumgarten et al., 2011; Oberleitner et al., 2020),

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and aquifer conditions, such as temperature (Munz et al., 2019; Storck et al., 2012), pH (Arias-Estévez et al., 2008; Kah et al., 2007), redox conditions (Bertelkamp et al., 2016c; Greskowiak et al., 2006), microbial activity and diversity (Poursat et al., 2019; Regnery et al., 2017), and dissolved organic carbon concentration and composition (Bertelkamp et al., 2016a; Regnery et al., 2015). Greskowiak et al. (2017) compared biodegradation rate constants of 82 emerging organic compounds (of which 8 pesticides) from 48 studies, and observed that most of the rate constants vary over >3 orders of magnitude. This indicates the large impact of the above-mentioned conditions on pesticide degradation.

Microbial adaptation is another factor influencing pesticide degradation. It is defined as the time needed for the microbial population to adjust to a new introduced chemical (Alexander, 1999). Adaptation times can vary between a few hours to several years (Alexander, 1999; Baumgarten et al., 2011), but generally do not exceed 6 months (Hoppe-Jones et al., 2012). During this time, the microbial community changes in composition and/or in abundances. Furthermore, biodegradation can be enhanced by introducing new types of bacteria - as naturally part of the infiltration water - to the aquifer during MAR (e.g., bioaugmentation). Microbial adaptation and bioaugmentation are both often indicated by increasing pesticide degradation rates over time (Fetter et al., 1999; Hoppe-Jones et al., 2012).

Degradation of pesticides or other organic micro pollutants have been studied before in full-scale MAR systems, for example, riverbank filtration sites (e.g., Hamann et al., 2016; Oberleitner et al., 2020), basin recharge systems (Kuster et al., 2010), and Aquifer Storage and Recovery (ASR) sites (e.g., Page et al., 2014; Stuyfzand et al., 2007). Many of these studies focused on MAR systems with travel times up to several years, which permitted the use of averaged input levels as water composition was substantially homogenized during aquifer transport (Wiese et al., 2011). This approach is not suitable for smaller scale systems as in the current study, as aquifer travel times between injection and abstraction can be relatively short (in the order of days to weeks) and concentrations of the injected water can fluctuate considerably (Huntscha et al., 2013).

Aquifer Storage Transfer and Recovery (ASTR) is one of the various methods of MAR, wherein water is stored in an aquifer during wet periods via well injection and abstracted from another well when needed. In the current study, we monitored an ASTR system, in which fresh tile drainage water is collected from an agricultural parcel during wet periods, injected and stored in the originally brackish coastal aquifer, and abstracted when needed (e.g. during droughts) for irrigation purposes on the same plot. We focused on the degradation of 7 common pesticides and 2 metabolites. The current research is a follow-up on the research performed by Kruisdijk et al. (2022). They studied pesticide sorption during ASTR in the same aquifer as the current study. The obtained sorption parameters in Kruisdijk et al. (2022) were used in the analysis of the current research, which is appropriate as about the same set of pesticides was studied at the same depths.

We hypothesized that conditions in the current MAR application are favorable for pesticide degradation, as injected tile drainage water contains electron acceptors (e.g., O₂, NO₃), nutrients, DOC, and likely biodegrading bacteria, besides the injected pesticides and metabolites. These factors can stimulate biodegradation (Aldas-Vargas et al., 2021; Luo et al., 2019), while in oligotrophic groundwater systems biodegradation is often limited due to limited carbon and nutrient sources (Egli, 2010). Push-pull tests were performed to assess pesticide degradation in the native aquifer before the start of ASTR operation. Furthermore, pesticide degradation was monitored during three storage periods of ASTR operation and by periodical operational monitoring. The research objectives of the current study were to (i) determine degradation rate constants for several pesticides and metabolites at 6 different depths within the aquifer to better assess the risks for groundwater contamination during MAR; (ii) assess if degradation rate constants increase over time in subsequent storage periods due to microbial adaptation

and/or bioaugmentation; (iii) compare the obtained degradation rate constants to those obtained for similar groundwater systems to assess if the injection of aerobic, nutrient- and DOC-rich, and microbially active tile drainage water favors pesticide degradation; and (iv) assess the utility of push-pull tests to assess pesticide degradation in MAR systems.

2. Methods

2.1. Field site description

Pesticide degradation was examined in an Aquifer Storage Transfer and Recovery (ASTR) system for agricultural use in the North-Western part of the Netherlands (coordinates: 52.8883, 4.8221). Injected water is collected from a tile drainage network approximately 1 m below the 10 ha agricultural parcel (Fig. 1). Tile drainage water in this network ends up in a collection drain, from where it is discharged to the ASTR system. The collected tile drainage water is injected in the aquifer by 2 wells (well screens ranging from 11.5 to 33.0 m below surface level (b.s.l.), injection well A and B). The water can be retrieved by 4 abstraction wells (well screens ranging from 12.0 to 23.0 m b.s.l.) in periods of drought and re-used for crop irrigation. A Holocene peaty clay layer confines the target aquifer, ranging from surface level to about 10 m-b.s.l. The sandy aquifer itself is of late Pleistocene and Holocene origin and reaches to about 45 m-b.s.l. For monitoring purposes, 2 sets of 6 piezometers (1-in. diameter) were constructed at 2.5 m (monitoring well (MW) 1–6) and at about 15 m (MW-B1-B6) distance from injection well A (Fig. 1). Kruisdijk et al. (2022) studied pesticide sorption at the same monitoring wells (MW1–6), and observed that the hydraulic conductivity was highest at the well screen depth of MW4, moderate at MW3 and 5, and relatively low at MW1,2, and 6.

2.2. Overview of study and ASTR operation

Fig. 2 shows an overview of the total injected volumes during ASTR operation. Before the start of ASTR operation, push-pull tests were performed from 25 February till 18 March 2019. ASTR operation started with the injection of 2700 m³ water in the first operation period. During operation period 2 and 3, 2900 and 4300 m³ of water were injected, respectively. Storage periods took place after each operation period: in winter 2019 (from 19 December 2019 to 2 February 2020), fall 2020 (from 14 October 2020 to 24 November 2020), and spring 2021 (from 18 March 2021 to 03 May 2021).

2.3. Push-pull tests

2.3.1. Method

Push-pull tests consist of a 'push'-phase during which water with a known quality is injected through a groundwater well, and a subsequent 'pull'-phase during which the injected water is gradually abstracted. Abstracted water is periodically sampled, after which the water quality changes of these samples were assessed.

Push-pull tests were performed in 6 monitoring wells (MW1–6) located at different depths ranging from 11.4 to 32.2 m b.s.l. (Table 1). Samples from the native groundwater were taken before the start of the push-pull tests. Injection water consisted of approximately 300 L tile drainage water, to which 0.1 mmol/L Br (as NaBr) was added as a conservative tracer, and a solution with pesticides and metabolites selected on the basis of a multi-criteria analysis (for more information see Kruisdijk et al. (2022)). The reactant solution was prepared in advance, and consisted of the pesticides bentazon, boscalid, chloridazon, fluopyram, flutolanil, imidacloprid, methoxyfenozide, and the metabolites of chloridazon: desphenyl-chloridazon (D-chloridazon) and methyl-desphenyl-chloridazon (MD-chloridazon). Approximately 9 mg of each pesticide was added to 6 L of distilled water. Next, the solution was mixed for 48 h using a magnetic stir plate. A small coagulate of the reactants developed in the bottle, which was removed from the solution.

