Modeling Subsurface Fate of S-Metolachlor and Metolachlor Ethane Sulfonic Acid in the Westliches Leibnitzer Feld Aquifer

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Pesticides and their metabolites have been increasingly detected in groundwater bodies in southeastern Austria in recent years. The main objective of this study was to model the fate of the herbicide S-metolachlor [2-chloro-N-[(1S)-2-methoxy-1-methylethyl]-N-(2-ethyl-6-methylphenyl)acetamide; SMET] and the main metabolite metolachlor ethane sulfonic acid (MESA) at the Westliches Leibnitzer Feld (WLF) aquifer. For this purpose, a modeling approach based on coupling the one-dimensional vadose zone model PEARL and the two-dimensional groundwater flow and solute transport model FEFLOW was developed. To calibrate the one-dimensional pesticide fate model, we used leachate concentrations of SMET and MESA from lysimeter experiments. Additionally, samples of representative soil types in the WLF aquifer were analyzed to infer SMET- and MESA-specific fate parameters (e.g., half-life DT50, Freundlich sorption coefficient Kfoc), which were used for the PEARL model. The results show that using SMET fate parameters derived from the lysimeter data considerably improved the fit of the simulation results with the field observations compared with the application of standard laboratory-derived fate parameters accounting for soil type differences. Although locally an overestimation of the monitoring data prevailed, the description of the subsurface fate of pesticides will improve the interpretation of concentration data and the design of mitigation measures.

Abbreviations: DT50, half-life; MESA, metolachlor ethane sulfonic acid; NSE, Nash–Sutcliffe model efficiency; OC, organic carbon; PPDB, Pesticide Property Database; SMET, S-metolachlor; WLF, Westliches Leibnitzer Feld.

In Austria, almost all drinking water is supplied by untreated groundwater. Approximately half of it originates from springs out of karstified or fractured rocks, while the other half is provided by pumping wells from sand and gravel aquifers. Because of the Austrian topography, sediment-filled river valleys and basins are also intensively used by numerous human activities such as settlements, manufacturing, and in particular agriculture. Monitoring results show that the greatest threats to groundwater quality in Austria and at the European scale originate from the application of fertilizers and plant protection products as well as the emergence of corresponding metabolites in agriculture (e.g., Loos et al., 2010).

Among the vast number of plant protection products, in our present research we focused on the environmental fate of the herbicide SMET, which is often applied to maize (Zea mays L.) to combat the emergence of grass weeds. It transforms into the main metabolite MESA, which is classified as irrelevant in Austria. Thus, rather than the European drinking water limit of 0.1 μg L−1, no general groundwater concentration limits for MESA apply (European Commission, 2003), although Austria has specified a threshold concentration in groundwater of 3 μg L−1.
In the GeoPEARL-Austria study (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2013), MESA concentrations in the leachate between 1 and 10 μg L\(^{-1}\) were computed for southeastern Austria. These numbers are related to maize being the dominant crop (~50%), which is grown to feed pigs.

In recent years (2013–2015), groundwater quality data from the WLF aquifer has shown MESA concentrations in groundwater at numerous locations and different times varying between 0.074 and 1.834 μg L\(^{-1}\) (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2017). Although the values are below the threshold, the consistent detection of MESA concentrations in groundwater provides evidence of leaching of this substance from the soil into the groundwater.

For assessing the leaching potential of specific plant protection products into the groundwater, lysimeters are very valuable tools because they allow the detailed study of water movement as well as the environmental fate of fertilizers and plant protection products in the vadose zone under natural or controlled conditions.

Because the application of SMET is widespread within agricultural land, monitored groundwater concentrations of MESA can only be understood within a regional spatially distributed and temporally explicit framework. This means that the variable natural conditions in the aquifer (i.e., soil and weather) have to be considered in describing the movement and fate of SMET and its main metabolite—in the vadose zone as well as the subsequent mixing into and advective transport with the lateral groundwater flow. This task can only be accomplished by using numerical models that address the most relevant processes along the subsurface pathway of the substances.

Several numeric models have been developed that describe the transfer of pesticides from the soil surface to leaching in the vadose zone. They are able to consider the major processes involved in the environmental fate of pesticides (e.g., sorption, degradation, leaching, volatilization, plant uptake, and wash-off) at varying degrees of complexity. Widely used models include PEARL (Leistra et al., 2001), MACRO (Larso and Jarvis, 2003), and PELMO (Klein, 1995), all of which are used for environmental risk assessment and registration purposes of plant protection products (FOCUS, 2009).

Baris et al. (2012) provided a comprehensive review of a number of pesticide leaching models. Marín-Benito et al. (2014) compared three pesticide fate models using equivalent parameterization with respect to the leaching of two herbicides under field conditions in an irrigated maize cropping system. They addressed the fact that some studies show an adequate description of the water and pesticide field data, whereas others show that models could not correctly simulate the monitored data. Because of the favorable performance of PEARL in these model assessments, and to be consistent with the GeoPEARL-Austria study, we used the model PEARL in our present research to simulate the monitored water movement and fate of SMET and MESA following herbicide applications on the Wagna lysimeter.

