

1 **How root nutrient uptake affects rhizosphere pH: A modelling study**

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21

22 **Abstract**

23 Rhizosphere pH is the consequence of numerous, complex processes and is a key factor of
24 biogeochemistry at the soil-root interface. This work aimed at evaluating the impact of
25 nutrient root absorption on rhizosphere pH using a mechanistic model formalizing major
26 nutrient cation and anion transport, under the influence of concentration, electric potential
27 gradients and of convection. The electrical neutrality of the system was maintained through a
28 H^+ root efflux or influx (or equivalent opposite OH^- fluxes). The model outputs were
29 compared to the rhizosphere pH of maize (*Zea mays* L.), ryegrass (*Lolium perenne* L.) and
30 Alpine pennycress (*Noccaea caerulescens* (J. & C. Presl) F. K. Mey.) grown in three different
31 soils, determined with planar optodes. A global sensitivity analysis was carried out in order to
32 highlight the dominating factors. The composition of 37 soil solutions from the literature was
33 used to predict rhizosphere pH. The model most of the time predicts the alkalisation of the
34 rhizosphere by up to +3.3 pH units, given that in aerobic soils, nitrate is the most absorbed
35 nutrient and its internalization is equilibrated by H^+ root absorption (or equivalent OH^-
36 excretion). This alkalisation is close to that observed in the rhizosphere of ryegrass and
37 Alpine pennycress. The rhizosphere pH predictions are very sensitive to the initial
38 composition of the soil solution and quite insensitive to root absorption kinetics and soil
39 buffer power for the various nutrients. Because it favours nitrate diffusion, water content is
40 positively correlated with rhizosphere alkalisation. Moreover, the lower the root density, the
41 lower the effect of the root uptake on both ion concentrations and on rhizosphere pH.
42 Convection has little influence on rhizosphere pH. This study confirms the prominent role of
43 mineral nutrition in the determination of rhizosphere pH. The model therefore constitutes a
44 tool for understanding and predicting rhizosphere pH.

45

46 **Keywords:** soil solution; nutrient; root uptake; nitrate; sensitivity analysis

47 **1. Introduction**

48 It has long been established that soil pH in the vicinity of the roots may differ from that of the
49 bulk soil, by up to two units. The sign of this difference, i.e. alkalisation or acidification of
50 the rhizosphere, and its intensity depends on plant and soil factors. Indeed, the root-mediated
51 pH changes in the rhizosphere has been explained by cation-anion exchange between root and
52 soil, root excretion of organic anions, root respiration (CO₂ production) and root-induced
53 redox processes (O₂ emission). These processes may be affected by nutritional constraints,
54 such as Fe and P deficiencies or Al toxicity, whose effect on rhizosphere pH varies according
55 to the soil buffering capacity (Hinsinger et al., 2003; Neumann and Römheld, 2012).

56 Of these different processes, the cation and anion exchange balance appears to be most
57 influential, because soil solution pH depends on the net charge from ions which do not react
58 to OH⁻ and H⁺ (Sposito, 1989) and all living plants have to take up ions (mainly as nutrients)
59 from this solution, modifying the net charge. The impact of plant mineral nutrition on
60 rhizosphere pH has often been shown to be strong (Haynes, 1990; Marschner et al., 1986).

61 When more cations than anions are absorbed by the root cells, protons are released into the
62 apoplast to compensate for the excess positive charges in the cell, thereby resulting in a
63 decrease in the rhizosphere pH. However, when more anions are absorbed, either H⁺ is taken
64 up, or OH⁻ or HCO₃⁻ (resulting from the reaction of OH⁻ with CO₂) is excreted, thence leading
65 to the alkalisation of the rhizosphere (Haynes, 1990; Riley and Barber, 1969; Riley and
66 Barber, 1971). The release or uptake of H⁺ by roots is therefore equivalent to the cation-anion
67 balance of root-absorbed ions (Hinsinger et al., 2003; Rufyikiri et al., 2001). However, it has
68 yet to be clearly established whether roots have a general tendency to acidify or to alkalise
69 their neighbourhood. Although Cunningham (1964) showed that on average, plants absorb
70 more anions than cations, plants are often considered to acidify their rhizosphere, arguing that
71 they absorb more cations than anions (Sposito, 2016).

72 These modifications to the rhizosphere pH can have a feed-back effect on the mineral
73 nutrition of plants. They can affect the roots' uptake properties through competition between
74 H^+ and OH^- for sorption sites in apoplast and cell membrane, through modification of the
75 external electrochemical gradient or alterations to the root metabolism (Chaignon et al., 2009;
76 Neumann and Römheld, 2012). However, the main effects of the rhizosphere pH on mineral
77 nutrition of plants occur through modification of the nutrient availability in soil. Rhizosphere
78 acidification can be regarded as a process selectively evolved in some species or group of
79 species to overcome P and Fe deficiencies. Indeed, most plant species, except *Poaceae*, can
80 be gathered into the Strategy I group, which possesses an enhanced capacity to excrete H^+ and
81 to reduce Fe(III) through a reductase system, in order to acquire Fe when it is poorly
82 available. Similarly, increased proton exudation can also be triggered by P deficiency in
83 various plant species (Hinsinger et al., 2003; Neumann and Römheld, 2012). Alternatively, an
84 alkalinisation of the rhizosphere can reduce the availability of elements as demonstrated for P
85 (Riley and Barber, 1971) and Cu (Bravin et al., 2009; Chaignon et al., 2009).

86 Mechanistic modelling based on the diffusion-convection equation of solutes in the
87 rhizosphere (Barber, 1995) has continuously developed in order to predict plant uptake of
88 both nutrients (Darrah et al., 2006; Keyes et al., 2013; Leitner et al., 2010; Ptashnyk et al.,
89 2011) and of metallic contaminants (Custos et al., 2014; Lin et al., 2014; Mullins et al., 1986;
90 Puschenreiter et al., 2005; Sterckeman et al., 2004). One approach to improving the solute
91 uptake model would be to couple it to a model predicting rhizosphere pH (Gérard et al., 2017;
92 Szegedi et al., 2010).

93 Nye (1972; 1981) was the first author to model the changes in rhizosphere pH from a constant
94 H^+ or HCO_3^- flux from the root surface and the diffusion of these species according to Fick's
95 law, taking into account the pH buffer capacity of the soil. Given that plants, except legumes,
96 on average absorb more anions than cations (Cunningham, 1964), root excretion of HCO_3^-

97 was fixed at a value estimated from the literature. The proton emission from well-nodulated
98 legume roots was fixed in a similar way. Close agreement between Nye's theory and
99 experimental results was found in the case of rhizosphere acidification of submerged rice
100 (Kirk and Bajita, 1995) or of the growth zone of maize root tip (Schaller and Fischer, 1985).
101 Nevertheless, these validations of Nye's model did not cover the case of a HCO_3^- efflux
102 which often occurs above root tips, in well-aerated soils where nitrate is the main form of
103 absorbed nitrogen (Blossfeld et al., 2010; Nye, 1981). Moreover, Nye's model is based on an
104 *a priori* setting, namely an estimated H^+ or OH^- (or HCO_3^-) proton efflux to fit a situation
105 known to cause an acidification or alkalinisation of the root vicinity, respectively. This
106 approach does not apply to the general case, when the efflux of acid-base species resulting
107 from the plant mineral nutrition is unknown. Therefore, a model determining the root efflux
108 of acid-base species from the balance of cation and anion root absorption would be an
109 improvement of the rhizosphere pH prediction.

110 We consequently developed such a model, and used it to evaluate the effect of major nutrient
111 root uptake on rhizosphere pH. The model describes the transport of major cations and anions
112 under the influence of both a concentration and an electric potential gradient, as well as their
113 reaction with the soil solid phase (soil buffer power). At the root surface, the elements are
114 taken up according to Michaelis-Menten kinetics and the electrical neutrality of the system is
115 maintained through a proton or hydroxyl efflux (Bouldin, 1989). The model was tested by
116 comparing its outputs with the pH measured in the rhizosphere of three plants species
117 (ryegrass, maize and Alpine pennycress) grown in three different soils, using a non-invasive
118 optical method (Blossfeld et al., 2010). A global sensitivity analysis was then carried out in
119 order to highlight the most influential factors on the rhizosphere pH. This approach was
120 completed by simulations using the composition of 37 soil solutions from various origins,
121 taken from the literature.

122

123 2. Materials and methods

124 2.1. Model development

125 The new and original model to compute the rhizosphere pH is derived rigorously from first
126 principles. A simplified description of the model is given here, while an extensive version can
127 be found in the [Supplementary Material](#). The soil is divided into two compartments: the soil
128 solution, where the electro-neutrality condition is verified locally and the solid phase,
129 including the very thin electrical double layer (thickness ≈ 10 nm) at the surface of the solid
130 phase. The electrical double layer is neglected because of its very small volume compared to
131 that of the pore solution. Its influence is supposed to be part of the buffer power.