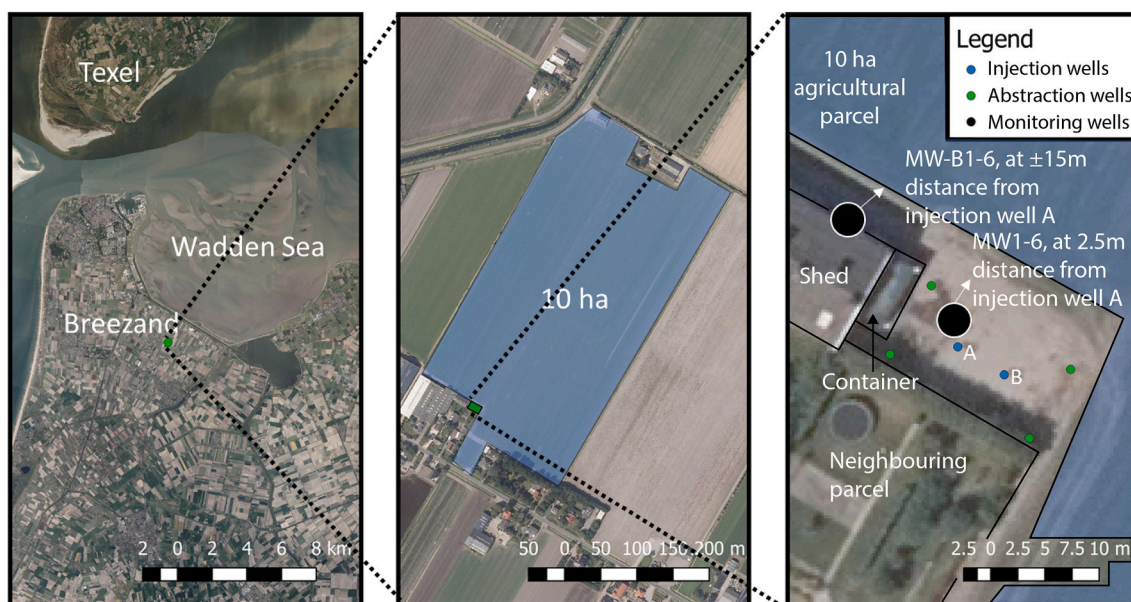


Fig. 1. Overview of the field site location in Breezand, in the North-Western part of The Netherlands. The left panel shows the ASTR pilot location. The drained agricultural field is shown in light blue in the middle panel, where the location of the ASTR system is displayed as a green square. The right panel shows the ASTR system and monitoring wells in detail. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

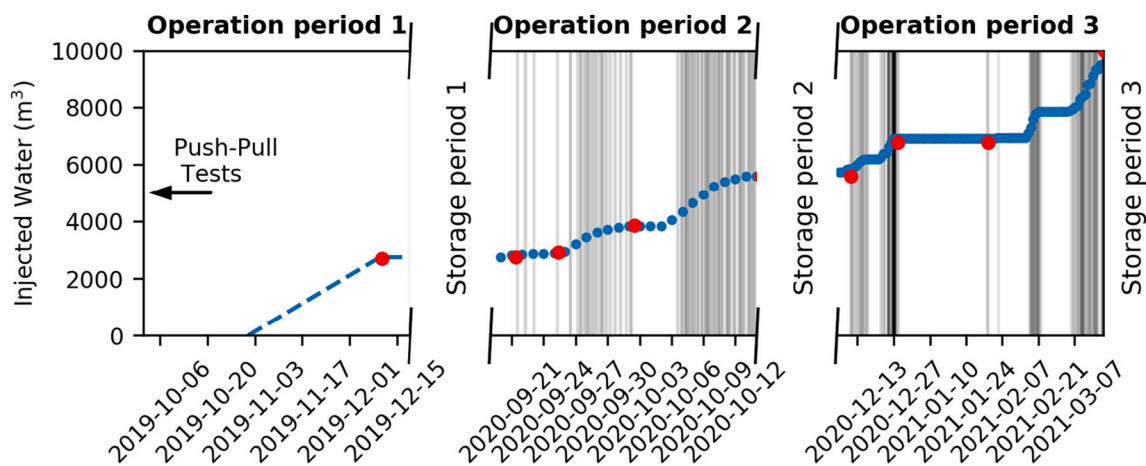


Fig. 2. Overview of the injected water volumes and the different experiments. The blue dots show the monitored injected volumes. In operation period 1, no monitoring was performed: the blue dashed line shows a linear interpolation between the start and measured end volume. The red dots display the manual control readings. The grey vertical bars in the background show the periods during which injection occurred (only for operation period 2 and 3). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Therefore, final reactant concentrations were somewhat lower than aimed at. Lastly, the obtained solution was divided over 6 glass bottles of 1 L, one bottle for each monitoring well. This would result in a maximum concentration of 5 $\mu\text{g/L}$ when added to the 300 L tile drainage water obtained from the collection drain, which fits inside the typical range of pesticide concentrations observed in tile drainage water observed in the current study (see Table 1). For each monitoring well, a storage tank containing tile drainage water plus reactants was prepared. In the storage tank, the tile drainage water was thoroughly mixed manually with a pole after adding the pesticide solutions.

Water in the storage tank was injected using a peristaltic pump (Eijkelkamp, the Netherlands) through each of the 6 monitoring wells in approximately 2.5 h, with a steady flow of about 2 L/min (push-phase). Four water samples were taken of the injected water equally spread over time. During the pull-phase, the period in between sampling was for the first samples 4 h but gradually increased until maximum three days in

between the last samples. The total push-pull test duration was 17 or 18 days, during which 14 water samples were taken. During the first 12 samples, 360 L water was abstracted (12×30 L, 30 L is substantially more than the max. Standing well volume of 17 L). On the last day, a total of 120 L was abstracted, during which 2 water samples were collected after abstraction of 60 and 120 L.

2.3.2. Data analysis

First-order degradation rate constants (k) were determined based on the well-mixed reactor model (Haggerty et al., 1998), which was successfully used in previous studies (e.g., Huntscha et al., 2013; Kruisdijk and van Breukelen, 2021; Vandenbohede et al., 2008). This model is shown to be accurate when the push-phase takes substantially less time than the pull-phase, which is valid in our case (push-phase: 2.5 h, pull-phase: ± 400 h). To assess the significance of the calculated rate constants, 95% confidence limits were calculated from the variance of the

Table 1

Composition of mean injected tile drainage water (TDW), ambient groundwater in monitoring wells. Mean tile drainage water concentrations and their standard deviations have been determined from 123 analyzed water samples during ASTR operation.

		Mean. TDW	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6
Sample date	–	25-02-2019: 18-03-2021	Between 25-02-2019 and 02-03-2019					
Depth filter	m-b.s.1	–	11.4–12.4	15.0–16.0	18.3–19.3	22.8–23.8	25.9–26.9	31.2–32.2
Temp	°C	10.5 ± 2.3	10.6	10.6	12.7	10.7	9.9	12.2
pH	–	7.45 ± 0.30	6.7	6.8	7.3	6.5	6.6	6.2
EC	µS/cm	1780 ± 389	1879	1823	1996	3331	5250	9219
DOC	mg/L	24.7 ± 4.2	8.96	7.45	7.13	6.11	3.78	3.74
Water composition								
O ₂	mg/L	6.4 ± 1.9	0	0	0	0	0	0
Cl	mg/L	160 ± 61	400	399	450	1010	1780	3170
Br	mg/L	0.4 ± 0.3	1.6	1.6	1.9	4.0	7.2	13.0
NO ₃	mg/L	14.1 ± 11.3	0	0	0	0	0	0
PO ₄	mg/L	5.21 ± 0.80	1.29	0.86	0.28	0.81	0.82	4.69
SO ₄	mg/L	193 ± 55	1.0	1.1	0.6	1.4	1.1	1.4
Alkalinity	mg/L	367 ± 13	254	186	124	143	82.1	77.8
Na	mg/L	90.4 ± 37.8	173	180	131	199	170	419
K	mg/L	52.3 ± 14.0	7.91	6.76	8.53	12.3	17.2	39.9
Ca	mg/L	172 ± 42.9	188	198	222	462	817	1200
Mg	mg/L	31.1 ± 7.4	27.4	31.1	33.4	67.2	132	154
NH ₄	mg/L	0.13 ± 0.11	1.49	0.86	0.84	1.73	1.50	8.25
Fe(II)	mg/L	0.14 ± 0.19	8.79	13.7	14.3	13.7	26.7	14.8
Mn(II)	mg/L	0.43 ± 0.14	1.89	1.03	0.94	1.94	3.99	6.82
As	µg/L	9.3 ± 2.3	<1.0	<1.0	1.01	<2.5	<5.0	<5.0
Pesticides and metabolites								
Bentazon	µg/L	0.075 ± 0.12	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Boscalid	µg/L	0.045 ± 0.026	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Chloridazon	µg/L	0.087 ± 0.13	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
D- chloridazon	µg/L	11 ± 3.7	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
MD-chloridazon	µg/L	1.9 ± 0.53	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fluopyram	µg/L	0.62 ± 0.20	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Flutolanil	µg/L	0.21 ± 0.12	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Imidacloprid	µg/L	0.044 ± 0.10	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Methoxyfenozide	µg/L	0.013 ± 0.019	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

degradation rate constants (Schroth et al., 2000).