To match the monitored MESA concentrations in groundwater, the hydrodynamic transport of the metabolite with lateral groundwater flow needed to be examined. For this purpose, we sequentially coupled the pesticide fate model PEARL with the groundwater flow and contaminant transport model FEFLOW (Diersch, 2009).

Stenemo et al. (2005) pursued a similar approach by loosely linking the pesticide fate model MACRO to the three-dimensional discrete fracture–matrix diffusion model FRAC3DVS to describe the transport of the pesticide mecoprop [2-(4-chloro-2-methylphenoxy)propanoic acid] in a fractured moraine till and local sand aquifer. However, they restricted their application to field dimensions of 40 by 40 m. They concluded that the temporal resolution of the boundary conditions were much more important with respect to simulated concentrations leaching to the regional aquifer than the spatially variable pesticide input conditions.

Loague et al. (1998a, 1998b) combined the pesticide fate model PRZM-2 with the groundwater flow model MODFLOW and the solute transport model MT3D to simulate the regional distribution of the nematocide DBCP (1,2-dibromo-3-chloropropane) concentrations in groundwater in Fresno County, California. For the period between 1960 and 1994, they generated an annual DBCP water table loading map based on 1172 individual PRZM-2 runs at a 1-km\(^2\) resolution of soil, land use, meteorology, irrigation, and groundwater table depth information. Loague et al. (1998b) inferred that nonpoint source application of DBCP was not responsible for the monitored hotspots in the study area. In both studies, the researchers stressed that it was not their intention to condition simulations to an individual site, but rather they used the best available models in an uncalibrated mode and then asked what-if questions at a regional scale, which were subsequently interpreted in terms of limiting assumptions.

Christiansen et al. (2004) added a macropore description to the coupled MIKE SHE/Daisy code and applied the model to a small catchment in Denmark. They concluded that although macropore processes have no dominating effect on groundwater recharge at the catchment scale, they will have significant effects on pesticide leaching to groundwater because some of the pesticides are transported rapidly downward in the soil to zones with less sorption and degradation. Bergvall et al. (2011) coupled the vadose zone model HYDRUS-1D to the groundwater flow model MODFLOW and the solute transport model MT3D to describe significant processes that govern the subsurface transport of the pesticide metabolite 2,6-dichlorobenzoamide in a glacifluvial esker aquifer. They reproduced the observed concentrations at the regional scale, attributed half of the model uncertainty to hydraulic conductivity...
in the aquifer and infiltration rate, and applied the model to optimize the location of extraction wells for remediation. Herbst et al. (2005) linked the models TRACE and 3DLEWASTE to reveal the behavior of the pesticide isoproturon \((N,N\text{-dimethyl-N'}\text{-[4-(1-methylethyl)phenyl]urea})\) at a 20-km\(^2\) test area in the lower Rhine embayment. The highest concentrations of isoproturon in groundwater were estimated for areas with a thin and permeable soil layer, whereby the researchers stressed the importance of the processes in the unsaturated zone.

It was the objective of our study to apply the sequentially coupled PEARL and FEFLOW models at the WLF aquifer. Additionally, we tested the use of lysimeter-derived pesticide fate data for regional modeling of MESA groundwater concentrations and compared the results against the use of standard laboratory-derived fate parameters for SMET and MESA considering soil type variability.

**Materials and Methods**

**Investigation Area**

The investigation area, the WLF (see Fig. 1), is located ~30 km south of Graz, Austria, and has a size of 44 km\(^2\). The hydrogeological characteristics of the area have already been depicted in Klammler et al. (2013) and Händel et al. (2013). The WLF aquifer comprises quaternary gravel with an average thickness of 8 m. Groundwater recharge in the investigation area is mainly provided by infiltrating precipitation without any predominant periods for groundwater recharge. The average groundwater depth is ~3.5 m. Aquifer hydraulic conductivities vary between \(1 \times 10^{-4}\) and \(7 \times 10^{-3}\) m s\(^{-1}\). The mean annual precipitation is 938 mm, with a maximum in August (125 mm) and a minimum in January (28 mm), while the average annual air temperature is 10.5°C (monitoring period 1991–2016).

Spatial soil information is available only for arable land according to the Austrian Soil Mapping (Bundesministerium für Land- und Forstwirtschaft, 1974; maximum exploration depth of 1 m). Thirty percent of this area is covered with sandy-clayey Dystric Cambisols, and in the floodplains along the rivers mainly Dystric Fluvisols can be found. Neighboring soil types were allocated to residential areas and forests for the simulations.

The WLF is intensively used for agriculture. At present, ~54% of the investigation area is arable land used for cultivating maize (50%), oil pumpkin \((Cucurbita maxima\) Duchesne) (13%), grassland (17%), and some other crops with minor portions (average percentages 1996–2014, based on the integrated administration and control system of the EU). Approximately 28% of the investigation area is used for residential purposes and 14% is forest.

