Macropore–matrix mass transfer of reactive solutes quantified by fluorescence imaging

Christoph Haas1 | Martin Leue2 | Ruth H. Ellerbrock | Horst H. Gerke1

1 Working Group “Hydropedology,” Research Area 1 “Landscape Functioning,” Leibniz Centre for Agricultural Landscape Research (ZALF), Eberswalder Strasse 84, D-15374, Müncheberg 15374, Germany
2 Working Group “Landscape Pedology,” Research Area 1 “Landscape Functioning,” Leibniz Centre for Agricultural Landscape Research (ZALF), Eberswalder Strasse 84, D-15374, Müncheberg 15374, Germany

Correspondence
Christoph Haas, Working Group “Hydropedology,” Research Area 1 “Landscape Functioning,” Leibniz Centre for Agricultural Landscape Research (ZALF), Eberswalder Strasse 84, D-15374, Müncheberg, 15374 Germany.
Email: christoph.haas@zalf.de

Assigned to Associate Editor Martine van der Ploeg.

Funding information
Deutsche Forschungsgemeinschaft, Grant/Award Numbers: GE 990/10-1, GE 990/14-1, LE 3177/1-2

Abstract
Horizontal infiltration experiments with a fluorescent dye (e.g., Na-fluorescein) potentially allow the quantification of the macropore–matrix mass transfer of reactive solutes through coated macropore surfaces. The objectives were (a) to determine the movement and map the spatial mass distributions of a reactive and fluorescent dye (i.e., Na-fluorescein) at the millimeter scale during horizontal tracer application to the intact structural surface of a soil aggregate, and (b) to validate the method by comparing total masses as quantified with Fluorescence imaging with total applied dye masses. For the quantification of dissolved masses of dye, millimeter-scaled distributed water contents obtained from horizontal flow simulation using Hydrus-1D were multiplied with mapped dye solution concentrations. The spatial distribution of dye concentrations was visualized and quantified with a fluorescence imaging technique at a pixel resolution length of ~100 μm. Submillimeter-scaled distribution maps of adsorbed dye concentrations were derived using the calibrated Freundlich adsorption model. The sorption isotherm predicted that most of the dye was adsorbed to soil. In total, 1,366 μg of dye was transferred through the coated matrix block, of which 1,181 μg was adsorbed to soil. The applicability of the method was validated by comparing applied and recovered Na-fluorescein masses, which corresponded relatively closely. Although the test of the approach presented here was limited by uncertainties regarding the local distributions of water contents and bulk density, the method could be applied to map two-dimensional horizontal distributions of dye in an intact soil clod for quantifying macropore–matrix mass transfer of the reactive solute.

1 | INTRODUCTION

Macropores are significantly larger than intergranular or intra-aggregate soil pores (Jarvis, 2007) and act as preferential flow paths for gas because they are air filled under field conditions, and for water and solutes during events with heavy precipitation. Dyes like Na-fluorescein (i.e., fluorescein disodium salt; C20H10Na2O5) are widely used to visualize flow paths of water and solutes in soils (Flury, & Fühler, 1995; Gerke, Sidle, & Tokuda, 2008; Vanderborght, Gähwiller, & Flühler, 2002). According to Flury

Abbreviations: FPI, fluorescence peak intensity; UV, ultraviolet; VG, van Genuchten; Vis, visible.
and and Wai (2003), dye patterns illustrate the behavior of sorbing molecules transported by the aqueous phase. More recently, Na-fluorescein has been used to determine dispersivity coefficients in porous media (Citarella, Cupola, Tanda, & Zanini, 2015) and also to help parameterize sorption properties of soils (Gerke et al., 2008; Haas, Horn, Ellerbrock, & Gerke, 2020).

The soil volumes surrounding preferential flow paths, like biopore walls or clay–organic mineral coatings at the surface of shrinkage cracks, show physicochemical soil properties different from those of the soil matrix. The microaggregation of coated macropore walls is a function of the macropore type (e.g., earthworm burrows or root channels) and of the distance from the crack surface (Haas & Horn, 2018). The geometry (Leue et al., 2019), the connectivity, and the tortuosity of the macropore system (Pagenkemper, Peth, Uteau, & Horn, 2013) differ as compared with the intra-aggregate pore network. This may result in varying values of parameters for describing transport processes (e.g., the gas diffusion; Haas & Horn, 2018) for macropore coatings as compared with the soil matrix. Thus, physical, chemical, and physicochemical macropore and coating properties control the macropore–matrix mass exchange of water and solutes (e.g., via the wettability, the hydraulic permeability, and the sorption properties; Jarvis, 2007). The relatively small sizes and volumes of interfaces of these two domains limit the spatial quantification of the permeability of water and air as demonstrated for the wettability (Haas, Gerke, Ellerbrock, Hallett, & Horn, 2018; Leue, Gerke, & Godow, 2015) and the relative oxygen diffusivity coefficient (Haas & Horn, 2018).

In two-domain models (Gerke & van Genuchten, 1993), adsorbate-specific and volume-related effective exchange parameters are used to describe the properties of macropore–matrix interfaces depending on the surface area and geometry of macropores that actively participate in preferential flow and transport (Gerke, Dusek, & Vogel, 2013).