First order reaction rate constants were estimated based on Eq. (1) developed by Haggerty et al. (1998), which is valid if the retardation factors of the tracer and reactants are identical,

$$\ln\left(\frac{C_r(t^*)}{C_r^*(t^*)}\right) = \ln\left[\frac{1 - e^{-kT_{inj}}}{kT_{inj}}\right] - kt^* \quad (1)$$

where $C_r^*(t^*)$ and $C_r(t^*)$ are normalized concentrations of respectively the reactant and the tracer (–) at time t^* (days), k is the first-order reaction rate constant of the reactant (day^{-1}), T_{inj} is the duration of the push-phase (days), and t^* is the time elapsed since the push-phase (days). Br was used as the tracer for MW1-MW4. Unfortunately, Br concentrations in injected water (8.2–9.6 mg/L) were relatively close to the native groundwater concentrations at MW-5 and MW-6 (7.2 and 13.0 mg/L, respectively). Cl concentrations varied more distinctly between injected (255–436 mg/L) and native groundwater for MW-5 and MW-6 (1780 and 3170 mg/L, respectively) and was used as the tracer at these depths. Rate constants were estimated by fitting a regression line to a plot of $\ln\left(\frac{C_r(t^*)}{C_r^*(t^*)}\right)$ versus t^* , which generates a line with a slope $-k$. Only the water samples were used where $C_r^*(t^*) > 0.2$. We assumed that assessing water samples where $C_r^*(t^*) < 0.2$ resulted in larger uncertainties as, (i) lower $C_r^*(t^*)$ infers that a larger part of the abstracted water originates from native groundwater, which means that the tracer and reactant concentrations become lower and measurement errors increasingly influence the obtained k , and (ii) tracer concentrations in groundwater are not 100% homogeneous, which leads to higher uncertainties for lower $C_r^*(t^*)$. Normalized concentrations were calculated for tracer and reactants following Eq. (2),

$$C_{tr}^* = \frac{C_{tr} - C_{gw}}{C_{inf} - C_{gw}}, C_r^* = \frac{C_r}{C_{1^{st} \text{ sample}}} \quad (2)$$

where C_{tr} is the tracer concentration during the ‘pull’-phase (mg/L), C_{gw} the concentration in native groundwater (mg/L), C_{inf} the mean concentration of the 4 samples taken during injection (mg/L), C_r the reactant concentration during the ‘pull’-phase (mg/L), and $C_{1^{st} \text{ sample}}$ the concentration of the first abstracted sample during the ‘pull’-phase (mg/L). Different equations were used for the normalized concentrations of the tracer and the reactants, because we observed unexpectedly higher concentrations in the first samples of the ‘pull’-phase than in the injection phase for some of the reactants. This suggests that the total concentration of the added reactant was not fully analyzed during the injection phase, for which we cannot provide a clear explanation. Therefore, we used $C_{1^{st} \text{ sample}}$ for the reactants instead of C_{inf} . C_{gw} was 0 for the reactants and could therefore be neglected. A nonlinear least-squares routine was used to fit Eq. (1) to the observed concentrations in python (Python v. 3.6.4).

The influence of pesticide retardation on the push-pull test breakthrough curves was analyzed based on the analytical equation proposed by Schroth et al. (2000),

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left\{ \left(\frac{V_{ext}}{V_{inj}} - 1 \right) \right\} / \left[\frac{16}{3} \frac{\alpha_L}{r_{max}} \left(2 - \left| 1 - \frac{V_{ext}}{V_{inj}} \right|^{0.5} \times \left(1 - \frac{V_{ext}}{V_{inj}} \right) \right) \right]^{0.5} \right\} \quad (3)$$

where V_{ext} is the cumulative extracted volume, V_{inj} the cumulative injected volume, α_L the longitudinal dispersivity, and r_{max} the maximum radius of the 50% front position which was calculated with the equation below,

$$r_{max} = \sqrt{\frac{V_{inj}}{\pi b n R}} + r_w \quad (4)$$

where b is the aquifer thickness, n the effective porosity which was assumed to be 0.3, R the retardation factor, and r_w the radius of the well.

2.4. ASTR storage periods

ASTR operation was not continuous. Idle periods resulted from droughts or maintenance of the system. Groundwater flow was minimal (<0.01 m/d) based on groundwater levels (obtained from the Netherlands Hydrological Instrument via www.grondwatertools.nl/gw-sinbeeld/ (De Lange et al., 2014)) and hydraulic conductivity (2.5–25 m/day) in the proximity of the system (obtained from the REGIS II model via www.dinoloket.nl/ondergrondmodellen (Gunnink et al., 2013)). Storage periods of about 45 days were investigated in winter 2019, fall 2020, and spring 2021. Before each storage period, substantial tile drainage water volumes were injected (2700–4300 m³, see Fig. 1), during which pesticides and metabolites were not manually added. Therefore, only the pesticides and metabolites could be assessed present in tile drainage water injected during ASR operation. Water samples were taken periodically from MW1–6 to assess pesticide degradation over time during these storage periods. Before each sample, 1.5× the internal volume of the monitoring well was abstracted. First-order degradation rate constants were obtained by fitting a first-order regression line through the pesticide concentrations by a least-squares routine (Python v. 3.6.4). In this study, all obtained k were converted to half-lives (DT50),

$$DT50 = \frac{\ln(2)}{k} \quad (5)$$

2.5. Water analysis

Groundwater samples were directly analyzed in the field on alkalinity, electrical conductivity (EC) (C4E, Ponsel, France), pH/temperature/redox (PHEHT, Ponsel, France), and dissolved oxygen (OPTOD, Ponsel, France). Furthermore, all samples were filtered (0.45 μm) on site and stored immediately in the dark at 4 °C. A 60 ml glass vial was used for pesticide analysis with Liquid Chromatography – Mass Spectrometry (LC-MS; Xevo TQ-S micro, Waters, U.S.A.), and another vial for DOC analysis (NDIR; TOC-V CPH, Shimadzu, Japan). For more information about the assignment of the pesticides, their chemical physical-properties, detection limits, and analysis see S2. A 15 mL PE vial was used for analysis of anions with Ion Chromatography (IC; Compact IC pro, Metrohm, Switzerland), and another 15 ml PE vial was acidified with HNO₃ (69%, 1:100) for analysis with Inductively Coupled Plasma – Mass Spectrometry (ICP-MS; PlasmaQuant MS, Analytik-Jena, Germany) and Discrete Analysis (DA; AQ400, Seal analytical, UK).

3. Results and discussion

3.1. Pesticide degradation in the native aquifer before aquifer storage transfer and recovery operation

3.1.1. Hydrochemical conditions during the push-pull tests

Before Aquifer Storage Transfer and Recovery (ASTR) operation, push-pull tests were conducted to assess the initial capacity of the native anoxic brackish aquifer to degrade pesticides and metabolites in injected tile drainage water. Tile drainage water was injected at 6 different depths via the monitoring wells 1–6 (MW1–6) located at 2.5 m from injection well A during the ‘push-phase’ of the push-pull tests (Fig. 1). Injected tile drainage water had O₂ concentrations ranging from 5.4 to 9.6 mg/L, dissolved organic carbon (DOC) concentrations between 20.8 and 23.8 mg/L, and relatively high nutrient concentrations (NO₃: 41.1–49.7 mg/L, PO₄: 6.54–9.98 mg/L, NH₄: 0.04–0.85 mg/L). Water

temperature ranged from 7.0 to 14.4 °C, and pH from 7.2 to 8.0.