**Lysimeter Setup in Wagna**

In the WLF aquifer, we have operated several lysimeters within an agricultural test field located in Wagna for >20 yr to investigate the impact of conventional and organic farming schemes on yield and leachate characteristics. The lysimeter setup has been repeatedly described in detail (von Unold and Fank, 2008; Klammler and

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Fig. 1. Location of the aquifer Westliches Leibnitzer Feld (WLF; marked by the cross) and the lysimeter in Wagna, including the land-use distribution, soil sampling locations, and the mean groundwater (GW) level.
The lysimeters were cultivated by local farmers with typical agricultural machinery (e.g., a plow) during which the upper ring of the lysimeter was removed. The lysimeter scale has a resolution of 35 g (0.035 mm water equivalent). Inside the monolith, various measurements can be taken at 10-min intervals at depths of 35, 60, 90, and 180 cm: (i) the water content using time-domain reflectometry probes, (ii) the hydraulic potential using tensiometers, and (iii) the soil temperature. A layer of suction cups is installed in the gravel filter layer to control the lower boundary condition of the lysimeter. An automatic vacuum pump is used to transfer the soil water tension—measured at 180 cm below the surface outside the lysimeter—to the suction cups at the lysimeter bottom. Thus, flow rates equivalent to those in the undisturbed field can be achieved. Leachate is sampled through the suction cup layer, whereby the amount of leachate is detected using a tipping bucket with 0.1-mm resolution.

**Application of S-Metolachlor on the Wagna Lysimeter**

The conventional lysimeter was cultivated with a crop rotation consisting of maize (2010, 2012, 2014), triticale (*Triticeaeae* spp.) (2011 and 2015) and pumpkin (2013). Outside the crop vegetation periods, typical catch crops (ryegrass [*Lolium multiformum* Lam.] or forage rye [*Secale cereale* L.]) were planted.

Gardo Gold (Syngenta Agro GmbH), containing SMET and terbutylazine [6-chloro-N-(1,1-dimethylethyl)-N’-ethyl-1,3,5-triazine-2,4-diamine], was applied on the lysimeter on 24 May 2012. Application rates were equivalent to 3.47 kg ha$^{-1}$ for SMET and 2.08 kg ha$^{-1}$ for terbutylazine. Dual Gold (Syngenta Agro GmbH), containing only SMET, was applied at a rate of 1.2 kg ha$^{-1}$ on 12 May 2013 and 0.96 kg ha$^{-1}$ on 10 May 2014. The plant protection products were applied postemergence as suspensions onto the soil surface of the field including the lysimeter without any additional irrigation. The field area was chosen for the application to ensure an even distribution of the pesticide on the lysimeter surface and minimize impacts from the surrounding area.

Leachate from the lysimeter was collected at an average sampling interval of 10 d (when sufficient leachate had been produced) and stored at −18°C prior to analysis. Samples were analyzed by liquid chromatography–mass spectrometry and direct injection after the addition of an internal standard.

Based on the Pesticide Property Database (PPDB; University of Hertfordshire, 2017), SMET is moderately soluble in water (480 mg L$^{-1}$), nonpersistent with a half-life (DT$_{50}$) value in the field of 21 d, and moderately mobile with a Freundlich $K_{foc}$ of 226.1 mL g$^{-1}$. It transforms into the key metabolites metolachlor oxanilic acid and MESA with estimated maximum occurrence fractions in soil of 0.109 and 0.124, respectively. Metolachlor ethane sulfonic acid is described as having a high solubility in water (212.461 mg L$^{-1}$), persistent with a typical DT$_{50}$ value of 132 d, and very mobile with a linear $K_{foc}$ of 9 mL g$^{-1}$.

**Regional Variation of Environmental Fate Parameters of S-Metolachlor and Metolachlor Ethane Sulfonic Acid**

The degradation of SMET was determined for seven representative soils (samples taken not deeper than 20 cm) and one deeper sample (between 40 and 60 cm) within the investigated area. The locations of the soil samples, which were taken at the beginning of May 2016, are shown in Fig. 1. One soil sample was taken at each of the two agriculture-operated lysimeters in Wagna, each having a different soil type.

The soil samples varied with respect to OC content (3.2–19.4 g kg$^{-1}$), clay (12–19%), cation exchange capacity (6.3–13.2 cmol$_{c}$ kg$^{-1}$), and pH (6.0–6.4). Degradation half-life was measured according to the Organization for Economic Cooperation and Development (2002) and at 18°C and 22 and 32% gravimetric water content, respectively. The DT$_{50}$ varied between 28.1 and 38.8 d for the surface soils and was much higher (DT$_{50}$ = 123.2 d) in the subsurface sample.

Freundlich adsorption coefficients of SMET were determined using a standard batch equilibrium method following the Organization for Economic Cooperation and Development (2000). The $K_{f}$ values ranged from 1.39 to 1.9 mL g$^{-1}$ ($K_{foc} = 93.7–121.9$ mL g$^{-1}$, $n = 0.71–0.77$) in four surface soils and was 0.19 mL g$^{-1}$ ($K_{foc} = 60.8$ mL g$^{-1}$, $n = 0.8$) in the subsurface soil. The most important soil property influencing the sorption was the OC content of the soil. The linear distribution coefficient ($K_{D}$) for MESA varied between 0.05 and 0.19 mL g$^{-1}$ ($K_{OC} = 6.4–14.6$ mL g$^{-1}$).