However, such adsorbate-specific exchange parameters are still under development; also, the quantified and experimental methods for independent determination are missing to date. The sorption behavior of a specific adsorbate on an absorbent is described with sorption isotherms (Flury, & Wai, 2003) and may strongly vary for different adsorbates and absorbents. Sodium fluorescein is a reactive tracer often used to visualize flow paths (Flury, & Flühler, 1995) and can be quantitatively analyzed (Gerke et al., 2008), potentially applicable as an example tracer for the parameterization of the macropore–matrix mass exchange.

Haas et al. (2020) introduced a fluorescence imaging technique, applicable to mapping the solid- and liquid-phase dye concentrations along intact soil structural surfaces at the submillimeter scale, derived from imaged grayscale values with only few requirements in equipment like a digital camera, a source for ultraviolet (UV) light, and a dark hood. Dye concentration maps can be used to derive mass maps if the spatial distributions of the solid (i.e., minerals and soil organic matter) and liquid soil phases are known. Mass maps may help to parameterize mass exchange parameters of dual-porosity models (Gerke & van Genuchten, 1993), for example by comparing measured and simulated values of the dye masses.

In this study, the water content distribution at the millimeter scale (i.e., the mass of the liquid phase of the soil) was derived from implementing a numerical model (Hydrus-1D), and the dry soil mass (i.e., the mass of the solid phase of the soil) was assumed to be homogenously distributed within the soil clod for calculations of the dye mass distribution. The objective was to determine experimentally millimeter-scaled macropore–matrix mass transfer of a reactive solute during horizontal tracer application at an intact crack surface of a soil clod, and to map the movement and the spatial distribution of Na-fluorescein as a tracer. The applicability of the method was validated by comparing applied and recovered Na-fluorescein masses.

2 | MATERIALS AND METHODS

2.1 | Mass transfer experiment on a soil clod

The soil clod sample was prepared out of a larger intact soil block sampled from the clay-enriched Bt horizon (0.4- to 0.6-m depth) of a Haplic Luvisol (IUSS Working Group WRB, 2006) profile developed on glacial till. The soil profile was located at the arable field of the CarboZALF-D experimental site, Holzendorf, near the village of Dedelow, Uckermark region, in northeastern Germany (53° 22′ 45″ N, 13° 47′ 11″ E; 48 m asl; mean annual precipitation of 501 mm; annual mean temperature of 8.7 °C). The sandy-loam Bt horizon was characterized by contents of 165 g clay kg⁻¹,
350 g silt kg\(^{-1}\), 485 g sand kg\(^{-1}\), and 3.1 g soil organic C kg\(^{-1}\), as described in a previous study (Haas et al., 2020).

For obtaining the soil water retention function, water contents were determined at defined pressure heads from cube-shaped soil clods (6-cm edge lengths), sampled at the same soil, and depth as the soil clod used in the mass-transfer experiment. These samples were first saturated by capillary rise on a kaolin bed to obtain the clods’ water content at saturation, \(θ_0\), representing the matrix pores of the bulk soil. The clods were then drained on the same kaolin bed and equilibrated at matric potential steps of \(-1\) and \(-6\), and at \(-30\) kPa using a ceramic suction plate. The water content after equilibration to \(-1,500\) kPa using a pressure chamber was assumed to represent the residual water content parameter, \(θ_r\), of the van Genuchten (VG) soil hydraulic model. The VG model parameters \(α\) and \(n\) were obtained by fitting using the RETC program (version 6.02; van Genuchten, Leij, & Yates, 1991).

For the mass-transfer and absorption experiment, an almost-cubed soil clod (i.e., block) of about 6-cm edge length was prepared out of a larger intact soil monolith. This block had a volume \((V)\) of 216 cm\(^3\), a mass \((M)\) of 376.4 g dry soil, and a bulk density \((ρ_b)\) of 1.74 Mg m\(^{-3}\) and was drained after capillary saturation to equilibrate with a matric potential head of \(-6\) kPa on a kaolin bed. The experimental procedure of dye application, soil slicing, and fluorescence imaging was identical to that described in Haas et al. (2020). Briefly, Na-fluorescein solution with an initial Na-fluorescein concentration \((c_i)\) of 100 mg L\(^{-1}\) was applied at a rate of 3.24 ml h\(^{-1}\) (assuming the density of the solution to equal 1 Mg m\(^{-3}\); i.e., 0.324 mg Na-fluorescein h\(^{-1}\)) by horizontally spraying the solution to the intact crack surface area \((A)\) of 21 cm\(^2\) at one side of the soil block for three hours with hourly interruptions. During each interruption (i.e., after one \([T1]\), two \([T2]\), and three hours \([T3]\)), an about 1-cm-thick soil slice was carefully removed from the clod surface as described in Haas et al. (2020) to obtain a horizontally plane surface for imaging the spatial distribution, and horizontal fluorescein movement inside of the clod between the application surface \((x = 0)\) and the opposite side \((x = L)\), with \(L = 6\) cm. Slicing reduced both the soil sample height \((H)\), and the surface area \((A)\) to which Na-fluorescein was sprayed. By replacing the reduced sample height by a sponge, superfluous dye was soaked up, and the spraying rate was kept constant during the experiment.

