

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

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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 cells¹⁻³, rapid tests of rocks and concrete^{4,5}, water purification⁶⁻⁹ and may play
41 an important role on enhanced and sustainable resources recovery¹⁰⁻¹². An important
42 environmental application of electrokinetic techniques is the remediation of soil and subsurface
43 porous media¹³⁻¹⁵, 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 bacteria¹⁶⁻¹⁹. 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 resources²⁰⁻²². 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 particles²³.
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 (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 applications²⁴⁻²⁷. We show that
63 background electrolyte concentrations control the delivery of the injected 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 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 \times 182 mm \times 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 \times 180 mm \times 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 (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 mol/m^3 . For all experiments, the concentration of the injected KMnO_4 was constant (3 mol/m^3)
110 whereas the background electrolyte concentration, consisting in a solution with a fixed ratio of
111 NaHCO_3 and Na_2CO_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^{28–33}:

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

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, Φ 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^{34,35}. 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 as²⁸:

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

146 Eq. 2 indicates that there are strong dependencies between the current density I and the
 147 conductivity of the electrolyte solution σ_e . In particular, as σ_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-Phreeqc³⁶ and NP-
 153 Phreeqc-EK³⁷ 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 PhreeqcRM³⁸, 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

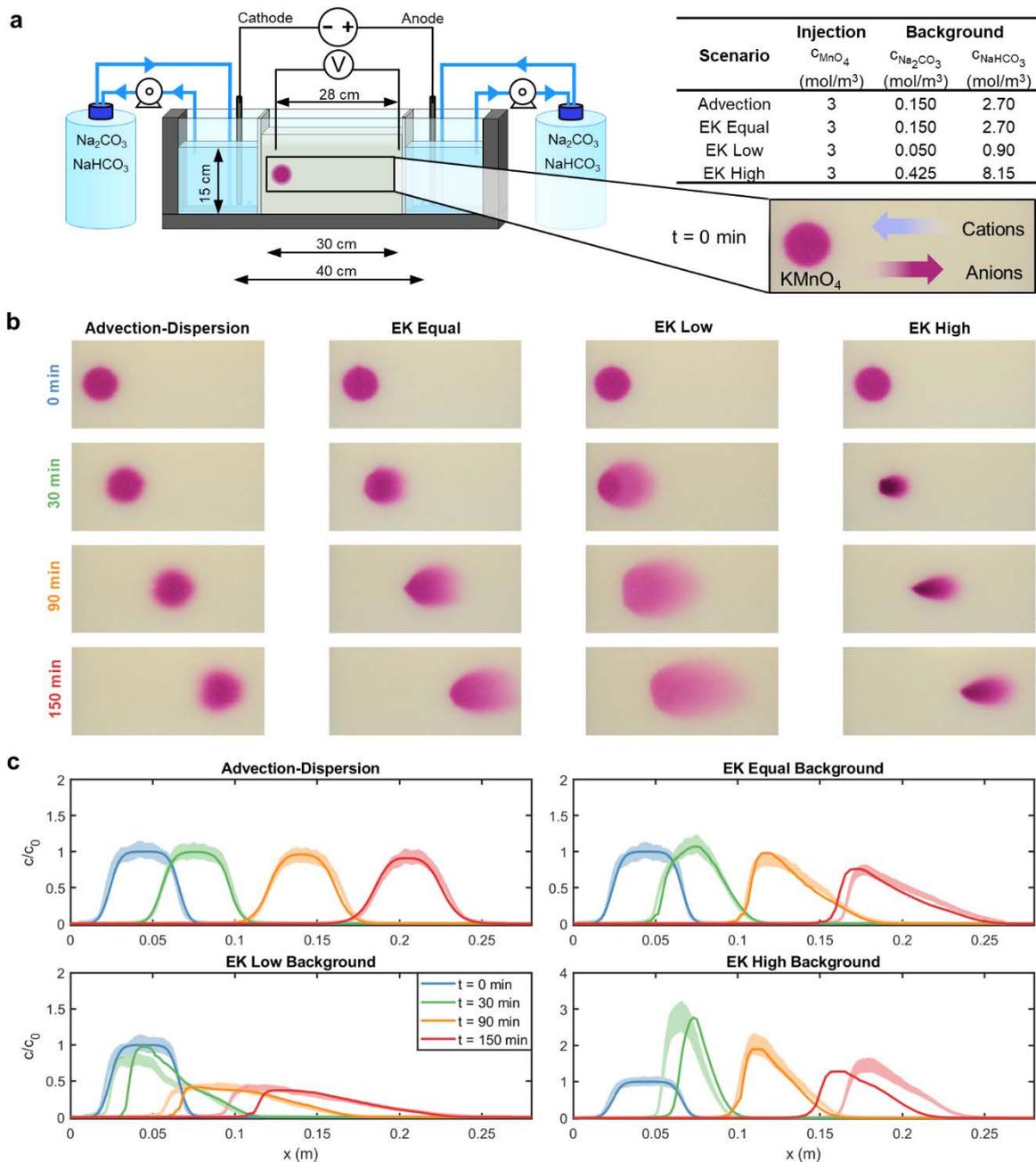
158 kinetically-controlled reactions. The coupling with the geochemical code accounts for the
159 composition and aqueous speciation of the pore water. The initial solution speciation for each
160 scenarios is reported in Tables S4 (Supporting Information).

