Intra aquifer variations in pesticide sorption during a field injection experiment

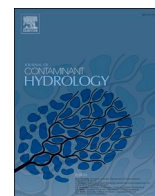Kruisdijk, Emiel; Zietzschmann, Frederik; Stuyfzand, Pieter J.; van Breukelen, Boris M.

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Intra aquifer variations in pesticide sorption during a field injection experiment

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ABSTRACT

A field injection experiment was performed in an anoxic sandy aquifer over 6 days to assess sorption characteristics of 7 commonly applied pesticides in agriculture and 2 frequently detected metabolites. Pesticide use changed considerably in the last decades, and there is insufficient knowledge of the fate of currently used pesticides in aquifers. Injected water arrival was monitored at 6 depth intervals of 1 m ranging from 11.4 to 32.2 m below surface level with varying organic carbon contents (0.057–0.91%d.w.) to examine intra-aquifer variations in sorption. Observed pesticide concentrations were fit using a non-linear least squares routine to an advection-dispersion equation, from which retardation factors (R) were obtained. Pesticide degradation did not significantly influence the simulated R during the experiment. We observed that bentazon and cycloxydim were most mobile with $R < 1.1$ at all depths. Desphenyl chloridazon, methyl desphenyl chloridazon, and imidacloprid were, on average, less mobile, with maximum R of 1.5. Boscalid, chloridazon, fluopyram, and flutolanil showed a larger range of R, and $R > 2.0$ were observed in the shallowest part of the aquifer. Largest R were observed at the top of the aquifer and decreased with depth. K_{oc} values varied similarly, which indicates that sorption is not only influenced by sedimentary organic matter (SOM) content but also by its sorption reactivity. Obtained sorption parameters were substantially lower than reported in a widely used pesticide sorption database, which suggests that sorption parameters are influenced by methodological differences and variations in the sorption reactivity of SOM. The large intra-aquifer variations in pesticide sorption highlights that aquifer heterogeneity should be considered in groundwater risk assessments.

1. Introduction

Pesticides and their metabolites are increasingly detected in groundwater systems over the last decades (Arias-Estevez et al., 2008; Burri et al., 2019). Heavy use of pesticides in agriculture adversely impacts groundwater resources. Understanding of pesticide transport processes is essential to assess the pesticide spreading risk through aquifers. These insights are even more urgent as managed aquifer recharge (MAR) technologies become more common (Sprenger et al., 2017; Zhang et al., 2020). MAR systems store freshwater in aquifers, often for later re-use (Dillon et al., 2019; Sprenger et al., 2017). Using available surface water or stormwater in MAR can introduce pesticides directly into groundwater systems. Examples are: (i) riverbank filtration

where surface water infiltrates and flows towards groundwater abstraction wells (Hiscock and Grischek, 2002; Ray, 2008), and (ii) Aquifer Storage (Transfer) and Recovery (AS(T)R) in which for example, stormwater can be directly injected into an aquifer using wells (Page et al., 2010; Vanderzalm et al., 2011).

Aquifer sorption parameters (retardation factors, partition coefficients (K_d), and organic carbon-water partition coefficients (K_{oc})) are commonly determined by batch experiments (Clausen et al., 2004; de Lipthay et al., 2007; Janniche et al., 2011; Kiecak et al., 2019; Madsen et al., 2000; Moreau and Mouvet, 1997; Rae et al., 1998). Sediment, water, and pesticides are combined and mixed, after which the pesticide decrease in the liquid-phase is determined (OECD, 2000). Limousin et al. (2007) acknowledge the difficulty of translating batch experiment

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results to porous media, as the solid/solution ratio and the hydrodynamic conditions differ largely. Column experiments have the benefit that sorption during advective transport can be studied under controlled conditions, although obtained results are mostly limited to the experiment scale and are not directly transferable to aquifers (Banzhaf and Hebig, 2016). In-situ experiments in aquifer sediments hold substantial advantages over column experiments: (i) experiments are done under field conditions and are therefore site specific, (ii) often larger volumes of aquifer sediments are studied, which make the results more representative, and (iii) risks of disturbance or contamination of aquifer materials are smaller, as no drilling and relocation of sediments is needed.

In-situ pesticide sorption studies in aquifers are limited (Broholm et al., 2001a; Broholm et al., 2001b; Pang and Close, 2001; Rügge et al., 1999a; Rügge et al., 1999b; Springer and Bair, 1998; Widmer and Spalding, 1995; Widmer et al., 1995; Živančev et al., 2019). All these studies conducted a (natural) gradient experiment, in which water (which contained pesticides) was injected into an aquifer after which the plume movement was monitored and analyzed. Aside of Živančev et al. (2019), the studies were all done more than 20 years ago, and since then pesticide use changed greatly. In Europe, this can be partly related to directive 2009/128/EC and EC 1107/2009 which both aim to achieve sustainable pesticide use. Of all pesticides examined in the previous in-situ pesticides sorption studies, only acetamiprid and bentazon are approved by the EC 1107/2009 regulation. In our study, we focus on the sorption of 6 commonly used present-day approved agricultural pesticides (bentazon, boscalid, chloridazon, cycloxydim, fluopyram, flutolanil), 2 regularly observed metabolites (desphenyl chloridazon and methyl desphenyl chloridazon), and the recently (2013) EU-banned pesticide imidacloprid (Gross, 2013).

Pesticide mobility is affected by aquifer heterogeneity. During and after genesis, intra-aquifer variations are developed, for example, lithology, mineral content, and organic carbon content. These variations result in fluctuations in pesticide sorption, which can be crucial to assess potential groundwater contamination risks. MAR sites facilitate studying this heterogeneity during the injection of a new type of water into an aquifer. To our knowledge, only Broholm et al. (2001b) studied in-situ intra-aquifer variations of 2-methyl-4,6-dinitrophenol (DNOC) sorption, which was done in a low organic carbon aquifer. During their field injection experiment, they studied a relatively small layer of 1 m at 3 different depths. Furthermore, they assessed a 3.5 m aquifer layer at 12 depths using batch experiments. They observed spatially varying DNOC sorption related to variations in clay minerals and pH. Organic carbon content is often the most important factor related to pesticide sorption when available (Delle Site, 2001; Fetter et al., 1999). In the current research, we examine an aquifer from ~11-33 m below surface level, with a wide range of organic carbon contents (0.057–0.91%d.w) at the 6 depth intervals studied. This range is significantly larger than in the previous in-situ pesticide sorption studies together (Broholm et al., 2001a; Broholm et al., 2001b; Pang and Close, 2001; Rügge et al., 1999a; Rügge et al., 1999b; Springer and Bair, 1998; Widmer and Spalding, 1995; Widmer et al., 1995; Živančev et al., 2019), where the aquifers examined had organic carbon contents ranging from 0.007–0.16%d.w.