**Calibration of PEARL on Lysimeter Data**

For modeling the monitored SMET and MESA concentrations in the leachate resulting from the three applications of plant protection products, we used the environmental fate model PEARL (FOCUSPEARL 4.4.4; Leistra et al., 2001). This one-dimensional model uses a convection–dispersion equation to simulate the transport of solutes in the vadose zone. Instantaneous equilibrium or kinetic sorption is described by either a linear or a Freundlich equation and degradation by first-order kinetics depending on soil water content, temperature, and depth. PEARL is linked with the SWAP (Soil, Water, Atmosphere, and Plant) model (Kroes et al., 2008), whose soil hydrology is described by the Richards equation. The SWAP model calculates the evapotranspiration according to a
modified Penman–Monteith equation (Monteith, 1965; Van Dam et al., 1997) or according to the Makkink equation (Makkink, 1957).

The van Genuchten–Mualem parameters for describing the hydraulic characteristics of the lysimeter were derived from in situ measurements of water contents and matrix potentials inside the lysimeters and are presented in Table 1. A dispersivity length of 0.1 m was assumed.

During the calibration, we used values from the PPDB and from the lysimeter-specific soil analysis in the laboratory to match the time series of SMET and MESA fluxes between April 2012 and June 2015. Based on the results of an upfront sensitivity analysis, we focused on $DT_{50}$ and $n^{-1}$ values for the fitting of SMET observations and $DT_{50}$ and $K_{foc}$ values as well as the coefficient of transformation for the matching of monitored MESA concentrations in the leachate in a manual trial-and-error procedure. We chose this method over an automated calibration procedure because of the higher flexibility to handle options to steer the numerous hydraulic and environmental fate parameters given the characteristics of the monitored time series.

**Application of PEARL to the Agricultural Part of the Aquifer**

To take the nonpoint-source nature of the application of plant protection products into account, the parameterization specified at the Wagna lysimeter needed to be transferred to the aquifer scale. For this purpose, the WLF aquifer was divided into homogeneous subunits that showed uniform soil, weather, and land-use (e.g., forests, settlements, farmland) conditions. In the area of the WLF aquifer, data from one meteorological station were available to drive the PEARL simulations.

The van Genuchten parameters required for the simulation of the 23 different soil types within the investigation area were derived by curve fitting to existing retention curves. For the definition of these curves, Murer (1998) used values for pore volumes and field capacities derived from the Austrian Soil Mapping (after AG Boden [1994] and Eisenhut [1990]). He also provided hydraulic conductivity curves, which were the basis for defining the required saturated hydraulic conductivities for PEARL.

The actual set of crops grown each year was recorded based on cadastral municipalities in Austria. The percentage of maize grown can vary among different municipalities in the same year and change between years in the same municipality. In the PEARL simulations, only cultivation of maize with the application of SMET as the sole herbicide was considered per subunit. The overlay between the spatial distribution of different soil types and the cadastral municipalities yielded a total of 79 homogeneous subunits in the vadose zone. During the PEARL simulations, different environmental parameter sets were used in the subunits, which are described below.

Because maize represents only a fraction of the crops grown, the computed time series of MESA fluxes needed to be reduced by multiplication with the corresponding maize percentage for this particular cadastral municipality and year. Moreover, we assumed that each farmer used the maximum dose of SMET (i.e., 1.25 L ha$^{-1}$) with no reduction for wind drift, surface runoff, or interception. Additionally, because of the effective absence of organic material, no decay in the vadose zone underneath the soil layers or in the saturated groundwater body was taken into account. Consequently, below the soil layers and in the saturated part of the groundwater body, only conservative transport of MESA along with groundwater flow was considered. This approach is consistent with the application practice of pesticide fate models (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2013).

**Sequential Coupling between PEARL and FEFLOW**

To match the monitored MESA concentrations in the groundwater, the pesticide fate model PEARL was sequentially coupled with the groundwater flow and contaminant transport model FEFLOW (Diersch, 2009). Because PEARL is a one-dimensional vertical model, this procedure is suitable only if lateral flow in the vadose zone can be neglected, which is the case in most porous media aquifers in river valleys and basin fills. The sequential coupling approach, which was developed to simulate the impact of diffuse N application as fertilizer, was discussed in detail by Klammel et al. (2013).