132 2.1.1. Transport in soil solution

133 The various ions contained in the soil solution are H_3O^+ , OH^- , HCO_3^- and n ionic species
134 $\text{M}_i^{z_i+}$ of valence z_i (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , NH_4^+ , Cl^- , NO_3^- , P ions and SO_4^{2-} as well as Zn^{2+}
135 in a specific soil). Organic ions, such as organic or amino acids were not taken into account.
136 The valence of the P ions is taken as -1.5, as in soil solution at pH around 7, phosphates in the
137 soil solution are constituted in nearly equal parts of H_2PO_4^- et HPO_4^{2-} (Barber, 1995). The
138 concentrations of the OH^- and HCO_3^- ions are given from the H_3O^+ concentration according
139 to the following equilibrium conditions:

$$140 \quad [\text{H}_3\text{O}^+][\text{OH}^-] = K_e \quad (1)$$

$$141 \quad [\text{H}_3\text{O}^+][\text{HCO}_3^-] = k_{\text{CO}_2} \quad (2)$$

142 where K_e is the water ionic product and k_{CO_2} is assumed to be proportional to the (uniform)
143 partial pressure of CO_2 (P_{CO_2}) in the soil. Micro-organism mediated processes and root
144 emissions of CO_2 were not formalized.

145 As the objective is to compute the pH, the electro-neutrality of the soil solution

146
$$[\text{H}_3\text{O}^+] + \sum_{j=1}^n z_j [\text{M}_j^{z_j^+}] = [\text{OH}^-] + [\text{HCO}_3^-] = \frac{K_e + k_{\text{CO}_2}}{[\text{H}_3\text{O}^+]} \quad (3)$$

147 has to be verified rigorously. Using Eqs. (1-3) gives for a given partial CO_2 pressure
 148 (P_{CO_2}) the concentrations $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$ and $[\text{HCO}_3^-]$ as a function of the sum of the ion
 149 charges ($\sum_{j=1}^n z_j [\text{M}_j^{z_j^+}]$). Fulfilling the electro-neutrality condition (i.e. adding Eq. (3) to the
 150 transport equations) requires adding a supplementary unknown, the (electric) streaming
 151 potential ψ . Therefore, the molar mass fluxes for the n ion species ($\text{M}_i^{z_i^+}$) are given as the
 152 sum of a convective term due to the water movement with the velocity \mathbf{v} , as well as a
 153 diffusive term written in the Nernst-Planck form to take into account the electric effects on the
 154 ions diffusive motion:

155
$$\mathbf{J}_{\text{M}_i^{z_i^+}} = [\text{M}_i^{z_i^+}] \mathbf{v} - \mathcal{D}_{\text{M}_i^{z_i^+}} \left(\nabla [\text{M}_i^{z_i^+}] + \frac{F z_i [\text{M}_i^{z_i^+}]}{RT} \nabla \psi \right) \quad 1 \leq i \leq n \quad (4)$$

156
$$\frac{\partial [\text{M}_i^{z_i^+}]}{\partial t} = -\nabla \cdot \mathbf{J}_{\text{M}_i^{z_i^+}} \quad 1 \leq i \leq n+3 \quad (5)$$

157 Similar equations are written for the molar flux of H_3O^+ , OH^- and HCO_3^- . The introduction
 158 of the diffusion equation in the Nernst-Planck form allows a rigorous determination of the
 159 evolution of the rhizosphere pH from the properties of the soil and the mineral nutrition of the
 160 plant for the mineral nutrients $[\text{M}_i^{z_i^+}]$ ($1 \leq i \leq n$) without any additional hypotheses.

161 Due to the electro-neutrality condition, adding the n transport equations for the nutrients plus
 162 the transport equations for H_3O^+ , OH^- and HCO_3^- weighted by the valence of each ion leads
 163 to

164
$$\nabla \cdot \mathbf{I}_c = 0 \quad (6)$$

165 with
$$\mathbf{I}_c = F \left(\sum_{i=1}^n z_i \mathbf{J}_{\text{M}_i^{z_i^+}} + \mathbf{J}_{\text{H}_3\text{O}^+} - \mathbf{J}_{\text{OH}^-} - \mathbf{J}_{\text{HCO}_3^-} \right) \quad (7)$$

166 The electric current in the soil solution is divergence free. The convective part being
 167 necessarily 0 due to the electro-neutrality condition, \mathbf{I}_c only depends on the $n+1$ gradients
 168 $\nabla[M_i^{z_i^+}]$ and $\nabla\psi$. As no electric current occurs in the soil, the electric current \mathbf{I}_c is locally
 169 zero in the soil solution (see SM for details) and the gradient of the streaming potential $\nabla\psi$ is
 170 easily deduced from the gradients of $\nabla[M_i^{z_i^+}]$ ($1 \leq i \leq n$). The molar flux $\mathbf{J}_{M_i^{z_i^+}}$ for the n
 171 $M_i^{z_i^+}$ species is consequently written:

$$172 \quad \mathbf{J}_{M_i^{z_i^+}} = [M_i^{z_i^+}] \mathbf{v} - \sum_{j=1}^n \mathbb{D}_{ij} \nabla[M_j^{z_j^+}] \quad 1 \leq i \leq n \quad (8)$$

173 where the diffusion coefficient \mathbb{D}_{ij} is given as a function of the molecular diffusive
 174 coefficients $\mathcal{D}_{M_j^{z_j^+}}$ as

$$175 \quad \mathbb{D}_{ij} = \mathcal{D}_{M_i^{z_i^+}} \left\{ \delta_{ij} + \frac{z_i z_j [M_k^{z_k^+}] (D_H - \mathcal{D}_{M_j^{z_j^+}})}{\sum_{k=1}^n z_k^2 \mathcal{D}_{M_k^{z_k^+}} [M_k^{z_k^+}] + \left([H_3O^+] + \frac{K_e + k_{CO_2}}{[H_3O^+]} \right) D_H} \right\} \quad 1 \leq i, j \leq n \quad (9)$$

176 where δ_{ij} is the Kronecker symbol and the diffusion coefficient D_H is given by

$$177 \quad \left(1 + \frac{K_e + k_{CO_2}}{[H_3O^+]} \right) D_H = \mathcal{D}_{H_3O^+} + \frac{K_e}{[H_3O^+]^2} \mathcal{D}_{OH^-} + \frac{k_{CO_2}}{[H_3O^+]^2} \mathcal{D}_{HCO_3^-} \quad (10)$$

178 Finally, the proton concentration $[H_3O^+]$ is computed from the electro-neutrality condition
 179 (Eq. 3).

180

181 **2.1.2. Transport in soil**

182 The transport equations in the soil solution are then up-scaled to the soil scale using a
 183 classical two-scale homogenization technique. At the interface between the soil solution and
 184 the solid phase (including the thin electric double layer), the $M_i^{z_i^+}$ species ($1 \leq i \leq n$) are
 185 adsorbed according to the soil buffer power $b_{M_i^{z_i^+}}$. A simultaneous flux of H_3O^+ , OH^- or

186 HCO_3^- is necessary to maintain the electro-neutrality of the soil solution. These fluxes are
 187 implicitly computed. The final result (see [Supplementary Material](#)) is

$$188 \quad \left(\theta + b_{M_i^{z_i^+}} \right) \frac{\partial [M_i^{z_i^+}]}{\partial t} + \mathbf{v}_D \cdot \nabla [M_i^{z_i^+}] = \nabla \cdot \left(\sum_{j=1}^n \mathbb{D}_{ij}^* \nabla [M_i^{z_i^+}] + S_{M_i^{z_i^+}} \right) \quad 1 \leq i \leq n \quad (11)$$

189 where θ is the volumetric liquid fraction of the soil (considered to be constant), and \mathbf{v}_D the
 190 Darcy velocity (water volumetric flux per unit surface area of the soil). The buffer power $b_{M_i^{z_i^+}}$
 191 is calculated as the ratio of the concentration of solid-phase sorbed ion (i.e. exchangeable, mol
 192 m^{-3} soil) to that of the ion in solution (mol m^{-3} solution) (Roose et al., 2001). No feedback
 193 effect of pH on soil buffer power for ions was taken into account. The source term $S_{M_i^{z_i^+}}$ is
 194 added in order to describe the production of nitrate from organic matter ([Supplementary](#)
 195 [Material](#)).

