Chemically Induced Flow in Contaminated Unsaturated Soil
Chiara Pasut,* Paolo Salandin, and Federico Maggi

Laboratory experiments and numerical modeling were conducted to assess the effects of glycerol concentration gradients on water flow through an unsaturated loamy sand (Yellow bush sand, Australia) at 46% glycerol mass fraction and 12.5% volumetric water content. When the contaminated and uncontaminated experimental soil sections were placed into contact, two opposite mechanisms were found to drive the flow: (i) the matric potential gradient affected by concentration-dependent surface tension, viscosity, and density repelled contaminated water; and (ii) the osmotic potential gradient had an opposite effect. Experiments demonstrated that the tested sand did not exhibit the complete semipermeable characteristic necessary to induce pure osmotic flow. Rather, physicochemical effects caused by dissolved glycerol were more relevant for water flow than those induced by the osmotic potential. We confirmed our experimental finding by numerical modeling that explicitly accounted for these effects compared with our experiments and earlier experiments conducted with 7% butanol–water mixtures as benchmarks. Our results were finally confirmed by a thermodynamic interpretation of matric and osmotic potentials. Experiments suggest that a rapid transient condition occurred on the first day and that equilibrium was recovered only after >60 d. The results support the hypothesis that chemically induced water flow in the vadose zone is contributed mainly by matric and only secondarily by osmotic effects, which have displaced 3 to 10% water during the initial transient condition. Predictive tools of contaminant hydrology in unsaturated soil may have to account for the osmotic effects in particular applications that involve soil with high osmotic efficiency.

Tracking contaminants in soil and understanding how water flow causes both transport and dilution has been an important target in hydrological sciences; the opposite effect, when the water flow is induced by gradients in contaminant concentration (i.e., chemical osmosis) has not yet received large attention, and many aspects remain unclear. Chemical osmosis has been recognized as one of the mechanisms driving water flow in saturated soil (and porous media in general) exposed to a solute concentration gradient. The Gibbs free energy can explain an osmotic water flow from a point in space with high dissolved chemical in soil water, the osmotic pressure would be overestimated by several orders of magnitude; for example, a NO₃⁻ concentration of 10⁻³ mol/L in a typical agricultural soil would result in Π = 2.477 kPa ≈ 0.25 m of water at T = 25°C, which is high enough to produce a pressure gradient capable of causing water flow rates far above observable ranges across small length scales. This has suggested that a real soil
cannot be considered to act as an ideal semipermeable membrane because solute mobility may be only partially restricted (Kemper and Rollins, 1966; Mitchell et al., 1973). Hence, the osmotic efficiency ε has been introduced as $\Pi = \varepsilon RTC$ to quantify how soil acts as a semipermeable medium, with $\varepsilon$ ranging between 0, when solute mobility is not restricted, to 1, when solute mobility is fully restricted (Fritz, 1986; Mitchell, 1993).

Experiments document that clays exhibit the highest solute restriction due to the development of a double-diffusion layer with the thickness comparable to the pore size (Marine and Fritz, 1981). In contrast, solute mobility is commonly very high in a coarse soil, and solutes can rapidly diffuse and decrease concentration gradients (Hillel, 1998; Mitchell, 1993). Estimated values of $\varepsilon$ in clays range between 0.001 and 0.8 (Barbour and Fredlund, 1989; Kemper and Rollins, 1966), while $\varepsilon$ in coarse soil has not been estimated and has only been thought to be negligible (Mitchell, 1993).

While consensus on chemical osmosis is consolidated relative to coarse saturated soil, accepted knowledge of whether this holds true under unsaturated compared with saturated conditions has not been reached yet. Unlike the hydrostatic pressure in a saturated soil, the capillary pressure in unsaturated soil is directly affected by dissolved chemicals that can alter the surface tension, the contact angle at the intersection line across the phases, and the water density and viscosity. Earlier works have shown substantial effects in the meniscus velocity within straight capillaries when mixtures of water and organic compounds were used—effects that were all ascribed to changes in the physicochemical characteristics of the water mixtures compared with pure water (Maggi and Alonso-Marroquin, 2012; Maggi, 2012). Hence, water flow in unsaturated soil where water also transports dissolved chemicals can be affected not only by the osmotic pressure $\Pi$ but also by other induced effects on the capillary pressure and hence on the soil matric potential $\psi_m$. Both experimental and numerical studies conducted in horizontal unsaturated sand columns half wetted by water and half wetted by water and organic surfactants have attributed the causes of water flow to the difference $\Delta \psi_m$ at the interface of the two halves induced by surface tension effects (Tschapek and Boggio, 1981; Bashir et al., 2008; Henry et al., 1999) and contact angle changes (Demond and Roberts, 1991), showing that these could move up to 50% of the water (Karkare and Fort, 1993). However, effects caused by the osmotic potential were not investigated and were excluded from modeling.

The aim of this work was to test the hypothesis that water flow in unsaturated soil is controlled by two different driving forces that depend on the characteristics of the medium and solute. Specifically: (i) osmotic flow always occurs but the magnitude depends on the soil texture and its efficiency to act as a semipermeable membrane; (ii) chemically altered capillary-driven flow occurs when a solute produces a substantial change in the physicochemical properties of the liquid phase; and (iii) their balance is dynamic and can result in backflow if the prevalence between osmotic and matric potential reverses.

The trade-off between the two effects cannot be anticipated given that they are nonlinear in the soil water content and the physicochemical characteristics, but scenarios such as one effect being prevalent on the other for part or the entirety of the transient state can be envisioned. This study therefore focused on how these two processes influence the net water flow in an unsaturated sand that does not work as an ideal membrane ($\varepsilon < 1$). Glycerol was selected as the target solute of this study because of its surfactant characteristic and its low toxicity. A specific laboratory experiment was designed to measure changes in water content across time and space induced by a glycerol–water mixture in a controlled experimental test box. Then, the Richards equation for unsaturated flow was modified to account for both processes and to analyze the condition that can induce backflow during the transient toward equilibrium. The model was first validated on experimental data from the literature (Bashir et al., 2008; Henry et al., 1999) to describe and assess the effect of osmotic flow induced by a butanol–water mixture. The model was next used with our experimental data related to a glycerol–water mixture: a flow analysis, a parametric sensitivity analysis, and a thermodynamics interpretation were conducted to complement our observations.