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 (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 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 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 the186 different experiments. **b** images showing the evolution of the permanganate plume in the four187 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 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^{36,37,39}. 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 media⁴⁰, 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 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”.

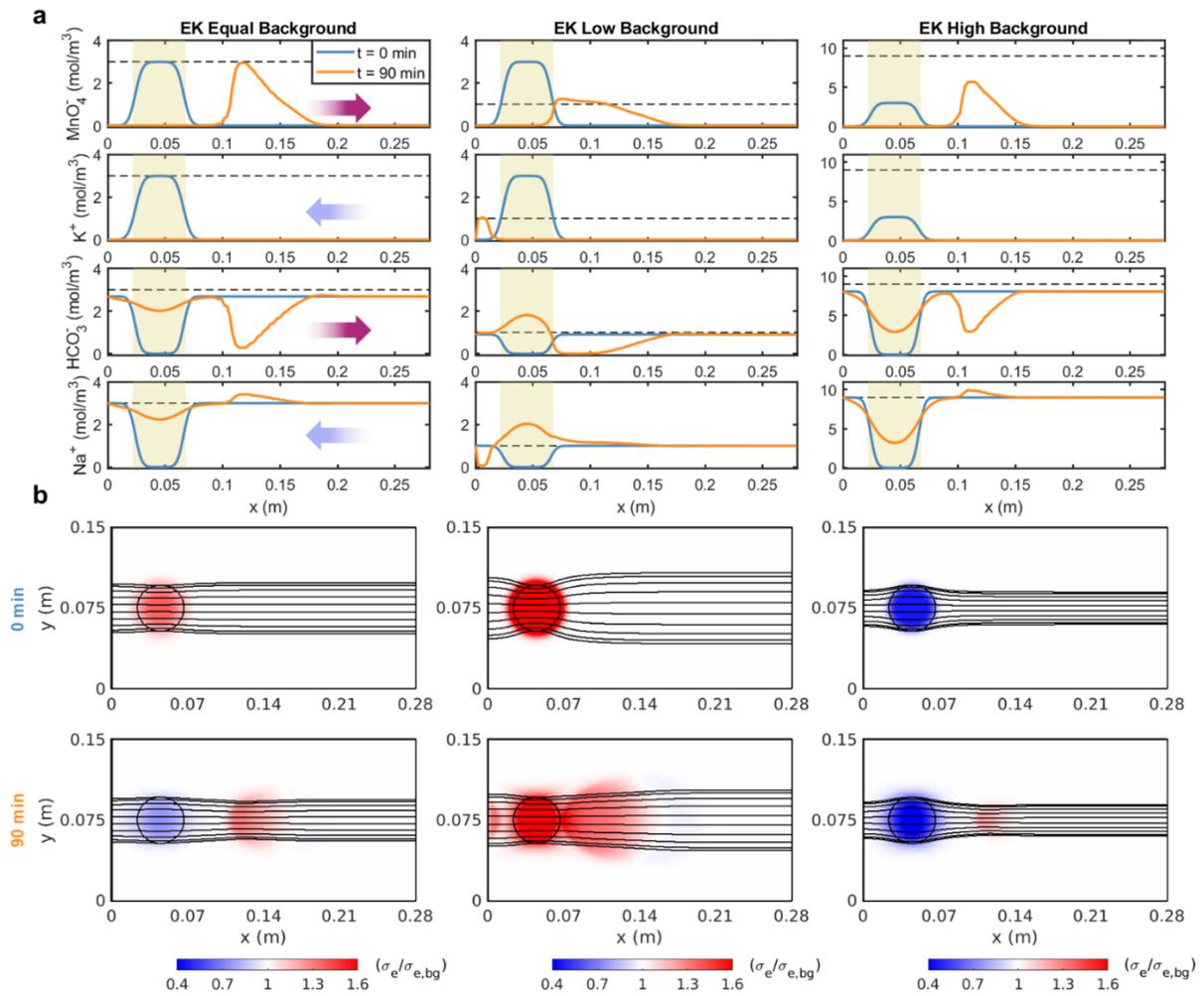
238

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, MnO_4^- moves towards the anode, whereas 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 KMnO_4 solution. Upon application of the electric potential,
250 HCO_3^- is transported towards the anode, in the same direction of MnO_4^- . At the same time, the
251 major cation in the system, 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 MnO_4^- and 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 MnO_4^-
256 and the low concentration of HCO_3^- are mainly due to their different aqueous diffusion
257 coefficients (i.e., 1.50×10^{-9} for MnO_4^- and 1.09×10^{-9} for HCO_3^-). The higher diffusivity of
258 MnO_4^- , leads to its faster transport. However, such tendency is slowed down by the coupling
259 with 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 (Na^+ and K^+), anions (HCO_3^- and 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 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 Na^+
281 and HCO_3^- in the injection zone increases to fulfil the charge balance in this portion of the
282 domain where higher amounts of K^+ and 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 Na^+ present in the background (moving
285 towards the cathode), which requires a higher concentration of MnO_4^- (moving towards the
286 anode) to comply with the condition of electroneutrality. In this scenario, also the concentration
287 of both Na^+ and HCO_3^- after 90 minutes in the initial area of injection is similar to the initial
288 concentration of K^+ and 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 KMnO_4 plume is higher as a
299 result of the higher diffusivity of MnO_4^- and K^+ compared to the background ions. After 90

300 minutes, the distribution of MnO_4^- can be directly related to the electrolyte conductivity map
301 with a higher σ_e , whereas the injection zone still shows a lower value of σ_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 σ_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 σ_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 σ_e) and then focusing in the
316 direction of permanganate transport. In this case, it is possible to observe an increase of σ_e as
317 a result of the progressive increase in 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 σ_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^{41,42}. 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 spreading⁴³. 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 plume⁴⁴. 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^{44,45} and quantify the capability of
365 the injected plumes to effectively mix with the background pore water. In the advection-