### 2.2 Calibration of fluorescence concentrations

For calibration, the fluorescence peak intensity (FPI) was related to the Na-fluorescein concentration dissolved in solution, \(c_{eq}\) (Haas et al., 2020). The FPI is defined as the peak value of the emitted spectra during excitation, obtained with an excitation wavelength of 420 nm in a UV–visible (UV–Vis) spectrometer (Aqualog, Horiba Scientific). Several FPI values were obtained from aqueous solutions with initial Na-fluorescein concentrations \((c_i)\) of 0, 25, 50, 75, 100, and 125 mg L\(^{-1}\) at a pH value of 7.05, adjusted by 0.05 M K\(_2\)HPO\(_4\)/KH\(_2\)PO\(_4\), and were related to the \(c_i\) values of the aqueous solutions to yield a relation as

\[
c_i - c_i^* = c_{eq} = \left(\frac{\text{FPI} - 66.79}{103.19}\right)
\]

where \(c_i^*\) is dye adsorbed to soil (mg (kg soil solution))\(^{-1}\). Note that \(c_i^* = 0\) mg kg\(^{-1}\) for the aqueous solutions.

Sieved soil <2 mm (see Haas et al., 2020, who used sieved soil <0.63 mm) was mixed with aqueous solutions (1:2.5 soil/water mass/volume ratio) at defined concentrations \((c_i)\) to parameterize the sorption characteristics. Samples were then treated by centrifugation and filtration as previously described (Haas et al., 2020). The FPI values of the liquid phase of each soil solution were determined with the UV–Vis spectrometer as described above. The values of \(c_{eq}\) were obtained from the FPI (Equation 1), assuming that \(c_i\) and \(c_{eq}\) can be linearly related as for the aqueous solution, and that adsorbed Na-fluorescein is not fluorescent. The remaining water-saturated soil was filled in excess into white plastic caps (25 mm in diameter, 3 mm in height) and used for fluorescence imaging. The Na-fluorescein concentration adsorbed to soil \((c_s,\ mg\ kg^{-1}\ soil)\) was obtained from

\[
c_s = \beta c_i^*
\]

with \(c_i^*\) (mg L\(^{-1}\) soil solution) from Equation 1, and \(\beta\) (0.025 L solution 0.01 kg\(^{-1}\) soil) is a unit conversion factor. The values of \(c_s\) and \(c_{eq}\), determined at defined \(c_i\) steps were used for parameterizing the Freundlich (Freundlich, 1907; Equation 3) sorption model:

\[
c_{s,F} = K_F c_{eq}^{1/k}
\]

Under the assumption that the solid phase concentration \((c_s)\) is in equilibrium with that of the liquid phase \((c_{eq})\), a value of \(K_F\) of 1.94 (L soil solution kg\(^{-1}\) soil), and a value of 1.044 for the dimensionless constant \(k\) (Equation 3) gave the best fit for the isotherm (Figure 1).

In the observed concentration range, values of \(c_s\) increased almost linearly with the value of \(c_{eq}\) (Figure 1).

### 2.3 Fluorescence imaging

Grayscale values (GS) were calculated from color values of RGB images taken in a dark hood (DH-50, Biostep), with a digital camera (EOS 700, Canon), and a special objective
Individual values (dots) and mean values (squares) with standard deviation (error bars) of Na-fluorescein (mg kg\(^{-1}\)) soil adsorbed to soil \((c_s)\) as a function of equilibrated concentration \((c_{eq})\) of Na-fluorescein (mg L\(^{-1}\) soil solution) in soil solution. The lines represent the best fit to Freundlich sorption model (solid red line), the linear relationship between \(c_{eq}\) and \(c_s\) (dotted black line), and the identity line (i.e., \(c_s\) equal to \(c_{eq}\); gray dashed line).

(EI 28 mm f/1.8 USM, Canon) mounted in a way where it photographs toward the ground (in vertical direction) under illumination with UV radiation, and an image integration time of 30 s, according to Haas et al. (2020). The resolution pixel length of these images was 98.4 μm. The relationship between the GS value and the Na-fluorescein concentration was fitted here, in contrast with using an exponential function (Haas et al., 2020), with a power function of the form

\[
c_{eq} = aGS^b
\]

where the values of parameters \(a = 20.88 \times 10^{-5}\) mg kg\(^{-1}\) soil and \(b = 2.501\) were obtained in terms of highest \(R^2\) values \((R^2 = .99)\).

The software GIMP (gimp.org) was used to “paint” all pixel white that were lying outside of the soil slice. The Python 2.7 scripting language (Python Software Foundation, 2020), and the additional python packages PIL (Wiredfool, Murray, Karpinsky, Gohlke, & Tolf, 2016), NumPy (NumPy Developers, 2018), and cv2 (Bradski, 2008), were used for image processing. After exclusion of white pixels, the sprayed side was aligned by shifting pixels to the leftmost side of the image such that only pixels of the soil slice were further evaluated. Data analysis was carried out with the statistical software R (R Development Core Team, 2020). Parameters of the sorption isotherm were fitted using the R implementation of the Levenberg–Marquardt algorithm (LMA) as described in Elzhov, Mullen, Spiess, and Bolker (2016).