196 A simple approximation of the homogenized diffusion coefficient at the soil scale is provided
 197 by the relation:

$$198 \quad \mathbb{D}_{ij}^* = \theta^{3/2} \mathbb{D}_{ij} \quad (12)$$

199 **2.1.3. Boundary conditions**

200 The model is solved in a cylindrical unit soil volume around the root. At the surface of the
 201 roots in cylindrical coordinates ($r = r_0$) the mass flux of species $M_i^{z_i^+}$ ($1 \leq i \leq n$) is given by
 202 a Michaelis-Menten relation ($\mathbf{v}_D < 0$):

$$203 \quad \mathbf{v}_D [M_i^{z_i^+}] - \sum_{j=1}^n \mathbb{D}_{ij} \frac{\partial [M_j^{z_j^+}]}{\partial r} \Big|_{r=r_0} = -I_{max}^i \frac{[M_i^{z_i^+}]}{K_m^i + [M_i^{z_i^+}]} \quad (13)$$

204 As with the interface conditions between the soil solution and the solid phase, a simultaneous
 205 flux of H_3O^+ , OH^- or HCO_3^- at the surface of the root is necessary to maintain the electro-
 206 neutrality of the system, which is implicitly calculated ([Eq. \(14\) in Supplementary Material](#)).

207 Note that all fluxes are in the soil and not in the plant as some chemical reactions (including

208 CO₂ release) may occur at the soil/plant interface, but with the constraint of charge
 209 conservation. The periodicity condition around each root is simulated by setting a null flux for
 210 each ionic species i at the boundary of the root zone of influence:

$$211 \quad v_D[M_i^{z_i^+}] - \sum_{j=1}^n D_{ij} \left. \frac{\partial[M_j^{z_j^+}]}{\partial r} \right|_{r=r_i} = 0 \quad (14)$$

212 The root absorption functions along the root, above the growth zone are assumed to be
 213 invariable in space and time for all the ions considered (Barber, 1995). This corresponds to
 214 young active and growing roots, as those for which variations in the rhizosphere pH have
 215 been measured (e.g. Blossfeld et al. (2010); Marschner and Römheld (1983); Marschner et al.
 216 (1986); Marschner et al. (1982)). The ion transport is supposed to be purely radial, in a zone
 217 sufficiently distant from the root apex for the growth effects (as described by Kim et al.
 218 (1999)) to be negligible. The realism of the simulated uptakes according to the mean plant
 219 composition is discussed in Supplementary Material (2.2, Table S1).

220 **2.1.4. Initial conditions**

221 The initial soil composition is assumed to be uniform. The initial value of P_{CO_2} is deduced
 222 from the initial pH and composition of the soil solution, according to Eq. (3) and does not
 223 vary with time.

224 **2.1.5. Model parameters and numerical solution**

225 The model parameters concern self-ionization of water, the solubility of CO₂ in water, soil
 226 water content, soil buffer power for each ion, diffusion properties of the ions in water, root
 227 geometry and root ion absorption properties (K_m^i and I_{max}^i for each nutrient $1 \leq i \leq n$). These
 228 are given in Table 1. The root absorption parameters are set at the same level for the three
 229 plant species, based on the relatively little data available from the literature (see
 230 [Supplementary Material](#)).

231 The equations were solved using the pdepe function of Matlab®, using hundred space steps
232 logarithmically distributed and an adaptive time step.

233

234 **2.2. Model validation**

235 The model was experimentally evaluated by comparing its output, *i.e.* the soil pH at the root
236 surface (rhizoplane), to pH measured in the rhizosphere of ryegrass (*Lolium perenne* L., Prana
237 cultivar), maize (*Zea mays* L. cv INRA MB862) and the Zn and Cd hyperaccumulator Alpine
238 pennycress (*Noccaea caerulea* (J. & C. Presl) F. K. Mey., Viviez population) grown in
239 three different soils. For this, data previously produced by Blossfeld et al. (2010) were used
240 (see 2.2.2).

241 **2.2.1. Plant cultivation**

242 Plants were grown on three soils, designated as A, B and C, sampled in the Ap horizon of
243 Cambisols (Table 2). Soils A and B were a loam with a pH (H₂O) of 6.2 and a silt loam soil
244 with a pH (H₂O) of 8.1, respectively. Soil C was chosen because it was also a loam and its
245 bulk soil pH fell between those of soils A and B. Soil C also enabled the measurement of pH
246 in the rhizosphere of ryegrass on a slightly acidic soil, as this plant only rarely grew on soil A
247 in pot cultivation, because of the toxicity of a highly available Zn content (Blossfeld et al.,
248 2010). This Zn level, however, affected neither the growth of Alpine pennycress which is
249 hypertolerant to this metal, nor that of maize, probably because this is still heterotrophic (see
250 below).

251 Plants were transplanted to or sown in PVC rhizoboxes (height 300 mm, width 150 mm,
252 depth 50 mm) that were filled with the soil. During cultivation, the rhizoboxes were placed on
253 a rack inclined at 45° in order to force the roots to grow along the front plates. The transparent
254 side being placed against the rack, the roots were protected from light. The plants were grown
255 and investigated in a growth chamber. The cultivation period of the three species in the

256 rhizoboxes prior to the measurements differed due to the specific root growth of individual
257 species, *i.e.* 6-8 weeks for alpine pennycress, 4-5 weeks for ryegrass and 8-9 days for maize.

258 **2.2.2. Measurement of rhizosphere pH**

259 Rhizosphere pH was measured using planar pH optodes, according to the device described by
260 Blossfeld *et al.* (2010). The optode, a 10 μm inert polymer film measuring a few square
261 centimetres, was placed on a single root or on several roots, at the soil surface, behind the
262 rhizobox glass. This film contained a dispersed and immobilized dye which reacts to protons.
263 The measurement was based on the fluorescence decay time of the dye and was carried out
264 *via* an optical glass fibre from outside the rhizobox, which was connected to a light source and
265 measuring device. The glass fibre was moved automatically by an x-y stepper motor device.
266 By this means, the pH value could be measured in a line scanning mode, at 2 to 3 mm steps
267 and 4 s intervals. This enabled the evolution of the pH in the rhizosphere to be mapped, as
268 illustrated in Blossfeld *et al.* (2010).

269 To evaluate the model, we used three types of measured data (Table 3):

- 270 • The average pH along the axis of a single root, which can be considered as the pH at
271 the rhizoplane. This was available for all the plant species in the three soils, except
272 ryegrass which did not grow in soil A.
- 273 • The average pH in a portion of the root network, a planar optode being placed on
274 several young roots. This was not available for ryegrass in soil A.
- 275 • The pH of the bulk soil as measured with the optode.

276 The latter was used as the initial pH value, while the other two were compared to the model
277 outputs. The pH measurements showed that the functioning of roots was rather uniform along
278 their axes, except for maize, as will be shown and discussed later.

279 **2.2.3. Analysis of the soil solution and rhizosphere pH simulations**

280 Because the initial concentrations of anions and cations in the soil solutions were not
 281 determined in the work of Blossfeld et al. (2010), these were measured *de novo* for the
 282 validation of the model, in the following manner. Approximately one kilogram of soil was put
 283 in a pot and maintained close to the water holding capacity (WHC) for 21 days by regular
 284 watering from the bottom. A microsuction cup (Rhizon soil moisture sampler, Eijkelkamp,
 285 Giesbeek, The Netherlands), placed in the centre of the soil, enabled us to sample the soil
 286 solution. The day before the solution sampling, the soil was watered to WHC. Less than 30
 287 minutes were required to sample around 10 ml of soil solution. Anions (Cl^- , NO_3^- , PO_4^{3-} ,
 288 SO_4^{2-}) and cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , NH_4^+) were determined using ionic chromatography
 289 (Dionex AS50/EG40/IC25, Sunnyvale, CA, USA) and a certified solution from Sigma-
 290 Aldrich (reference number 89886). Induced coupled plasma atomic emission spectrometry
 291 (iCAP 6300 DUO, Thermo Scientific, UK) was used to determine Al, Fe, Mn and Zn in the
 292 solution. In this case, three certified solutions from SCP Science were used (reference
 293 numbers 701-021-067, 701-021-432 and 140-025-038).

294 Using these soil solution compositions (Table 4), soil pH at the root surface or in the
 295 rhizosphere (mean value over r_l) was simulated for the three plant species (for Alpine penny-
 296 cress, ryegrass and maize) in the three soils (A, B and C), fixing the initial pH at the value in
 297 the bulk soil and neglecting the nitrate source, so $S_{M_i^{z_i+}} = S_{\text{NO}_3^-} = 0$. The simulation
 298 conditions were adapted to the root age and density (Table 3). In total, the model outputs were
 299 compared to 15 measurements of the rhizosphere pH.

300 2.3. Sensitivity analysis

301 A sensitivity analysis was carried out using Matlab® in order to evaluate which of the 41
 302 factors (including the nitrate source) had the greatest impact on the variation of the pH at the
 303 root surface (ΔpH):

$$304 \quad \Delta pH = Y = pH_f - pH_i \quad (15)$$

305 where pH_i is the initial pH, corresponding to that of the non-rhizospheric (bulk) soil and pH_f
 306 is the soil pH at the end of the simulation.

