

Electrokinetic Delivery of Reactants: Pore Water Chemistry Controls Transport, Mixing, and Degradation

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Electrokinetic Delivery of Reactants: Pore Water Chemistry Controls Transport, Mixing, and Degradation / Sprocati, R., Gallo, A., Sethi, R., Rolle, M.. - In: ENVIRONMENTAL SCIENCE & TECHNOLOGY. - ISSN 0013-936X. - ELETTRONICO. - 55:1(2021), pp. 719-729. [10.1021/acs.est.0c06054]

*Availability:*

This version is available at: 11583/2869731 since: 2021-02-05T09:32:28Z

*Publisher:*

American Chemical Society

*Published*

DOI:10.1021/acs.est.0c06054

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1           **Electrokinetic delivery of reactants: pore water chemistry controls**  
2                           **transport, mixing and degradation**

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4  
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14

15 **Abstract**

16 Electrokinetics in porous media entails complex transport processes occurring upon the  
17 establishment of electric potential gradients, with a wide spectrum of environmental  
18 applications ranging from remediation of contaminated sites to biotechnology. The resulting  
19 electric forces cause the movement of pore water ions in opposite directions, leading to charge  
20 interactions that can affect the distribution of charged species in the domain. Here, we  
21 demonstrate that changes in chemical conditions, such as the concentration of a background  
22 electrolyte in the pore water of a saturated porous medium, exert a key control on the  
23 macroscopic transport of charged tracers and reactants. The difference in concentration  
24 between the background electrolyte and an injected solute can limit or enhance the reactant  
25 delivery, cause non-intuitive patterns of concentration distribution, and ultimately control  
26 mixing and degradation kinetics. With non-reactive and reactive electrokinetic transport  
27 experiments combined with process-based modeling, we show that microscopic charge  
28 interactions in the pore water play a crucial role on the transport of injected plumes and on the  
29 mechanisms and rate of both physical and chemical processes at larger, macroscopic scales.  
30 Our results have important implications on electrokinetic transport in porous media and may  
31 greatly impact injection and delivery strategies in a wide range of applications, including in  
32 situ remediation of soil and groundwater.

33

34 **Keywords**

35 Electrokinetic remediation; Porous media; Charge interactions; Reactive transport; Mixing

36

## 37 **Introduction**

38 Electrokinetics in porous media has important applications in many different disciplines, as  
39 well as an enormous and yet unexplored potential. For instance, electrokinetics (EK) is used in  
40 microbial fuel cells<sup>1-3</sup>, rapid tests of rocks and concrete<sup>4,5</sup>, water purification<sup>6-9</sup> and may play  
41 an important role on enhanced and sustainable resources recovery<sup>10-12</sup>. An important  
42 environmental application of electrokinetic techniques is the remediation of soil and subsurface  
43 porous media<sup>13-15</sup>, in which the use of low-intensity electric fields can lead to the mobilization  
44 of contaminants and to the effective delivery of reactants and amendments, including  
45 bacteria<sup>16-19</sup>. Particularly promising is the capability of electrokinetic processes to distribute  
46 reactants in impervious, low-permeability porous media, which are not accessible by hydraulic  
47 flushing and can represent long term sources of contamination for soils and groundwater  
48 resources<sup>20-22</sup>. An important feature for many subsurface applications is that EK empowers  
49 effective delivery and mobilization strategies through the transport mechanisms induced by the  
50 application of an electric potential gradient. Such mechanisms include electromigration,  
51 consisting in the movement of ions in opposite directions depending on their charge,  
52 electroosmosis, resulting in an advective flow caused by the movement of ions in proximity of  
53 the solid grains' surfaces, and electrophoresis, affecting the transport of charged particles<sup>23</sup>.  
54 Despite the large number of current and potential applications, the quantitative understanding  
55 of electrokinetic phenomena in porous media remains a daunting challenge due to the  
56 complexity of the controlling processes that depend on physical, chemical and electrical  
57 properties of both fluids and solid matrices.

58 Here, we focus on electromigration transport of charged solutes in saturated porous media and  
59 we experimentally demonstrate that the electrolyte composition of the pore water greatly  
60 impacts the macroscopic dynamics of electrokinetic transport. We consider permanganate  
61 ( $\text{MnO}_4^-$ ) as a colored charged tracer due to its visible properties and its widespread use as strong

62 oxidant for the degradation of organic contaminants also in EK applications<sup>24-27</sup>. We show that  
63 background electrolyte concentrations control the delivery of the injected  $\text{MnO}_4^-$ , its spatial  
64 distribution and its mixing behavior with the surrounding pore water. Furthermore, in our  
65 experiments we study reactive transport of  $\text{MnO}_4^-$ , oxidizing a non-charged organic solute  
66 initially present in the porous domain. We illustrate the mechanism and impact of  
67 electrokinetically-induced charge mixing, in which the concentration of the background  
68 electrolyte affects both the extent of mixing and the kinetics of the mixing-controlled reaction.  
69 The electrokinetic experiments are compared with transport by advection and dispersion: the  
70 radically different dynamics of EK-induced transport and electrolyte-controlled reactions are  
71 systematically analyzed with the support of process-based numerical simulations.

72

### 73 **Materials and Methods**

74 To evaluate the displacement mechanisms of a tracer under different conditions of advective-  
75 dispersive and electrokinetic transport and to illuminate the role of charge interactions, we  
76 designed a quasi-two-dimensional experimental setup, schematically illustrated in Figure S1a-  
77 b (Supporting Information). The system consists of a tempered glass chamber (inner size 795  
78 mm × 182 mm × 11 mm) held by an aluminum structure with an internal polyethylene layer.  
79 The porous medium (glass beads, with grain size 0.40-0.60 mm, Sigmund Lindner, Germany)  
80 was included in the central part of the system (300 mm × 180 mm × 11 mm), delimited by two  
81 acrylic separators with honeycomb mesh and covered by a fabric layer.

82 For the advection-dispersion experiments (Figure S1a), recirculation between the reservoirs  
83 was established to ensure the desired hydraulic gradient. The flow rate was controlled with a  
84 high-precision, multi-channel peristaltic pump (ColeParmer, United States), and steady-state  
85 conditions could be reached in few minutes. The pump was operated with 5 channels, providing  
86 a constant seepage velocity in the porous medium of 6.5 cm/h.