### 2.4 Water content distribution, and mass transfer calculation

The Hydrus-1D programming code (Šimůnek, Šejna, & van Genuchten, 2005) was used to calculate the one-dimensional water content distribution as a function of the spraying time of solution application, and the distance to the sample’s coated crack surface. For this horizontal flow experiment, gravity was neglected in Hydrus-1D by entering a cosine of the angle for the decline from the vertical axis of zero. A finite element mesh was constructed by dividing the horizontal soil slice into 100 linear elements with 101 nodes of equal distance of 0.6 mm.

The single-porosity van Genuchten–Mualem model with an air-entry value of –0.02 m was used to describe the hydraulic properties. The water content (\(\theta\)) and the unsaturated hydraulic conductivity (\(K\)) were described (Mualem, 1976; van Genuchten, 1980) as

\[
\theta = \theta_s + (\theta_s - \theta_r)\left(1 + |\alpha h|^{n}\right)^{-m}
\]

where the coefficients denote the saturated (\(\theta_s\)) and residual (\(\theta_r\)) water contents, and empirical parameters \(\alpha\) (cm\(^{-1}\)), \(n\), and \(m\) \((m = 1 – 1/n)\), and where the effective water saturation \((S_e)\) is defined as \(S_e = (θ - \theta_r)/(\theta_s - \theta_r)\). The one-dimensional isothermal horizontal soil water flow in variably saturated rigid porous medium is described with the Richards equation as

\[
\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K(h)\frac{\partial h}{\partial x}\right]
\]

in the form for water movement along the horizontal axis (\(x\)) as a function of time (\(t\)).

The VG model parameters (\(\theta_s\), \(\theta_r\), \(\alpha\) [cm\(^{-1}\)], \(n\), and \(m\) = 1 – 1/n), and the saturated hydraulic conductivity \((K_s)\) were (a) taken from a previous study of intact core samples (Rieckh, Gerke, & Sommer, 2012) and (b) estimated directly from data of the experiment (Table 1). With the VG parameters of the previous study as initial estimates, the constraint VG model was fitted to the water contents determined after equilibration of the soil clod to matric potentials of –1, –6, and –30 kPa on a sand bed using the RETC program and assuming the fixed \(\theta_s\) and \(\theta_r\) values at water
TABLE 1 Parameters of the constrained van Genuchten soil hydraulic model (with \( m = 1 - 1/n \)), and saturated hydraulic conductivity \( (K_s) \) for the Bt horizon soil clod sample used in the numerical simulation (Hydrus-1D) of the horizontal water content distribution, obtained from a reference Bt horizon (Rieckh et al., 2012), and by fitting (RETC) to data of soil clods obtained from the Bt horizon (Figure 2).

| Method | \( \theta_s \) | \( \theta_r \) | \( n \) | \( \alpha \) | \( K_s \) |
|--------|--------|--------|------|------|-------|
| Reference | 0.358 | 0.048 | 1.1720 | 0.6160 | 816.40 |
| RETC | 0.323 | 0.078 | 0.50 | 0.433 | 1.4232 |

Note. \( \theta_s \), saturated water content; \( \theta_r \), residual water content; \( \alpha \) and \( n \), van Genuchten model parameters.

FIGURE 2 Soil water retention plot of the clod sample from a Luvisol Bt horizon that were used here, with the constraint van Genuchten retention curves (lines) plotted for the reference function (Rieckh et al., 2012), and fitted with the RETC program (RETC) to data obtained directly from the experiment (dots); see Table 1 for the van Genuchten model parameters.

contents after capillary saturation, and drying at 105 °C for 24 h, respectively (Figure 2). The \( K_s \) value was adapted such that the simulated position of the moisture front matched that of the observed one; an adaption of the \( K_s \) value was necessary to account for the absence of coarser pores, like shrinkage cracks, when analyzing the soil matrix in the form of clods and aggregates.

The initial condition was a uniform water content distribution after equilibration at a matric potential of \(-6 \text{kPa}\). At the coated application side, \( x = 0 \), a flux-type condition was imposed, defined in Hydrus-1D as the atmospheric boundary condition. The flux of 0.153 cm h\(^{-1}\) corresponded to the rate of 3.24 ml water h\(^{-1}\) applied to the area of 46 × 46 mm. Evaporation losses of water during the application were not considered in the simulations. The boundary condition at the opposite clod side, at \( x = L \), was defined as a zero-flux condition.

The simulated water content distribution, \( \theta(x) \), and the concentrations obtained from image analyses were used to calculate the Na-fluorescein mass \( (M_T) \) in the soil slices based on the pixel distance \( (i = 1, \ldots, N) \) along the one-dimensional horizontal profile as

\[
M_T = M_{\text{ads}} + M_{\text{sol}} = \bar{c}_s \rho_b V + \sum_{i=1}^{N} c_{eq}(i) \cdot \theta(i) \cdot V(i)
\]

where \( M_{\text{ads}} \) is mass adsorbed to soil, \( M_{\text{sol}} \) is mass remaining in the liquid phase, \( \bar{c}_s \) is the mean concentration of adsorbed dye averaged over the soil slice, \( c_{eq}(i) \) is pixel-based dye concentration in the liquid phase, \( V \) is total, and \( V(i) \) pixel-based volume of the soil slice, and \( \theta(i) \) is the pixel-based local volumetric water content that was derived by linearly interpolating \( \theta(x) \) of two nodes that enclose the pixels \( i \), and \( N \) is the number of pixel along the slice length, \( L \). The total mass of Na-fluorescein \( (M_T) \) transferred across the application side of the soil slice at the three times \( t \) (T1, T2, and T3) was calculated as

\[
M_T(t) = M_{\text{ads}}(t) + M_{\text{sol}}(t)
\]

The total mass of Na-fluorescein \( (M_T) \) in the slice, determined from image analysis (Equation 9), was compared with the applied mass \( (M_{\text{appl}}) \) of 0.324 (T1), 0.648 (T2), and 0.972 mg (T3).