307 Factors (X_j) were ranked according to standardized regression coefficients (SRC) (Faivre et
 308 al., 2013; Saltelli et al., 2004).

$$309 \quad SRC_j = \beta_j \sqrt{\frac{Var(X_j)}{Var(Y)}} \quad (16)$$

310 in which $Var()$ is the variance, β_j is the regression coefficient of X_j , according to the
 311 correlation

$$312 \quad Y = \sum_{j=1}^N \beta_j X_j + \varepsilon \quad (17)$$

313 where Y is the output of the model and ε the model error, $N = 41$.

314 The factors were sampled using random sampling of uniform distributions (Table S2). The
 315 initial pH (Figure S3) was calculated according to Eq. 3, randomly sampling P_{CO_2} , as follows.

316 After sampling all the concentrations of the transported ions, their charge balance (CB , mol_c
 317 m⁻³) was calculated according to

$$318 \quad CB = \sum_{j=1}^n z_j [M_j^{z_j^+}] \quad (18)$$

319 as well as the sum of absolute charges:

$$320 \quad \sum_{j=1}^n |z_j| [M_j^{z_j^+}] \quad (19)$$

321 Solution compositions were retained when the relative charge balance (CB_r , dimensionless)
 322 satisfied the following condition:

$$323 \quad 0 < CB_r = \frac{\sum_{j=1}^n z_j [M_j^{z_j^+}]}{\sum_{j=1}^n |z_j| [M_j^{z_j^+}]} < 0.2 \quad (20)$$

324 Negative charge balances were discarded, as they led to very acidic initial pH, falling beyond
 325 of the range of natural pH. The upper limit of CB_r (0.2) was chosen by rounding the mean
 326 relative charge balance measured on soils worldwide (see 2.4), which is 0.12. P_{CO_2} was then
 327 randomly sampled between $3 \cdot 10^3$ ppmv and 10^5 ppmv (Sposito, 2016), to calculate the

328 corresponding solution pH according to Eq. (3). The final sample size was 20,000. The model
329 was run for two durations: one and four weeks.

330

331 **2.4. Simulating rhizosphere pH in 37 soils sampled worldwide**

332 As the 20,000 random cases simulated in the sensitivity analysis could not all be
333 representative of the reality of soil solution composition, we analysed the output of the model
334 on a set of data originating from real soils. In Tables 7.2 and 7.3 of his book, Wolt (1994)
335 summarized the solution composition of soil horizons sampled worldwide by various authors.
336 From this data set, we kept the solution composition from 35 surface horizons, for which our
337 calculations based on Eq. 3 led to an initial pH close to that measured. Indeed, for some of
338 them, it was impossible to reproduce the measured pH, probably because of errors or missing
339 data in the reported solution composition. In most of the solutions, there was no phosphate
340 content, probably because this ion was below the detection limits. The NH_4^+ and the SO_4^{2-}
341 contents were not always available. However, as will be shown later, these ions have a limited
342 influence on rhizosphere pH and the simulations could usefully be carried out with null values
343 for P ions, NH_4^+ and SO_4^{2-} . The solution composition of soils used to validate the model, i.e.
344 soils B and C were added to those from Wolt (1994). Solutions from soil A were not used
345 because of its exceptionally high Zn content. The 37 solutions (Table S3) were used to
346 simulate ΔpH . For these simulations, nitrate source ($S_{\text{NO}_3^-}$), soil buffer powers and root
347 absorption parameters of the different ions were taken as averages of the distributions used in
348 the sensitivity analysis (Table S2). The root radius (r_0), the mean distance between roots (r_l)
349 and the volumetric water content (θ) were taken as $1 \cdot 10^{-4}$ m, $5.5 \cdot 10^{-3}$ m (Lin et al., 2016) and
350 0.25, respectively. P_{CO_2} was taken as $3 \cdot 10^3$ ppmv (around 10 times the atmospheric pressure).
351 The water volumetric flux v_D was $2.5005 \cdot 10^{-8}$ m s⁻¹ and $S_{\text{NO}_3^-}$ was zero. The model also

352 enabled a calculation of other variables, such as the final composition of the rhizosphere
353 solution and the amounts of ions taken up by the root.

354

355 **3. Results and discussion**

356 **3.1. Model validation**

357 **3.1.1. Ryegrass and Alpine pennycress**

358 The simulated rhizosphere pH was compared to 15 measured values (Table 5). In the case of
359 ryegrass and Alpine pennycress, along the surface of a single young root and in root network,
360 an alkalinisation of the rhizosphere was systematically measured. In soil A, the alkalinisation
361 ranged from 1.2 to 1.4 pH unit. In soil B, this ranged from 0.4 to 0.9 pH units, while in soil C,
362 it varied between 0.3 and 1.7 pH units. It must be noted that pH measured in the bulk soil with
363 the planar optodes was close to that determined with dry soil dispersed in a 0.01 M CaCl₂
364 solution, and was slightly lower than that measured in water (Table 2).

365 All the simulations predicted a clear alkalinisation of the rhizosphere. In soil A, the simulated
366 pH at the root surface was 6.4, i.e. 0.8 units above the initial pH (= 5.6) and 0.4 units below
367 the measured value (Table 5). In the root network, the simulated pH was 7.7, i.e. 0.7 unit
368 above the measured one. In soil B, the simulation produced a rhizoplane alkalinisation of 0.2
369 pH unit. The rhizoplane pH was 0.2 units below that measured at the rhizoplane of ryegrass
370 (7.6 against 7.8) and 0.8 units below that measured at the rhizoplane of Alpine pennycress
371 (7.6 against 8.4). For root networks, the simulations (pH = 8.0) were closer to the measured
372 values (pH = 7.9) in both ryegrass and Alpine pennycress. In soil C, the simulated rhizoplane
373 pH was 0.7 pH units above that in the bulk soil (= 6.2). It was 0.9 units below that measured
374 at the rhizoplane of Alpine pennycress (6.9 against 7.8), but 0.4 units above that measured at
375 the rhizoplane of ryegrass (6.9 against 6.5). In all the simulations, the initial P_{CO_2} fell within

376 the range that has been observed in soils [up to 100 times the atmospheric partial pressure
377 (Sposito, 2016)].

378 Overall, these results show a reasonably good fit between the model predictions and the
379 measured pH values at the root surface of ryegrass and Alpine pennycress. To interpret the
380 differences between measurements and simulations, it is important to bear in mind the
381 relationship between the solution pH, the ion charge balance (*CB*) and the CO₂ partial
382 pressure (P_{CO_2}) (Eq. (3), Figure 1). There is a quasi-discontinuity in the function $pH = f(CB)$
383 at $CB = 0$. Therefore, when the charge balance is close to zero, the pH varies strongly with
384 even a very small changes in charge balance. Moreover, in the case of a positive charge
385 balance, the value at which P_{CO_2} is fixed also has a considerable impact on the calculated pH,
386 as shown by the curves for different P_{CO_2} . The characteristics of the function determining the
387 pH explain the variability of the deviations between measured and simulated rhizospheric pH.
388 Indeed, this law may transform small uncertainties in the composition of the soil solution and
389 the CO₂ pressure, related to sampling and analysis, into wide variations in the pH calculation.
390 However, this does not prevent the model from being used. Indeed, instead of using the initial
391 solution composition to predict the initial soil pH, the latter measured in the bulk soil can be
392 imposed, thereby slightly adjusting the composition of the soil solution or of the partial CO₂
393 pressure. To illustrate this, slightly increasing the NO₃⁻ content of 0.08 mol m⁻³ in soil A, i.e.
394 +0.7% of the total charges in solution, gives a simulated alkalinisation of the rhizosphere of
395 1.3 pH units (corresponding to the measured alkalinisation), instead of 0.8 units.

396 **3.1.2. Maize**

397 This adequation was not observed in the case of maize, whose rhizosphere pH was clearly
398 different from that of the two other species and from the simulation results. Indeed, when
399 measured along a single young root, the rhizoplane pH decreased from 0.2 to 0.7 pH units
400 (Table 5). At the rhizoplane of a single older root, this increased by only 0.1 to 0.3 pH units

401 when measured in soils B and C, while it decreased by 0.1 units in soil A. None of the
402 rhizoplane pH simulations led to an acidification, but did generate alkalisation which most
403 frequently, was above that of the single older root in soil B and C.