87 For the EK experiments (Figure S1b), graphite rod electrodes ( $\varnothing 6 \times 300$  mm, Elektrokul,  
88 Denmark) were placed in the glass chamber, in two reservoir zones outside the porous medium.  
89 The distance between the two electrodes was 400 mm for all experiments. An electrolyte  
90 solution was recirculated in two external reservoirs to provide additional volume to reduce the  
91 impact of electrolysis reactions on the system pH. To recirculate water in the reservoirs, a four-  
92 channel peristaltic pump (Ole Dich, Denmark) was operated with 2 channels, providing a  
93 constant flowrate of 40 mL/min. The graphite electrodes were connected to a power supply  
94 (EA Elektro-Automatik, EA-PSI 5200-10A, Germany) by means of electric wires. The voltage  
95 provided by the power supply throughout the experiments was kept constant at 200 V. The  
96 current in the system was measured by connecting the wire from the power supply to the anode  
97 through a multimeter (PeakTech 3315, Germany). The effective potential drop within the  
98 porous media was measured by means of two wire electrodes (exposed tip 2 mm) placed  
99 centered in the setup, 10 mm below the water table and at a distance of 280 mm. The potential  
100 reading was performed with a second digital multimeter (PeakTech 3315, Germany). Voltage  
101 and current measurements were recorded with the multimeter at every hour of operation and  
102 were found to be in a range 122.1-148.7 V and 3.0-24.8 mA, respectively. The values measured  
103 in the different experiments are reported in the Supporting Information (Table S1).

104 Advection-dispersion and EK transport have been studied performing injections of potassium  
105 permanganate ( $\text{KMnO}_4$ ) on the left-side of the domain. To investigate the role of charge  
106 interactions on the transport of ions, we performed first a set of conservative, non-reactive  
107 experiments followed by a second set of reactive experiments, in which glucose (Sigma-  
108 Aldrich, United States) was added to the background solutions to reach a concentration of 8  
109  $\text{mol/m}^3$ . For all experiments, the concentration of the injected  $\text{KMnO}_4$  was constant ( $3 \text{ mol/m}^3$ )  
110 whereas the background electrolyte concentration, consisting in a solution with a fixed ratio of  
111  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  to reach a pH of 9, was varied for the different investigated scenarios.

112 In all cases, the injected tracer solution displaces the background fluid and creates a circular  
113 plume shape and a conductivity difference in the system.

114 The experiments were conducted in a dark room and the glass chamber was illuminated from  
115 the back with an electroluminescent panel (1000 mm × 300 mm, EL-Technik, Germany) and  
116 from the front with a light bulb (Philips 4000K, 806 lm, 100 mA, 9.5W). A calibration  
117 procedure was developed to relate the color intensity of permanganate with its concentration  
118 and to quantify the spatial distribution of the permanganate plumes in the porous medium at  
119 different times. Details about the setup and the image analysis and calibration techniques are  
120 provided in Supporting Information (Section S2).

121

## 122 **Theoretical background**

123 The transport of dissolved species in saturated porous media occurs as a result of concentration,  
124 electric potential and pressure gradients. These phenomena result in diffusion/dispersion,  
125 electromigration and advective fluxes, which are described by the Nernst-Planck equation<sup>28–33</sup>:

$$\mathbf{J}_i^{Tot} = \underbrace{-nD_i \nabla c_i}_{\mathbf{J}_i^{Dif}} \underbrace{-nD_i \frac{z_i F}{RT} c_i \nabla \Phi}_{\mathbf{J}_i^{Mig}} + \underbrace{n\mathbf{u}c_i}_{\mathbf{J}_i^{Adv}} \quad (1)$$

126 where  $n$  is the porosity,  $c_i$  is the molar concentration,  $D_i$  is the pore diffusion/dispersion  
127 coefficient,  $z_i$  is the charge number,  $\Phi$  is the electric potential and  $\mathbf{u}$  is the seepage velocity.

128 In absence of advective fluxes, transport by electromigration, provided sufficient electric  
129 potential gradients, is the dominant component. Such situation is typical of electrokinetic  
130 applications, in which the transport of ions by electromigration depends on the applied electric  
131 potential, on the diffusive/dispersive properties and on the charge of the individual ions. This  
132 makes anions and cations move in presence of an electric field in opposite directions, whereas  
133 non-charged solutes are not affected by the applied voltage. Considering a porous medium,  
134 ions in solution need to comply with the electroneutrality condition  $\sum_{i=1}^N z_i c_i = 0$ , which

135 corresponds to the Poisson's equation under the assumption of overall zero charge density in  
 136 the domain<sup>34,35</sup>. Given that ions in aqueous solutions have different diffusion coefficients  
 137 (Table S3, Supporting Information), under the application of an electric field they will move  
 138 with different electromigration velocities. Such properties, in combination with the  
 139 electroneutrality condition, imply that the electrokinetic transport of ions is affected by the  
 140 overall electrolyte composition of the system, thus making charge interactions play a key role  
 141 for the movement of the different charged species.

142 Considering that the application of an electric current in a porous medium results in a flux of  
 143 ions, it is possible to define the current density from the definition of total fluxes in Eq. 1. As  
 144 an external current can result in significant electric potential gradients, it is possible to assume  
 145 that the current density can be approximated as<sup>28</sup>:

$$I = F \sum_{i=1}^N J_i^{Mig} z_i = F^2 \sum_{i=1}^N z_i^2 \frac{nD_i}{RT} c_i \nabla \Phi = \sigma_e \nabla \Phi \quad (2)$$

146 Eq. 2 indicates that there are strong dependencies between the current density  $I$  and the  
 147 conductivity of the electrolyte solution  $\sigma_e$ . In particular, as  $\sigma_e$  changes in the system, the current  
 148 density and the electric potential gradient are also spatially and temporally variable in the  
 149 porous medium domain. Indeed, changes in electric potential gradients impact the intensity and  
 150 direction of migration fluxes, which ultimately affect the concentration and distribution of ionic  
 151 species in the system.