In the current study, we assess pesticide sorption during the first operation of an ASTR system, in which agricultural tile drainage water containing pesticides is injected in the aquifer for later re-use as irrigation water. We follow a similar set-up as the previous mentioned in-situ pesticide sorption studies, with the key differences: (i) tile drainage water (TDW) from an agricultural field, was used as injection water, (ii) intra aquifer variations were examined with monitoring wells at 6 different depths, and (iii) an extensive sedimentological and geochemical characterization of the aquifer was performed. The objectives of this study are to, (i) determine sorption parameters of 7 commonly applied pesticides and 2 regularly detected metabolites injected during this in-situ experiment at 6 different depths with a wide

range of organic carbon content, (ii) compare obtained sorption parameters to a widely used literature database, and (iii) assess the effects and implications of intra-aquifer variations with depth on sorption.

2. Material and methods

2.1. Field site description

The study site is located in an agricultural area in a polder in the North-Western part of the Netherlands (coordinates: 52.8883, 4.8221). Here, an Aquifer Storage Transfer and Recovery (ASTR) system stores water during wet periods in the underlying confined aquifer using wells and re-uses this water in dry periods to irrigate flower bulbs. For additional information about the field site see Supplementary Information 1 (S1). Tile drainage water (TDW) containing pesticides is collected from 10 ha of agricultural land and injected via a vertical well in a sandy anoxic aquifer (11.5–33.0 m below surface level (b.s.l)) of late Holocene and Pleistocene origin, below a confining Holocene clay/peat layer. The aquifer studied consists of sediments from three different geological Formations, based on the Dutch national database of subsurface information (TNO-NITG, 2021). The Boxtel Formation extends from approximately 8-19 m b.s.l., and consists mostly of aeolian and fluvial sands deposited from early Holocene untill middle-Pleistocene (Schokker et al., 2005). The Eem Formation is situated below, from about 20-28 m b.s.l., and consists mostly of marine sands deposited during the early-Pleistocene (Bosch et al., 2003). Below, the Drenthe Formation is situated from about 29-34 m b.s.l. built up mostly from glacial sands in the middle-Pleistocene (Bakker et al., 2003). A monitoring well screen is situated in the gravel pack of the injection well. Furthermore, monitoring wells (MW1–6) placed at 6 depths (from 11.4 to 32.2 m-b.s.l, for specific depths see Table 1) are distributed over 3 boreholes at 2.5 m distance from the injection well. The three shallowest monitoring wells (MW1, 2, and 3) are situated in the Boxtel Formation, MW4 and 5 in the Eem Formation, and MW6 in the Drenthe Formation.

2.2. Description field injection experiment

The field injection experiment took place from 1 to 6 November 2019, during which a total of about 440m^3 TDW was injected during ASTR operation. TDW contained pesticides originating from agriculture in environmental concentrations, rather than elevated concentrations often used in laboratory experiments. Furthermore, Cl concentrations were notably lower in TDW in comparison to the native brackish groundwater. Injection occurred continuously during daytime. Water quality was monitored before, during, and after the arrival of the injected TDW at MW1–6, and at the injection well. Injected TDW was sampled with a peristaltic pump (Eijkelkamp, the Netherlands) from the monitoring well in the gravel pack of this injection well, every 30 min. At the start of each day, about 60 L was abstracted from this monitoring well, to remove the standing volume of the well (ca. 11 L). Concurrently, every 30 min a water sample was collected from a specific monitoring well, such that each monitoring well was sampled every 3 h (6 monitoring wells x 30 min = 3 h). The standing volume of the wells (max. 17 L) was removed before sampling by abstracting 30 L using a diaphragm pump (Liquiport NF1.100, KNF Verder, the Netherlands).

2.3. Estimation of longitudinal dispersivity

Longitudinal dispersivities were estimated independently for each well screen depth interval of MW1–6. We assumed that the major flow path between the injection well and the monitoring wells was radial 1 dimensional (1D), as (i) the aquifer studied is anisotropic, which means here that the horizontal hydraulic conductivity is significantly larger compared to the vertical, and most importantly (ii) the model did simulate conservative transport remarkably well at all different depths as shown in Fig. 1.

Table 1

Composition of native groundwater in monitoring wells and injected TDW, and geochemical aquifer characteristics, D50, and the calculated longitudinal dispersivities with their standard deviation at the depth of the monitoring well screens. Mean TDW concentrations and their standard deviations have been determined from 43 analyzed water samples during the field injection experiment.