404 As already shown by Blossfeld et al. (2010) (particularly in Fig. 6 of their article), there was
405 an acidification of the rhizosphere of maize, at about 15 to 25 mm from the apex. This
406 phenomenon had already been observed by other authors (Peters and Felle, 1999; Pilet et al.,
407 1983) Schaller and Fischer (1985). This acidification could be explained by the acid growth
408 theory (Rayle and Cleland, 1992), which states that growing cells excrete protons into the
409 cell-wall at an enhanced rate, resulting in a cell-wall loosening to facilitate the root
410 elongation. This acidification zone is alternatively explained by a higher nutrient uptake in the
411 growth zone that would constitute a large nutrient sink, particularly for K^+ , whose root
412 absorption would be equilibrated by proton excretion (Kim et al., 1999; Taylor and Bloom,
413 1998).

414 On the other hand, the lower alkalisation observed here in the root network or in older
415 maize roots (i.e. away from the apex) could be due to a much lower nitrate uptake by the
416 maize than by ryegrass and Alpine pennycress. Indeed, maize is completely heterotrophic
417 from 0 to around 75 degree-days (about 7 days after germination) and completely autotrophic
418 from around 250 degree-days (Girardin, 2000; Nadeem et al., 2014). Between 75 degree-days
419 and 250 degree-days, maize becomes progressively autotrophic. Therefore, 8-9 day-old maize
420 seedlings (that is 88 to 99 degree-days), as used in the present experiment, were only slightly
421 autotrophic. That means that the seedling was mostly provided with mineral nutrients from
422 the caryopsis reserves and that it absorbed only a minor part of these nutrients from the soil
423 solution. Nadeem et al. (2014) demonstrated that phosphorus was exclusively provided by the
424 maize seed until 75 degree-days and was increasingly absorbed from the soil solution from
425 that date until complete autotrophy was attained and the seed P reserves were exhausted.

426 Similar schemes could be drawn for the other nutrients, and particularly for nitrogen (Mollier,
427 2015, personal communication). Eight to nine day-old maize would therefore consume
428 nitrogen mostly from the seed reserves and absorb fewer nitrates from the soil solution than
429 ryegrass and Alpine pennycress, which are much older and completely autotrophic. Therefore,
430 at the rhizoplane of maize behind the acidification zone, the sum of charges is only slightly
431 higher, as is, consequently the pH of the solution.

432

433 **3.2. Sensitivity analysis**

434 **3.2.1. Simulating root uptake over one week**

435 Those ions which most frequently accumulated at the root surface, i.e. their concentrations at
436 the rhizoplane was higher at the end of the simulations than at in the initial condition, were
437 Ca^{2+} , Mg^{2+} , Na^+ , SO_4^- and Cl^- . In contrast, K^+ , NH_4^+ NO_3^- and P ions⁻ were clearly depleted
438 (Fig S2). The sum of these balances led to a positive final charge balance of the transported
439 ions, resulting from the mostly negative initial and final charge uptakes (Fig 2). As a
440 consequence, in the vast majority of the cases, ΔpH was positive, reflecting an alkalinisation
441 of the rhizosphere, whose mean value was 0.36 (Fig 2).

442 The most influential factor on ΔpH was the initial nitrate concentration in the soil solution
443 ($[\text{NO}_3^-]$) (Fig. 3) ($\text{SRC} = 0.81$). The more NO_3^- in the soil solution, the more the pH increased
444 at the root surface. This is due to the root uptake of NO_3^- , as shown by the depletion of this
445 ion in the rhizosphere in most of the simulations (Fig. S2), which is compensated for by the
446 root absorption of H^+ (or equivalent excretion of OH^-). Nitrate was the most taken-up ion,
447 representing 64% of the absorbed ion absolute charges (Table 6).

448 The second factor was the initial Ca^{2+} concentration ($[\text{Ca}^{2+}]$) in the soil solution ($\text{SRC} = -$
449 0.63). This could be explained by the fact the higher $[\text{Ca}^{2+}]$, the higher its uptake by the roots

450 in exchange for H^+ , which tended to reduce ΔpH . However, this explanation would be
451 contradictory to the fact that, Ca^{2+} generally accumulated at the root surface (Fig. S2). The
452 explanation can be found in another phenomenon. During the random sampling for the
453 constitution of the simulation dataset, the initial solutions with a negative charge balance were
454 discarded (Eq. (20)). This process favoured the higher $[Ca^{2+}]$, as can be seen from the initial
455 distribution of this factor (Fig. S3). Because the initial charge balance is a linear combination
456 of the charges of each ion, there is therefore a positive correlation between the initial charge
457 balance and the $[Ca^{2+}]$. Moreover, the relationship between the pH and the charge balance
458 (Fig. 1) shows that the pH curve slope decreases as the charge balance increases. Therefore,
459 as $[Ca^{2+}]$ rises, the initial charge balance increases and the higher it is, the lower ΔpH will be.

460 The initial sulphate concentration had a positive effect on ΔpH ($SRC = 0.55$). One could
461 expect that the root absorption of SO_4^{2-} would alkalinise the rhizosphere, as that of NO_3^- did.
462 However, SO_4^{2-} accumulated in the rhizosphere (Fig. S2). Again, the explanation of the $[SO_4^{2-}]$
463 effect relies on the dataset sampling process and the calculation of the initial charge balance,
464 which made the initial sulphate concentration negatively correlated to that of the initial charge
465 balance (Fig. S3). The relationship between the pH and the charge balance (Fig. 1) shows that
466 in the vicinity of a zero charge balance, the slope of the pH curve strongly increases as the
467 charge balance decreases. It is this trend which explains that the higher the $[SO_4^{2-}]$, the lower
468 the initial charge balance and pH and the greater the variation in pH (ΔpH) will be.

469 The fourth influential factor is $[Mg^{2+}]$, with $SRC = -0.26$. Its effect can be explained in a
470 similar manner to that of $[Ca^{2+}]$, although being less intense, because the initial concentration
471 of Mg^{2+} is lower than that of Ca^{2+} (Fig. S3).

472 The average distance between roots r_I , also had a negative effect on ΔpH (Fig. 3, $SRC = -$
473 0.15). This can be explained by the fact that the higher r_I , the greater the amount of ions in the

474 rhizosphere and as a consequence, the lower the effect of the root uptake on ion
475 concentrations and therefore, on solution pH. The water content θ also had a positive effect on
476 ΔpH ($SRC = 0.12$). This variable takes part in the calculation of the element content in soil
477 (term $(\theta + b_{M_i^{z_i+}}) \frac{\partial [M_i^{z_i+}]}{\partial t}$ in Eq. (11)), although its contribution is very slight when compared
478 to the buffer power $b_{M_i^{z_i+}}$. θ is also involved in the calculation of the homogenized diffusion
479 coefficient at the soil scale (Eq. (12)). Increasing θ enhances ion diffusion in general and NO_3^-
480 in particular, whose contribution dominates those of the other ions. Therefore, θ is positively
481 correlated to ΔpH because it favours NO_3^- uptake.

482 It must be noted that although absorbed by the root in such a way that their concentrations
483 decreased in the rhizosphere during uptake, K^+ , NH_4^+ and P ions had no strong effect on ΔpH
484 because their concentration variations (and those of the associated charges) was small
485 compared to that of NO_3^- . Whatever the ion, the buffer power and the root absorption
486 parameters had very little or no significant influence on the variation of pH in the rhizosphere.
487 The nitrate source term ($S_{\text{NO}_3^-}$) had no significant influence: over one week, it represented on
488 average only 2% of the initial stock of NO_3^- .

489 **3.2.2. Simulating root uptake over four weeks**

490 After a four-week uptake, ΔpH had a mean value of 0.45 and was therefore slightly more
491 positive than after a one-week uptake (Fig. 2). This again corresponded to the positive final
492 charge balance of the transported ions.

493 The four most influential factors were the same as for the one-week uptake simulations -
494 $[\text{NO}_3^-]$ ($SRC = 0.97$), $[\text{Ca}^{2+}]$ ($SRC = -0.75$), $[\text{SO}_4^{2-}]$ ($SRC = 0.70$) and $[\text{Mg}^{2+}]$ ($SRC = -0.32$) -
495 and ΔpH were affected in the same sense, but a little more intensively, as reflected by higher
496 SRC (Fig 4). Compared to the one-week simulations, r_I regressed to the seventh place ($SRC =$

497 -0.08), indicating that the buffer effect of the rhizosphere volume would decrease with uptake
498 duration, because of the depletion of nitrate in the rhizosphere solution. In contrast, θ gained
499 one place compared to the one-week uptake, as did $[\text{Cl}^-]$, which appears to positively affect
500 ΔpH because, as with $[\text{SO}_4^{2-}]$, this is negatively correlated to the initial charge balance. As
501 after four weeks, $S_{\text{NO}_3^-}$ represented only 8% of the initial NO_3^- stock, the nitrate source only
502 slightly reduced the nitrate depletion and had nearly no effect on ΔpH .