152 Process-based numerical modeling was performed with the codes NP-Phreeqc<sup>36</sup> and NP-  
 153 Phreeqc-EK<sup>37</sup> for the cases of advection-dispersion and electrokinetic transport, respectively.  
 154 These simulators are based on a coupling between COMSOL Multiphysics and the  
 155 geochemical code PhreeqcRM<sup>38</sup>, operated through a MATLAB LiveLink interface. For  
 156 electrokinetic transport, NP-Phreeqc-EK solves the Nernst-Planck-Poisson equations in  
 157 multidimensional domains and is able to account for a wide range of equilibrium and

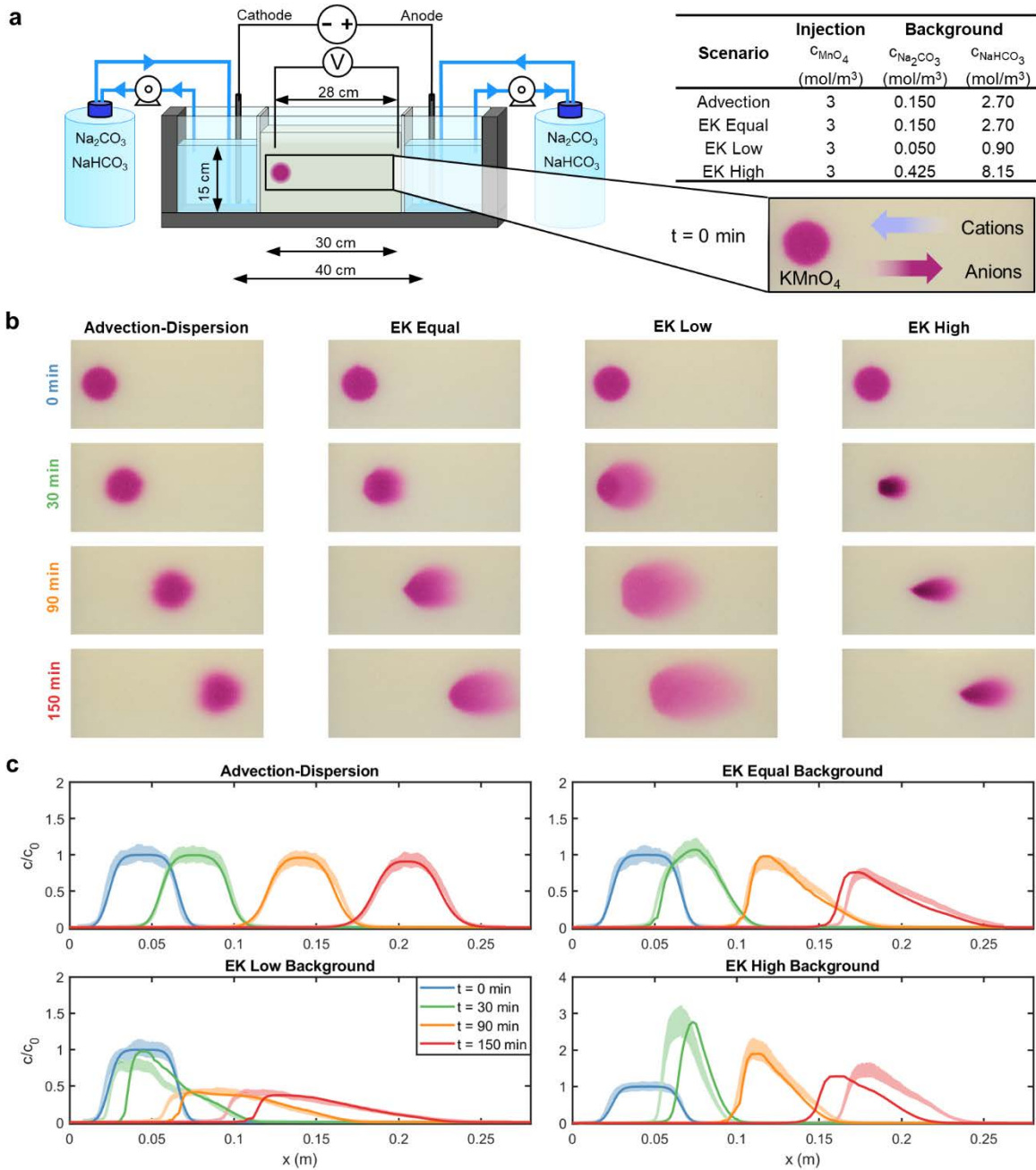
158 kinetically-controlled reactions. The coupling with the geochemical code accounts for the  
159 composition and aqueous speciation of the pore water. The initial solution speciation for each  
160 scenarios is reported in Tables S4 (Supporting Information).

161

## 162 **Results and discussion**

### 163 *Conservative transport experiments*

164 For the set of conservative experiments, the first scenario focuses on the movement of the  
165 purple-colored permanganate ion ( $\text{MnO}_4^-$ ) undergoing advective-dispersive transport induced  
166 by a simple pressure head gradient and without applying any electric potential difference  
167 between the electrodes (Figure 1). Three experimental scenarios were then dedicated to the  
168 investigation of EK transport. In these experiments, the application of a constant electric  
169 potential at the electrodes resulted in transport of the injected permanganate by  
170 electromigration. The electric potential in the system was set to provide an electromigration  
171 velocity comparable with the seepage velocity in the advective-dispersive experiment.  
172 Therefore, the electromigration velocity of  $\text{MnO}_4^-$  in the system was approximately 6.5 cm/h.  
173 The considered EK transport scenarios were characterized by three different electrolyte  
174 concentrations of the background pore water solution. We refer to “EK equal” for the scenario  
175 in which the sum of all cations (or anions) in the pore water is equal to the one of the injected  
176  $\text{KMnO}_4$  solution. Scenarios “EK low” and “EK high” represent situations in which the sum of  
177 cation equivalents in the background electrolyte solution is, respectively, three times lower and  
178 three times higher than the concentration of the injected tracer. Upon application of an electric  
179 field, the anions (including permanganate) move towards the anode on the right, whereas the  
180 cations are transported towards the cathode on the left. Figure 1a shows a sketch of the  
181 experimental setup and summarizes the injection and pore water concentrations in the different  
182 experiments.



184

185 **Figure 1.** *a* Illustration of the experimental setup and summary of concentrations used in the  
 186 different experiments. *b* images showing the evolution of the permanganate plume in the four  
 187 different experiments. *c* concentration profiles evaluated through the longitudinal axis of the  
 188 permanganate plume. The shaded area represents the experimental observations relating color  
 189 intensity to concentration including uncertainty bands ( $\pm 2\sigma$ ), whereas the solid lines are the  
 190 simulation outcomes.