|		Mean. TDW (n = 43)	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6
Sample date	–	01 Nov 2019 – 06 Nov 2019	25 Sep 2019	25 Sep 2019	25 Sep 2019	25 Sep 2019	25 Sep 2019	25 Sep 2019
Depth well screen	m-b.s.l	–	11.4–12.4	15.0–16.0	18.3–19.3	22.8–23.8	25.9–26.9	31.2–32.2
Water composition								
Temp	°C	11.7 ± 0.3	10.6	10.6	12.7	10.7	9.9	12.2
pH	–	7.18 ± 0.17	6.71	6.83	6.77	6.69	6.63	6.52
EC	µS/cm	1440 ± 39	1860	1910	1990	3280	5090	8930
DOC	mg/L	26.3 ± 0.5	8.6	7.2	7.8	5.8	3.7	3.5
O$_2$	mg/L	2.48 ± 2.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cl	mg/L	139 ± 20	440	455	498	1110	1810	2760
Bentazon	µg/L	0.062 ± 0.010	0.022	0.009	<0.001	<0.001	<0.001	0.012
Boscalid	µg/L	0.051 ± 0.024	<0.01	<0.01	<0.01	<0.01	0.018	<0.01
Chloridazon	µg/L	0.059 ± 0.012	0.037	0.041	0.010	<0.005	<0.005	0.019
D-Chloridazon	µg/L	11 ± 0.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
MD-Chloridazon	µg/L	2.1 ± 0.12	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cycloxydim	µg/L	0.030 ± 0.006	0.016	0.007	<0.005	<0.005	<0.005	0.007
Fluopyram	µg/L	0.69 ± 0.10	0.075	0.076	0.018	0.003	0.002	0.017
Flutolanil	µg/L	0.25 ± 0.09	0.035	0.042	0.012	<0.01	<0.01	<0.01
Imidacloprid	µg/L	0.030 ± 0.007	0.037	0.024	<0.005	<0.005	<0.005	<0.005
Sediment composition								
SOC	%d.w.	–	0.91	0.14	0.38	0.088	0.057	0.066
Clay	%d.w.	–	5.5	1.1	3.4	0.74	0.49	1.1
Carbonate	%d.w.	–	6.5	0.35	11	1.3	1	0.61
Al + Fe	%d.w.	–	4	1.9	4.5	2.3	1.7	1.6
Median grainsize (D50)	µm	–	132	200	148	321	287	352
Longitudinal dispersivity (αL)	cm	–	6.53 ± 1.43	31.1 ± 6.39	10.8 ± 2.32	2.52 ± 0.32	16.6 ± 2.93	10.7 ± 1.80
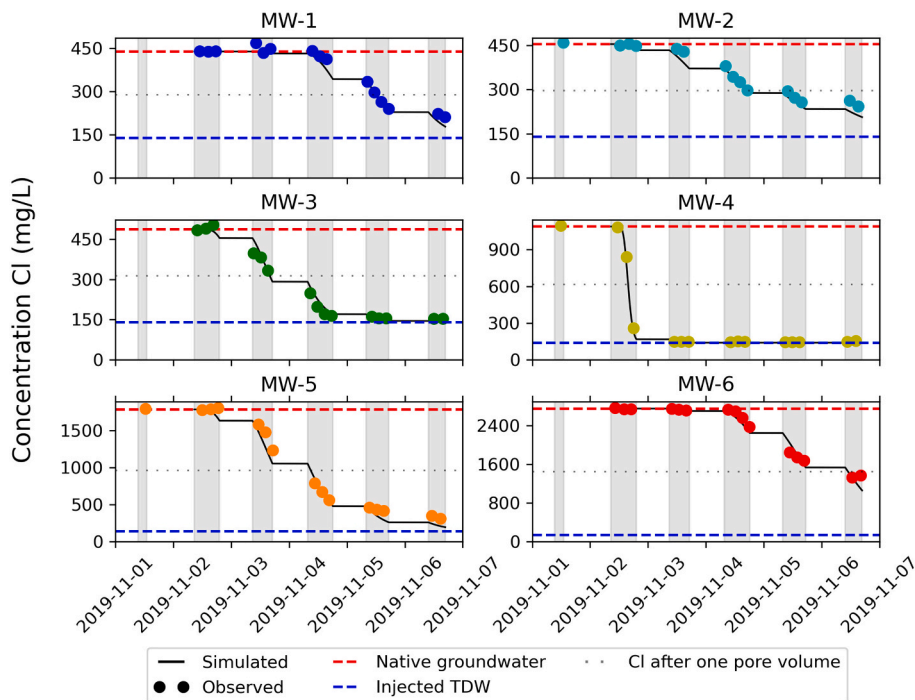
Fig. 1. Arrival of the spreading front based on the observed Cl concentrations in the different monitoring wells. The colored dots show the observed Cl concentrations at each monitoring well. The black line presents the concentrations simulated (Sim) using the estimated dispersivity. The vertical grey bars in the background show the injection periods. The red dashed line shows the initial native groundwater Cl concentration and the blue colored dashed line the mean injection water (TDW) Cl concentration. The grey dotted line in the middle of the panels represents the Cl concentration related to the arrival of the spreading front. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Observed Cl concentrations were fit to the approximate 1D solution for dispersion in radially diverging flow to obtain longitudinal dispersivities (Eq. 7–163 in Bear (2012)):

$$C(r,t) = C_i + \left(\frac{C_0 - C_i}{2}\right) * erfc\left(\frac{r - r_{50}}{\sqrt{\frac{4}{3}\alpha_L r_{50}}}\right) \quad (1)$$

where $C(r,t)$ are the observed Cl concentrations (mg/m^3) at MW1–6 observed at distance r (2.5 m) at time t after the start of injection, C_i the Cl concentration of the initial groundwater (mg/m^3), C_0 the mean concentration of the injected TDW (mg/m^3), r_{50} the calculated 50% front position of the injected water at time t (see eq. 2) (m), and α_L the longitudinal dispersivity (m). Negligible dispersion was expected during periods without injection, as groundwater flow was expected to be

negligible (<0.01 m/d) based on groundwater levels (obtained from www.grondwatertools.nl) and hydraulic conductivity in the proximity of the system (obtained from www.dinoloket.nl). These periods were excluded from time t. Diffusion was not simulated, as the effects were expected to be minor on the timescale of this experiment.

Eq. 2 was used to determine the 50% front position at time t after the start of injection, assuming a cylindrical expansion of the infiltration water:

$$r_{50} = \sqrt{\frac{QtK_n}{\varepsilon_N \pi KD}} \qquad (2)$$

where Q is the mean injection rate (m³/d), t is the time since start of injection (d), K_n the horizontal hydraulic conductivity of layer N (m/d), ε_N the porosity of layer N (−), and KD the transmissivity of the target aquifer (m²/d). K_n, ε_N, and KD are not exactly known, but their combined value $\left(\frac{K_n}{\varepsilon_N KD}\right)$ was determined at the arrival of the spreading front (breakthrough). At this moment, the r_{50} and Q are known, and t can be estimated via Eq.2.

Dispersivities were estimated separately for MW1–6. Eq. 1 was fit to observed chloride concentrations, using a non-linear least squares routine in python (Python v. 3.6.4). Furthermore, the standard deviation of the dispersivity was calculated by taking the square root of the variance of the fit multiplied with 1.96.

2.4. Estimation of retardation factors

A similar method was used to estimate retardation factors (R) of the pesticides, assuming 1D transport, and instantaneous equilibrium sorption. Periods without injection were disregarded, as no additional sorption would occur. Eq. 2 was adjusted to simulate retardation, by dividing t (time since start of injection) by R. R was estimated for the pesticides at the screen depths of MW1–6. The adjusted equation was fit to the observed pesticide concentrations to obtain R, using a non-linear least squares routine in python (Python v. 3.6.4).