Within the sequential coupling between PEARL and FEFLOW, the results of unsaturated water and MESA fluxes were provided as an upper boundary condition time series to FEFLOW (i.e., as a source term for flow or mass). By adding a gravel horizon underneath the soil layers that was sufficiently deep to cover the varying thickness of the vadose zone as a result of the fluctuating groundwater level, PEARL results were stored at a depth interval of 10 cm for daily time steps, generating a corresponding depth–time matrix. A specific add-in module for FEFLOW was developed to use these depth–time matrices of unsaturated water flow and MESA mass

<table>
<thead>
<tr>
<th>Depth</th>
<th>$\theta_{sat}$</th>
<th>$\theta_{res}$</th>
<th>$\alpha$</th>
<th>$n$</th>
<th>$K_{sat}$</th>
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<tr>
<td>cm</td>
<td>m$^3$ m$^{-3}$</td>
<td></td>
<td>1 cm$^{-1}$</td>
<td></td>
<td>m s$^{-1}$</td>
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<tr>
<td>0–30</td>
<td>0.39</td>
<td>0.16</td>
<td>0.05</td>
<td>1.33</td>
<td>$5.0 \times 10^{-6}$</td>
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<tr>
<td>30–50</td>
<td>0.38</td>
<td>0.19</td>
<td>0.04</td>
<td>1.44</td>
<td>$6.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>50–80</td>
<td>0.44</td>
<td>0.11</td>
<td>0.065</td>
<td>1.2</td>
<td>$6.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>80–130</td>
<td>0.20</td>
<td>0.03</td>
<td>0.25</td>
<td>1.4</td>
<td>$5.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>&gt;130</td>
<td>0.14</td>
<td>0.03</td>
<td>0.25</td>
<td>1.9</td>
<td>$1.2 \times 10^{-4}$</td>
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Table 1. Parameters of the van Genuchten model used for the PEARL simulation, including saturated and residual water content ($\theta_{sat}$ and $\theta_{res}$, respectively), shape fitting parameters $\alpha$ and $n$, and saturated hydraulic conductivity ($K_{sat}$).
as look-up-tables, that is, FEFLOW picked up water and MESA fluxes from the look-up-tables for the depth of the groundwater table at the corresponding time step.

**Groundwater Flow and Conservative Transport Model for the Aquifer**

Groundwater transport of MESA driven by lateral groundwater flow was simulated with the groundwater flow and transport model of the WLF aquifer described by Klammler et al. (2013). It is a two-dimensional groundwater model implemented in FEFLOW covering the time period between 1993 and 2009 and it has recently been extended to 2015. Because NO₃ and MESA can both be treated as conservative substances in the saturated domain, we assumed that the saturated transport model derived by Klammler et al. (2013) could also be used to simulated groundwater transport of MESA. In this context, we followed a practical approach by not aiming to exactly match a monitored time series of metabolite concentrations in the groundwater but rather attempting to reproduce the essential patterns of the concentration time series behavior.

The dynamic groundwater recharge input distribution into the groundwater under agriculture was computed at a daily time interval using the soil water and N transformation model SIMWASER–STORASIM (Feichtinger, 1998). Groundwater recharge for nonagricultural areas in the WLF aquifer (e.g., forests) was calculated using the FAO Penman–Monteith method (Allen et al., 1998) to estimate evapotranspiration. Groundwater recharge from residential areas was determined following a combined approach, whereby precipitation falling on paved areas was collected and infiltrated directly into the aquifer by drainage shafts. Groundwater recharge from grassland was simulated by running the one-dimensional vertical soil water movement and plant growth model SIMWASER (Stenitzer, 1988).

Groundwater recharge for the cultivation of maize was computed with the SWAP model within the coupled PEARL–FEFLOW approach. For representative subunits, these groundwater recharge time series were compared with those resulting from the approach described by Klammler et al. (2013) for agricultural land to ensure that the two groundwater recharge patterns were compatible and could be used in the same model domain. The comparisons showed a favorable match, whereby implementing the groundwater recharge time series computed with PEARL into the existing groundwater flow and transport model did not introduce a systematic error in the further computations.

**Modeling of Metolachlor Ethane Sulfonic Acid Groundwater Concentrations in the Aquifer**

Aquifer-wide MESA groundwater concentrations were simulated for four different versions of fate parameter distributions (shown in Table 2) and application doses. The simulated MESA groundwater concentrations were assessed at six monitoring wells (for locations, see Fig. 4) representing areas of different MESA groundwater concentration levels:

1. In Version 1, the most likely SMET and MESA fate parameters from the PPDB (University of Hertfordshire, 2017) were uniformly applied to simulate the MESA groundwater concentrations in the WLF aquifer to illustrate the situation whereby no site-specific fate information is available (i.e., no knowledge from calibration on lysimeter data or soil-specific physicochemical analysis). For plant uptake, values according to Briggs et al. (1982) were used since there are no values specified in the PPDB.

2. In Version 2, the SMET and MESA fate parameters as derived from the calibration of the Wagna lysimeter concentration data were used uniformly distributed across the 23 different soil types in the model domain.

3. In Version 3, the effect of reducing the overall applied volume of SMET by 30% on the resulting MESA groundwater concentrations was evaluated in combination with the fate parameters from Version 2 to consider the fact that not all farmers might have used the SMET compound as a herbicide. The selected percentage is only an assumption to quantify the sensitivity of the input dosage uncertainty.