191

192 For every scenario we monitored the evolution of the tracer plume in the porous medium by  
193 collecting pictures every minute for 150 minutes; Figure 1b presents four successive images of  
194 each experiment. Considering the advection-dispersion case, the permanganate plume has a  
195 regular and symmetric shape and moves with the water at the average linear pore water  
196 velocity. Conversely, in the EK transport cases, although the nominal migration velocity is  
197 comparable to the average pore water velocity in the advection-dispersion case, the shapes are  
198 very different and the plumes appear to be substantially deformed with respect to the initial  
199 circular shape. For instance, in scenario “EK equal”, the permanganate plume becomes  
200 elongated and a smooth concentration gradient develops at the front. A similar but more  
201 pronounced behavior is observed for scenario “EK low”, in which the permanganate plume has  
202 a lower color intensity and is significantly more stretched in the longitudinal and transverse  
203 directions. In contrast, in scenario “EK high”, the permanganate plume initially contracts and  
204 assumes a darker color. Successively, as the plume migrates towards the anode, it develops an  
205 elongated shape parallel to the applied electric field. The velocity of plume displacement for  
206 “EK equal” and “EK high” is similar and comparable with the advection-dispersion scenario.  
207 In these cases, the center of mass of the plume has traveled a distance of approximately 150  
208 mm after 150 min. The small electrolyte concentration in the case “EK low” has a clear effect  
209 of retarding the plume. After 150 min and despite the application of the same electric potential  
210 gradient, the centroid of the “EK low” plume has covered only 2/3 of the distance (~100 mm)  
211 of the other plumes.

212 Figure 1c illustrates the longitudinal profiles of the  $\text{MnO}_4^-$  concentrations at different times.  
213 Such profiles were evaluated both from the pictures, using a calibration function relating the  
214 color intensity to the tracer concentration, and from the outcomes of a 2-D forward model,  
215 describing the physical and electrostatic processes in the setup<sup>36,37,39</sup>. The simulation results,

216 showing the two-dimensional spatial distribution of the permanganate plumes at the different  
217 times, are presented in Figure S4. In the first experimental scenario, with transport induced by  
218 the hydraulic gradient, the permanganate concentration profiles are regular and follow the  
219 classic theory of transport in porous media<sup>40</sup>, as shown by the good agreement of the  
220 experimental observations with the advection-dispersion simulations (Figure 1c). The transport  
221 becomes radically different when  $\text{MnO}_4^-$  is displaced by electromigration. For instance, in the  
222 “EK equal” experiment, the plume develops a smoother concentration front, whereas the back  
223 of the plume presents a steep concentration profile even at late times. This behavior, inherently  
224 dissimilar from advective-dispersive transport, can be simulated considering the charge  
225 interactions and the coupled Nernst-Planck fluxes of the different charged species in the  
226 domain.

227 The results of the numerical simulations allowed us to reproduce the experimental observations  
228 very well, including the concentration values as well as the shape and the evolution of the  
229 permanganate plume in the setup. In the scenario “EK low”, the permanganate plume starts to  
230 expand and slowly displaces with a lower concentration with respect to the previous scenarios.  
231 The peak concentration ( $\sim 1 \text{ mol/m}^3$ ) is in the order of the low background electrolyte  
232 concentration in the pore water. Both the pictures and the longitudinal profiles also clearly  
233 show a slower movement of the permanganate plume compared to the other experimental  
234 scenarios. Conversely, in the scenario with high electrolyte background (“EK high”), the  
235 concentration of the permanganate plume initially increases, with the highest value almost three  
236 times the injected concentration. Successively, the plume migrates towards the anode with  
237 similar velocity and smooth concentration fronts as in the scenario “EK equal”.