3 | RESULTS

3.1 | Fluorescence image of millimeter-scale solute distributions

An unprocessed, plan-view fluorescence image of a horizontal cross-section of the aggregated soil clod (Figure 3a) shows that most dyed soil regions are in a narrow range of \(~20 \text{mm} \) to the sprayed surface, which is located at the leftmost side of the photo. Some regions of the soil remained undyed, whereas the surrounding soil was intensely dyed. The mapped Na-fluorescein concentration in soil solution \( (c_{eq}) \), as calculated from grayscale values of Figure 3a, showed increased values of \( c_{eq} (>1 \text{mg L}^{-1}, \text{typical values} = 1-10 \text{mg L}^{-1}) \) in a narrow band to the sprayed side (Figure 3b). Values of \( c_{eq} \) decreased with increasing distance from the sample surface towards a “background”
value of $\leq 1$ mg L$^{-1}$. Most values of $c_{\text{eq}}$ were smaller than the sprayed concentration ($c_i$) of 100 mg L$^{-1}$ with a few outliers. A result of the image processing procedure (shifting) is exemplarily shown in Figure 3c, with the surface to which the dye was applied aligned to the leftmost side. Derived averaged Na-fluorescein concentrations in soil solution ($c_{\text{eq}}$) as a function of the distance from the sprayed surface at each slicing time showed increased $c_{\text{eq}}$ within 15–18 mm from the sprayed surface (Figure 4). A background value of close to 0 mg L$^{-1}$ is reached with distances $> 15$ mm (for T1 and T2), and $> 18$ mm (for T3). Maximum values of $c_{\text{eq}}$ increased with spraying time. However, averaged $c_{\text{eq}}$ for T1 and T2 were similar, whereas $c_{\text{eq}}$ was found increased for T3 as compared with T1 and T2.

The mapped solid phase dye concentrations ($c_s$, Figure 5) were generally larger than the liquid phase concentrations ($c_{\text{eq}}$, Figure 3c).

### 3.2 Water content distribution

The two sets of VG parameters (Table 1) result in characteristically different simulated water content distributions (Figure 6a). Water contents slightly decreased with increasing distance from the sprayed surface with VG parameters published by Rieckh et al. (2012), or wetting fronts appeared within 15 mm after 1 h of spraying, within 25 mm after 2 h of spraying, and within 32 mm in distance from the sprayed surface after 3 h of spraying when parameters were estimated (RETC) from soil clods (Figure 6a).

Masses of dye in soil solution ($M_{\text{sol}}$) were higher for water content distributions derived from aggregates (RETC) as compared with those derived from VG parameters published by Rieckh et al. (2012) (Table 2, Figure 6b). Most of the dye was adsorbed to soil ($M_{\text{ads}}$) as compared with $M_{\text{sol}}$ (Figures 6b and 7). Values representing masses at T2 increased only a little as compared with masses at T1, whereas the increase of values at T3 was more...
pronounced as compared with before (Figures 6b, and 7, Table 2).

3.3 Cumulative mass transfer as a function of time

Cumulative masses of dissolved ($M_{sol}$) of adsorbed ($M_{ads}$) and of total dye ($M_T$) increased with application time (Table 2). The increase was stronger for $M_{ads}$ than for $M_{sol}$ (Table 2). Total and adsorbed cumulative masses of Na-fluorescein increased with T1 and T3 as compared with applied masses of dye (Figure 8) by up to 76 % for $M_T$, as indicated by relative mass ratios. Values of $M_T$ for T2 were in the range of $M_{appl}$, as indicated by values of ~1 for relative mass ratios (Table 2). Cumulative masses of Na-fluorescein in soil solution, $M_{sol}$, increased slightly from T1 to T2 but increased overproportionally after 3 h of spraying time (Figure 8). Values of $M_{sol}$, and of $M_T$, were smaller for water content distributions derived from VG parameters by Rieckh et al. (2012) as compared with those estimated with VG parameters using RETC (Table 2).