Table 1 shows the native groundwater composition at the well screen depths of MW1–6 before the push-pull tests and ASTR operation. The native groundwater was anoxic (O₂ and NO₃ below detection limit), with mainly Mn(IV)- and Fe(III)-reducing conditions based on the relatively high concentrations of Mn(II) and Fe(II), respectively (Table 1). The shallow part of the aquifer was relatively fresh (Electrical conductivity (EC) at MW1, 2, and 3 (11.4–19.3 m below surface) was between 1850 and 2000 μS/cm) and turned more saline with depth (EC at MW4, 5, and 6 (22.78–32.2 m below surface) was 3280, 5090, and 8930 μS/cm, respectively). During the ‘pull-phase’ of the push-pull tests, redox conditions changed rapidly in the abstracted water as shown in more detail in S3.2. Injected water became anoxic within 1 day of residence in the aquifer, and subsequently, NO₃-reducing conditions were observed at all depths. Furthermore, reductive dissolution of Fe and Mn-oxides probably occurred. SO₄ reduction was not observed, except at MW2. Any degradation of pesticides and metabolites thus occurred at about neutral pH under mostly NO₃ and/or metal-oxide reducing conditions during the push-pull tests.

3.1.2. Observed pesticide degradation during the push-pull tests

Fig. 3 shows the push-pull test results of fluopyram for a selection of depths (the classes stated in the labels will be explained later in this section). The results are shown for the other depths and pesticides/metabolites in S3.3. In the left panels, concentrations of the tracer (Br or Cl) and fluopyram gradually decreased because of dispersive mixing with native groundwater during the abstraction phase of the push-pull tests. Except for MW5 and MW6 (S3.3), where Cl concentrations were higher in native groundwater compared to injected tile drainage water due to the higher salinity at larger depths in the aquifer. Similar trends were observed for the normalized concentrations in the middle panels, where the occurrence of degradation was suggested by a faster decline of normalized fluopyram concentrations compared to those of the conservative tracer. In the right panel, linear regression was performed on the natural logarithm of the normalized fluopyram concentrations divided by the normalized tracer over time, from which the first-order degradation rate constants and half-lives (DT50) were estimated by Eq. (1). The calculated 95% confidence intervals were used to denominate the obtained k values as statistically significant when they excluded $k = 0$.

3.1.2.1. Influences of retardation on obtained DT50. The performed method is only valid when retardation is assumed negligible, as pesticide retardation can also result in decreasing pesticide concentrations which can influence the estimated DT50 value (Schroth et al., 2000). Degradation is indicated by normalized pesticide concentrations lower than those of the conservative tracer during the entire ‘pull’ phase (Haggerty et al., 1998), whereas sorption is indicated by initially lower concentrations until the arrival of the 50% front position (i.e. where the normalized tracer concentration = 0.5) followed by higher concentrations afterwards (Schroth et al., 2000) (see S3.1). Analytical solutions are not available which can disentangle sorption from degradation. Kruisdijk et al. (2022) obtained retardation factors (R) of about the same set of pesticides and metabolites at the same depths in the aquifer. For a short description of the method see S3.4. Most (32 out of 38) R values range between 0.8 and 2.0 (Table 2). The highest R values were observed at the top of the aquifer and generally decreased with depth, which corresponded with the higher sedimentary organic matter contents at the top of the aquifer compared to the bottom.

Before the onset of the push-pull tests, we simulated the influence of pesticide retardation on the push-pull test breakthrough curves using Eqs. (3) and (4). Schroth et al. (2000) stated that methodological errors of ≤14% could be expected in a physically and chemically homogeneous aquifer by using these equations. However, errors could be larger under more heterogeneous conditions. The variation in pesticide concentrations was <5%, ((1-relative concentration when $R = 2$ /relative

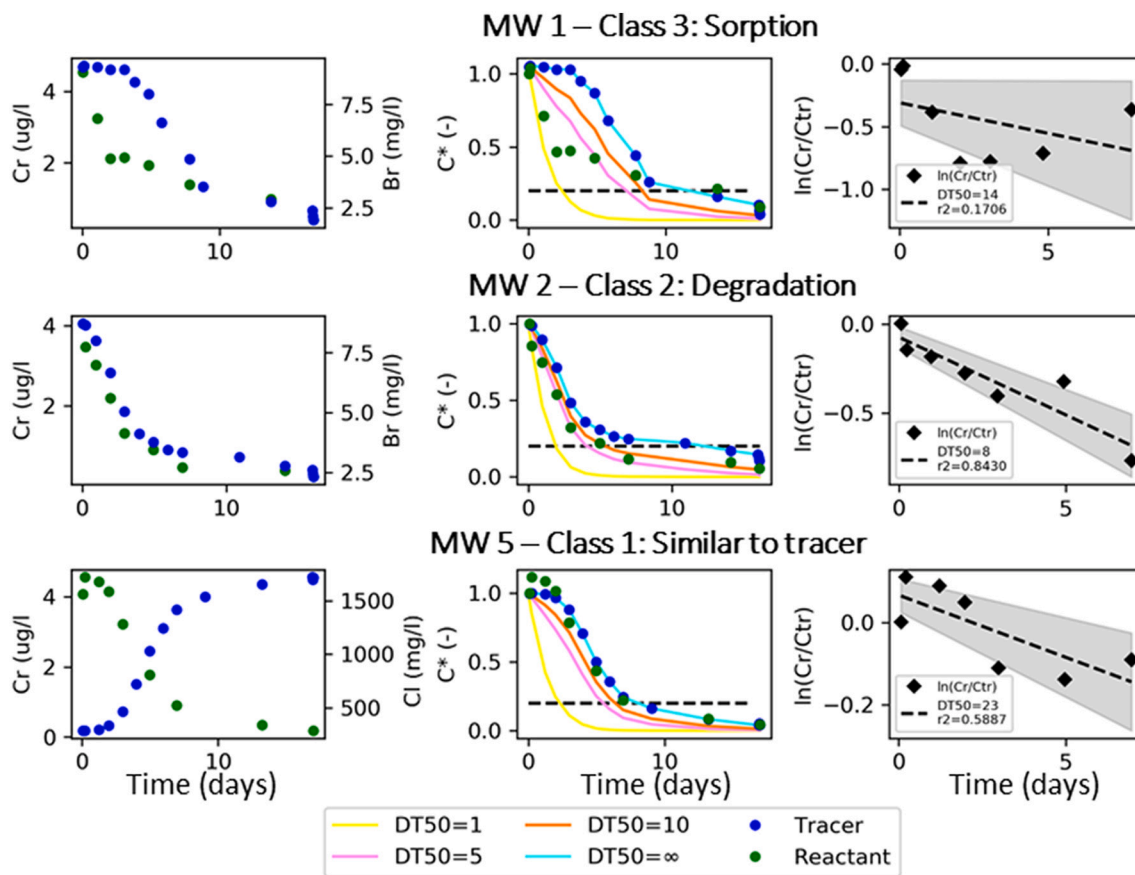


Fig. 3. Observed fluopyram concentrations and the calculated DT50 values from the push-pull tests for a selection of depths. The left panel shows the absolute concentrations of reactant and tracer. The middle panel displays the normalized concentrations of tracer and reactant including simulations for DT50 = 1, 5, 10 and infinity (∞ ; i.e. no degradation) days. The dashed line represents $C^* = 0.2$, all samples below this line were discarded for the estimation of the DT50. The right panel shows the natural logarithm of the normalized reactant divided by the normalized tracer concentration, from which the DT50 value is estimated by linear regression. The grey area behind the fitted line represents the 95% confidence intervals.

Table 2

Estimated DT50 value, the results of the qualitative degradation versus sorption assessment, and the retardation factors obtained from Kruidijk 2021 for the 7 studied pesticides and 2 metabolites. DT50 value followed with an asterisk are significant. The orange cells highlight the pesticides and metabolites and depths where the qualitative assessment indicates degradation. The grey cells show the pesticides/metabolites and depths for which no retardation factor was obtained and the red cell the negative DT50 values.