2.5. Determination of K_d and K_{oc}

R values obtained were converted to partition coefficients (K_d: L/kg) and organic carbon-water partition coefficients (K_{oc}: L/kg) with eq. 3 (Appelo and Postma, 2004; Fetter et al., 1999):

$$K_d = \frac{(R-1)\varepsilon}{\rho_b}, where\ K_{oc} = \frac{K_d}{f_{oc}} \qquad (3)$$

where ρ_b is the bulk density of the aquifer matrix (kg L⁻¹) calculated as $(1-\varepsilon)\rho_s$, where ρ_s is the density of mainly quartz solids in the aquifer matrix (=2.65 kg L⁻¹), and f_{oc} is the fraction of organic carbon in the aquifer matrix at the well screen depths of MW1–6 (−). The porosity (ε) is assumed to vary between 0.2 and 0.35 (−), based on Table 3.1 from Appelo and Postma (2004). A minimum and maximum K_d and K_{oc} was calculated using ε=0.2 and 0.35.

2.6. Comparison obtained sorption parameters to literature data

K_d and K_{oc} values obtained in the current study were compared to values from the pesticides properties database (PPDB). This database is evidence-based, and contains data of, for example, the chemical identity, physical chemistry, human health, and ecotoxicology of pesticides from regulatory dossiers, peer reviewed publications, and manufacturer datasheets. Therefore, it provides an extensive dataset, which can be used for pesticide risk assessments (Lewis et al., 2016). The PPDB database contains information on linear sorption isotherms, but most of the sorption parameters describes Freundlich sorption isotherms. The equation below shows the linear sorption isotherm:

$$S = K_d C \rightarrow K_d = \frac{S}{C} \qquad (4)$$

where S is the mass of solute sorbed per dry unit weight of solid (mg/mg), and C is the pesticide concentration in solution (mg/m³). The equation below presents the Freundlich sorption isotherm:

$$S = K_f C^n \qquad (5)$$

where K_f is the Freundlich constant and n a constant which describes the nonlinearity of the Freundlich isotherm. The K_d value valid at a specific concentration can be derived from the Freundlich parameters, by combining eqs. 4 and 5:

$$K_d = \frac{K_f C^n}{C} \rightarrow$$

$$log(K_d) = log(K_f) + n \bullet log(C) - log(C) \rightarrow$$

$$log(K_d) = log(K_f) + (n-1) \bullet log(C) \qquad (6)$$

We calculated ranges of K_d values for the concentration range in this study from K_f and n values using eq. 6, in order to compare the K_d values obtained at our field site with the sorption data in the PPDB database. The K_d range was calculated for the pesticide concentration in TDW which represented the pesticide concentration after the full arrival of the injected TDW and the minimum K_d, to pesticide concentration is 0.005 µg/L which represented the lowest pesticide detection limit and the maximum K_d.

2.7. Hydrochemical analysis

Water quality was monitored in the field using a flow cell, for EC (C4E, Ponsel, France), pH/temperature/redox (PHEHT, Ponsel, France), and dissolved oxygen (OPTOD, Ponsel, France). Water samples were filtered (0.45 µm, Chromafil Xtra PES-45/25, Macherey-Nagel, Germany) on site. Pesticides were analyzed with Liquid Chromatography – Mass Spectrometry (LC-MS; Xevo TQ-S micro, Waters, U.S.A.). For more information about the selection of pesticides for analysis and the analytical methods, see S2. Dissolved anions (Br, Cl, F, NO_2, NO_3, and SO_4) were measured with Ion Chromatography (IC; Compact IC pro, Metrohm, Switzerland). Na, K, Ca, Mg, Fe, Mn, Al, Si, S, P, and various trace metals such as Ni, Zn, and As were analyzed with Inductively Coupled Plasma – Mass Spectrometry (ICP-MS; PlasmaQuant MS, Analytik-Jena, Germany). Alkalinity, PO_4, and NH_4 were determined with a Discrete Analyzer (DA; AQ400, Seal analytical, UK). DOC contents were analyzed after high temperature combustion with a TOC analyzer (TOC-V CPH, Shimadzu, Japan).

2.8. Sediment sampling and geochemical analysis

Sediment samples were obtained using a 2 m sonic drill aqualock system using a core catcher from 2 m to 36 m-b.s.l at the location of MW4 and 6 (S1) (Oele et al., 1983). Sediment was stored in PVC liners of 1 m length and 103 mm inner diameter. Slight variations in diameter of the thin-wall tubes (103 mm internal diameter (ID)) and the sonic drill aqualock system (97 mm ID) resulted in compaction of the sediment. A correction was applied to the core lengths and depths for this variation. The top and bottom 20 cm of sediments were discarded, due to possible contamination. Subsamples were taken of every 10 cm of each core, from which a mixed sample was made, representing depth intervals of about 1.0 m. The representative contents of geochemical parameters at well screen depth (screen length: 100 cm) were determined by multiplying the fraction of the well screen that overlapped the depth interval of a specific mixed sample with the geochemical content of that mixed sample. The contributions of the two neighboring mixed samples were added together afterwards. Variations in the contents of reactive

constituents are assumed to be small in lateral directions, as the aquifer sediments are all deposited horizontally, and the lateral scale of the experiment is limited (2.5 m).

Sedimentary organic carbon (SOC) was analyzed by high temperature combustion with non-dispersive infrared detection, carbonate mineral content by thermogravimetric analysis, and the Al and Fe content by x-ray fluorescence after lithium borate fusion. A HELOS/KR laser particle sizer (Sympatec GmbH, Germany) determined the grain size distribution, including the clay size fraction (< 2 µm, called lutum fraction) and median diameter (D_{50}) after removal of sedimentary organic matter and carbonates.

3. Results and discussion

3.1. Hydrochemical conditions field site

Most pesticide measurements (59%) were below the limit of quantification (LOQ) in ambient groundwater before infiltration (Table 1). Some pesticides were already observed in groundwater (max. 0.076 µg/L), resulting from previous push-pull tests. These traces do not result from agricultural practice at ground level because infiltration of water is negligible at the land surface, as shown by the (i) groundwater seepage flux of about 4.7 mm/year in the polder (Boekel et al., 2014), and (ii) the negative base exchange index (BEX) of the ambient groundwater, which indicates that salinization is occurring by inflow of groundwater from larger depths (Stuyfzand, 1993). Groundwater was relatively fresh at the well screen depths of MW1, 2, and 3 (EC between 1850 and 2000 µS/cm), but got more saline deeper in the aquifer at MW4, 5, and 6 (EC = 3280, 5090, 8930 µS/cm respectively). The redox state is anoxic, with mostly Mn(IV) and Fe(III) reducing conditions.