4 DISCUSSION

The molecular structure of the dye helps explain the dye staining patterns. Sodium fluorescein is a relatively large organic molecule, and its spatial distribution depends on interactions with other solutes, and solids, and the liquid phase. As stated by Flury and Wai (2003), dye patterns illustrate the behavior of a sorbing molecule, carried by the aqueous phase. However, Na-fluorescein inadequately depicts the spatial patterns of the water
The assumption of uniform water content distributions as estimated by using values derived from one-dimensional water content simulations may not be valid for the present experiment, because Ellerbrock, Gerke, and Böhm (2009), Leue, Gerke, and Ellerbrock (2013), and Haas et al. (2018) showed that wettability-related soil properties are heterogeneously distributed at macropore surfaces. Contact angles are moisture dependent, and partial wetting, or partial nonwetting with contact angles ranging from 0 to <90° and from 90 to <180°, respectively, were found at macropore surfaces (Fér, Leue, Kodešová, Gerke, & Ellerbrock, 2016; Haas et al., 2018), which alters the water retention curve (Bachmann, Deurer, & Arye, 2007) and consequently θ at the submillimeter scale. An increased deviation between the relative cumulated total masses and applied masses for T1 as compared with T2 and T3 (Figure 8) could indicate that the difference in the soil water contents within the sample are not as uniform as suggested by the simulated distribution. Increasing wettability would also lead to increasing accessibility of sorption sites; in addition, the cation exchange capacity among other properties can be heterogeneously distributed at the millimeter scale (Leue, Beck-Broichsitter, Felde, & Gerke, 2019).

Differences between applied and cumulated masses (Figure 8) were probably caused by uncertainties introduced by the assumed water content distributions. An overestimation of the water content would coincide with an overestimation of calculated Na-fluorescein masses. In contrast, an underestimation of the local water contents would lead to an underestimation of cumulative masses of dye. Unstained soil regions (Figure 3a) indicate the heterogeneity of soil properties at the millimeter scale. Staining patterns can be affected by the spatial distribution of hydraulic conductivity, wettability, and sorption properties (Leue et al., 2015; Rogasik, Schrader, Onasch, Kiesel, & Gerke, 2014). Theoretically, in a homogenous soil, a spatially homogenous wetting front and spatially homogenous dye patterns are expected. Thus, the actual three-dimensional soil water content distribution within the soil clod may differ from the simulated one-dimensional distribution. Consequently, submillimeter-scaled maps of the actual water content, the wettability, and the amount and accessibility of sorption sites (Leue et al., 2019) would help to better explain deviations between applied and recovered masses.

The comparison of applied and recovered mass indicated that the method was relatively well applicable to quantify the small-scaled spatial Na-fluorescein mass distribution and the mass transfer. The calculated mass of Na-fluorescein, as derived from simulated water content distributions and averaged dye concentration distributions, ranged from 102 to 176% of the applied masses (Table 2). Overestimated values of the applied masses may
be due to several reasons, like (a) the assumed equilibrium between the liquid and the solid phase concentrations, (b) the parameterization of the adsorption, which were assumed to be equal for the soil matrix and the coated macropore, and (c) using sorption characteristics in modeling that were derived from air-dried and sieved soil. In such soil samples, the soil structure is homogenized, increasing the specific surface area and the accessibility of sorption sites compared with intact aggregates (Horn, Fleige, Lal, & Zimmermann, 2018). Considering that sorption sites are not fully accessible by a soil-structure-related parameter, for example, may be helpful to better match recovered and applied masses.

Another methodical issue is that the bulk density was assumed to be uniform within the soil clod. Peth, Nellesen, Fischer, and Horn (2010) visualized the impact on the bulk density of crack formation due to drying stress. Schrader, Rogasik, Onasch, and Jégou (2007) calculated the millimeter-scaled bulk density distribution in the vicinity of an earthworm burrow. Both studies showed that the bulk density is not homogenously distributed within single aggregates but is increased for crack surfaces as compared with the aggregate interiors, which would also have an impact on water content and dye mass distributions. Gerke and Köhne (2002) showed that physical and hydraulic soil properties of the coatings of soil aggregates differed from those of the aggregate interior. The hydraulic conductivity near saturation of the clayey coating material was reduced by ∼70% as compared with the value of the matrix, whereas the specific porosity of coating material was around 10% larger than that of the interior. In this study, coating and aggregate interior material could not be clearly distinguished. Differing VG parameters for the coating as compared with the soil matrix would influence the mass of dye in solution, due to varying water, and dry soil masses (Equation 8). In future studies, VG parameters should be derived separately for aggregate coatings and soil matrix. Regarding the identification of the spatial distribution of the coating material via the composition of the organic matter components, the combination with the diffuse reflectance infrared spectroscopy technique would be useful (Haas et al., 2018; Leue et al., 2013). More detailed water content distributions (e.g., as derived with neutron radiography) and dry mass distributions (e.g., derived from computed tomography measurements) would further improve the mass transfer calculations with this approach.

5 | CONCLUSIONS

The study aimed at experimentally determining the millimeter-scaled macropore–matrix mass transfer of a reactive solute during horizontal tracer application at the intact crack surface of a soil clod, and to map the movement and the spatial distribution of Na-fluorescein. The applicability of the method was validated by comparing applied and recovered Na-fluorescein masses.

Dye mass distribution maps of an aggregated soil block and the movement of the dye were derived during a horizontal infiltration experiment using fluorescence imaging to determine the tracer concentration and simulated one-dimensional water content distributions. Sorption characteristics were derived from sieved soil, and the separation of Na-fluorescein adsorbed to soil and dissolved in the liquid phase was possible after calibration.

The results suggest that the accessibility of adsorption sites of the aggregated soil should be considered, since the adsorption of the dye is highly relevant. The spatial distribution of adsorbed dye should be determined directly to calibrate the presently indirect method.