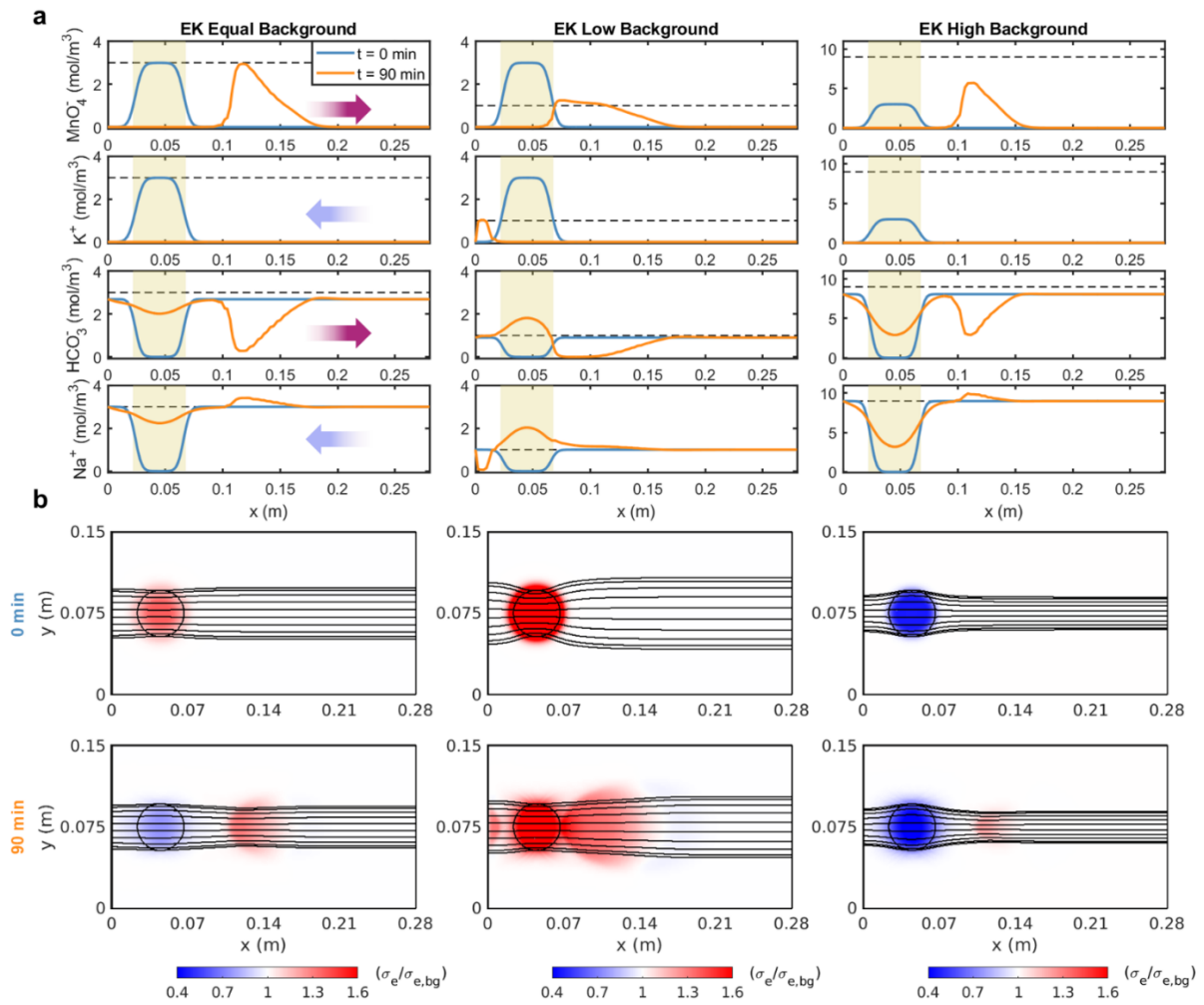
238

239 *Charge interaction mechanisms*

240 Process-based numerical modeling is essential to mathematically describe electrokinetic  
241 transport mechanisms, to visualize the spatial distribution of the delivered and of the  
242 background charged species, to illuminate their coupled displacement and, ultimately, to allow  
243 a quantitative interpretation of the experimental observations.

244 Figure 2a presents the simulated longitudinal concentration profiles of the different ions in the  
245 experimental setup at the initial time and after 90 minutes. In the EK scenario with equal  
246 background,  $\text{MnO}_4^-$  moves towards the anode, whereas  $\text{K}^+$  exits the porous medium to the  
247 cathode reservoir. In such scenario, the major background ions (sodium and bicarbonate) are  
248 uniformly present in the domain at the beginning of the experiment, except in the area where  
249 they were displaced by the injected  $\text{KMnO}_4$  solution. Upon application of the electric potential,  
250  $\text{HCO}_3^-$  is transported towards the anode, in the same direction of  $\text{MnO}_4^-$ . At the same time, the  
251 major cation in the system,  $\text{Na}^+$ , moves in the opposite direction towards the cathode. Note that  
252 in every point, due to the condition of electroneutrality, the sum of equivalents of both cations  
253 and anions must be the same. Consequently, the shape of the profiles of  $\text{MnO}_4^-$  and  $\text{HCO}_3^-$   
254 appear to be complementary as one anion can replace the other although together they cannot  
255 exceed the charge that is carried by the cations in the same location. The smooth front of  $\text{MnO}_4^-$   
256 and the low concentration of  $\text{HCO}_3^-$  are mainly due to their different aqueous diffusion  
257 coefficients (i.e.,  $1.50 \times 10^{-9}$  for  $\text{MnO}_4^-$  and  $1.09 \times 10^{-9}$  for  $\text{HCO}_3^-$ ). The higher diffusivity of  
258  $\text{MnO}_4^-$ , leads to its faster transport. However, such tendency is slowed down by the coupling  
259 with  $\text{HCO}_3^-$ , which needs to be displaced and the overall charge in the system has to be  
260 balanced. As a result, only a fraction of the permanganate front is able to proceed at the nominal  
261 electromigration velocity imposed by the voltage difference at the electrodes, thus resulting in  
262 a smooth front progressively advancing in the domain.

263



264

265 **Figure 2.** Simulated concentrations of major cations ( $\text{Na}^+$  and  $\text{K}^+$ ), anions ( $\text{HCO}_3^-$  and  $\text{MnO}_4^-$ )  
 266 ) in the pore water and 2D electrolyte conductivity at different times. **a** cross-section  
 267 illustrating the transport of the major ions in the system at  $t=0$  and  $t=90$  minutes for all three  
 268 EK scenarios. The dashed lines represent the sum of all positive or negative charge equivalents  
 269 in the system whereas the shaded area indicates the initial zone where the tracer has been  
 270 injected. **b** normalized electrolyte conductivity maps with respect to the background  
 271 conductivity for the three EK scenarios at  $t=0$  and  $t=90$  minutes (upper and bottom rows,  
 272 respectively). The lines are the computed electric field streamlines passing through the central  
 273 zone of the porous medium, where the tracer was injected.

274

275 In the experiment with lower background (“EK low”), the concentration of  $\text{MnO}_4^-$  during  
276 transport decreases significantly and approaches the values corresponding to the sum of the  
277 equivalents of all cations in the background solution (dashed line in Figure 2a). This is the  
278 result of the lower concentration of cations in the pore water, which limits the delivery of  
279 permanganate. Only a fraction of the injected plume can enter the volume initially occupied by  
280 the background electrolyte and starts to move towards the anode. The concentrations of  $\text{Na}^+$   
281 and  $\text{HCO}_3^-$  in the injection zone increases to fulfil the charge balance in this portion of the  
282 domain where higher amounts of  $\text{K}^+$  and  $\text{MnO}_4^-$  were initially injected. Finally, in the  
283 experimental scenario with high background electrolyte (“EK high”), the increase of  
284 permanganate concentration is the result of the high  $\text{Na}^+$  present in the background (moving  
285 towards the cathode), which requires a higher concentration of  $\text{MnO}_4^-$  (moving towards the  
286 anode) to comply with the condition of electroneutrality. In this scenario, also the concentration  
287 of both  $\text{Na}^+$  and  $\text{HCO}_3^-$  after 90 minutes in the initial area of injection is similar to the initial  
288 concentration of  $\text{K}^+$  and  $\text{MnO}_4^-$ . Such situation is particularly interesting since the increase in  
289 concentration, caused by electromigration fluxes (Figure S5) and resulting from the charge  
290 interactions in the multicomponent ionic system, occurs against the natural concentration  
291 gradient (Figure S6).