## Methods

### Theory of Chemically Induced Water Flow

In an unsaturated horizontal soil column initially uniformly wetted, $P_{m,0}$ is the initial matric pressure reflecting the water content. If a solute is injected uniformly in the right side at time $t_0$, and the soil acts as an ideal semipermeable membrane ($\varepsilon = 1$), a pressure difference ($P_{m,0} - \Pi$) between the two volumes develops. When the water movement recovers the equilibrium (denoted with subscript $\infty$), the final pressure at both sides is $P_{m,\infty}$ but the water content on the left is higher due to the water received from the right side; therefore, the initial concentration $C_{0}$ on the right side decreases to the equilibrium concentration $C_{\infty}$ but remains equal to 0 on the left side (Fig. 1a). However, soil does not behave as an ideal membrane ($0 < \varepsilon < 1$), hence the solute can diffuse into the clean water side (on the left side) and slowly decrease the osmotic pressure (on the right side) with time (Fig. 1b). This transient state lasts until solute diffusion reduces the chemical pressure gradient completely and then causes a backflow of the water initially moved toward the contaminated side back to the clean water side. When soil does not apply any solute restriction ($\varepsilon = 0$), solutes can freely diffuse and decrease the chemical gradient (Fig. 1c). Equilibrium (when $\varepsilon < 1$) corresponds to uniform solute concentration and water content in the two halves. The osmotic pressure $\Pi$ of the van’t Hoff equation in soil is defined as (see the thermodynamic derivation in Appendix A)

$$\Pi = \varepsilon RTC \quad [1]$$

The osmotic potential can then be calculated as

$$\psi_o = \frac{\Pi}{\rho g} \quad [2]$$
where $\rho$ is the fluid density and $g$ is the gravitational acceleration. In contrast, the matric potential $\psi_m$ can be defined as (Bear, 2012)

$$\psi_m = -\frac{2\sigma \cos(\gamma)}{\rho g r} \tag{3}$$

where $\sigma$ is the surface tension, $r$ is the equivalent radius of soil capillaries, and $\gamma$ is the contact angle measured at the solid–liquid–gas interface.

Equations [2] and [3] are functions of the liquid composition, thus are functions of dissolved contaminants. For a soil that works as a leaky semipermeable membrane ($0 < \varepsilon < 1$), any change in $C$, and therefore in $\sigma$, $\gamma$, and $\rho$, can produce changes in $\psi_o$ and $\psi_m$. It is therefore evident that when water carries dissolved chemicals at concentration $C$, the trade-off between $\psi_o$ and $\psi_m$ can determine if water flow is prevalently controlled by osmotic or matric suction and whether one of them may prevail during some part or the entirety of the transient state described in Fig. 1. The experiments and analyses conducted here are expected to shed light on the balance between the osmotic and matric potentials.

**Earlier Experiments and Modeling**

Only a minor number of studies have been conducted on the dynamics of water flow caused by surfactants in unsaturated sand. Henry et al. (1999) used a horizontal column 13.7 cm long, half wetted by deionized water and half wetted by a 7% butanol–water mixture, both at 18% water content. Similar experiments were conducted in a horizontal column 40 cm long, 10.2 cm wide, and 4.5 cm high, with Ottawa graded sand and a 7% butanol–water mixture at 15% initial water content by Bashir et al. (2008). In those works, water was repelled from the contaminated half because butanol is a highly soluble organic substance that reduces $\sigma$ from 72 to 26 mN/m at 25°C.

Henry et al. (2001) used HYDRUS 5.0 and implemented water retention hysteresis using polynomials to account for the solute effect on physicochemical properties as $s/s_0 = 1 - b[\ln(c/a) + 1]$ and $m/m_0 = [1 - c\ln(c/d + 1)]^{-1}$ (Adamson, 1990) to match experimental data in Henry et al. (1999). The soil water potential was scaled using Leverett (1941), and the hydraulic conductivity was scaled for the viscosity effects. The same model was used by Bashir et al. (2008) to conduct a sensitivity analysis on pore connectivity and pollutant dispersion. However, all approaches excluded the effect of osmotic potential and adsorption, thus leaving an open question of whether an explicit accounting of these effects could improve the interpretation of experimental results.

**Experimental Apparatus and Procedure**

To produce an abrupt gradient in $\psi_o$ and $\psi_m$ within a test soil, we designed an experiment similar to those reported above. The control volume consisted of two identical rectangular Perspex halves (1 cm thick, 20 cm long, 6 cm wide, and 9 cm high) attached horizontally and closed by a lid (Fig. 2). The two halves were used for water and a 46% glycerol–water mixture, respectively. Eight penetration holes in the lid hosted the water content sensors (Vegetronix VH400); those at the interface of the two halves were located more closely than the others to detect variations in water content near the interface at a higher spatial resolution (Fig. 2). The sensors were inserted vertically across the entire depth of the control volume, and the setup was powered by a PowerTech DC voltage regulator to maintain constant voltage and power supply.
The tested soil was a commercial sand (Yellow bush sand, Australia). This sand was dried and sieved using a 600-µm mesh size. The mineral density was 2550 kg/m³, while the bulk density was 1657 kg/m³ with porosity \( \phi = 0.35 \). Deionized water was used in one half of the test box, while glycerol (BP 1 mL/mL, Gold Cross) at 46% mass fraction was used as the solute for the glycerol–water mixture in the other half. Density, viscosity, and surface tension of the glycerol–water solution were determined using literature data for the temperature \( T \) and glycerol mass fraction \( X \) dependence (Glycerine Producers’ Association, 1963) with the polynomial interpolator of the generic physical quantity \( Z \) (based on Maier and Kelley, 1932)

\[
Z = a \log\left(\frac{T}{T_0}\right) + b + c T + d T X + e T X^2 + f X + g X^2
\]  

where \( Z \) represents either \( \rho, \sigma, \text{ or } \mu \), and \( a, b, c, d, e, \text{ and } f \) are dimensional fitting parameters. Equation [4] was used also to describe the properties of pure water when \( X = 0 \). The curves obtained for the glycerol–water mixture as a function of \( X \) and \( T \) are compared against experiments at temperature \( T = 22^\circ\text{C} \) (Fig. 3).