	MW1 11.4-12.4 m-b.s.l.			MW2 15.0-16.0 m-b.s.l.			MW3 18.3-19.3 m-b.s.l.			MW4 22.8-23.8 m-b.s.l.			MW5 25.9-26.9 m-b.s.l.			MW6 31.2-32.2 m-b.s.l.		
	DT50	Class	R	DT50	Class	R	DT50	Class	R	DT50	Class	R	DT50	Class	R	DT50	Class	R
Bentazon	32*	3		23*	1		40*	1	1	35*	1	1.1	45*	1	1	130	1	0.8
Boscalid	36	3	>2.0	8	4	>3.5	23	4	2.7	50	4	1	45	4	1.1	-15	4	1.2
Chloridazon	15*	3	>2.0	9*	2		27*	3		50	3	1	-609	1	1.1	-96	1	1
D-chloridazon	32	3	1.3	36	1	1.1	44*	3	1.1	-337	3	1	-56	1	0.8	-25	1	0.8
MD-chloridazon	20*	3	1.5	13*	2	1.2	38*	1	1.2	76	1	1	-116	1	0.9	-43	1	0.9
Fluopyram	14*	3	>2.0	7.9*	2	1.8	21*	5	1.5	34*	3	1.1	23*	1	1	-1115	3	1
Flutolanil	-19	3	>2.0	7.1	4		10*	4	1.7	-52	4		20	4	0.9	-12	4	1
Imidacloprid	10*	3		5.2*	2		13*	5		20*	5		15*	5	1.4	18*	5	1.2
Methoxyfenozide	14*	3		7.5*	2		43*	3		37*	3		25*	1		-103	1	

Classes:

1 = The reactant behaves similarly as the conservative tracer.

The reactant's behavior is different from the conservative tracer, due to:

2 = Degradation, 3 = Sorption, 4 = Unknown reasons (e.g., scattered concentrations), 5 = Sorption or degradation.

concentration when $R = 1$) $\times 100$) when estimating pesticide concentrations by $R = 2$ compared to $R = 1$ (S3.1). Based on these outcomes, we did not expect major interferences from pesticide retardation in the current study.

To examine the actual influence of sorption in the obtained data

during the push-pull tests, we first visually examined the trends observed in the Figs. S3-11 in S3.3 and categorized these trends in 5 classes (Table 2): (1) the reactant behaves similarly as the conservative tracer; or the reactant acts differently, due to (2) degradation, (3) sorption, (4) unknown reasons (e.g., scattered concentrations), or (5)

sorption or degradation (no clear distinction). Fig. 3 shows an example of the categorization of the push-pull test results for a selection of depths of fluopyram, where the trend at MW1 was categorized as sorption (class 3), at MW2 as degradation (class 2), and at MW5 as similar to the conservative tracer (class 1).

Table 2 presents the estimated DT50 values, the results of the qualitative assessment, and the retardation factors obtained from Kruisdijk et al. (2022). Kruisdijk et al. (2022) observed $R < 1$ at 2 depths for a few pesticides. The mechanism behind the $R < 1$ remained unclear, although a relation with DOC-associated transport seemed unlikely. Most estimated DT50 values were positive (51 out of 64). Negative DT50 values were observed during the push-pull tests but were all insignificant. Significant DT50 values (39 out of 64) ranged from 5.2 to 45 days.

At MW1, all pesticide and metabolite concentration trends resembled those associated with sorption. This corresponds with the retardation factors in Table 1, which show that pesticide sorption was most substantial at MW1 compared to the other depths. Nevertheless, sorption influences were not only observed if $R > 2.0$ (as suggested by the calculations using Eq. (3), S3.1), but also for $R = 1.3$ (D-chloridazon) and $R = 1.5$ (MD-chloridazon) at MW1. At the other depths, the influence of sorption was observed for 7 pesticides/metabolites where R was lower than 2 and was even observed when R was estimated about equal to 1. This shows that sorption played a substantially bigger role than expected based on the analytical equation of Schroth et al. (2000), which is additionally shown by the relatively large occurrence of the sorption related class 3 ($\pm 31\%$). The discrepancy between the analytical solution and the observed results is probably resulting from physical or chemical heterogeneity of the aquifer layers in the current study, which Schroth et al. (2000) stated as a drawback of this method. This made it impossible to estimate a realistic DT50 value for the pesticides and metabolites which were influenced by sorption.

3.1.2.2. Outcomes push-pull tests. The orange cells represent class 2, where a clear pesticide degradation trend was observed. Remarkably, such a degradation trend was only observed for 5 pesticides/metabolites (chloridazon, MD-chloridazon, fluopyram, imidacloprid, and methoxyfenozide) and only at MW2. These trends represented some of the lowest DT50 values (5.2–13 days). We question these degradation trends observed at MW2, as (i) we deem it unlikely that degradation only occurred at this depth for no apparent reason; (ii) no influences of sorption are observed while the R values are only slightly lower compared to MW1; and (iii) the results do not agree with the results obtained during the storage periods (Section 3.2). Nevertheless, no clear explanation can be given for the observed trends observed at MW2, despite degradation. DT50 values were also estimated for class 1: the class in which pesticides and metabolites visually act similar as the conservative tracer. In class 1, the minimum positive DT50 value was 23 days. Estimated DT50 values $> \pm 20$ days seem highly uncertain, as these DT50 values are substantially larger than the durations of the push-pull tests (7–12 days) which makes it troublesome to disentangle degradation and the scatter of pesticide concentrations.

In the current study, the obtained DT50 have a relatively low reliability, due to the unexpected effects of pesticide retardation and the relatively short time span of the push-pull tests in combination with the mostly high DT50 obtained. We learned that push-pull tests are only useful when pesticide degradation is relatively fast (here DT50 values < 20 days) and pesticide retardation is negligible. Huntscha et al. (2013) successfully obtained first-order degradation rate constants using push-pull tests but studied non-retarding organic micropollutants which degraded much faster (k values in order of hour^{-1}). From the data in the current study, we can conclude that degradation could have occurred for some pesticides and metabolites at MW2 before the start of ASTR operation, but generally it did not or was too small to observe (DT50 values $> \pm 20$ days).

3.2. Pesticide degradation during storage periods of ASTR operation

3.2.1. Hydrochemical conditions during storage periods

Periods of injection and storage periodically alternated depending on the availability of tile drainage water during ASTR operation. We assessed pesticide degradation during the storage periods when groundwater was stagnant. Collected groundwater samples were anoxic at wells MW1–6 at 2.5 m distance from infiltration well A during the storage periods. O_2 was thus fully consumed during transport of tile drainage water from the injection well to the monitoring wells. Similarly, NO_3 was already fully consumed at MW3 before the winter 2019 storage period started, and at MW6 for all storage periods (S4.2). NO_3 was initially present in all other cases (MWs and storage periods), but its concentrations were steadily decreasing until depletion reflecting ongoing denitrification during storage. Fe concentrations mostly gradually increased, which indicates reductive dissolution of Fe-(hydr)oxides. SO_4 concentrations were increasing at most depths during the storage periods, which is explained by pyrite oxidation linked to NO_3 -reduction. SO_4 concentrations decreased pointing to occurrence of SO_4 reduction at some depths and storage periods (all storage periods at MW2, winter 2019 storage period at MW3, and spring 2021 storage period at MW6). The simultaneous occurrence of different redox conditions likely points to aquifer heterogeneity at the grain-scale, and therefore different conditions in pore spaces (Jakobsen, 2007; Jakobsen and Postma, 1999). Abstracted water had a temperature range of 8.7–10.2 °C during storage period 1 (winter 2019), 11.7–13.9 °C during storage period 2 (fall 2020), and 7.2–13.7 °C during storage period 3 (spring 2021). During all storage periods, pH ranged from 6.6 to 7.3, DOC concentrations from 14.0 to 26.3 mg/L, PO_4 from 0.05 to 2.60 mg/L, and NH_4 from < 0.1 –1.3 mg/L. Pesticide degradation was, therefore, studied under mostly NO_3 - and metal-oxide reducing conditions in the presence of mostly relatively high DOC and nutrient concentrations.