Tile drainage water (TDW) contained 9 pesticides above LOQ of the 20 pesticides in our measurement method (Table 1): bentazon, boscalid, chloridazon, desphenyl chloridazon (D-chloridazon), methyl desphenyl chloridazon (MD-chloridazon), cycloxydim, fluopyram, flutolanil, and imidacloprid. Boscalid, chloridazon, cycloxydim, and fluopyram were applied in 2018 and/or 2019 by the flower bulb grower. Observed concentrations were relatively low, mostly in between 0.01 and 0.15 µg/L. Exceptions were observed for fluopyram, flutolanil, and the metabolites D-chloridazon and MD-chloridazon with concentrations between 0.15 and 12 µg/L. D-chloridazon and MD-chloridazon concentrations were about 100 times larger than their parent compound chloridazon. Most pesticide concentrations were relatively stable over time in the injected TDW. The 10% and 90% percentiles of the temporal pesticide concentrations in TDW did not deviate more than 25% from the mean concentrations, except for boscalid and flutolanil. Boscalid showed a decreasing concentration during the first day of injection (from about 0.15 to 0.05 µg/L) after which concentrations remained relatively stable in the following 4 days. Observed flutolanil concentrations were more scattered: the 10% and 90% quantile deviated about 55% from the mean concentration. TDW was relatively fresh (average EC is 1440 µS/cm), oxic, and had relatively high DOC concentrations (on average 26.3 mg/L).

The contents of reactive constituents were relatively high in sediment samples of MW-1 and 3 (Table 1). MW-1 had the highest SOC (=0.91%d.w.) and clay contents (=5.5%d.w.), and MW-3 the highest carbonate (=11.0%d.w.) and Al + Fe contents (=4.5%d.w.). Reactive constituents were relatively low in MW-2 (e.g., SOC: 0.14%d.w.; clay: 1.1%d.w.), and even lower in MW4, 5, and 6 (e.g., SOC: 0.057–0.066%d. w.; clay: 0.49–1.1%d.w.).

3.2. Simulation of conservative transport

TDW had significantly lower Cl concentrations compared to ambient groundwater from all monitoring wells at 2.5 m distance from the injection well (Table 1), which made Cl an ideal conservative tracer for the dispersivity estimations.

The tracer curves showed that at least one pore volume had been injected at the well screen depths of MW1–6 (Fig. 1). The earliest arrival occurred in MW-4 after about 110 m^3 injection and the latest in MW-6 after 420 m^3 injection. Longitudinal dispersivities (α_L) were estimated at all well screen depths (Table 1). Dispersivities fit well to the observed Cl concentrations for the different monitoring wells (Fig. 1, minimum r^2 = 0.945). The α_L values are all within 1 order of magnitude, MW-2 and 4 excluded. MW-4 shows the lowest α_L (2.52 cm), MW-2 the highest (31.1 cm).

3.3. Obtained retardation factors

Retardation factors were obtained by fitting the analytical equation to the observed pesticide concentrations. Generally, good fits were obtained, with ~60% of the fits showing r^2 > 0.7 and ~ 40% of the fits r^2 > 0.9. Fits with r^2 < 0.7 were discarded from further interpretation. The experimental duration was too short to observe the arrival of all pesticides. The delayed arrival of these pesticides is expected to be caused by sorption. For these cases, the minimum R was obtained (for example, see Fig. 2: subplot MW-1). In total, 37 R values were obtained for further analysis, with more than 80% below 2.0.

Pesticide degradation can influence pesticide arrival, and consequently also the deduced R. Potential occurrence of degradation can most easily be determined in MW-3, 4, and 5, where mostly complete break-through curves were observed (S3). Note that sorption is not influencing observed concentrations after arrival and degradation is reflected by concentrations consistently lower than injected concentration levels. Degradation was only observed for chloridazon in MW-4 and probably also in MW-5. Chloridazon concentrations decreased during aquifer transport to about the 10% percentile of the injection water concentrations. The obtained R value was not significantly affected by degradation during the experiment, as the fit to the observed concentrations during arrival was good.

Fig. 2 shows the observed concentrations, the associated model fits, and the obtained R for fluopyram at the different depths in the aquifer. We show here only the results of fluopyram as example, as it shows an interesting variation of R within the aquifer. Figures for the other pesticides can be observed in the Supporting Information (S3). Observed concentrations gradually increase in all monitoring wells during the experiment, except for MW-1. The determined R values decrease with depth. Relatively high R values were observed at MW-1, 2, and 3 (>2.0, 1.64, and 1.52, respectively), and low values at MW-4 (R = 1.09), and at MW-5 and MW-6 (both close to 1).

The deduced R values are not influenced by non-equilibrium sorption, as the center of mass of a breakthrough curve is independent of kinetic constraints (Brusseau, 1994; Brusseau et al., 1989), whereas non-equilibrium sorption results in fronting and tailing during arrival of TDW (Bouchard et al., 1988; Burke et al., 2013). For fluopyram in Fig. 2, observed pesticide concentrations show no distinct tailing and fronting. This suggests that retardation is resulting from equilibrium sorption. A similar trend is observed for most other pesticides (S3). Exceptions hold for chloridazon in MW-3, and imidacloprid in MW-3 and 4. However, prior investigations did not detect non-equilibrium sorption of chloridazon (Sánchez-Martín and Sánchez-Camazano, 1991) and imidacloprid (Cox et al., 1998a; Cox et al., 1997) and could simulate their sorption with equilibrium sorption isotherms.