Two equal masses of dry sand were pre-wetted with either deionized water (Elga Micromeg purified water) or a glycerol–water mixture and were vigorously mixed to homogenize their wetness. After 4 h, 70 g of sand was incrementally added to the two halves of the test box and were mechanically compacted to 1-cm thickness to ensure that the same compaction energy was used on each side of the box. Thereafter, the soil moisture sensors were slid vertically into each penetration hole. The sensors were connected to a 32-channel datalogger (NI 6092 National Instrument), and the signal was transferred and saved to a personal computer. The sampling frequency was one sample per minute; successively, a moving mean window of 10 points was applied during the post-processing to smooth high-frequency signal fluctuations. The experiment lasted for 7 d, at

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**Fig. 2.** Top view (left) and cross-section (right) of control volume and sensor positions (S1–S8). Lengths are in centimeters.

**Fig. 3.** (a) Glycerol density \( \rho \), (b) surface tension \( \sigma \), and (c) viscosity \( \mu \) against mass fraction at \( T = 18, 20, 22, \) and \( 25^\circ\text{C} \). Markers represent \( \rho, \sigma, \) and \( \mu \) at the experimental temperature \( T = 22^\circ\text{C} \).
which point the total evaporation was weight measured with an accuracy of 0.01 g. Experiments were run under nearly isothermal conditions (T = 22 ± 1°C was recorded throughout the experiments).

**Model Description**

To model our and earlier experiments, we modified the Richards equation and solved it in a one-dimensional horizontal domain along the x direction. Its original form is

\[
\frac{\partial \theta}{\partial t} - \frac{\partial}{\partial x} \left[ K \left( S_e \right) \frac{\partial \psi \left( S_e \right)}{\partial x} \right] + Q = 0
\]  

where \( K \) is the hydraulic conductivity and \( S_e = (\theta - \theta_r)/(\phi - \theta_r) \) is the effective water saturation, \( \theta_r \) and \( \phi \) are the residual water content and porosity, respectively, and \( Q \) is a contribution to changes in \( \theta \) such as from boundary conditions. For the modeling purpose of this work, \( Q \) included only losses by evaporation. The water potential \( \psi \) included the matric potential \( \psi_m \) modified to account for the effect of a solute on the fluid physical properties, and the osmotic potential \( \psi_o \). The matric potential for pure water was calculated using van Genuchten (1980):

\[
\psi_m \left( S_e \right) = \alpha \left( S_e^{-1/m} - 1 \right)^{1 - m} 
\]  

where \( \alpha \) and \( m \) are soil-specific parameters. Leverett (1941) was used to rescale \( \psi_m \) including density and surface tension change effects as

\[
\psi_m \left( S_e, X \right) = \frac{\sigma X \rho_0}{\sigma_0 \rho_X} \psi_m \left( S_e \right) 
\]  

Explicit effects of the solute on the contact angle were neglected, but implicit effects were taken into account as explained below. The osmotic potential following the van’t Hoff Eq. [1] was written as

\[
\psi_o = \frac{RTC}{\rho X g} \frac{\sigma X \rho_0}{\sigma_0 \rho_X} \psi_m \left( S_e \right) 
\]  

for the density \( \rho_X \) of the water mixture. Values of \( \sigma X \), \( \rho_X \), and \( \mu_X \) at solute mass fraction \( X \) were calculated using Eq. [4]. Finally, the unsaturated hydraulic conductivity at solute mass fraction \( X \) was calculated as (Mulem, 1976)

\[
K \left( S_e, X \right) = \frac{k \rho X g S_e^2}{\sigma X} \left( 1 - \left( S_e^{-1/m} \right)^{m_k} \right)^2 
\]  

where \( k \) is the soil absolute permeability, \( m_k \) is a curve-fitting parameter, and \( \lambda \) is the pore connectivity parameter.

Substituting Eq. [7] and [8] into Eq. [5], the Richards equation for the rate of change in soil water content \( \theta \) was then written as

\[
\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left[ k \rho X g S_e^2 \left( 1 - \left( S_e^{-1/m} \right)^{m_k} \right)^2 \right] \times \frac{\partial \psi_m}{\partial x} \left( \frac{\sigma X \rho_0}{\sigma_0 \rho_X} \alpha \left( S_e^{-1/m} - 1 \right)^{1 - m} + \frac{RTC}{\rho X g} \right) + Q
\]  

while the rate of change in solute concentration \( C \) was described using the advection–diffusion–reaction equation:

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} - v_x C \right) + F
\]  

where \( D_X = (D_x \theta_x + D_x + dx \theta_x + dx)/2 \) is the effective diffusion coefficient calculated as the weighted averaged of the water content at two adjacent positions \( x \) and \( x + dx \), \( v_x \) is the Darcy’s velocity along direction \( x \), and \( F \) is a sink or source of solute. Adsorption to and desorption from sand minerals were the only processes accounted for in \( F \), and they were described by a linear equilibrium using the mass action law

\[
C_{ads} = k_{ads} C
\]  

where \( C_{ads} \) is the adsorbed concentration and \( k_{ads} \) is the adsorption equilibrium constant.