3.2.2. Observed pesticide degradation during storage periods

3.2.2.1. Degradation of Fluopyram. DT50 values were calculated during storage periods of ASTR operation. Fig. 4 presents the DT50 values of fluopyram (which are calculated based on the obtained first order rate constants (k)) at the different aquifer depths during the three storage periods. The 95% confidence intervals show the significance of the obtained k values. The obtained k values were denominated statistically significant if the confidence interval excluded $k = 0$. The normalized standard error (NSE) is a measure of the scatter of the observed pesticide concentrations, where a low NSE indicates a more accurate DT50 value. For example, a NSE of 0.1 represents a mean deviation of the regression line of 10%. We show again the results of fluopyram, because significant degradation was observed during one of the storage periods and the NSE of the fitted data are smaller than those of most other pesticides and metabolites (S4.4).

Degradation of fluopyram is slow or not significant (DT50 values > 158 days or negative), except for the fall 2020 storage period for which a DT50 value of 59 days was estimated at MW 2. After the winter 2019 storage period, the ASTR system was not in operation for another 275 days (from 19 December 2019–19 September 2020). To assess long-term trends, water samples were taken 219 days (25 July 2020) after the start of this first storage period. These samples likewise show that degradation is slow, as observed concentrations after 219 days were only slightly lower than the concentrations during the storage period.

3.2.2.2. Degradation of all pesticides and metabolites. Table 3 shows the deduced DT50 values during the winter 2019 (W '19), fall 2020 (F '20), and spring 2021 storage period (S '21). All first order rate constants and their 95% confidence intervals can be found in S4.3. Most of the calculated DT50 values were significant (99 out of 162). Note that $\pm 26\%$ of the determined DT50 values was negative reflecting an

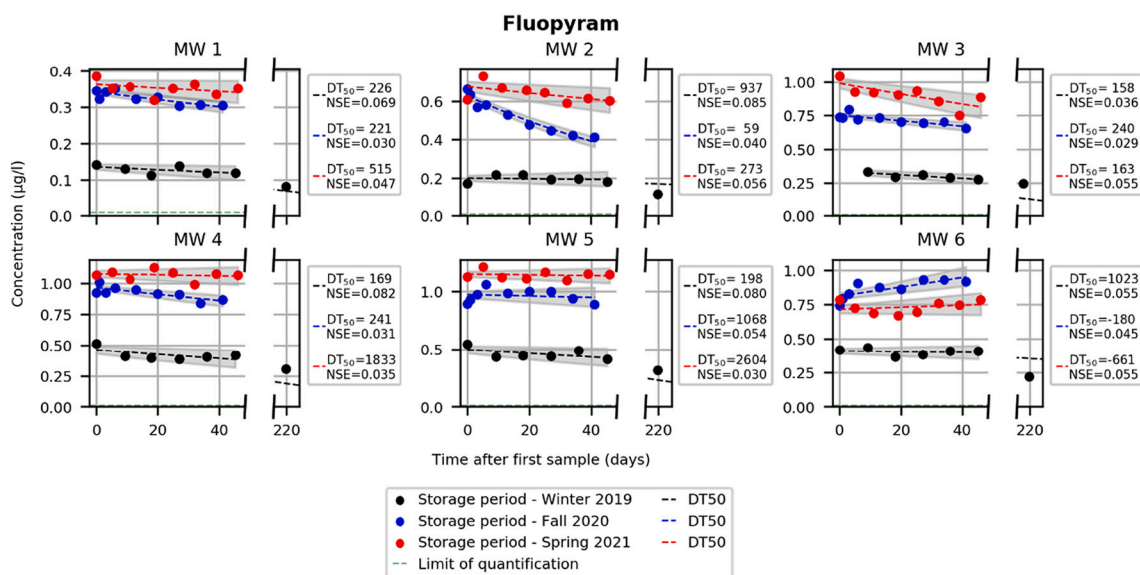


Fig. 4. Calculated DT50 values of fluopyram for the 6 different depths (MW1–6) and the three storage periods. Black, blue, and red dots show the observed concentrations during storage in winter 2019, fall 2020, and spring 2021, respectively. The dashed lines are fitted to the observed concentrations, from which the DT50 values are obtained. The grey area behind the fitted line represents the 95% confidence intervals. The limit of quantification (0.01 µg/L) is not visible in all panels, due to the scale. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Deduced DT50 values (days) at the different depths during the winter 2019 (W '19), fall 2020 (F '20), and spring 2021 storage period (S '21). DT50 values followed with an asterisk are significant. The green cells show the DT50 values where the NSE < 0.1. The grey cells display the storage periods where pesticide concentrations were below LOQ.

	MW 1			MW 2			MW 3			MW 4			MW 5			MW 6		
	W '19	F '20	S '21	W '19	F '20	S '21	W '19	F '20	S '21	W '19	F '20	S '21	W '19	F '20	S '21	W '19	F '20	S '21
Bentazon	-225*	877	283	-419	-147*	-188	-134	345	-145*	449	151*	-640	193	247	-387	209	-144	-334
Boscalid				72	-458	63*	227*	106	41*	54*	285	43*	63*	521	7006	-821	-160*	
Chloridazon	150*	-23035	210	171*	53*	76*	102*	312	232*	152*	155*	291	236	1794	164	172*	110*	304
D-chloridazon	196*	470*	-10528	112*	100*	1010	134*	-134*	499*	153*	-14679	-174*	754	492	394*	220*	-199*	257*
MD-chloridazon	-1445	63417	-594*	164*	185*	1004	176*	527	1448	264*	333*	-134*	586*	331*	177*	263*	-570*	274*
Fluopyram	226*	221*	515	937	59*	273*	158*	240*	163*	169*	241*	1833	198*	1068	2604	1023	-180*	-661
Flutolanil	30*	138*	179	-95	66*	-115	29*	260	83*	28*	116*	103*	27*	71*	1131	186	503	104*
Imidacloprid	147	92*	87	122*	39*	131	-1129	111*	86*	-280*	211*	-209	101*	139*	-325	-7431	-132*	216
Methoxyfenozide		-150*	-196		177*	-346		-597	1228		184*	137*		-235*	-309		171	107*

increasing concentration trend. Substantially low negative DT50 values were not observed (maximum negative DT50 value = -95 days, median = -280 days), but some of the negative DT50 values were significant. These significant negative DT50 values point to some uncertainty of the applied method as will be explained later in more detail. Faster degradation (0 < DT50 < 100 days) occurred mostly for the pesticides boscalid, flutolanil and imidacloprid. The lowest positive DT50 value (i. e. fastest degradation) observed is 27 days (flutolanil, MW 5), but the median positive DT50 value is 184 days which shows that degradation is mostly slow. This also corresponds with the pesticide concentrations in the samples taken 219 days after the start of the first storage period, as concentrations were above the limit of detection for 37 out of 64 pesticides at all depths. Most DT50 values <100 days were observed for pesticides at MW2 in the fall 2020 storage period. This seems to agree with the seemingly highest degradation rates at MW2 during the push-pull tests. It should be noted, however, that (i) the observed DT50 values during the push-pull tests were generally more than a factor 5 lower than observed during the storage periods, and (ii) these lower DT50 values were only observed during the 2nd (fall 2020) storage period, making it less likely that this layer in the aquifer has for some unknown reason special degradation capabilities.

3.2.2.3. Reliability obtained DT50 during storage periods. Our DT50 calculation method assumes for simplicity that (i) pesticide concentrations in the injected tile drainage water were constant over time, and (ii) that degradation was negligible during transport from the injection well to the monitoring wells. We can largely verify the second assumption, as the average age of sampled tile drainage water (2.4–5.77 days, S4.1) and the maximum age (~8.5 days, S4.1) at the start of the storage phase was considerably lower than the total duration of the storage phase (almost 50 days). Based on both assumptions, pesticide concentrations would be constant across the entire radius of abstraction (0.23–0.54 m, for calculation see S4.1) of the total sampled water volume during the storage period. Any occurrence of degradation during storage would then lead to a decline in concentrations over time while being homogeneous in space.