Fig. 3 shows the R values for all pesticides at all well screen depths. Large variations in R are observed between the different depths for most pesticides, with R generally being largest in MW-1 and 2, and lowest in MW-4, 5, and 6. Bentazon and cycloxydim were the most mobile pesticides with R < 1.2 at all depths. D-chloridazon, MD-chloridazon, and imidacloprid were slightly less mobile, with R ranging between 0.8 and 1.5. Boscalid, chloridazon, fluopyram, and flutolanil show a larger range of R, with maximum R > 2.0 in MW-1. The largest R value was determined for boscalid in MW-2: R > 3.5. R of all pesticides never exceeded R = 1.2 in MW-4, 5, and 6, except for imidacloprid in MW-5.
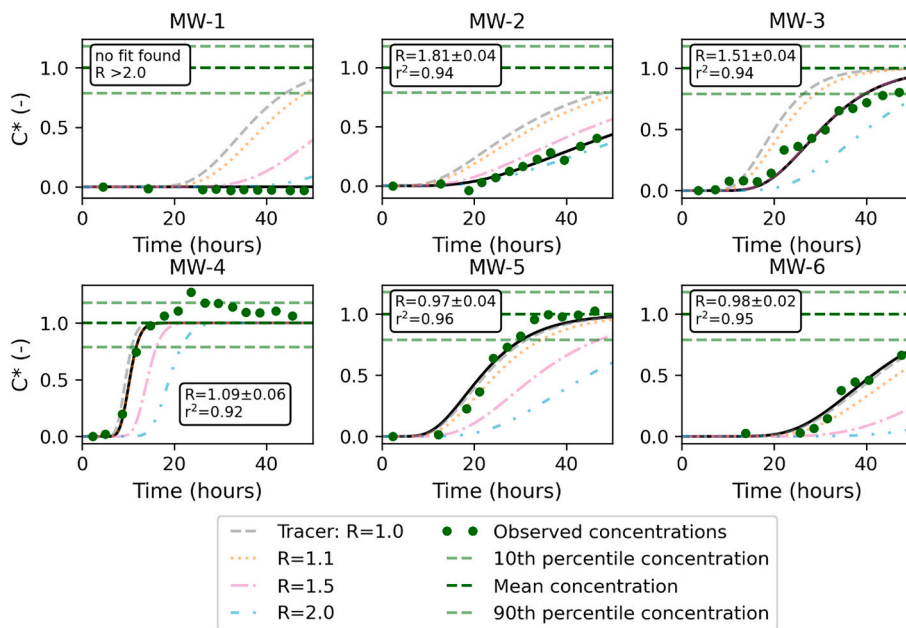
Fig. 2. Retardation factor (R) of fluopyram at different aquifer depths. The green dots show the normalized observed concentrations. The black line shows the best fit to these concentrations, from which R was obtained. The mean injected concentration is shown with a dashed dark green line, its 10% and 90% percentiles with light green dashed lines. The dashed, grey, orange, pink, and cyan lines display breakthrough with indicated R values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
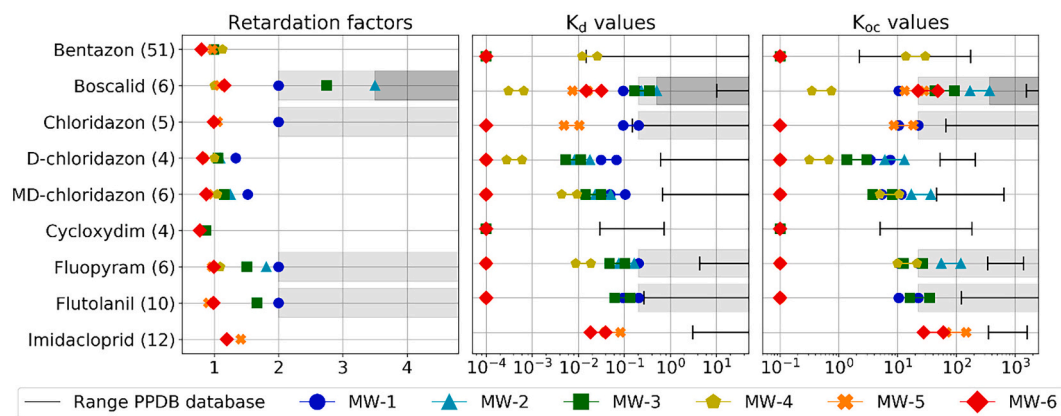

Fig. 3. Calculated pesticide retardation factors (R), partition coefficients (K_d), and organic carbon-water partition coefficients (K_{oc}). Retardation factors are not shown for model fits with $r^2 < 0.7$. The different colors and symbols present the data from the different well screen depths. The light and dark grey background indicates R > 2.0 and R > 3.5 respectively, and the K_d and K_{oc} that are determined based on this R. $K_d = 0$ were set to 10^{-4} and $K_{oc} = 0$ were set to 10^{-1}. The minimum K_d and K_{oc} is calculated based on $\varepsilon = 0.2$, and the maximum based on $\varepsilon = 0.35$, based on Table 3.1 from Appelo and Postma (2004). The ranges in black present the PPDB database ranges. The number in parenthesis behind the pesticide names show the number of studied soils which are reported in the PPDB database.

3.4. Retardation versus intra aquifer variations in geochemical properties

Pesticides observed during the experiment can be divided in 3 groups (based on pKa and isoelectric point calculations (S2)): (i) anionic pesticides, which consists of bentazon and cycloxydim; (ii) non-ionic hydrophilic pesticides (log $D_{ow} < 2$), which consist of chloridazon plus its metabolites, and imidacloprid; and (iii) non-ionic hydrophobic pesticides (log D_{ow} between 2 and 4.5), which consist of boscalid, fluopyram, and flutolanil.

As bentazon and cycloxydim retardation was not significant, Al^{3+} and Fe^{3+} hydroxide (Borggaard and Gimsing, 2008) or organic matter (Kah and Brown, 2006; Tülp et al., 2009) sorption of anionic pesticides appear subordinate mechanisms in the current study.

Several prior researches studied sorption of polar pesticides to different soil sorbents. Sánchez-Martín and Sánchez-Camazano (1991) studied chloridazon adsorption in 18 different natural soils (SOC content ranging from 0.05 to 7.70%d.w., calculated from sedimentary organic matter (SOM) content with a conversion factor of 2.0 (Pribyl, 2010)). They observed that organic matter content accounted for 72% of the

variance in adsorption. Effects of clay content on extent of adsorption were relatively small. Cox et al. (1997) studied imidacloprid sorption in soils. They discovered a strong correlation between K_f (Freundlich partition coefficient) and SOC content ($r^2 = 0.995$, 3 soils, SOC content ranged from 1.4–4.1%d.w.). Cox et al. (1998b) observed a similar correlation between K_f and SOC content ($r^2 = 0.94$) for 7 natural soils (SOC content ranged from 0.29–3.95%d.w.). These findings correspond with the higher R observed for chloridazon and imidacloprid in the current project at the depths with higher SOC contents. Therefore, we can assume that SOC is the major sorbent for the hydrophilic pesticide group.

To our knowledge, no relevant sorption studies were performed on the sorption of the specific compounds in the hydrophobic pesticide group. SOC is generally the main sorbent for hydrophobic pesticides (Fetter et al., 1999; Wauchope et al., 2002). This corresponds with the observed R in this study, which mostly increase when SOC content increases.

In the current research, pesticide R at the different depths showed the strongest correlations with SOC contents, compared to the other geochemical parameters (Table 2). Nonetheless, all observed

Table 2

Pearson correlation coefficients for the retardation factors of the different pesticides with the geochemical parameters, and between the geochemical parameters. The first part (Geo) shows the correlation between the different geochemical parameters, and the second (R) the correlation between the retardation factors and the geochemical parameters. The third column (n) shows the number of estimated sorption parameters used in the correlation. The asterisks behind the value shows the significance of the correlation.