292 These experiments clearly show that the background electrolyte concentration controls the  
293 mechanisms of electrokinetic transport and, thus, the delivery, the shape and the evolution of  
294 the injected permanganate plumes. The driving force is indeed the electric potential gradient in  
295 the system, which in turn is influenced by the electrolyte conductivity. The latter is a spatially  
296 variable quantity in the considered setup, as illustrated in Figure 2b for all EK scenarios at  $t=0$   
297 and  $t=90$  minutes. In scenario “EK equal”, despite the concentrations of the background and  
298 the tracer solutions are the same, the conductivity of the injected  $\text{KMnO}_4$  plume is higher as a  
299 result of the higher diffusivity of  $\text{MnO}_4^-$  and  $\text{K}^+$  compared to the background ions. After 90

300 minutes, the distribution of  $\text{MnO}_4^-$  can be directly related to the electrolyte conductivity map  
301 with a higher  $\sigma_e$ , whereas the injection zone still shows a lower value of  $\sigma_e$  due to the lower  
302 diffusion coefficients of the background ions that occupied the injection's pore space. At this  
303 later time, also the electric field streamlines are different and appear to focus on the area of the  
304 permanganate plume, which has higher  $\sigma_e$  and has moved towards the anode. Similarly, in the  
305 scenario with low background concentration, a strong focusing of the streamlines occurs in the  
306 zone with initial injection of the plume where the higher  $\sigma_e$  results from the higher  
307 concentration of the injected permanganate solution with respect to the background. This  
308 phenomenon is due to the focusing of the electric field streamlines in zones with higher  
309 electrolyte conductivity, where the intensity of the electric field is higher. Also in this case, a  
310 subsequent defocusing of the streamlines causes a larger spreading of the permanganate plume.  
311 At later times, the progressive distribution of the mass from the initial injection and the limiting  
312 effect of the background electrolyte concentrations tend to suppress the differences in  
313 conductivity.

314 For the scenario with high background electrolyte concentration, the streamlines show an  
315 opposite pattern, first defocusing in the injection zone (low  $\sigma_e$ ) and then focusing in the  
316 direction of permanganate transport. In this case, it is possible to observe an increase of  $\sigma_e$  as  
317 a result of the progressive increase in  $\text{MnO}_4^-$  concentration, as the permanganate plume shrinks  
318 during its displacement towards the anode.

319 Overall, the computed 2D maps of electrolyte conductivity illustrate the evolution of this  
320 property in the domain and the effects on the electric potential streamline patterns, which  
321 directly affect the observed shape and propagation of the permanganate plume in the  
322 experimental setup. Interestingly, during EK also the initial conditions of the system such as  
323 local differences in  $\sigma_e$  between the injected tracer solution and the background are maintained  
324 at later times and such effects only dissipate slowly as a result of diffusion.

325

326 *Plume spreading and mixing*

327 Transport of solutes in porous media results from complex pore-scale flow and mass transfer  
328 processes that determine the macroscopic shape and evolution of injected plumes. Metrics  
329 allowing the quantification of plume spreading and mixing are essential to describe solute  
330 transport in porous domains<sup>41,42</sup>. The second central spatial moments, quantifying the mean  
331 displacement of the concentration distribution from the plume centroid, are typically evaluated  
332 to characterize plume spreading<sup>43</sup>. Here we determine the moments of the permanganate  
333 plumes observed in our experiments as well as in the model simulations. To determine plume  
334 mixing, instead, we use the concept of the dilution index, a metric based on the Shannon  
335 entropy that quantifies the effective volume occupied by the plume<sup>44</sup>. Plume spreading and  
336 mixing are evaluated for all conservative scenarios with the equations summarized in the  
337 Supporting Information (Section S4). Figure 3a shows the permanganate plumes after 90  
338 minutes from the injection for the four considered experimental scenarios. The pictures clearly  
339 show different plume shape, mass distribution and solute concentration resulting from the  
340 transport and electrostatic mechanisms in the experiments performed. The longitudinal and  
341 transverse second central moments exhibit a distinct behavior in the experiments (Figure 3b).  
342 In the advection-dispersion scenario, the longitudinal and transverse moments show a gradual  
343 increase due to hydrodynamic dispersion at the plume fringes. In the EK scenario with the same  
344 background concentration (“EK equal”), instead, the permanganate plume spreading is larger  
345 both in the longitudinal and in the transverse directions. Spreading in both directions is very  
346 pronounced in the experiment with low concentration of the background electrolyte in which  
347 the observed permanganate concentrations are low and the plume spreads over a large portion  
348 of the porous medium. The trends of the computed moments show higher slope at the  
349 beginning, indicating that the spreading enhancement is more effective at early times. In the

350 scenario “EK high”, the plume initially shrinks and then spreads. Such behavior is apparent  
351 from the computed moments, showing decreasing values from the initial injection followed by  
352 an increase as the plume is displaced towards the anode. The rate of increase is more  
353 pronounced in the longitudinal direction, resulting in higher moments at late times compared  
354 to the advection-dispersion case. For all the cases, the spatial moments from the 2-D  
355 simulations allow capturing the trends computed from the experimental data.

356

357

358 **Figure 3.** *Metrics of spreading and mixing. a images of the permanganate plumes for the*  
359 *different scenarios at t=90 minutes. b Second central spatial moments, dilution index and peak*  
360 *concentration expressed as a function of time. The solid lines indicate model predictions*  
361 *whereas the shaded areas represent the experimental results.*

362

363 Figure 3b also shows the evolution of the dilution index and the peak concentration of the  
364 permanganate plumes. Such metrics are intrinsically related<sup>44,45</sup> and quantify the capability of  
365 the injected plumes to effectively mix with the background pore water. In the advection-