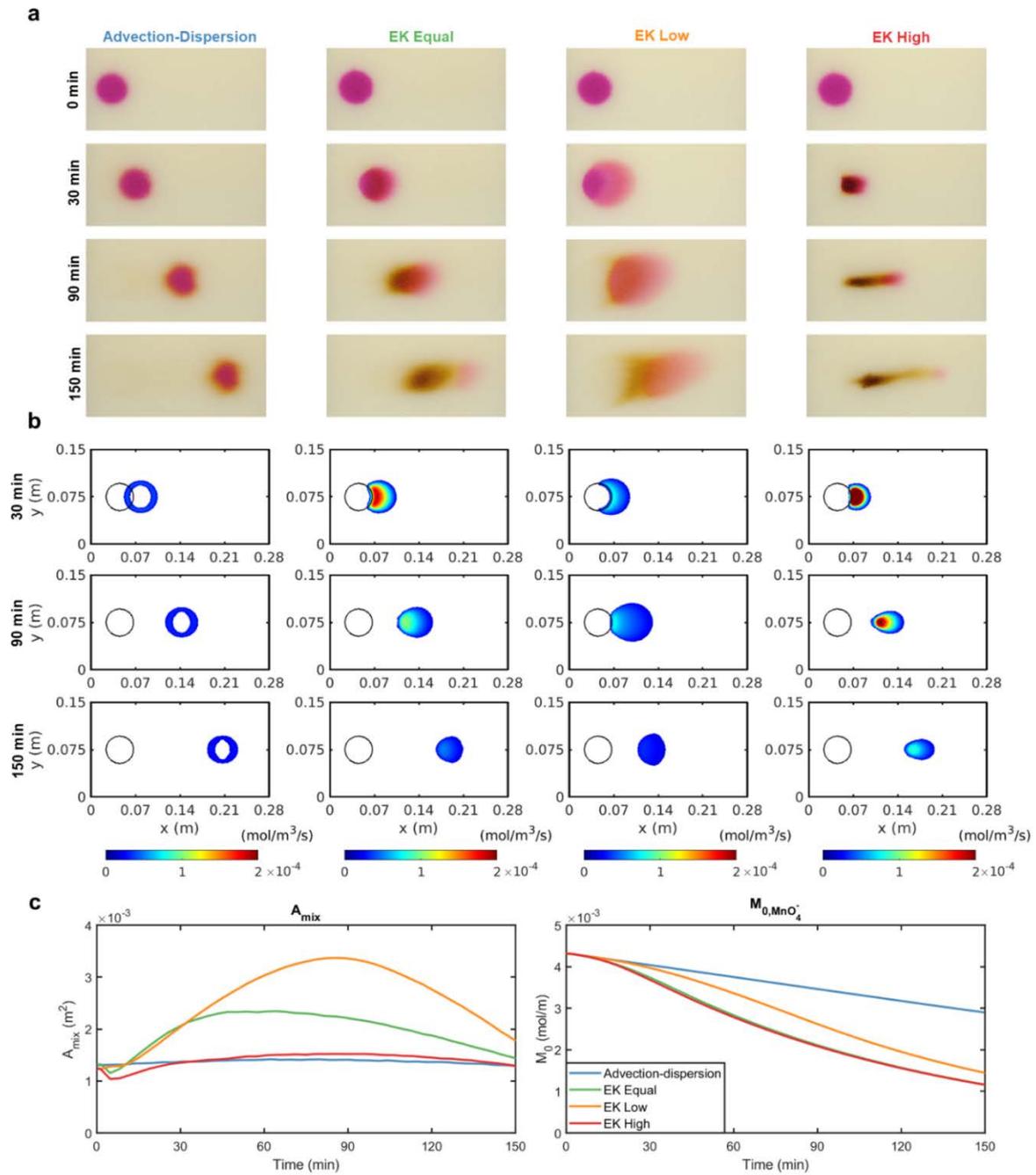
366 dispersion case the dilution index shows a mild linear increase, as expected for transport in a
367 two-dimensional homogeneous porous medium, $E \sim t^{n/2}$, where n is the dimensionality of the
368 system⁴⁴. Dilution appears to be stronger in the “EK equal” and “EK low” scenarios. In
369 particular, 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 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 MnO_4^- under
384 advective-dispersive and electrokinetic transport. Permanganate was delivered in the porous
385 media with a background electrolyte containing glucose (8 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 2×10^{-5} mol/m³/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 MnO₄⁻ 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 MnO_4^- has been consumed. In the case with low background electrolyte
417 concentration, the 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 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^{39,46-48} and reactants⁴⁹⁻⁵² 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^{25,26} 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 limitations⁵³ 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^{54,55}.

487

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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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