	Pesticide	n	SOC	Clay	Carbonates	Al + Fe
Geo	SOC	6	1.00			
	Clay	6	0.98***	1.00		
	Carbonate	6	0.64	0.76*	1.00	
	Al + Fe	6	0.78*	0.86*	0.97**	1.00
R	Bentazon	4	−0.72	−0.73	−0.76	−0.64
	Boscalid	4	0.99***	0.98**	0.99***	0.96*
	D- Chloridazon	6	0.87**	0.83**	0.53	0.71
	MD-Chloridazon	6	0.87**	0.83**	0.51	0.69
	Fluopyram	5	0.68	0.58	0.45	0.53
	Flutolanil	4	0.99**	0.99**	0.99**	0.96*

*,** and *** indicate significance at $P < 0.1$, 0.05 and 0.01, respectively.

geochemical parameters are positively correlated with pesticide R, and are also positively correlated with each other. We can safely assume that SOC is the major sorbent for most pesticides studied, as this corresponds with this and prior studies. Therefore, we converted R to organic carbon-water partition coefficients (K_{oc}), which are presented in Fig. 3. At shallow depths (MW-1, 2 and 3), K_{oc} values are remarkably higher than at the depths of MW-4, 5, and 6, while K_{oc} would be expected in the same range because SOC is the main soil sorption parameter. Therefore, we can conclude that the content of SOC is not the only factor controlling pesticide sorption; the sorption reactivity of SOC probably plays a role as well.

3.5. In-situ field sorption parameters versus literature parameters

Literature sorption parameters were not available from aquifer studies (column or field studies) for the pesticides examined, except for bentazon (e.g., Tuxen et al. (2000): $R = 1.00$, Madsen et al. (2000): $R = 1.00–1.25$, Broholm et al. (2001a): $R < 1.1$). Instead, obtained R values were compared to sorption parameters retrieved from the PPDB database (Lewis et al., 2016), which is often used in pesticide transport studies (e.g., Lefrancq et al., 2017; Rouzies et al., 2019). Freundlich sorption parameters were converted to linear K_d values applicable for a defined concentration range (lowest detection limit (0.005 µg/L to maximum concentration in TDW) based on eq. 6. These Freundlich sorption parameters have mostly been obtained from batch experiments with topsoils, performed for regulatory purposes. K_d and K_{oc} obtained in this study are both considerably lower for all pesticides than the range retrieved from the PPDB database (Fig. 3).

3.6. Explanations for low K_d and K_{oc} and intra-aquifer variations

Temperature, aquifer heterogeneity, and DOC-associated transport seem not the cause of the relatively low K_d and K_{oc} observed as argued in the following.

Sorption generally decreases with increasing temperature (Delle Site, 2001) while aquifer temperatures (10–12 °C) were lower than applicable for standard batch experiments (room temperature: ±20 °C).

Aquifer heterogeneity can cause lower sorption than expected. Clay and SOC contents are significantly correlated in this study (Table 2), which reflects that less permeable and more clayey aquifer section contain the most SOC. The SOC content in the more permeable parts of the aquifer is therefore probably lower than the average SOC content determined for these aquifer layers. Consequently, less sorption may be observed than expected based on the SOC content of the entire layer. We deem in unlikely that the lower sorption is caused by aquifer heterogeneity, as small clay layers were only observed at the well screen depth

of MW-2 and MW-3 (for more information see S4) and relatively low K_{oc} were observed at all depths.

DOC-associated transport is an additional, and often rapid, transport pathway for pesticides, which can result in an increased mobility (Fetter et al., 1999). It can be indicated by larger velocities of the pesticides than the average groundwater, which can result in $R < 1.0$ (Enfield et al., 1989; Fetter et al., 1999). The larger velocities are resulting from size-exclusion effects, which are observed as molecules or ions are restricted to travel through larger pores due to their size, where groundwater velocities are greater than average (Fetter et al., 1999). This is observed for bentazon, D-chloridazon, MD-chloridazon, and cycloxydim at MW-5, 6 (and for cycloxydim at MW-3), which could suggest the occurrence of DOC-associated transport. However, we deem it unlikely that DOC-associated transport has more than a minor control at this site. As first, DOC itself does not show R < 1.0, while pesticides sorbed to the DOC travel with the same speed (Fig. 4). During the field injection experiment, sorption and/or degradation of DOC is suggested by the lower concentrations compared to the conservative concentrations during and after the breakthrough at all depths. Two analytical solutions were fitted to the observed DOC concentrations, one simulating only retardation and the other only degradation. A clearly better fit was observed for the solution simulating degradation only, which suggests that retardation of DOC is limited but not <1.0 in this aquifer (for more information see S5). Second, DOC-associated transport is only likely when a substantial fraction of the pesticide is bound to DOC, which is unlikely as the pesticides with R < 1.0 are the most hydrophilic of those pesticides studied (S2). It is therefore unclear which mechanism caused the observed $R < 1.0$.

Methodological differences and a low sedimentary organic matter (SOM) sorption reactivity probably caused the lower sorption observed in this study compared to the PPDB database. Batch experiments can result in outcomes unrealistic for aquifers, as they are often performed with different solid/solution ratios and/or dissimilar hydrodynamic conditions (Banzhaf and Hebig, 2016; Limousin et al., 2007). A low SOM sorption reactivity can also result in less sorption and can have different causes, such as the oxygen exposure extent of SOM during and after deposition (Grathwohl, 1990; Hartog et al., 2004); SOM chemical composition (Ahmad et al., 2001; Karapanagioti et al., 2000); coating and masking of SOM (El Arfaoui et al., 2012); and SOM aging (Weber and Huang, 1996). It is therefore possible that the SOM sorption reactivity of the aquifer sediments is generally lower than from the experiments performed for the sorption parameters in the PPDB database.

Furthermore, we observed remarkably lower K_{oc} values at shallow depths (MW-4, 5 and 6) compared to MW-1, 2, and 3. The higher K_{oc} at shallower depths correspond to the aeolian and fluvial aquifer sediments of the Boxtel Formation. We assume that the higher K_{oc} at the shallow depths are mainly caused by a higher SOM sorption reactivity in these aquifer sediments, compared to the marine and glacial sediments from the other Formations (Eems and Drenthe) composing the aquifer.