**Numerical Solution and Parameter Estimation**

Equation [10] and [11] were solved with a finite difference scheme across 10 evenly spaced elements using a variable time step with \( 10^{-4} \) lower bound. An initial uniform distribution in \( \theta \) was used in all tests and corresponded to the experimentally imposed values. A step function equal to zero for all elements on the uncontaminated side and equal to the experimental solute concentration on the contaminated side was used. No mass boundary fluxes were used for the literature experiments because the control volume was isolated and the experiment lasted for only 1 d, while the measured evaporation was imposed in our experiments because we explicitly measured it.

The model was first validated on the butanol–water mixtures data and next used with our experimental data. Four numerical analyses (T1–T4) were implemented to account for increasing model complexity, model comparison, and the number of estimated parameters. Specifically, T1 accounted for only the solute effect on the physicochemical properties (\( \rho_X \), \( \sigma_X \), and \( \mu_X \)) but excluded osmotic potential \( \psi_o \) and adsorption \( F \) and was used only with data from Henry et al. (1999) and Bashir et al. (2008) to initially assess the model; T2 allowed the hydraulic parameters in Eq. [6] to be adjusted to improve fitting against the experiments with butanol– and glycerol–water mixtures but excluded osmotic potential and adsorption; T3 extended T2 by including osmotic potential \( \psi_o \) as in Eq. [8]; and T4 extended T3 by including also adsorption \( F \). Next, the same parameters of T4 were used excluding first adsorption (T3b) and then osmosis (T2b) to check the extent to which the hydraulic parameters estimated in the most complex model combination (T4) were applicable also in other (simpler) cases. Table 1 reports the parameters estimated and imposed in each numerical analysis.

The parameters \( \theta_r, \phi, K_{ads}, \lambda, \) and \( m \) were estimated individually as listed in Table 1. Parameters \( m_k = m \) and \( \lambda = 0.5 \) were used for the glycerol–water mixture due to the lack of information on the hydraulic properties of the tested material. In contrast, \( k, \alpha, \)}
Glycerol-Water System

Figure 6 shows the experimental volumetric water content profile across space and time obtained in our glycerol-water system. The permeability \( k = 3.7 \times 10^{-12} \) estimated by Henry et al. (2008) was used in these numerical analyses to retrieve \( c \) and \( e \) from the lumped parameters \( A \) and \( B \) as anticipated above. The uncertainty in hydraulic parameters (see below for more analyses) suggests a strong correlation between modeled and observed data across space and time. The proposed coupling of (10) and (11) that models both the effect of physicochemical properties and in describing water flow induced by a dissolved surfactant (i.e., adsorption) was applied in describing the drainage of the medium. While T2 and T2 only approximated the experiments (Fig. 4a and 4b), the results of T2b and T3b (Table 2) demonstrated that the models performed well in the experiments. The original modeling work by Henry et al. (2008) and Bashir et al. (2019) for the corresponding experiments parameters that were estimated in the T4 parameter analysis† were limited to twice the standard deviation to exclude about 5% extreme values of the Gaussian tails.

Results

Experiments by Henry et al. (1999) and Bashir et al. (2008) show that the parameter values of the most complete model (T4) butanol–water model assessment and adsorption (Henry et al., 2001 and Bashir et al., 2008) for the corresponding experiments parameters that were estimated in the T4 parameter analysis† were limited to twice the standard deviation to exclude about 5% extreme values of the Gaussian tails.

<table>
<thead>
<tr>
<th>Parameter System</th>
<th>Description</th>
<th>Numerical analysis†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lumped parameters</td>
<td>System</td>
<td>Individual parameters</td>
</tr>
</tbody>
</table>

Table 1. Summary of estimated and fixed parameters in each numerical analysis.

where \( X \) and \( Y \) represent the model and experimental water content, respectively, and \( X \) is the number of experimental points. A stochastic sensitivity analysis was performed on \( A, B \) and \( N \), by extracting 100 independent values for each parameter and by estimating the central limit theorem from the normal distribution function for each parameter. The standard deviation for each parameter was estimated to exclude about 5% extreme values of the Gaussian tails.
mixture experiments. In these experiments, water always moved from the glycerol–water mixture (right) toward the clean water (left), thus suggesting that physicochemical effects of the matric potential $\psi_m$ prevailed over the osmotic potential $\psi_o$. The water content profile showed a wave pattern with time; the prevailing flow from the glycerol–water mixture side toward the water side significantly slowed down during the transient state at about the end of the first day, after which the water content only decreased uniformly due to evaporation (Fig. 6a). The greatest change in water content mainly occurred at the interface between 7.75 and 10 cm due to the presence of a steep glycerol concentration gradient and did not involve the two column ends, probably because the high viscosity of the glycerol–water mixture (see Fig. 3c) slowed down the water flow rate. Drainage occurred between 2 and 3.5 cm, when water presumably moved toward the center of the box; one possible explanation for this observation is that the initial water content was higher at time $t = 0$ at 2 cm and that therefore water moved by matric potential toward the right.

The model described above was used for the numerical analyses T2 to T4 with $l = 0.5$ and $m_k = m$ for comparison with our experiments. The goodness-of-fit and the estimated parameter values are summarized in Table 3. Model predictions approximated only qualitatively the overall water content across time and space ($R^2 = 0.77$ and NRMSE = 20%), and the water content increases in the clean water side were underestimated. The best match occurred on the side with the glycerol–water mixture. The model could not reproduce drainage in the far end of the clean water side observed in the experiments.

Fig. 4. Comparison of modeling and experiments of the relative change in volumetric water content (VWC) for each numerical analysis: T1 (literature data), T2 (no osmosis), T3 (no adsorption), and T4 (osmosis and adsorption) at (a) $t = 2.5$ h and (b) $t = 24$ h, and (c) scatterplot from $t = 0$ to 24 h. Filled markers indicate each sensor’s reading at time $t = 24$ h. Experimental data were redrawn from Henry et al. (1999), where shaded areas represent the standard deviation of two tests under the same experimental conditions, and earlier model data were redrawn from Henry et al. (2001).