503 **3.2.3. Main lessons from the sensitivity analysis**

504 The first conclusion which can be drawn from the sensitivity analysis is that the general trend
505 to rhizosphere pH is alkalisation. The second point is that the main factor affecting the
506 alkalisation level is by far the initial nitrate concentration in solution. The third conclusion
507 is that the soil buffer power and the root absorption parameters (K_m and I_{max}), whatever the
508 ion, have little or no influence on the rhizosphere pH. This justifies the use of the same root
509 absorption parameters for the three different plant species. The sensitivity analysis also
510 showed that the root density (or r_l) and the soil humidity could both have an influence on the
511 rhizosphere pH.

512 The final conclusion concerns the sensitivity analysis itself. Despite the conditions imposed
513 for the sampling of the ion concentrations in the initial solution (Eq. (20)), there was a
514 dependency of the initial charge balance on major ion concentrations (Ca^{2+} , Mg^{2+} , SO_4^{2-}),
515 which artificially made the latter influential variables. This bias in the sensitivity analysis also
516 shows how strongly ΔpH depends on the initial ionic composition of the solution. This
517 justifies a statistical analysis of the model using more realistic soil solution compositions.

518

519 **3.3. Simulating rhizosphere pH in 37 soils**

520 To test the model in more realistic conditions, the rhizosphere pH was simulated using a well-
521 documented series of various soil solutions taken from Wolt (1994).

522 **3.3.1. General trend of rhizosphere pH and effect of solution composition**

523 Let us consider first the results of the simulation of a four-week uptake of ions. The simulated
524 initial pH was close to the measured one (Fig. S4). On average, the rhizosphere pH increased
525 by 1.1 units (Table S4). For each soil, the sign of ΔpH corresponded to that of ΔCB , the
526 variation in charge balance in the soil solution at the root surface being expressed as

$$527 \quad \Delta CB = CB_f - CB_i \quad (21)$$

528 with the subscript f for “final” ($t = 1$ or 4 week) and i for “initial” ($t = 0$). CB_f results from ion
529 root uptake and ion accumulation at the root surface through convection.

530 In 32 of the 37 soils (i.e. 86% of the soils), ΔpH was positive. In 26 soils over the 32 where
531 ΔpH was positive, the charge balance of the ions absorbed by the roots (RCB , $\text{mol}_c \text{ m}^{-1}$) was
532 negative, indicating that the root absorbed mainly anions (Table S4). This absorption of
533 anions caused the alkalinisation of the rhizosphere. This alkalinisation was not perturbed by
534 the accumulation of ions due to convection, *i.e.* the convection leading to the accumulation of
535 cations or the accumulation of anions was not sufficient to counteract anion root absorption.

536 In these 26 cases, NO_3^- uptake represented 80% (against an overall mean of 62%) of the total
537 absolute charge uptake, showing that the rhizosphere alkalinisation was mainly the
538 consequence of nitrate uptake. Fourteen soils had a particularly high ΔpH , ranging from
539 nearly 1.7 to 3.3. These values explain the mean ΔpH of 1.1, higher than that estimated during
540 the sensitivity analysis ($\Delta pH = 0.45$ after 4 weeks of uptake), the rest of the soils having a
541 mean ΔpH of 0.30. Thirteen of these high ΔpH soils had an initial pH between *ca* 4.7 and 6.0,
542 which corresponds to the pH zone, where a small change in charge balance can strongly affect
543 the solution pH (Fig. 1). One of them (Tujung), had an initial pH of 7.0, beyond the high

544 variation zone of this parameter. However, this soil with high initial cation contents, showed a
545 very positive charge balance ($23.7 \text{ mol}_c \text{ m}^{-3}$ versus $5.2 \text{ mol}_c \text{ m}^{-3}$ on average) after 4 weeks,
546 due to an elevated uptake of NO_3^- (representing 91% of the absorbed charges).

547 In 6 soils out of the 32 where ΔpH was positive (for instance in soils Cecil unamended,
548 Fyfield, and Grove), RCB was positive (i.e. dominated by cation absorption) (Table S4). In
549 these cases, however, ΔCB was still positive, leading to a positive ΔpH . Although the root
550 absorption, after 4 weeks of uptake, tended to acidify the rhizosphere, this was not sufficient
551 to significantly reduce the positive charge balance created at the rhizoplane after the initial
552 uptake. This shows that the initial uptake plays an important role in rhizosphere pH, in
553 determining a charge balance which will be slow to modify afterwards. At the beginning of
554 uptake, nitrate is quickly absorbed, causing alkalinisation at the rhizoplane. Afterwards,
555 although nitrate is less absorbed than cations, the absorption of cations is not quick enough to
556 acidify the rhizoplane solution.

557 In the 5 soils where ΔpH was negative, correlatively with ΔCB , RCB was positive, indicating
558 that the plant predominantly absorbed cations, which was compensated for by an acidification
559 at the rhizoplane. In these soils, nitrate represented only 3.6% of the absorbed charges, while
560 K^+ represented 68%. This is due to a lack of NO_3^- in the initial solution ($0.03 \text{ mol}_c \text{ m}^{-3}$ against
561 $8.3 \text{ mol}_c \text{ m}^{-3}$ on average), and not to an excess of K^+ ($0.25 \text{ mol}_c \text{ m}^{-3}$ against $0.85 \text{ mol}_c \text{ m}^{-3}$ on
562 average).

563 **3.3.2. Effect of uptake duration**

564 The results obtained after a one-week uptake simulation were close to those of a four-week
565 uptake. ΔpH after a one-week uptake was on average 0.2 unit lower than that after a four-
566 week uptake (Table 7). Up to 1 week of uptake, concentrations of Ca^{2+} , Cl^- , Mg^{2+} , Na^+ and
567 SO_4^{2-} in the soil solution increased slightly because of convection and then stabilized over

568 time, probably because of an equilibrium between convection and retro-diffusion.
569 Concentrations of K^+ , NH_4^+ , NO_3^- and P ions decreased because of root absorption. The
570 decrease rate of NO_3^- was much higher than that of the other ions (Table 7). The charge
571 balance in the rhizoplane solution regularly increased from $+1.20 \text{ mol}_c \text{ m}^{-3}$ to $+8.12 \text{ mol}_c \text{ m}^{-3}$
572 after 12 weeks. The proportion of Ca^{2+} , Mg^{2+} , K^+ , P ions and SO_4^{2-} in the total absolute
573 charge uptake continuously increased, while that of NO_3^- strongly decreased from 69.8% to
574 51.7% as did that of NH_4^+ also, but to a far lesser extent (Table 8).

575 As mentioned above, the first week of uptake determined most of ΔpH at the rhizoplane even
576 for the consecutive weeks and on average, increasing the simulation time to 8 and 12 weeks
577 only slightly increased ΔpH , by a few hundredths of pH units. This is due to the fact that
578 within the first week, there is a strong decrease in anion (i.e. mainly nitrate) concentration in
579 the solution, and therefore an increase in the charge balance and in the pH. This initial
580 increase in rhizosphere pH is sharp, because of the discontinuity in $pH = f(CB)$ (Figure 1).
581 However, after this increase, the same function shows that pH only slightly increases with
582 CB. In some cases, ΔpH after four weeks was slightly lower than those after one week (Table
583 S4), indicating the beginning of a depletion of the rhizosphere solution with the ions
584 dominating the initial root uptake. This was particularly the case in the Xanthozem soil, which
585 ΔpH was clearly positive after one week (+2.5), decreased to 0.6 after 4 weeks and became
586 negative (-0.55) after 8 weeks of uptake. In this exceptional soil, nitrate uptake was relatively
587 low after 8 weeks, representing only 15% of the absorbed charges, while it was 50% after 1
588 week. The uptake of K^+ after 8 weeks was higher, with 24% of the absorbed charges, and
589 NH_4^+ exceptionally high, with 53%. This is the consequence of an exceptionally high
590 ammonium concentration in the soil solution ($4.03 \text{ mol}_c \text{ m}^{-3}$ against $0.75 \text{ mol}_c \text{ m}^{-3}$ on average).

591 Simulations taking into account a nitrate source ($S_{NO_3^-}$) in the model were also carried out.
592 After a one-week uptake, with the nitrate source, ΔpH was on average 2.3% lower than
593 without a source. After 12 weeks, the difference was 0.6% (Table S4). This confirms the
594 sensitivity analysis which showed that nitrification had nearly no effect on rhizosphere pH
595 variation.