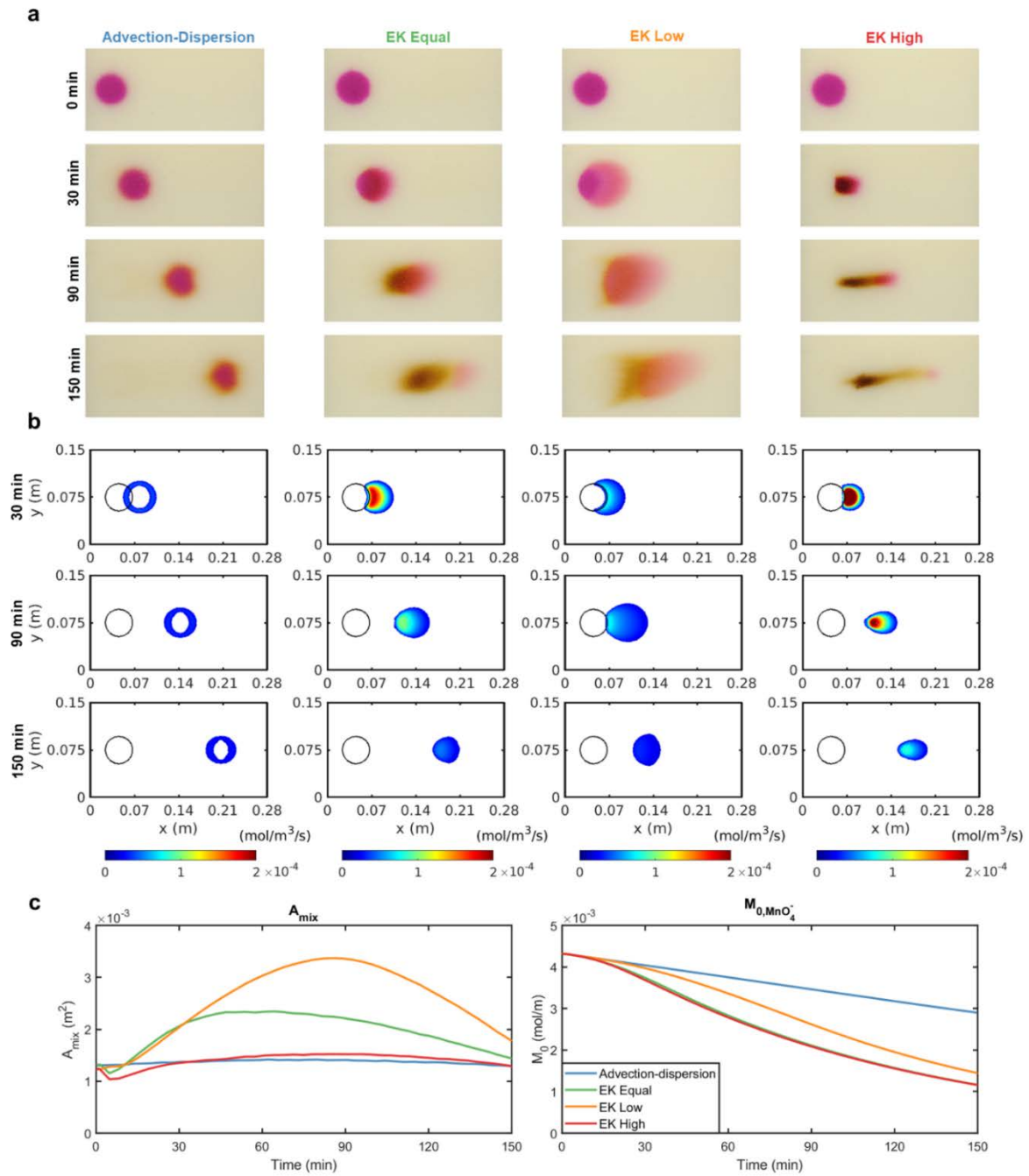
366 dispersion case the dilution index shows a mild linear increase, as expected for transport in a  
367 two-dimensional homogeneous porous medium,  $E \sim t^{n/2}$ , where  $n$  is the dimensionality of the  
368 system<sup>44</sup>. Dilution appears to be stronger in the “EK equal” and “EK low” scenarios. In  
369 particular, the latter case exhibits more than double increase in the plume dilution. These results  
370 show the capability of EK transport to effectively distribute the mass of the injected tracer over  
371 a larger pore water volume. Different, and perhaps even more interesting, is the case “EK high”.  
372 In such scenario the dilution index shows a non-monotonic trend with an initial decrease  
373 (approximately half of the initial value during the first 30 minutes) followed by an increase to  
374 a level similar to the dilution of the injected circular plume. The initial trend of the dilution  
375 index of the  $\text{MnO}_4^-$  plume is counterintuitive based only on conventional mass transfer  
376 mechanisms, since it indicates that the plume decreases its entropy. However, as explained  
377 above, the plume shrinking, the peak concentration increase (almost three times the injected  
378 values) and the dilution decrease are due to the electrostatic interactions with the ions present  
379 at high concentration in the background pore water electrolyte and to the electroneutrality  
380 constraint.

381

### 382 *Reactive transport experiments*

383 These experiments explored the displacement and degradation reaction of  $\text{MnO}_4^-$  under  
384 advective-dispersive and electrokinetic transport. Permanganate was delivered in the porous  
385 media with a background electrolyte containing glucose ( $8 \text{ mol/m}^3$ ) as model organic  
386 compound. When these two reactants come into contact an oxidation-reduction reaction occurs,  
387 which is described as a bimolecular reaction kinetics. In this set of reactive transport  
388 experiments, the same EK scenarios with equal, low and high background concentration of  
389 electrolytes were investigated and the results are illustrated in Figure 4.

390



391

392 **Figure 4.** Reactive transport experiments and model analysis. **a** images showing the temporal  
 393 evolution of the reactant plumes. **b** simulated reaction rates, considering a limiting threshold  
 394 of  $2 \times 10^{-5}$  mol/m<sup>3</sup>/s for all scenarios that allows the visualization of the different reaction  
 395 patterns. **c** evaluation of the area for the mixing-controlled reaction and of the MnO<sub>4</sub><sup>-</sup> mass  
 396 simulated in the different scenarios.

397

398 Figure 4a shows the evolution of the reactive system for the different scenarios over time. In  
399 case of advection-dispersion, the reaction occurs at the fringe of the plume, where the  
400 permanganate mixes with the glucose in the background pore water by hydrodynamic  
401 dispersion. When the two solutes come into contact, the mixing-controlled reaction occurs. The  
402 reaction area is visible from the pictures showing the formation of oxidation products at the  
403 plume fringe and also from the numerical simulations. In this scenario the reactive fringe moves  
404 with the permanganate plume in the same direction of the advective flow (Figure 4b).