Fig. 5. Comparison of modeling and experiments of the relative change in volumetric water content (VWC) for each numerical analysis: T1 (literature data), T2 (no osmosis), T3 (no adsorption), and T4 (osmosis and adsorption) at (a) $t = 2.5$ h and (b) $t = 24$ h, and (c) scatterplot from $t = 0$ to 24 h. Filled markers indicate each sensor’s reading at time $t = 24$ h. Experimental and model data were redrawn from Bashir et al. (2008).
The scatterplot in Fig. 6c quantifies the high correlation between experimental and modeled water content in the glycerol–water mixture side (S5–S8) compared with the clean water side (S1–S3). The modeled water content on the left side was more uniformly distributed across the column section rather than between 5 and 7.75 cm, probably due to boundary wall effects not accounted for in the model.

Once $A$ and $B$ were calibrated (see Table 3), and using an average silty sand permeability of $k = 10^{-13}$ m$^2$ (Freeze and Cherry, 1979), we retrieved $\alpha = k/A \approx 0.1$ 1/cm and $\varepsilon = B/k \approx 10^{-6}$. These values can be acceptable for the tested material, and the small value of $\varepsilon$ means that osmosis was very small or negligible. Removing osmosis, such as in T2b, did not introduce significant changes in the goodness-of-fit; we tested also the contribution of adsorption

### Table 2. Estimated parameters and goodness-of-fit† for butanol–water experiments for each numerical analysis. Square brackets mean that parameters were estimated in Henry et al. (2001) (c) or Bashir et al. (2008) (d); parentheses mean that parameters were estimated in Test T4; no parentheses or brackets means that parameters were estimated in that test.

<table>
<thead>
<tr>
<th>Numerical analysis‡</th>
<th>$\theta_0$</th>
<th>$\gamma$</th>
<th>$m$</th>
<th>$m_k$</th>
<th>$\lambda$</th>
<th>$A$</th>
<th>$B$</th>
<th>$\alpha$</th>
<th>$\varepsilon$</th>
<th>$k_{ads}$</th>
<th>$R^2$</th>
<th>NRMSE</th>
<th>System§</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>[0.050]c</td>
<td>[0.297]c</td>
<td>[0.889]c</td>
<td>[0.889]c</td>
<td>[3.75]c</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[0.021]c</td>
<td>–</td>
<td>0.95</td>
<td>11.30</td>
<td>a</td>
</tr>
<tr>
<td>[0.047]d</td>
<td>[0.285]d</td>
<td>[0.875]b</td>
<td>[1.036]d</td>
<td>[1.72]d</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[0.057]d</td>
<td>–</td>
<td>0.76</td>
<td>28.90</td>
<td>b</td>
<td></td>
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<tr>
<td>T2</td>
<td>0.007</td>
<td>0.300</td>
<td>0.791</td>
<td>0.801</td>
<td>2.80</td>
<td>2.870</td>
<td>–</td>
<td>0.013</td>
<td>–</td>
<td>–</td>
<td>0.98</td>
<td>5.90</td>
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<tr>
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<td>0.751</td>
<td>–</td>
<td>0.049</td>
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<td>–</td>
<td>0.97</td>
<td>6.81</td>
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<tr>
<td>T2b (0.052)</td>
<td>(0.300)</td>
<td>(0.844)</td>
<td>(0.844)</td>
<td>(2.50)</td>
<td>(1.770)</td>
<td>–</td>
<td>(0.021)</td>
<td>–</td>
<td>–</td>
<td>0.98</td>
<td>7.84</td>
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<tr>
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<td>(0.300)</td>
<td>(0.511)</td>
<td>(0.988)</td>
<td>(1.15)</td>
<td>(0.728)</td>
<td>–</td>
<td>(0.048)</td>
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<td>6.89</td>
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<tr>
<td>T3</td>
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<td>0.813</td>
<td>3.19</td>
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<td>1.200</td>
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<td>3.200</td>
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<td>0.767</td>
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<td>0.710</td>
<td>–</td>
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<td>6.81</td>
<td>b</td>
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</tr>
<tr>
<td>T3b (0.052)</td>
<td>(0.300)</td>
<td>(0.844)</td>
<td>(0.844)</td>
<td>(2.50)</td>
<td>(1.770)</td>
<td>(1.230)</td>
<td>(0.021)</td>
<td>(3.270)</td>
<td>–</td>
<td>0.98</td>
<td>6.23</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>(0.070)</td>
<td>(0.300)</td>
<td>(0.511)</td>
<td>(0.988)</td>
<td>(1.15)</td>
<td>(0.728)</td>
<td>(0.254)</td>
<td>(0.048)</td>
<td>(0.710)</td>
<td>–</td>
<td>0.97</td>
<td>6.83</td>
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<tr>
<td>T4</td>
<td>0.052</td>
<td>0.300</td>
<td>0.844</td>
<td>0.844</td>
<td>2.50</td>
<td>1.770</td>
<td>1.203</td>
<td>0.021</td>
<td>3.270</td>
<td>0.200</td>
<td>0.99</td>
<td>4.85</td>
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<td>0.070</td>
<td>0.300</td>
<td>0.511</td>
<td>0.988</td>
<td>1.15</td>
<td>0.728</td>
<td>0.254</td>
<td>0.048</td>
<td>0.710</td>
<td>0.0002</td>
<td>0.97</td>
<td>6.82</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.96</td>
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<tr>
<td>b1</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.91</td>
<td>17.67</td>
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</tr>
<tr>
<td>b2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>0.91</td>
<td>17.54</td>
<td></td>
</tr>
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</table>

† $\theta_0$, residual volumetric water content; $\gamma$, contact angle; $m$ and $\alpha$, soil-specific parameters; $m_k$, curve-fitting parameter; $A$ and $B$, lumped parameters; $\varepsilon$, osmotic efficiency; $k_{ads}$, adsorption equilibrium constant; NRMSE, normalized root mean square error.