596 **4. Conclusions**

597 Many simplifications have been made during the modelling, because of a lack of knowledge
598 and for the sake of mathematical and numerical simplicity: the same absorption parameters
599 were used for the three plant species, soil water content was considered to be constant, micro-
600 organism mediated processes and root emissions of O_2 and CO_2 were not formalized, no
601 feedback effect of pH on soil buffer power for ions was taken into account and organic ion
602 release and uptake was neglected. However, the model predicted the same alkalisation trend
603 as that measured with the planar optodes. The simplifications therefore appear reasonable and
604 the result supports the theory that the nutrient root uptake, in aerobic soils, is the important
605 process responsible for the modification of the pH in the root vicinity (Hinsinger et al., 2003).
606 The simulations also suggest that among the nutrients, nitrogen is the one which most
607 influences the rhizosphere pH. In aerobic soils without ammonium fertilization, nitrate is
608 around 5 to 400 times more absorbed than the other ions. As its depletion in the root vicinity
609 is compensated for by the root absorption of H^+ (or the equivalent excretion of OH^-), the
610 rhizosphere of non-leguminous crops in non-flooded soils might generally be more alkaline
611 than the bulk soil.
612 This work also showed that the variations in the rhizosphere pH were dependent on the initial
613 pH, more than on its evolution through root ion absorption. It highlighted how extremely this
614 initial pH was sensitive to the initial composition of the soil solution, in such a way that small
615 errors in analyses would produce a strong uncertainty about the calculated initial pH.

616 Therefore, it seems nearly impossible to precisely predict the initial pH from the initial
617 solution composition. This is contrary to the pH at the rhizoplane which after a few weeks of
618 root uptake, should generally stabilize from then on. However, it is the charge balance (*CB*)
619 which determines the trend of the rhizosphere pH and generally, the plant roots increase *CB*,
620 as they take up nitrates more than the other ions. Therefore, there is no doubt that most
621 frequently the rhizosphere pH is higher than that of the bulk soil. Moreover, despite the
622 uncertainty on the initial pH prediction, the model can be used to predict the rhizosphere pH,
623 fixing the initial pH (which can be measured in 0.01 CaCl₂).

624 The model considers that the partial pressure of carbon dioxide is constant, being adjusted to
625 the initial solution composition. However, in presence of roots and micro-organisms, P_{CO_2}
626 probably vary, influencing both the pH and the solution composition. Therefore, it would be
627 logical that P_{CO_2} should be measured, in the rhizosphere and CO₂ concentration taken into
628 account in the model. Indeed, excretion of CO₂ could for instance limit the extent of the
629 alkalisation zone.

630

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635

636

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755 **Figure captions**

756

757 **Fig. 1.** Relationship between pH, partial CO₂ pressure (P_{CO_2}) and sum of ion charges

758 $(\sum_j z_j [M_j^{z_j+}])$ in soil solution, as deduced from Eq. (3).

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760 **Fig. 2.** Global sensitivity analysis of the model. Frequency distribution of a) ΔpH and b) of

761 the charge balance (CB , Eq. (18)) after 1 and 4 weeks of uptake. Mean values of ΔpH are 0.36

762 and 0.45 for 1 and 4 weeks of uptake, respectively. Mean values of CB are 3.12 mol_c m⁻³, 7.35

763 mol_c m⁻³ and 9.72 mol_c m⁻³ for initial, 1 and 4 weeks of uptake, respectively.

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765 **Fig. 3.** Global sensitivity analysis of the model. Ranking of the model variables based on their

766 standardized regression coefficients (SRC) for the simulation of ΔpH after one week of uptake

767 (Eqs. (16) and (17)). Variables are described in Table 1.

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769 **Fig. 4.** Global sensitivity analysis of the model. Ranking of the model variables based on their

770 standardized regression coefficients (SRC) for the simulation of ΔpH after four weeks of

771 uptake (Eqs. (16) and (17)). Variables are described in Table 1.

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Symbol	Definition	Value
K_e	Water self-ionization constant	$10^{-14} \text{ mol}^2 \text{ L}^{-2}$
k_{CO_2}	CO ₂ dissolution constant	$3.7 \cdot 10^{-8} P_{\text{CO}_2} / \ln 10$ in $\text{mol}^2 \text{ L}^{-2} \ddagger$
$\mathcal{D}_{\text{H}_3\text{O}^+}$	Diffusion coefficient of H ₃ O ⁺ in water	$9.31 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \ddagger$
$\mathcal{D}_{\text{HCO}_3^-}$	Diffusion coefficient of HCO ₃ ⁻ in water	$1.18 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \ddagger$
$\mathcal{D}_{\text{OH}^-}$	Diffusion coefficient of OH ⁻ in water	$5.27 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \ddagger$
$\mathcal{D}_{\text{Ca}^{2+}}$	Diffusion coefficient of Ca ²⁺ in water	$7.93 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1} \ddagger$
\mathcal{D}_{K^+}	Diffusion coefficient of K ⁺ in water	$1.96 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \ddagger$
$\mathcal{D}_{\text{Mg}^{2+}}$	Diffusion coefficient of Mg ²⁺ in water	$7.05 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1} \ddagger$
$\mathcal{D}_{\text{Zn}^{2+}}$	Diffusion coefficient of Zn ²⁺ in water	$7.15 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$
$\mathcal{D}_{\text{Na}^+}$	Diffusion coefficient of Na ⁺ in water	$1.13 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \ddagger$
$\mathcal{D}_{\text{NH}_4^+}$	Diffusion coefficient of NH ₄ ⁺ in water	$1.98 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \ddagger$
$\mathcal{D}_{\text{Cl}^-}$	Diffusion coefficient of Cl ⁻ in water	$2.03 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \ddagger$
$\mathcal{D}_{\text{NO}_3^-}$	Diffusion coefficient of NO ₃ ⁻ in water	$1.90 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \ddagger$
$\mathcal{D}_{\text{SO}_4^{2-}}$	Diffusion coefficient of SO ₄ ²⁻ in water	$1.07 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \ddagger$
\mathcal{D}_P	Diffusion coefficient of P ions in water	$7.9 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$
θ	Volumetric water content	$0.24 \text{ m}^3 \text{ m}^{-3}$
$b_{M_i^{z_i+}}$	Buffer power	See Table 2
r_0	Mean root radius	$10^{-4} \text{ m} \S \P$
r_1	Thickness of the rhizosphere	$2.5 \cdot 10^{-2} \text{ m} \S$
I_{max}^{Ca}	Maximum root influx of Ca ²⁺	$1.042 \cdot 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \#$
K_m^{Ca}	Michaelis constant for Ca ²⁺	$3.9 \cdot 10^{-2} \text{ mol m}^{-3}$
I_{max}^{K}	Maximum root influx of K ⁺	$5.02 \cdot 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$
K_m^{K}	Michaelis constant for K ⁺	$3.2 \cdot 10^{-2} \text{ mol m}^{-3}$
I_{max}^{Mg}	Maximum root influx of Mg ²⁺	$6.5 \cdot 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$
K_m^{Mg}	Michaelis constant for Mg ²⁺	0.44 mol m^{-3}
I_{max}^{Na}	Maximum root influx of Na ⁺	0
K_m^{Na}	Michaelis constant for Na ⁺	-
$I_{max}^{\text{NH}_4}$	Maximum root influx of NH ₄ ⁺	$1.0 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$
$K_{max}^{\text{NH}_4}$	Michaelis constant for NH ₄ ⁺	$5.4 \cdot 10^{-2} \text{ mol m}^{-3}$
$I_{max}^{\text{Zn-Nc}}$	Maximum root influx of Zn ²⁺ in <i>N. caerulea</i>	$1.66 \cdot 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$
$K_m^{\text{Zn-Nc}}$	Michaelis constant for Zn ²⁺ in <i>N. caerulea</i>	$2.83 \cdot 10^{-3} \text{ mol m}^{-3}$
I_{max}^{Zn}	Maximum root influx of Zn ²⁺ in other species	$9 \cdot 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$
K_m^{Zn}	Michaelis constant for Zn ²⁺ in other species	$2.8 \cdot 10^{-3} \text{ mol m}^{-3}$
I_{max}^{Cl}	Maximum root influx of Cl ⁻	0
K_m^{Cl}	Michaelis constant for Cl ⁻	-
$I_{max}^{\text{NO}_3^{\text{CH}}}$	Constitutive maximum root influx of NO ₃ ⁻	$3.75 \cdot 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$
$K_m^{\text{NO}_3^{\text{CH}}}$	Constitutive Michaelis constant for NO ₃ ⁻	$1.6 \cdot 10^{-2} \text{ mol m}^{-3}$
$I_{max}^{\text{NO}_3^{\text{IH}}}$	Induced maximum root influx of NO ₃ ⁻	$1.9 \cdot 10^{-7} \text{ mol NO}_3^- \text{ m}^{-2} \text{ s}^{-1}$

$K_m^{NO_3^{IH}}$	Induced Michaelis constant for NO_3^-	$8.5 \cdot 10^{-2} \text{ mol m}^{-3}$
$I_{max}^{SO_4}$	Maximum root influx of SO_4^{2-}	$1.1 \cdot 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$
$K_m^{SO_4}$	Michaelis constant for SO_4^{2-}	$7 \cdot 10^{-2} \text{ mol m}^{-3}$
I_{max}^P	Maximum root influx of P ions	$3.26 \cdot 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$
$K_m^{P^4}$	Michaelis constant for P ions	$5.8 \cdot 10^{-3} \text{ mol m}^{-3}$
$S_{NO_3^-}$	Source of NO_3^- from mineralization	$1.70 \cdot 10^{-7} \text{ mol m}^{-3} \text{ s}^{-1} \#$

778 † Source: Nye (1972).