405 In case of EK transport, the mixing mechanisms and the resulting patterns of reactants and  
406 products distribution are completely different (Figure 4a-b). The applied electric field causes  
407 the displacement of permanganate by electromigration but has no effect on the non-charged  
408 glucose. Therefore, the mixing pattern resembles chromatographic mixing with an effective  
409 overlap of the displaced permanganate with the immobile organic compound in the pore water.  
410 The reactive zone is large, extending to the whole area of the plume, and is not restricted to a  
411 thin fringe at the plume boundary. Indeed, in case of EK transport, more extensive degradation  
412 and more effective consumption of permanganate are observed. It is also of interest to note the  
413 effects of the different background electrolyte concentrations in the distinct EK reactive  
414 transport experiments. When the electrolyte background solution has an equal concentration  
415 with respect to the injected permanganate, the reaction occurs effectively and, after 150  
416 minutes, almost all  $\text{MnO}_4^-$  has been consumed. In the case with low background electrolyte  
417 concentration, the  $\text{MnO}_4^-$  plume spreads significantly and its concentration in the porous  
418 medium is limited by the background electrolyte. Such behavior results in a large mixing area  
419 but in a considerably slower reaction kinetics leading to only partial consumption of the  
420 oxidant. Therefore, the slow kinetics of the redox reaction is the overall rate-limiting step,  
421 resulting in the presence of a significant permanganate plume even after 150 minutes. Lastly,  
422 in the experimental scenario with higher background concentration, the permanganate plume

423 shrinks and its concentration is increased. The mixing area is smaller but reactive mixing is  
424 effective due to the higher concentration of  $\text{MnO}_4^-$  leading to faster reaction kinetics and to an  
425 almost complete consumption of the permanganate plume.

426 Figure 4b illustrates the spatial and temporal distribution of the mixing-controlled reactive  
427 zones in the different scenarios. The evolution of the computed mixing area and of the reaction  
428 efficiency, quantified through the computed mass of permanganate in the domain, are shown  
429 in Figure 4c. The mixing area is larger in the cases “EK equal” and “EK low” in which  
430 permanganate electromigration and the composition of the background electrolyte solution lead  
431 to an extended mixing zone. Such area of contact between the reactants reaches a maximum  
432 and, successively, starts to decrease due to the consumption of the permanganate plume. The  
433 mixing area is considerably more limited in the “Advection-Dispersion” and “EK high”  
434 experiments. In these cases the values reached are similar but, as discussed above and  
435 illustrated in Figure 4a-b, the shape of the mixing zone is completely different due to the  
436 different transport mechanisms. Considering the degradation of the permanganate plumes upon  
437 reaction with the glucose in the pore water, the simulations show nonlinear decreasing trends  
438 of the remaining mass with significantly higher permanganate consumption in presence of  
439 electrokinetic transport. In particular, the cases “EK equal” and “EK high” show the highest  
440 efficiency and the lowest mass of permanganate in the system at the end of the simulation. In  
441 these cases the simulation outcomes show that 75% of the initial permanganate mass was  
442 consumed. A smaller efficiency (70% of the initial mass consumed) characterized the scenario  
443 “EK low”, whereas the lowest efficiency was observed in the advection-dispersion case in  
444 which only 35% of the initial permanganate mass was consumed.

445

#### 446 **Implications for electrokinetic applications**

447 Our investigation highlights important aspects and mechanisms of both scientific and practical  
448 relevance for electrokinetic transport of charged species in porous media, which is of crucial  
449 importance in different disciplines and has a wide range of current and potential applications  
450 in geological, environmental, industrial and biological systems. We demonstrate that the pore  
451 water chemistry and microscopic Coulombic interactions can both limit and/or enhance the  
452 delivery of charged tracers by electrokinetics. The EK transport experiments performed clearly  
453 show that when the background concentration of the cations or anions is significantly smaller  
454 than an injected charged tracer, the tracer concentration that it possible to deliver by  
455 electromigration is limited by the concentration level of the background electrolyte solution.  
456 The ionic composition of the pore water also controls the tracer displacement, impacting the  
457 movement of the center of mass as well as the shape and spreading of the plume both in  
458 longitudinal and lateral directions. Moreover, the dilution of the injected tracer depends on the  
459 background electrolyte that, when present at high concentration, can even lead to a decrease of  
460 the dilution and the entropy of the plume and to an increase of its peak concentration. Of  
461 environmental significance are also the outcomes of the reactive transport experiments showing  
462 fascinating aspects of electrokinetically-induced charge species' mixing, leading to different  
463 mass removal efficiencies and to quantitatively important effects of the pore water chemistry  
464 on the kinetics of mixing-controlled degradation.

465 This investigation opens interesting perspectives on the possibility to employ microscopic  
466 charge interactions to control macroscopic transport and to design innovative delivery  
467 strategies in porous media that can be effectively implemented in practical applications, such  
468 as soil and groundwater remediation. The mechanistic understanding of the fundamental role  
469 of background electrolyte composition for the delivery of charged species during EK and the  
470 developed process-based model, will allow the improvement of the performances of  
471 electrokinetic distribution techniques for nutrients<sup>39,46-48</sup> and reactants<sup>49-52</sup> in subsurface

472 porous media. Specific examples include the quantitative assessment of the amounts and  
473 distribution of delivered species, the optimization of voltage values, and the planning of  
474 delivery strategies such as alternating active/inactive EK phases. Applications for subsurface  
475 remediation encompass both low-permeability zones<sup>25,26</sup> but may also be employed to enhance  
476 mixing and degradation of contaminant plumes in permeable aquifer systems, where poorly  
477 mixing flow and transport regimes and mass transfer limitations<sup>53</sup> represent typical bottlenecks  
478 to effective remediation. The detailed process knowledge obtained in this study will also be  
479 instrumental for quantitative understanding of electrokinetic transport in heterogeneous porous  
480 media, where high spatial variability of physical and chemical properties (e.g., permeability,  
481 porosity, surface charge and pore water composition) will affect the electrokinetic delivery of  
482 reactants, and where strong interactions between the different electrokinetic transport processes  
483 will impact the effectiveness of in situ EK interventions. Finally, the combined experimental  
484 and process-based modeling approach proposed in this study could be extended and further  
485 developed for the use of different tracers and reactants, including micro- and nanomaterials for  
486 subsurface remediation<sup>54,55</sup>.

487

488 **Acknowledgments**

489 The authors would like to acknowledge the support of the Capital Region of Denmark, the H.C.  
490 Ørsted Fond and the PhD fellowship at Politecnico di Torino (DIATI Department), as well as  
491 the help of Emil Bay Frantzen in the experimental activities. Constructive comments of three  
492 anonymous reviewers helped improving the quality of the manuscript.

493

494 **Associated content**

495 *Supporting Information*

496 Details of the experimental setup, image analysis, governing equations, metrics of spreading,  
497 dilution and mixing, and numerical modeling approach. 2-D model results of permanganate  
498 transport at different times for the four conservative scenarios, simulated 2-D advective and  
499 electromigration fluxes and diffusive/dispersive fluxes. Tables summarizing experimental  
500 conditions (e.g., voltage, current, pH and temperature) and parameters used for the process-  
501 based numerical modeling.

502

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