‡ T1, literature parameters; T2, no osmosis or adsorption; T2b, parameter of T4 excluding osmosis; T3, no adsorption; T3b, parameters of T4 excluding adsorption; T4, osmosis and adsorption.

§ a, experimental data from Henry et al. (2001); b, experimental data from Bashir et al. (2008); b1, pore connectivity test from Bashir et al. (2008); b2, dispersivity test from Bashir et al. (2008).
by removing it in T3b, and the goodness-of-fit did not substantially change, thus suggesting that adsorption was also negligible (see corresponding $R^2$ and NRMSE in Table 3).

### Flow Analysis

Water flow in our model is contributed by the matric potential (Eq. [7]) and the osmotic potential (Eq. [8]), and an analysis of the two terms allowed us to investigate the strength of their contributions to flow in time and space. In the butanol–water experiment by Henry et al. (1999), the matric-driven flow (black solid line in Fig. 7a) was prevalent at the beginning of the experiment, while the osmotic flow (red dashed line) was about one order of magnitude smaller (see flow velocity across time and space in Fig. 7a). The matric-driven flow slowed down after approximately 2 h from the beginning of the experiment. By that time, the osmotic and matric-driven flow had similar intensity but pointed in opposite directions, thus resulting in no or negligible water flow from that time on.

The osmotic flow in the experiment of Bashir et al. (2008) was negligible because we found $\varepsilon = 7.0 \times 10^{-5}$ (Table 2). This suggests that the tested sand was not characterized by semipermeable properties (Fig. 7b), thus flow was mainly caused by physicochemical effects on the matric potential. In fact, the matric-driven flow coincided with the net flow (black solid line in Fig. 7b).

A similar phenomenon occurred in our glycerol–water experiment, where the osmotic efficiency was estimated to be $\varepsilon \simeq 10^{-6}$. In this case, the water flow velocity was between two and three orders of magnitude smaller than the experiments with butanol–water mixtures. The reason for this difference is that the presence of glycerol induced smaller changes in $\sigma_X$ compared with butanol, but we do not exclude that a high viscosity change in $\mu_X$ could have caused slow flow velocity in the glycerol–water system.

Despite the different conditions, the three experiments have in common the shape of the water front, which was initially located at the interface between the two solutions and then extended toward the right side. All of the three systems showed a prevalent flow direction with no inversion, at least for the first day. A thermodynamic analysis may help to explain which condition can trigger a reverse flow and return to an even water distribution.

### Thermodynamic Interpretation

Different state variables and thermodynamic potentials can equally describe the system since the chemical potential is linked to the Gibbs free energy $G$ via $\mu_w = dG/dn_w$ (see Appendix A). The chemical potential in soil solutions can be described as (Sposito, 1981)

### Table 3. Estimated parameters and goodness-of-fit† for glycerol–water mixture experiments for each numerical analysis. Parentheses mean that parameters were estimated in Test T4. No parentheses means that parameters were estimated in that test.

<table>
<thead>
<tr>
<th>Numerical analysis‡</th>
<th>$\theta_0$</th>
<th>$\gamma$</th>
<th>$m$</th>
<th>$A$</th>
<th>$B$</th>
<th>$\alpha$</th>
<th>$\varepsilon$</th>
<th>$k_{ads}$</th>
<th>$R^2$</th>
<th>NRMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2</td>
<td>0.062</td>
<td>0.350</td>
<td>0.779</td>
<td>1.002</td>
<td>–</td>
<td>0.099</td>
<td>–</td>
<td>–</td>
<td>0.77</td>
<td>20.18</td>
</tr>
<tr>
<td>T2b (0.062)</td>
<td>(0.062)</td>
<td>(0.350)</td>
<td>(0.778)</td>
<td>(2.55)</td>
<td>–</td>
<td>(1.0)</td>
<td>–</td>
<td>–</td>
<td>0.77</td>
<td>20.80</td>
</tr>
<tr>
<td>T3</td>
<td>0.062</td>
<td>0.350</td>
<td>0.802</td>
<td>1.002</td>
<td>9.7</td>
<td>1.0</td>
<td>9.7</td>
<td>–</td>
<td>0.77</td>
<td>20.19</td>
</tr>
<tr>
<td>T3b (0.062)</td>
<td>(0.062)</td>
<td>(0.350)</td>
<td>(0.778)</td>
<td>(2.55)</td>
<td>(0.1)</td>
<td>(1.0)</td>
<td>(0.1)</td>
<td>–</td>
<td>0.77</td>
<td>20.21</td>
</tr>
<tr>
<td>T4</td>
<td>0.062</td>
<td>0.350</td>
<td>0.778</td>
<td>2.55</td>
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<td>1.0</td>
<td>0.10</td>
<td>6.48</td>
<td>0.77</td>
<td>20.13</td>
</tr>
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</table>

† $\theta_0$, residual volumetric water content; $\gamma$, contact angle; $m$ and $\alpha$, soil-specific parameters; $A$ and $B$, lumped parameters; $\varepsilon$, osmotic efficiency; $k_{ads}$, adsorption equilibrium constant; NRMSE, normalized root mean square error.

‡ T1, literature parameters; T2, no osmosis or adsorption; T2b, parameter of T4 excluding osmosis; T3, no adsorption; T3b, parameters of T4 excluding adsorption; T4, osmosis and adsorption.
where $\mu_w$ is the chemical potential of the soil gas phase. Application of Eq. [14] to our experiment implies that the first and last terms on the right-hand side can be neglected because the experiment was conducted in isothermal conditions and constant atmospheric air pressure. The second term represents the rate of change in activity relative to changes in pressure, which is $\psi_o$ in this case; the third and the fourth terms can be summed together in $(\partial \mu_w / \partial n)_{P,T,m_{aq}}$, which represents $\psi_m$ and accounts for the solute dissolved in the system (Sposito, 1981). Eventually, Eq. [14] can be written as

$$d\mu_w = d\psi_o + d\psi_m = d\psi$$

thus showing that $d\mu_w$ is equivalent to $d\psi$, that is, $\mu_w$ is equivalent to $\psi$ if other effects are excluded.