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<tbody>
<tr>
<td>DT₅₀, d</td>
<td>21 (11–31)†</td>
<td>33</td>
<td>41</td>
<td>132 (94–169)</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>Kₘₚ des. mL g⁻¹</td>
<td>226 (110–369)</td>
<td>226</td>
<td>131</td>
<td>9 (3–22)</td>
<td>18.3</td>
<td>7.8</td>
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<tr>
<td>n⁻¹</td>
<td>1.06 (1.053–1.071)</td>
<td>0.95</td>
<td>0.79</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>FacUpt</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
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<tr>
<td>Coefficient of transformation</td>
<td>na</td>
<td>na</td>
<td>0.124#</td>
<td>0.06</td>
<td>0.07</td>
<td></td>
</tr>
</tbody>
</table>

† DT₅₀, half-life; Kₘₚ des. Freundlich sorption coefficient related to organic content; n⁻¹, Freundlich exponent; FacUpt, coefficient for plant uptake.
‡ The range of measured values as presented within the PPDB provided in parentheses.
§ Values according to Briggs et al. (1982); not specified in the PPDB.
¶ na, not applicable.
# Estimated maximum occurrence fraction.
4. In Version 4, soil-specific fate parameters were applied to ~50% of the agricultural area in the WLF aquifer following the results of the laboratory analysis for the investigated surface soil types. In this version, the 30% dose reduction from Version 3 was still used.

**Results**

**Modeling of S-Metolachlor and Metolachlor Ethane Sulfonic Acid Application at the Wagna Lysimeter**

Figure 2 shows the cumulative leachate amount for crop periods with a Nash–Sutcliffe model efficiency coefficient (NSE; Nash and Sutcliffe, 1970) value of 0.56 ($n = 195$). It can be seen that the general level and the behavior of the measured leachate is well represented by the simulation (especially in 2010, 2011, and 2012, including the period without any leachate between autumn 2011 and spring 2012), which was based on daily values. Nevertheless, there are still periods in which measured leachate rates do not fit well to the modeled curve (e.g., during the peak in spring 2013, the catch crop in winter 2013–2014, or the fallow period in autumn and winter 2015). The mean annual leachate water rates between 2010 and 2014 were 371 and 367 mm for monitored and simulated leachate, respectively.

The simulation results for leaching of SMET and MESA are presented in Fig. 3 and were based on the calibrated parameters (Version 2) given in Table 2. It can be seen that the first occurrences of SMET in the leachate in the summer of 2012 could not be reproduced with PEARL (top image of Fig. 3). However, the nature of the monitored SMET concentrations between August 2014 and June 2015 were well represented by PEARL, although there was a slight delay in the simulated results. Because the analysis of leachate SMET concentrations was terminated in June 2015, the predicted peak in SMET concentrations in autumn 2015 could not be compared against data. The NSE for SMET computed between May 2012 and June 2015 is 0.19.

For MESA, the comparison between monitored and simulated leachate concentrations (bottom image of Fig. 3) looks different. While the monitored first arrival of MESA in the leachate (in October 2012) could be matched with PEARL, the simulated values thereafter clearly overestimated the monitored concentrations until November 2013. The second and third coherent appearances of MESA in the leachate were better reproduced with PEARL, yet absolute single peak values were noticeably underestimated by the model. Therefore, corresponding NSE values are low and vary between ~0.19 for the period between May 2012 and June 2015 and 0.16 for the time span between February 2014 and June 2015.

**Comparison between Computed Time Series of Metolachlor Ethane Sulfonic Acid Groundwater Concentrations and Observations**

The location of the selected monitoring wells (observation wells) is shown in Fig. 4 against the background of the simulated MESA groundwater concentrations averaged between 2011 and 2015. The overall distribution pattern of the simulated MESA groundwater concentrations (based on an average node distance of 27 m in the computational mesh) is dominated by areas with low predicted values gradually changing into adjacent regions with medium range MESA groundwater concentrations. Two distinct areas showing high averaged MESA groundwater concentrations emerge in the eastern and the far southwestern part of the WLF aquifer.
Figure 5 shows the comparison between the MESA groundwater concentration time series for the four simulation versions and the available observations at selected monitoring wells. At OW45212 (a region of high simulated MESA groundwater concentrations; top left image in Fig. 5), the fluctuation range of the MESA groundwater time series based on the four different versions reduced from between ~4 and 10 μg L\(^{-1}\) for Version 1 to between roughly 1 and 3 μg L\(^{-1}\) for Version 2. The time series at OW45212 tended to have an annual concentration maximum in the summer followed by a 4- to 5-mo decline. The uniform application of the fate parameter set derived at the Wagna lysimeter within the entire WLF aquifer (Version 2) significantly shifted the simulated MESA groundwater concentrations toward the observations. Reducing the application dose of SMET by 30% (Version 3) further improved the simulated MESA groundwater concentrations through lowering them on average by 0.5 μg L\(^{-1}\). Assigning the soil-specific fate parameters to the dominant (~50%) soil type in the WLF aquifer (Version 4) yielded roughly the same MESA groundwater concentrations as uniformly using the lysimeter-derived fate parameters.