The concentration data, however, do show some degree of scatter which is much larger than the analytical measurement uncertainty and, in some cases, result in increasing concentration trends over time. We expect that these trends primarily reflect the temporal variation of pesticide concentrations in injected tile drainage water. A collected sample essentially presents a mixture of (slightly) different ages of injected tile drainage water, where with each subsequent collected

sample, the range in ages in the sample increases somewhat. When degradation is absent or very slow as in this aquifer, the scattering should mostly reflect temporal variations in pesticides concentrations in tile drainage water at the time of injection. Very low groundwater flow velocities (resulting in <0.5 m displacement over 50 days of storage) during storage may contribute to this effect. On the one hand, decreasing concentrations over time might in fact only reflect temporal variations in injected tile drainage water, while degradation does not occur. On the other hand, it should be noted that in the aforementioned case degradation might in fact be higher than calculated when in subsequent samples there is a tendency towards collecting tile drainage water which initially had higher concentrations. The bottom line is that calculated DT50 values are prone to some degree of uncertainty as concentrations in tile drainage water were not completely constant. The fact that (i) overall decreasing concentration time trends were observed, and (ii) most DT50 values were positive, points to general occurrence of degradation in the aquifer albeit at very low rates.

3.2.2.4. Outcomes storage periods. We arbitrarily decided to highlight pesticide trends with a minimum NSE of 0.1 (displayed in green in Table 3), as we considered these trends convincing after a visual inspection of the figures in S4.4. In this selection, only 6 of 86 DT50 are larger than 0 and smaller than 100 days. Despite the uncertainty in some of the DT50 values, this learns us that pesticide degradation is mostly slow (DT50 values >100 days or insignificant) during storage periods of ASTR operation. Furthermore, we do not see an increase in pesticide degradation rates, as an effect of microbial adaptation of the aquifer or bioaugmentation of the aquifer by the injected tile drainage water microbiome. Therefore, we expect that their effects (i) already occurred before the first storage period in the aquifer, or (ii) did not quantifiably occur in the aquifer during the storage periods.

3.3. Pesticide degradation during operational monitoring

Pesticide concentrations were periodically measured at the

monitoring wells ± 15 m away from injection well A during the entire period of ASTR operation. Fig. 5 shows the results for D-chloridazon and chloride (Cl). D-chloridazon is shown here as it was the only pesticide above the detection limit at MW-B4 and B3, together with bentazon. Results for the other pesticides can be found in S6.1. Cl was used as a natural conservative tracer, as concentrations were lower in injected tile drainage water compared to the native groundwater. Decreasing Cl concentrations, therefore, demonstrated the arrival of the injected tile drainage water at the monitored monitoring wells. Cl concentrations are relatively stable and indicative of native brackish-saline groundwater at MW-B1, 2, 5, and 6. Freshening is occurring to some extent due to the arrival of fresh tile drainage water at MW-B3 and more distinct at MW-B4. This shows that the hydraulic conductivity of the aquifer is higher at MW-B3 and B4 compared to the other depths. Injected tile drainage water preferentially flows through these layers, and, therefore, freshening is only observed here. At MW-B4, the Cl concentration decreased almost to that of injected tile drainage water (mean injected tile drainage water concentrations can be found in Table 1). D-chloridazon was detected above the detection limit only during the last sampling event at these 2 depth levels where the tile drainage water arrived.

Based on Eq. (2), normalized Cl and pesticide concentrations were calculated, where a normalized concentration of 1 presents injected tile drainage water and a normalized concentration of 0 the native groundwater. Pesticide concentrations can decrease due to degradation or sorption, while Cl as tracer is conservative and does not react. The fraction of pesticide left in the sample was calculated and corrected for the fraction of Cl, by dividing the normalized reactant concentration by the normalized tracer concentration: $\left(\frac{C_p(t)}{C_p(t^0)}\right) \left(\frac{C_{Cl}(t^0)}{C_{Cl}(t)}\right)$. Bentazon and D-chloridazon were the only pesticides observed above the detection limit at MW-B3. Only 45% of the injected bentazon concentration was observed, and for D-chloridazon approximately 9%. Retardation was small for bentazon ($R = 1.1$) and negligible for D-chloridazon ($R = 1.0$) (Table 2), and therefore the decreasing concentration is mostly related to degradation. The other monitored pesticides had larger R and did therefore not yet arrive. The time between the start of ASTR operation and the

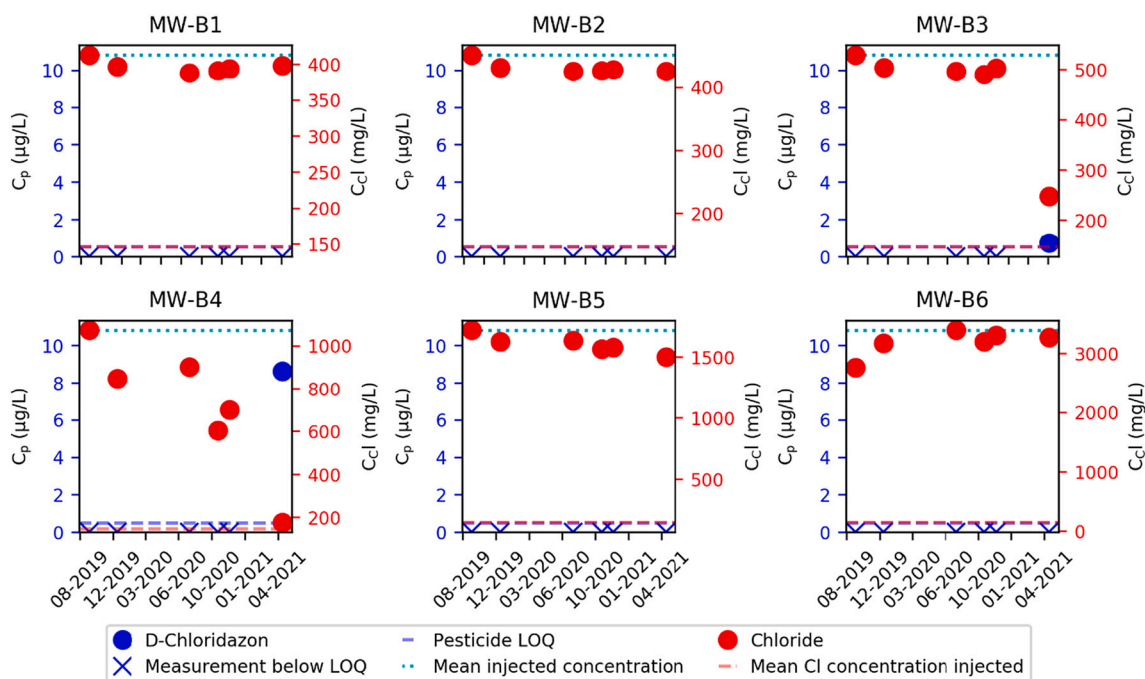


Fig. 5. Observed chloride and D-chloridazon concentrations at different depths in the aquifer at 15 m distance from injection well A. The blue crosses present D-chloridazon concentrations below LOQ, and the blue dots (only 2) concentrations above. The blue dashed line displays the pesticide LOQ. The red dots present the observed Cl concentrations, and the red dashed line the mean Cl concentration in tile drainage water during the full period of ASTR operation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

arrival of the 50% front position was estimated at 485 days for MW-B3 and 334 days for MW-B4. DT50 values calculated were 433 and 141 days for bentazon and D-chloridazon (Table 4), respectively, at MW-B3 (S6.2). Bentazon, boscalid, chloridazon, D-chloridazon, MD-chloridazon, fluopyram, flutolanil, and methoxyfenozide were observed above the detection limit at MW-B4. Negligible degradation ($(\frac{C_r(t)}{C_r(0)}) > 0.99$) was observed for chloridazon, MD-chloridazon, and flutolanil. For the other pesticides, between 61% and 74% of the injected concentrations were observed, even for bentazon and fluopyram which were prone to small retardation (R = 1.1). Degradation rates could be higher in reality for bentazon and fluopyram, as also retardation could be the cause of the lowered concentrations. Note that retardation factors were not available for flutolanil and methoxyfenozide (Table 2). Table 4 shows the estimated DT50 values for all pesticides at MW-B3 and MW-B4. The observed DT50 values for bentazon are similar at MW-B3 and MW-B4, while for D-chloridazon the DT50 value at MW-B3 are almost an order of magnitude lower. The observed DT50 values during operational monitoring fall mostly within the range of the DT50 observed during the storage periods.