779 ‡ Source: Li and Gregory (1974).

780 § Source: Blossfeld et al. (2010);

781 ¶ Source: Sterckeman et al. (2004).

782 # Source: for root absorption parameters and source of nitrate, references are given in

783 Supplementary Material.

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786 **Table 2.** Main characteristics of the soils used to validate the model.

Soil parameter	Soil A	Soil B	Soil C	
Particle size distribution (g kg ⁻¹)	Clay	208	162	204
	Silt	469	602	454
	Sand	323	236	342
pH (H ₂ O)	6.2	8.1	6.3	
pH (CaCl ₂)	5.7	7.4	5.9	
CaCO ₃ (g kg ⁻¹)	0	13	<1	
Organic C (g kg ⁻¹)	26.4	16.9	15.7	
P Olsen (mg P kg ⁻¹)	4.6	34.1	5.5	
C/N ratio	16.8	12.9	8.9	
CEC cmol _c kg ⁻¹	11.8	12.0	11.0	
Exchangeable cations (cmol _c kg ⁻¹) 1)	Ca ²⁺	7.1	12.6	9.0
	K ⁺	0.6	0.5	0.3
	Mg ²⁺	1.2	0.4	3.5
Buffer power, $b_{M_i^{z_i+}}$	Ca ²⁺	30.3	33.5	14.6
	Mg ²⁺	22.4	20.9	8.5
	K ⁺	23.1	23.7	48.3
	Na ⁺	23.0	23.0	23.0
	Zn ²⁺	300	2760	270
	Cl ⁻	0.4	0.4	0.4
	NO ₃ ⁻ †	0.4	0.4	0.4
SO ₄ ²⁻ †	6.0	6.0	6.0	

787 † Source: Barber (1995)

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789 **Table 3.** Conditions of the model validation. The pH measurement conditions refer to
 790 Blossfeld et al. (2010).

pH measurement conditions	Simulation conditions		
	r_l mm	Time days	pH location
	Ryegrass		
Average pH along the surface of a single young root	25.0	4	Rhizoplane
Average pH in root network	5.5	28	Mean in simulation domain
	Alpine pennycress		
Average pH along the surface of a single young root	25.0	4	Rhizoplane
Average pH in root network	5.5	42	Mean in simulation domain
	Maize		
Average pH along the surface of a single young root	25.0	4	Rhizoplane
Average pH along the surface of a single young root	25	8	Rhizoplane

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799 **Table 4.** Ionic composition of the soil solutions of soils A, B and C.

Ion	Unit	Soil A	Soil B	Soil C
Ca ²⁺	mol m ⁻³	1.638	2.632	4.322
K ⁺		0.363	0.295	0.087
Mg ²⁺		0.375	0.134	2.868
Mn ²⁺		0.029	< 7.1 10 ⁻⁶	< 7.1 10 ⁻⁶
Na ⁺		0.399	0.023	0.636
NH ₄ ⁺		0.071	< 1.9 10 ⁻³	0.020
Zn ²⁺		0.411	< 7.8 10 ⁻⁶	< 7.8 10 ⁻⁶
Cl ⁻	mol m ⁻³	0.480	0.436	1.242
NO ₃ ⁻		3.842	3.219	11.907
P ions		< 2.5 10 ⁻⁴	0.174	< 2.5 10 ⁻⁴
SO ₄ ²⁻		0.653	0.416	0.793
Charge balance	mol _c m ⁻³	0.112	1.102	0.387

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802 **Table 5.** Comparison of measured and simulated pH in the rhizosphere of three plant species grown in three soils. The simulation conditions are
803 given in Table 3.

pH measurement conditions	Soil A		Soil B		Soil C	
	Measured	Simulated	Measured	Simulated	Measured	Simulated
	Ryegrass					
Average pH along the surface of a single young root			7.8***	7.6	6.5*	6.9
Average pH in root network			7.9***	8.0	7.7***	7.6
Bulk soil (start of simulation)			7.4	7.4	6.2	6.2
	Alpine pennycress					
Average pH along the surface of a single young root	6.8***	6.4	8.4***	7.6	7.8***	6.9
Average pH in root network	7.0***	7.7	7.9***	8.0	n.d.‡	7.7
Bulk soil (start of simulation)	5.6	5.6	7.5	7.5	6.1	6.1
	Maize					
Average pH along the surface of a single young root	4.9***	6.4	7.1***	7.6	6.0	6.9
Average pH along the surface of a single older root	5.5***	6.5	7.5***	7.6	6.5*	6.9
Bulk soil (start of simulation)	5.6	5.6	7.4	7.4	6.2	6.2

804 ‡ n.d.: not determined.

805 * Significant at the 0.05 probability level

806 *** Significant at the 0.001 probability level

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809 **Table 6.** Global sensitivity analysis. Mean percentage of each ion in the total absolute charge
810 uptake.

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Ion	Part in the total absolute charge uptake (%)	
	1 week	4 weeks
Ca ²⁺	0.83	1.36
K ⁺	16.69	21.10
Mg ²⁺	3.65	6.01
NH ₄ ⁺	6.79	5.91
NO ₃ ⁻	63.69	54.88
P ions ⁻	7.51	9.32
SO ₄ ²⁻	0.85	1.40

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821 **Table 7.** Simulation of the rhizosphere pH using the composition of 37 soils sampled
822 worldwide. Mean ion concentrations at the rhizoplane after 0, 1, 4, 8 and 12 weeks of root
823 uptake.

Ion	Concentration at the rhizoplane, mol m ⁻³				
	Initial	1 week	4 weeks	8 weeks	12 weeks
Ca ²⁺	4.81	5.10	5.16	5.16	5.16
Mg ²⁺	1.02	1.09	1.10	1.10	1.09
K ⁺	0.72	0.68	0.66	0.63	0.61
NO ₃ ⁻	7.83	6.69	4.39	2.48	1.26
SO ₄ ²⁻	1.57	1.70	1.70	1.70	1.70
NH ₄ ⁺	0.28	0.24	0.20	0.18	0.16
P ions	4.70E-03	3.20E-03	2.74E-03	2.51E-03	2.36E-03
Na ⁺	1.05	1.11	1.11	1.11	1.11
Cl ⁻	1.54	1.60	1.60	1.60	1.60
Charge balance	+1.20	+2.74	+5.08	+6.95	+8.12
ΔpH	0	0.9	1.1	1.1	1.1

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838 **Table 8.** Simulation of the rhizosphere pH using the composition of 37 soils sampled worldwide. Cumulated root uptake of the different ions and
 839 part in the total absolute charge uptake after 1, 4, 8 and 12 weeks of root uptake.

Ion	Cumulated root uptake, mol m ⁻¹				Part in the total absolute charge uptake, %			
	1 week	4 weeks	8 weeks	12 weeks	1 week	4 weeks	8 weeks	12 weeks
Ca ²⁺	3.85E-07	1.54E-06	3.08E-06	4.62E-06	1.0	1.4	1.8	2.1
Mg ²⁺	1.26E-06	5.07E-06	1.01E-05	1.52E-05	2.8	3.5	4.3	4.9
K ⁺	1.55E-05	6.10E-05	1.20E-04	1.76E-04	20.3	26.8	32.0	35.2
NO ₃ ⁻	1.20E-04	3.95E-04	6.28E-04	7.79E-04	69.8	61.8	55.6	51.7
SO ₄ ²⁻	2.95E-07	1.18E-06	2.36E-06	3.54E-06	0.9	1.2	1.5	1.7
NH ₄ ⁺	7.45E-06	2.54E-05	3.96E-05	4.87E-05	4.8	4.7	4.1	3.7
P ions	3.20E-07	1.27E-06	2.54E-06	3.80E-06	0.4	0.5	0.7	0.8
Na ⁺	0	0	0	0	0	0	0	0
Cl ⁻	0	0	0	0	0	0	0	0
Cations					29.0	36.5	42.2	45.8
Anions					70.6	63.0	57.1	53.3
Charge balance	-9.47E-05	-2.99E-04	-4.51E-04	-5.27E-04				

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