At OW12292 (center left image in Fig. 5), using the fate parameter set of Version 2 and the reduced SMET application (Version 3) led to a decrease in the simulated MESA groundwater concentrations by a factor of approximately five compared with the simulated values using Version 1. The two MESA groundwater observations could be well described by either Version 2 or 3, which was not the case for Version 1. For OW22232 (bottom left image in Fig. 5), a pattern of annual MESA groundwater concentration maxima in autumn can be observed throughout the time series, whereas the MESA groundwater concentration minima do not show a clear distribution. The order of magnitude and the trend of the MESA groundwater concentration measurements were well captured by the corresponding time series applying parameters from Versions 2 and 3. The MESA groundwater concentrations from Version 4 were slightly higher than those from Version 2, which was also true for OW12292.

The same basic features can also be found by comparing the simulated time series of MESA groundwater concentrations at further monitoring wells OW12022 (top right image of Fig. 5), OW12202 (center right image of Fig. 5), and OW45312 (lower right image of Fig. 5). However, at OW12202 and OW45312, the time series using the input sets from Versions 2 and 3 consistently overestimated the monitored MESA groundwater concentrations, albeit these are small absolute differences only. At OW12202, the trend of the monitored MESA groundwater concentrations was properly met by the simulated values. Using the laboratory-derived fate parameters for the dominant soil type (Version 4) led to a worse reproduction (i.e., higher absolute values) of the observed MESA groundwater concentrations than Version 2 for wells OW12202 and OW45312, whereas it yielded about the same results for OW12022.

**Discussion**

With PEARL, the major characteristics of the monitored time series of SMET mass leached in the lysimeter at the 180-cm depth could be captured well. However, this was not the case for MESA leachate concentrations where, particularly after the first SMET application in 2012, the simulation results clearly overestimated the monitored MESA leachate concentrations. The discrepancies between the monitored and the modeled time series can also be seen in the low (i.e., close to zero) NSE values, which mainly were due to the mismatch of monitored and modeled spikes. Thus, the predictive power of the fitted model is limited given that an NSE value of 1 indicates a perfect match.

It was not possible to find a single fate parameter set with which the observed MESA leachate concentrations from the first SMET
application and the two consecutive applications could be reproduced. This also may be related to the fact that experimental conditions during the 2012 SMET application were different (i.e., individual maize plants were covered during the application, a handheld spray gun was used, and some of the maize plants were removed from the lysimeter), which could not be implemented in the PEARL model, probably leading to an overestimation of the simulated MESA concentrations. Hence, during the calibration process, the focus was placed on matching the second and third groups of MESA occurrences in the leachate with PEARL. Water contents at different depths were calibrated separately and yielded NSE values between 0.48 and 0.62.

For modeling the fate of SMET and MESA, it was a great benefit to have site-specific fate parameters available instead of using only parameter values given in the PPDB. Only the Freundlich sorption coefficient for SMET and the Freundlich exponent for MESA were used as the most likely values from the PPDB, whereas the majority of the parameter values were modified sometimes even beyond the parameter range indicated in the PPDB (e.g., DT50 and n−1 for SMET) because of the physicochemical characterization of the lysimeter soil type. This implies that if no lysimeter data from a compound application and no physicochemical analysis of local soils are available, the use of the most likely values from the PPDB for environmental fate parameters might lead to only a coarse description of the leaching features for a given compound or unrealistic fitted parameters that will not be appropriate for predictions. Thus, it can be deduced that the use of environmental fate parameters derived from calibrating leachate concentration time series in a lysimeter represents a central element within our regional model approach because the concentration time series in lysimeters also include the impacts of flow processes on the leaching characteristics of the compounds.

The transfer of the resulting groundwater recharge and MESA fluxes to the saturated domain from PEARL was implemented
Aquifer-wide MESA groundwater concentrations were simulated for four different versions of fate parameters and application doses. At some monitoring wells, a tendency of overestimation of the observed MESA groundwater concentrations by the simulated wells can be noted (OW45312, OW12202, and OW45212 in part) even for the best-performing version. The overestimation cannot be explained only by the moderate success in calibrating the MESA leachate concentration time series at the Wagna lysimeter because in 2013 and 2014, the simulated mass flux was lower than the monitored fluxes. The extent to which these findings are compound specific and dependent on the prevalent vertical profile (i.e., coarse sand and gravel underlying soil layers) and weather conditions must be further investigated.

As a surprising outcome, the simulated MESA groundwater concentrations in Version 4 increased, leading to a clear overestimation of the observations whereby the overall simulation results deteriorated. Nonetheless, making use of the laboratory-derived fate parameters improved the calibration of the lysimeter leachate data. Thus, it can be inferred that the use of spatially distributed, laboratory-derived fate parameters without placing them in a hydraulic context (as with the lysimeter experiment) does not necessarily improve regional groundwater concentration simulation results.