3.7. Insights on MAR operation and groundwater risk management

Obtaining in-situ R is only possible while performing a field injection experiment, if there is a distinct difference in pesticide concentration between the infiltrated water and ambient groundwater, and if degradation can be ruled out. The easiest and often only possibility to perform this experiment is at the start of MAR operation, although R does not necessarily stay constant afterwards. Pesticides were more mobile in this aquifer than expected based on literature sorption parameters from the PPDB database. This shows the large uncertainty which is involved by using literature sorption parameters to assess pesticide transport in aquifers. The relatively low R observed in this study can both be a positive and negative outcome for AS(T)R operation at this location. Low R simplifies restoration of the aquifer to native conditions after AS(T)R operation is stopped, as it is easier to reclaim the injected pesticides. Contrarily, injected pesticides travel further within the aquifer,
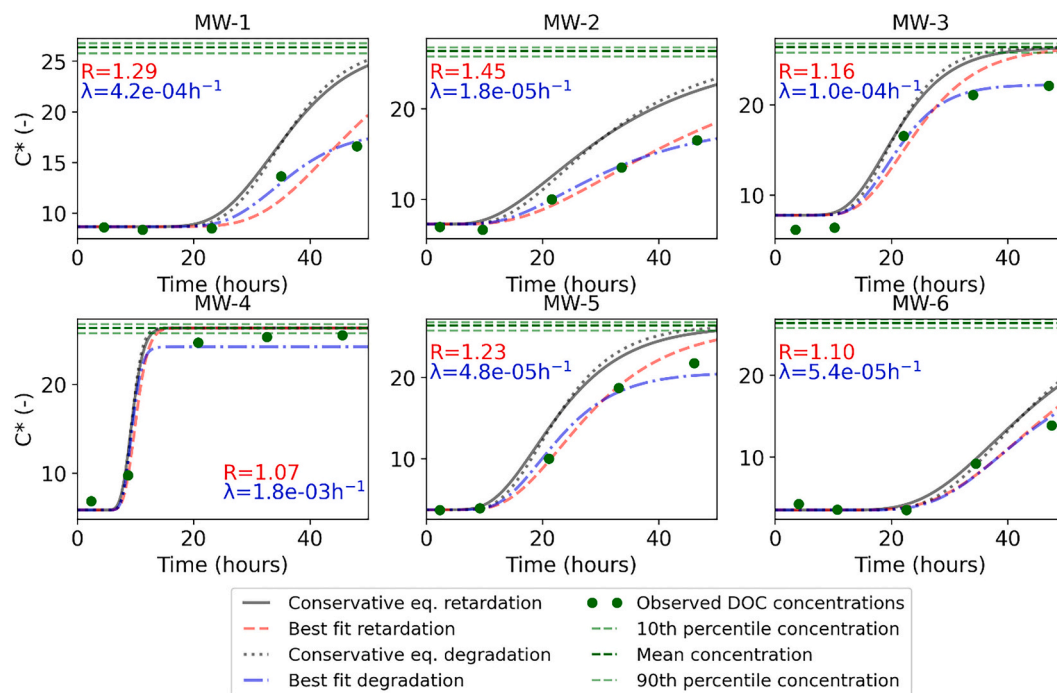
Fig. 4. Observed DOC concentrations (green dots) at different aquifer depths, and the best fit for solute transport including either retardation (dashed red line) or degradation (dotted blue line). The corresponding retardation factor (R) or first-order degradation rate constant (λ) are shown in the subplots. The grey lines show the conservative concentrations based on the 2 equations used to simulate retardation and degradation, with $R = 1$ and $\lambda = 0$. The mean injected concentration is shown with a dashed dark green line, its 10% and 90% percentiles with light green dashed lines. For more information see S5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

which increases the risk of groundwater contamination. In the current study, the pesticides examined were originating from agricultural use. Pesticide legislation changed considerably in the last decades, which resulted in a large group of new pesticides applied. There is insufficient knowledge of the fate of currently used pesticides in aquifers. More field pesticide sorption studies are needed to better understand transport of these present-day approved pesticides in aquifers.

We show the large impacts of aquifer heterogeneity on pesticide mobility in the current study. Intra-aquifer variations in hydraulic conductivity resulted in large variations in pesticide mobility, for example, in MW-6 almost $4\times$ the water volume was injected before arrival occurred compared to MW-4. These variations in mobility were strengthened by pesticide sorption. A low permeability is related to a higher clay content, and clay content is here significantly positively correlated with SOC. Therefore, aquifer parts with high permeability show often less pesticide sorption than low permeability parts. Taking aquifer heterogeneity in account is essential for an appropriate groundwater risk assessment, as pesticide mobility can vary substantially within an aquifer.

4. Conclusion

In this study, we determined sorption parameters of 7 commonly applied pesticides and 2 regularly detected metabolites during a field injection experiment in an aquifer with a wide range of sedimentary organic carbon contents. This experiment was performed at 6 depths, which enabled us to assess the effects and implications of variations in sorption. Lastly, we compared the obtained sorption parameters to a widely used literature database. Retardation factors (R) were obtained by fitting observed pesticide concentrations to an advection-dispersion equation using a non-linear least squares routine at each depth. The results were not influenced by pesticide degradation during the experiment. The most mobile pesticides were bentazon and cycloxydim, with $R < 1.1$ at all depths. The pesticides desphenyl chloridazon, methyl

desphenyl chloridazon, and imidacloprid were generally less mobile, with a maximum R observed of 1.5. Least mobile were the pesticides boscalid, chloridazon, fluopyram, and flutolanil, which showed a larger range of R with a maximum of $R > 2.0$. Pesticide retardation was largest in the shallow aquifer and decreased in the deeper aquifer. The comparison of the pesticide sorption parameters with the literature database showed that sorption in the currently researched aquifer was remarkably lower than expected based on the sorption parameters obtained mostly from batch experiments in the pesticide sorption database. The lower sorption observed in this research was most likely resulting from a lower sorption reactivity of sedimentary organic matter in the studied aquifer and/or a dissimilar solid/solution ratio and hydrodynamic conditions during the batch experiments compared to the aquifer studied. The relatively low R observed can be positive for aquifer storage (transfer) and recovery, as it is easier to reclaim all injected pesticides after operation. On the other hand, pesticides advance further into the aquifer, which increases the risk of groundwater contamination. Besides the decreasing R with depth, we also observed a decrease of K_{oc} with depth. We think it is likely that the variation in K_{oc} results from variations in sorption reactivity of the sedimentary organic matter. This study shows large intra-aquifer variations in pesticide sorption, which demonstrates the importance of taking aquifer heterogeneity in account for appropriate groundwater risk assessments.

CRediT authorship contribution statement

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.

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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.2022.104015.

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