We used our model to describe the long-term dynamics of the three experiments considered in this work, and we found that the presence of a contaminant increased the potential $\mu_w$ according to Eq. [3] and [8]. Hence, the originally clean water side had a lower potential than the contaminated side, aligning with both the experimental results and numerical simulations in Fig. 4, 5, and 6 that show that contaminated water moved toward uncontaminated water.

Specifically, the presence of butanol induced an abrupt change in water potential between the two sides of the box, which can move a high amount of water that rapidly recovers this sudden change before the end of Day 1 (Fig. 8a and 8b). In contrast, glycerol induced a smaller water potential change, which persisted up to Day 60 (Fig. 8c). This may result from the significant change in viscosity (Fig. 3) induced by glycerol that slows down the water flow toward the clean water side. In fact, only the water potential around the interface (7–13 cm, Fig. 2) changed during the first 60 d, while it remained constant in the two far ends of the box.

Figure 8b represents the total potential from Day 30 to Day 60 (small frame on the top right). The water potential was almost uniform across the sample, and there was only 0.2 cm difference between the two sides. However, the lower potential was in the butanol–water mixture side. By that time, the solute had diffused into the initially clean side, decreasing the chemical potential gradient, and thus the effect of the water content on the water potential prevailed over the chemical effect (as described in Eq. [6] and [7]). Thus, the water started moving following the water pressure gradient. In conclusion, the recovery process, or backflow, strongly depends on the contaminant diffusion coefficient and, considering the difference in water potential between the two sides, it is expected to take a long time to recover an even concentration and water content across space. In fact, an uneven water distribution was still present at Day 60 (Fig. 9).

**Sensitivity Analysis**

A sensitivity analysis was conducted to understand which parameter affected our simulations most, causing a biased interpretation of the dynamics of water and contaminant, to increase the confidence in our modeling results (Saltelli et al. (2008)) and to diagnose possible weaknesses in some part of the model formulation (Mara and Tarantola (2008)) such as the collection of multiple parameters into one (i.e., $k/\alpha = A$, and $k_c = B$).

All three systems were particularly sensitive to variations in the hydraulic parameter $m$. In addition, the response to increasing standard deviation was not linear; this was evident in $m$, that is, the standard deviation increasing from 5 to 10% resulted in a space-average standard deviation of the modeled water content increasing from about 0.6 to about 1.8% in the butanol–water system tested by Henry et al. (1999) (Fig. 10a). The response was not dissimilar in the other experiments. In contrast, a negligible sensitivity in water content resulted from variations in $A$, $B$, and $k_{ads}$, that is, the space-average standard deviation was <0.1%. This
suggested that our estimates of $e$, $k$, and $\alpha$ from $A$ and $B$ was relatively reliable.

Discussion

A series of considerations can be inferred from our results.

First, our experimental results are consistent with earlier experiments by Henry et al. (1999) and Bashir et al. (2008) even if the displaced water volume was smaller in our experiments and confined to only the interface. Despite this, our experiment with the glycerol–water mixture and the earlier experiments with butanol–water mixtures showed a first transient phase reaching an uneven water distribution during the first day. The counteracting drivers of observed uneven water distribution were ascribed mainly to the effect of physicochemical alterations of the dissolved contaminant on the matric potential and only partially to the presence of an osmotic potential. The osmotic potential, however, was found to be a minor contributor to water flow because the osmotic efficiency $e$ of the tested soil was relatively small (less than about $10^{-5}$), suggesting that no or only very poor physical restriction occurred in the sand. The only exception was the experiment by Henry et al. (1999), for which we estimated $e = 3.27 \times 10^{-4}$, meaning that the tested sand showed some osmotic characteristics and restriction of the dissolved butanol. The same sand presented the highest adsorption capacity, meaning that negligible adsorption may be the signature of a soil that does not act as a semipermeable membrane and therefore exhibits a low osmotic efficiency.

Second, the butanol–water system modeling was satisfactory and produced better results than the original modeling. Introduction of the osmotic flow, i.e., a flow directed in the opposite direction to the matric potential flow (see Eq. [13]), helped to better describe the V shape in water content of Henry et al. (1999) at the interface even without introducing hysteresis in the water tension–saturation relationship. Although hysteresis is well described in the literature and was used in the modeling of Bashir et al. (2008) and Henry et al. (2001), we think that a prevalent flow that does not invert direction frequently does not necessarily require the introduction of hysteresis modeling even if the water content was observed to undergo a minor decrease after rising in the uncontaminated side during the first few hours. Furthermore, hysteresis is expected to be largely reduced when the sample is pre-wetted, as in our experiments. The time scale during which a minor drying or wetting occurred was on the order of 1 d, thus it presumed a slow Darcy’s velocity. In contrast, our model neglects explicit contaminant effects on the contact angle, which may lead to underestimating the matric gradient and thus the water flow rate. However, $A$ allows implicit estimation of constant effects of the contact angle $\gamma$ in the glycerol–water system compared with pure water if $A$ is assumed to be written as $A = k/\left[\cos(\gamma)/\cos(\gamma_X)\right]$. Note that earlier analyses by Maggi (2012) showed that the dynamic contact angle is only relevant to the flow in capillaries when steep accelerations occur; hence we can exclude that missing an explicit accounting of the contact angle in our modeling and possible changes with time biased the numerical analysis.