From a technical perspective, the implementation of the sequential coupling between PEARL and FEFLOW to simulate the continuous subsurface pathway of SMET and MESA as well as the related fate processes appears to be a promising approach. The variability of soil types and agricultural practices (i.e., percentages of maize cultivated per cadastral municipality) led to a total of 79 PEARL simulation models to be set up. This number is still small compared with gridded nationwide studies about the leaching potential of numerous plant protection products, which can include several hundred thousand simulation runs (e.g., Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2013).

The one-dimensional vertical representation in PEARL implies that horizontal flow processes in the vadose zone hold minor significance and can be neglected, which is the case for the WLF aquifer and most river valleys and basins where agricultural production is conducted. Moreover, there is no process-driven need for feedback between the saturated and the vadose model domain in the WLF aquifer (i.e., the groundwater table is below the reach of plant roots), whereby the sequential coupling approach can be followed without further limits of applicability.

If horizontal flow exists in the vadose zone, a three-dimensional model needs to be applied to simulate flow and environmental fate processes. The resulting recharge and leaching mass time series can subsequently be coupled with a groundwater flow and pollutant transport model. Alternatively, a three-dimensional model that describes water flow and solute movement in variably saturated media could be applied (e.g., as an extension to the approach described by Bergvall et al., 2011). In the case of shallow groundwater tables, where plant roots reach into the groundwater, the coupling of models between the vadose and the saturated zone has to be implemented at an appropriate time interval (e.g., 1 d, depending on the temporal dynamics of the dominating processes); current results from the groundwater model (i.e., groundwater level and compound concentration) are then used as the lower boundary conditions for the following time step in the vadose zone model. Subsequently, the results from the vadose zone model (i.e., water flux and leachate mass) are back-transferred to the groundwater model as the upper boundary conditions for solution of the actual time step.

We highly recommend using lysimeter experiments to understand groundwater concentrations of a given compound because the derived environmental fate parameters from lysimeter data reflect the interplay between hydraulic and physicochemical processes in the vadose zone. Soil-specific environmental fate parameters determined in the laboratory narrow the range of parameter values indicated in the PPDB and assist in the modelling of leachate data from lysimeter experiments. If no lysimeter experiments for the targeted compound in a given aquifer exist, it is challenging to specify a general modeling protocol. For aquifer-scale modeling, our findings indicate that difficulties in modeling the observed groundwater concentrations may arise. Nonetheless, we still suggest using a groundwater transport model to run scenarios whereby vadose zone processes can be related to groundwater concentration data.

In general, the overall modeling approach (i.e., sequential coupling between PEARL and FEFLOW) is transferable to other aquifers and for different compounds and allows a transparent methodology to study the impact of different agricultural practices on groundwater concentrations of plant protection products and their metabolites. Additionally, it denotes a reasonable modeling procedure to link the risk assessment of plant protection products to groundwater protection goals for drinking water use based on which groundwater quality monitoring schemes can be developed. Because of lower detection limits and lower analysis costs per sample, it can be expected that in the near future the frequency of compound concentrations in the groundwater exceeding the corresponding detection limit will increase and thus the available database for matching simulation results will quickly grow.

Conclusions
We have implemented the sequential coupling between PEARL and FEFLOW models to describe the subsurface fate of MESA at
the aquifer scale. The parameterization of PEARL was supported by an experimental application of SMET on a well-established lysimeter in the WLF aquifer and laboratory analysis of soil samples to delineate location-specific fate parameters. Nonetheless, matching the monitored MESA leachate concentration time series with PEARL proved a challenging task and did not lead to satisfactory results for high application doses of SMET.

The lysimeter-derived fate parameter set was used to simulate the leaching of MESA into the groundwater body at the aquifer scale considering the distribution of soil types and maize cultivation percentages. For the transfer of groundwater and MESA fluxes to groundwater model inputs, the actual groundwater table was taken into account and therefore the complete vadose zone passage is represented. Monitored MESA groundwater concentrations were simulated by running the coupled models with four different combinations of fate parameter sets and application dosages. For the given compounds and prevailing natural conditions, the application of specific fate parameters for the dominant soil type in the WLF aquifer notably drives the simulation results toward the magnitude of monitored MESA groundwater concentrations. An assumed 30% reduction of the SMET application (Version 3) improves the simulated MESA groundwater concentrations at some locations. We also tested the additional use of specific fate parameters for the dominant soil type in the WLF aquifer, which surprisingly resulted in a deterioration of the simulated MESA groundwater concentrations. Thus, it can be inferred that lysimeter experiments and the subsequent modeling of leachate dynamics yield integrated parameter sets that are better suited for regional groundwater quality simulations than the use of spatially distributed laboratory-derived fate parameters.

Overall, the developed model system is well suited and robust for describing the entire subsurface pathway and fate of plant protection products including groundwater transport at the aquifer scale. Although a lot of site-specific information was available and has been implemented to the best of our understanding, the simulated MESA groundwater concentrations at some locations tended to overestimate the observations, which may be associated with uncertainties about the real application dose of SMET throughout the WLF aquifer.

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