The recovery rates in the range of 102–176% of applied masses suggest that the approach is limited since information on small-scaled heterogeneities of soil properties regarding the mass distributions of the liquid and solid soil phases are missing. Beside uncertainties regarding the submillimeter-scaled distributions of water and dry soil masses, the method seems applicable to map and to quantify the macropore–matrix mass transfer, and the movement of the reactive dye. Still, more detailed millimeter-scaled distributions of components in liquid and solid soil phases would help improve the imaging based technique.

ACKNOWLEDGMENTS

This study was financially supported by the Deutsche Forschungsgemeinschaft (DFG), Bonn, in the framework of Projects GE 990/10-1 “Solute mass transfer through the macropore-matrix interface during preferential flow in structured soils: Model development” (SOMATRA), GE 990/14-1 “The exchange flow between preferential flow paths and matrix in soils: from pore to continuum scale with tensors” (FLEXPO), and LE 3177/1-2 “Quantification of small-scale physicochemical and microbiological properties of intact macropore surfaces in structured soils.”

Open access funding enabled and organized by Projekt DEAL.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

ORCID
Christoph Haas © https://orcid.org/0000-0002-5272-4428
Martin Leue © https://orcid.org/0000-0002-8392-4545
REFERENCES

Bachmann, J., Deurer, M., & Arye, G. (2007). Modeling water movement in heterogeneous water-repellent soil: 1. Development of a contact angle-dependent water-retention model. Vadose Zone Journal, 6, 436–445. https://doi.org/10.2136/vzj2006.0060

Bradski, G. (2008). The OpenCV library. Dr. Dobb's Journal of Software Tools, 4.

Citarella, D., Cupola, F., Tanda, M. G., & Zanini, A. (2015). Evaluation of dispersivity coefficients by means of a laboratory image analysis. Journal of Contaminant Hydrology, 172, 10–23. https://doi.org/10.1016/j.jconhyd.2014.11.001

Ellerbrock, R. H., Gerke, H. H., & Böhm, C. (2009). In situ DRIFT characterization of organic matter composition on soil structural surfaces. Soil Science Society of America Journal, 73, 531–540. https://doi.org/10.2136/sssaj2008.0103

Elzhov, T. V., Mullen, K. M., Spiess, A. N., & Bolker, B. (2016). Package minpack.lm. R package version 1.2-1. Comprehensive R Archive Network. Retrieved from https://cran.r-project.org/web/packages/minpack.lm/minpack.lm.pdf

Fér, M., Leue, M., Kodešová, M., Gerke, H. H., & Ellerbrock, R. H. (2016). Droplet infiltration dynamics and soil wettability related to soil organic matter of soil aggregate coatings and interiors. Journal of Hydrology and Hydromechanics, 64, 111–120.

Flury, M., & Flühler, H. (1995). Tracer characteristics of Brilliant Blue FCF. Soil Science Society of America Journal, 59, 22–27. https://doi.org/10.2136/sssaj1995.03615995005900010003x

Flury, M., & Wai, N. N. (2003). Dyes as tracers for vadose zone hydrology. Reviews of Geophysics, 41(1). https://doi.org/10.1029/2001RG000109

Freundlich, H. M. F. (1907). Über die Adsorption in lösungen. Zeitschrift für Physikalische Chemie, 57U, 385–471.

Gerke, H. H., & van Genuchten, M. Th. (1993). A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media. Water Resources Research, 29, 305–319. https://doi.org/10.1029/92WR02339

Gerke, H. H., & Köhne, J. M. (2002). Estimating hydraulic properties of soil aggregate skins from sorptivity and water retention. Soil Science Society of America Journal, 66, 26–36. https://doi.org/10.2136/sssaj2002.2600

Gerke, K., Sidle, R., & Tokuda, Y. (2008). Sorption of uranium on forest soils. Hydrological Research Letters, 2, 32–35. https://doi.org/10.3178/hrl.2.32

Gerke, H. H., Dusek, J., & Vogel, T. (2013). Solute mass transfer effects in two-dimensional dual-permeability modeling of bromide leaching from a tile-drained field. Vadose Zone Journal, 12(2). https://doi.org/10.2136/vzj2012.0091

Haas, C., Gerke, H. H., Ellerbrock, R. H., Hallett, P. D., & Horn, R. (2018). Relating soil organic matter composition to soil water repellency for soil biopore surfaces different in history from two Bt horizons of a Haplic Luvisol. Ecohydrology, 11(6). https://doi.org/10.1002/eco.1949

Haas, C., & Horn, R. (2018). Impact of small-scaled differences in microaggregation on physicochemical parameters of biopore walls in two Bt horizons of a Haplic Luvisol. Frontiers in Environmental Science, 6, 10. https://doi.org/10.3389/fenvs.2018.00090

Haas, C., Horn, R., Ellerbrock, R. H., & Gerke, H. H. (2020). Fluorescence imaging for mm-scale observation of macropore-matrix mass transfer: Calibration experiments. Geoderma, 360. https://doi.org/10.1016/j.geoderma.2019.114002

Horn, R., Fleige, H., Lal, R., & Zimmermann, I. (2018). Soil health and functions as a basic requirement for advancing the SDGs. In R. Lal, R. Horn, & T. Kosaki (Eds.), Soils and sustainable development goals (pp. 52–60). Stuttgart, Germany: Catena Soil Sciences.