3.4. Comparison obtained DT50 values with previous studies

Table 5 gives an overview of the DT50 values of the studied pesticides and metabolites as deduced or reported in (i) this study, (ii) the PPDB database, which is an international database for risk assessment and management, based on regulatory files (Lewis et al., 2016), and (iii) previous pesticide degradation studies in field or column studies of aquifer systems. Several aquifer studies investigated the fate of bentazon and chloridazon. Bentazon DT50 values ranged from about 700–7000 days (Bertelkamp et al., 2016b; Broholm et al., 2001; Stuyfzand et al., 2007; Tuxen et al., 2000). Only Stuyfzand et al. (2007) studied the fate of bentazon in groundwater under various redox conditions. They observed a persistent behavior in suboxic and anoxic groundwaters, which corresponds with the results obtained in the current study. DT50 values of chloridazon ranged from 0.2 to 0.5 days in previous performed column studies with sands from a riverbank filtration site (Bertelkamp et al., 2015; Bertelkamp et al., 2016a; Bertelkamp et al., 2016c), which was substantially faster than observed in our study. Nevertheless, the DT50 values of chloridazon from the PPDB database are mostly in the same range as observed in this study. To our knowledge, degradation rate constants were not determined for the other pesticides in aquifer sediments. Therefore, we compared our results with the PPDB database, which consists mostly of DT50 values for topsoils collected from regulatory files. The “water phase only” DT50 values from the PPDB database are generally a little lower than in the current study, but the water-sediment, and the aerobic DT50 values are mostly within the same range.

Table 6 shows the detection of the pesticides assessed in the current study in groundwater monitoring campaigns in Europe. Bentazon was

Table 4

DT50 values estimated based on the periodical operational monitoring data at the monitoring wells at 15 m distance from injection well A. The DT50 was not estimated for the pesticides and depths for which a dash is presented in the table.

	MW-B3	MW-B4
	DT50 (days)	DT50 (days)
Bentazon	433	462
Boscalid	–	770
Chloridazon	–	∞
D-chloridazon	141	1155
MD-chloridazon	–	∞
Fluopyram	–	578
Flutolanil	–	∞
Imidacloprid	–	–
Methoxyfenozide	–	770

Table 5

Overview of obtained DT50 values in the current study from storage periods with an NSE < 0.1 where negative and insignificant DT50 values are interpreted as DT50 = ∞ and from operational monitoring, which were compared to the PPDB database and previous aquifer pesticide sorption studies.

	This study	PPDB			Literature range
	DT50 (days)	DT50 aerobic* (days)	Water-sediment (days)	Water phase only (days)	DT50 (days)
Bentazon	209-∞ (n = 7)	3.0–35.0 (20 soils)	716	80	693–6930 ^(c, e, f, g)
Boscalid	54-∞ (n = 5)	103–1214.4 (9 soils)	545	5	–
Chloridazon	53-∞ (n = 10)	3–173.9 (unknown)	137	51.5	0.21–0.47 ^(a, b)
D-chloridazon	112-∞ (n = 20)	80–360 (unknown)	–	–	–
MD-chloridazon	164-∞ (n = 19)	118–170 (unknown)	–	–	–
Fluopyram	59-∞ (n = 19)	93.2–717 (unknown)	1077	20.5	–
Flutolanil	66-∞ (n = 2)	60.4–1000 (16 soils)	320	90.5	–
Imidacloprid	92-∞ (n = 9)	77–425 (unknown)	129	30	–
Methoxyfenozide	171-∞ (n = 5)	81- > 1000 (unknown)	208.6	–	–

Aquifer studies: (a) Bertelkamp et al. (2015), (b) Bertelkamp et al. (2016a), (c) Bertelkamp et al. (2016b), (d) Bertelkamp et al. (2016c), (e) Broholm et al. (2001), (f) Stuyfzand et al. (2007), (g) Tuxen et al. (2000).

* Combination of lab and field studies, soils for both type of studies are added together.

Table 6

Pesticides observed in groundwater monitoring studies in Europe. Pesticides that were not measured are displayed as n.m.

	Observed in groundwater in:				
	The Netherlands (a, b, c)	Spain (d)	UK (e)	Italy (f)	Pan-Europe (g)
Bentazon	yes	yes	yes	yes	yes
Boscalid	n.m.	n.m.	n.m.	yes	n.m.
Chloridazon	yes	no	yes	yes	n.m.
D-chloridazon	yes	n.m.	n.m.	–	yes
MD-chloridazon	yes	n.m.	n.m.	–	yes
Fluopyram	n.m.	n.m.	n.m.	–	n.m.
Flutolanil	yes	n.m.	yes	–	n.m.
Imidacloprid	n.m.	n.m.	n.m.	–	n.m.
Methoxyfenozide	n.m.	n.m.	n.m.	–	n.m.

(a) Swartjes et al. (2016), Bijlage D (in Dutch), (b) Schipper et al. (2008), (c) Sjerps et al. (2017), (d) Jurado et al. (2012), Table S1, (e) Stuart et al. (2011), Appendix 2, (f) Meffe and de Bustamante (2014), Table A1 (g) Loos et al. (2010).

observed in groundwater at all monitoring networks in at least 1 of the monitored wells. Similarly, boscalid, chloridazon metabolites, and flutolanil were observed in all monitoring programs when analyzed. Chloridazon was observed in groundwater in the Netherlands, United Kingdom (UK), and Italy, but not in Spain. This shows that these pesticides are often persistent in groundwater systems. The mostly low degradation rates observed during the storage periods and the

operational monitoring in this study corresponds with the data from the European groundwater monitoring programs.

4. Conclusion

In this study, we assessed degradation of 7 commonly used pesticides and 2 metabolites before and during aquifer storage transfer and recovery (ASTR). Tile drainage water containing pesticides (ranging between 0.013 and 10.8 µg/L) was collected from a 10-ha agricultural parcel, injected in an anoxic brackish/saline aquifer, and abstracted when water was needed for irrigation purposes. We hypothesized that injection of fresh, oxic, nutrient and dissolved organic carbon (DOC) rich (mean concentrations NO₃: 14.1 mg/L, NH₄: 0.13 mg/L, PO₄: 5.2 mg/L, DOC: 24.7 mg/L), and probably microbially active tile drainage water would stimulate pesticide degradation. Push-pull tests were performed to assess pesticide degradation in the native aquifer at 6 depths before ASTR operation. Retardation, likely caused by pesticide sorption to sedimentary organic matter, interfered unexpectedly with the degradation assessment for some of the pesticides. Therefore, we could not obtain accurate DT50 values for all pesticides. For the other pesticides, degradation was not convincingly observed during the push-pull tests which lasted for ±18 days. We recommend the use of push-pull tests in future studies only when fast pesticide degradation (DT50 values < 20 days) and negligible retardation is expected. Subsequently, pesticide degradation was studied during 3 storage periods of ±45 days spread out over a period of 1.5 years of ASTR operation. Obtained DT50 values were prone to some uncertainty, related to variations in pesticide concentrations in the injected and later abstracted tile drainage water. Nonetheless, generally decreasing pesticide concentrations were observed and mostly positive DT50 values, which indicates degradation albeit at low rates with high half-lives of at least 53 days. Degradation rate constants did not increase during the consecutive storage periods suggesting no influences of microbial adaptation and/or bio-augmentation. Operational monitoring was performed at the wells at ±15 m distance from the injection well. Pesticides were detected at only two depths after a travel time of approximately 485 and 334 days, respectively. Estimated DT50 values were relatively high and exceeded 141 days. Lastly, the obtained DT50 values were compared to existing literature, and corresponded mostly to previous pesticide degradation studies in aquifers and groundwater monitoring studies. Therefore, we found no strong evidence that pesticide degradation is stimulated by the co-injection of electron acceptors (O₂, NO₃), DOC, nutrients, and biodegrading bacteria as contained in tile drainage water. The relatively high DT50 values consequently result in relatively high pesticide concentrations in abstracted ASTR water. Furthermore, the persistent pesticides in the non-abstracted water constitute a risk for contamination of the native brackish groundwater.

CRedit authorship contribution statement

Emiel Kruidijk: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing – original draft, Visualization. **Pieter J. Stuyfzand:** Conceptualization, Writing – review & editing, Supervision. **Boris M. van Breukelen:** Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jconhyd.2022.104094>.

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