Third, the discrepancies between experimental data and modeled results can be partially caused by experimental errors such as an uneven porosity and initial water content distribution during the sample preparation. For example, in our experiments, the sample preparation could last approximately 15 min, time during which some water may already have moved and blurred the actual time at which the datalogging started. Experimental constraints did not allow quantifying this initial error precisely, and we relied on data logged from about $t = 20$ min after the mounting of the two sides of the control volume. An additional experimental error occurred at the moment when the sensors were inserted in the sample, causing both soil disturbance and some interference in the water flow. Nonetheless, the discrepancy between experiments and modeling in the glycerol–water system was more significant than...
the earlier experiments analyzed here. Part of the error may be the result of uncertainty in the hydraulic parameters highlighted above, but it is also possible that the high glycerol mass fraction used in our experiment may have introduced additional nonlinearities not accounted for in our model. In fact, the viscosity difference between the two sides of the experimental volume was around one order of magnitude (from 0.68 to 3.96 g/ms).

Fourth, particular consideration should be paid to the uneven shape of transient water distribution reached approximately at the end of the first day. Figures 4a, 4b, 5, and 6a show an extension of the drainage area into the initially uncontaminated side. This phenomenon was caused by the moving of the solute front and the consequent changing in the matric potential, as highlighted by Bashir et al. (2008). However, no explanation exists for why the water content profile follows a very pointed V shape across the extended drainage and the initially contaminated side (see Fig. 4a for water content between 4 and 14 cm). None of the models can perfectly reproduce the water dynamic in that area. Recent studies have suggested that the presence of an abrupt discontinuity, such as a concentration gradient and a change in $\rho$, can cause a quick nonlinear shock wave known as the Burgers soliton (Caserta et al., 2017; Merlani et al., 2011). Hence, the processes detailed here may not be enough to describe the water and contaminant dynamics, but they may be extended to account for an initial contribution of soliton waves.

Fifth, it takes a long time to reach the final equilibrium because the water potential gradient was low in all the experiments after 2 h, as shown in our thermodynamics analysis. Factors such as column length, diffusion coefficient, and viscosity act in important roles in these experiments. Longer columns mean a longer time for the solute to advect to the end of the column and reduce the chemical gradient. Similar reasoning applies to diffusion. The effect of viscosity is more evident in the glycerol–water experiment, where the high glycerol viscosity significantly reduced the hydraulic conductivity; therefore the water flow rate appeared evident only at the interface where the steep potential gradient occurred.

Finally, the sensitivity analyses showed that the model is substantially sensitive to the specific soil parameter $m$, thus suggesting that minor uncertainties in this parameter may affect the quality of model fitting to experiments. However, there are still significant uncertainties in the magnitude of the $\varepsilon$ effect on water movement. Further modeling improvement should focus on linking this parameter to water content, contaminant concentration, and adsorption.

Conclusion

In this study, we experimentally and numerically investigated the occurrence of water flow in unsaturated soil induced by a concentration gradient and the ability of soil to act as a semipermeable membrane. In the presence of organic compounds such as butanol and glycerol, the induced matric potential always prevailed over the osmotic potential. However, the introduction of the osmotic flow in modeling the butanol–water system helped to describe the dynamics at the interface where the two driving gradients were comparable but pointed in opposite directions. Modeling of the glycerol–water system, although it replicated the experiments relatively well, may require further development and improvements such as accounting for the solute effect on the contact angle and a more in-depth understanding of the high viscosity effect on the hydraulic conductivity.

In general, this study showed that accounting for water flow induced by a concentration gradient into hydraulic models may be necessary in some particular cases of steep concentration gradients, when high evaporation rates increase the concentration of solutes such as salts and hydrocarbons, or when these may become important drivers for water flow in fine soils. However, the actual contribution of osmosis has been found to be minor, and an osmotic gradient can generally be neglected in the majority of the cases in coarse soil.

Appendix A. Thermodynamic Derivation

The Gibbs free energy can explain osmotic flow from a point with high to a point with low solute concentration. Using the van’t Hoff equation for two volumes of pure water in equilibrium with each other (called $L$ for left and $R$ for right) and separated by an ideal semipermeable membrane ($\varepsilon \neq 0$), their chemical potentials are

\[ \mu_w (P)_{L} = \mu_w (P)_{R} + \varepsilon \]

at a given temperature $T$ and pressure $P$. The value of $\mu_w (P)|_L$ decreases due to mixing if a solute is added to the left volume, which reflects in a decrease in $P$. Water will move according to the pressure gradient and will raise the pressure head on the left side until an equilibrium is reached such that

\[ \mu_w (X, P + \Pi)_{L} = \mu_w (P)_{R} \]

where $\Pi$ is the osmotic pressure and $X$ is the solute mass fraction. The chemical potential $\mu_w$ can also be expressed as a function of the solution activity $\sigma_w$ as

\[ \mu_w (X, P + \Pi)_{L} = \mu_w (P + \Pi)_{L} + RT\log(\sigma_w) \]

where $R$ is the universal gas constant. Because

\[ \mu_w = \frac{dG}{dn_w} \bigg|_{T,P,n_w} \]

where $G$ is the Gibbs free energy, and $n_w$ and $n$ are the moles of solvent and solute, respectively, at $T$ and $P$ (Sposito, 1981), and because

\[ \left( \frac{dG}{dP} \right)_{T,n} = V \]

where $V$ is the volume of the solution, then it is possible to write

\[ \left( \frac{d\mu_w}{dP} \right)_{T,n} = \frac{d^2G}{dPdn_w} = \left( \frac{dV}{dn_w} \right)_{T,n} = V_s \]
where $V_s$ is the molar volume. Separating the variables and integrating in $\mu$ and $d\mu$ results in
\[
\mu_s (P + \Pi) \int_{\mu_0}^{\mu} = \mu_s (P) + \int_{P}^{P+\Pi} V_s (P^*) dP^* \tag{A7}
\]
which leads to
\[
-RT \log(a_w) = \int_{P}^{P+\Pi} V_s (P^*) dP^* = \Pi \tag{A8}
\]
assuming that the solvent is incompressible. For a diluted solution, i.e., \[\log(a_w) = \log(1 - X) \approx -n/n_w = -C, \] the osmotic pressure is $\Pi = RT C$.

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References