IUSS Working Group WRB. (2006). World reference base for soil resources. Rome: FAO.

Jarvis, N. J. (2007). A review of non-equilibrium water flow and solute transport in soil macropores: Principles, controlling factors and consequences for water quality. European Journal of Soil Science, 58, 523–546. https://doi.org/10.1111/j.1365-2389.2007.09915.x

Leue, M., Beck-Broichsitter, S., Felde, V. J. M. N.L., & Gerke, H. H. (2019). Determining millimeter-scale maps of cation exchange capacity at macropore surfaces in Bt horizons. Vadose Zone Journal, 18(1). https://doi.org/10.2136/vzj2018.08.0162

Leue, M., Gerke, H. H., & Ellerbrock, R. H. (2013). Millimetre-scale distribution of organic matter composition at intact biopore and crack surfaces. European Journal of Soil Science, 64, 757–769. https://doi.org/10.1111/ejss.12098

Leue, M., Gerke, H. H., & Godow, S. C. (2015). Droplet infiltration and organic matter composition of intact crack and biopore surfaces from clay-illuvial horizons. Journal of Plant Nutrition and Soil Science, 178, 250–260. https://doi.org/10.1002/jpln.201400209

Leue, M., Uteau, D., Peth, S., Nellessen, J., Kodešová, R., & Gerke, H. H. (2019). Separation of soil macropore types in three-dimensional X-ray computed tomography images based on pore geometry characteristics. Vadose Zone Journal, 18(1). https://doi.org/10.2136/vzj2018.09.0170

Mualem, Y. (1976). A new model predicting the hydraulic conductivity of unsaturated porous media. Water Resources Research, 12, 513–522. https://doi.org/10.1029/WR012i003p00513

NumPy Developers. (2018). NumPy: The fundamental package for scientific computing with Python. Numpy. Retrieved from http://www.numpy.org/

Pagenkemper, S. K., Nellesen, J., Uteau, D., & Horn, R. (2010). Non-invasive 3D analysis of local soil deformation under mechanical and hydraulic stresses by μCT and digital image correlation. In S. H. Anderson & J. W. Hopmans (Eds.), Soil–water–root processes: Advances in tomography and imaging (Vol. 61, pp. 69–96). Madison, WI: SSSA. https://doi.org/10.2136/sssascpepub1c4

Peth, S., Nellessen, J., Fischer, G., & Horn, R. (2010). Non-invasive 3D analysis of local soil deformation under mechanical and hydraulic stresses by μCT and digital image correlation. Soil and Tillage Research, 111, 250–260. https://doi.org/10.1016/j.soiltex.2010.02.007

Python Software Foundation. (2020). Python language reference, version 3.7. Python Software Foundation. Retrieved from www.python.org

R Development Core Team. (2020). R: A language and environment for statistical computing. Vienna: R Foundation for Statistical Computing. Retrieved from http://www.R-project.org

Rieckh, H., Gerke, H. H., & Sommer, M. (2012). Hydraulic properties of characteristic horizons depending on relief position and structure in a hummocky glacial soil landscape. Soil Tillage Research, 125, 123–131. https://doi.org/10.1016/j.still.2012.07.004
Rogasik, H., Schrader, S., Onasch, I., Kiesel, J., & Gerke, H. H. (2014). Micro-scale dry bulk density variation around earthworm (*Lumbricus terrestris* L.) burrows based on X-ray computed tomography. *Geoderma, 213*, 471–477. https://doi.org/10.1016/j.geoderma.2013.08.034

Schrader, S., Rogasik, H., Onasch, I., & Jégou, D. (2007). Assessment of soil structural differentiation around earthworm burrows by means of X-ray computed tomography and scanning electron microscopy. *Geoderma, 137*, 378–387. https://doi.org/10.1016/j.geoderma.2006.08.030

Šimůnek, J., Šejna, M. & van Genuchten, M. Th. (2005). The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Riverside, CA: University of California.

van Genuchten, M. Th. (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal, 44*, 892–898. https://doi.org/10.2136/sssaj1980.03615995004400050002x

van Genuchten, M. Th., Leij, F. J., & Yates, S. R. (1991). The RETC code for quantifying the hydraulic functions of unsaturated soils. Riverside, CA: U. S. Salinity Laboratory.

Vanderborght, J., Gähwiller, P., & Flühler, H. (2002). Identification of transport processes in soil cores using fluorescent tracers. *Soil Science Society of America Journal, 66*, 774–787. https://doi.org/10.2136/sssaj2002.0774

Wiredfool, Clark A., Murray, A., Karpinsky, A., Gohlke, C., & Tolf, F. (2016). Pillow: 3.1.0. Zenodo. https://doi.org/10.5281/zenodo.44297

How to cite this article: Haas C, Leue M, Ellerbrock RH, Gerke HH. Macropore–matrix mass transfer of reactive solutes quantified by Fluorescence Imaging. *Vadose Zone J.* 2020;19: e20078. https://doi.org/10.1002/vzj2.20078