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ABSTRACT

Many people around the world are overexposed to cadmium through their consumption of plant products. A model predicting Cd content in crops would improve risk assessment and cultural practices. As no such model exists, we evaluated different methods to simulate the root uptake of Cd and its translocation to the aerial parts of maize.

Using non-equilibrium thermodynamics, the Cd flux ($J_{A,B}$) from one compartment (A) to another (B) was considered to be proportional to the difference in electrochemical potential between the compartments and given by an equation of the type $J_{A,B} = \beta_{A,B}\ln(K_B C_A / K_A C_B)$, where $\beta_{A,B}$ and K_B are constants and C_A and C_B the actual Cd concentrations in compartments A and B. The compartments considered were rhizosphere solution (Rh), root cortex (Co), xylem sap (X) and aerial tissues. The model was evaluated against the experimental uptake of Cd by maize exposed for 8 h to a constant Cd concentration in the rhizosphere solution.

The formalism made it possible to describe the flow of Cd from the rhizosphere to the root cortex, with $\beta_{Rh,Co} = 8.7\text{E-}11$ mol m^{-2} s^{-1} and $K_{Co} = 73$. This questions the common use of Michaelis-Menten kinetics to model root absorption over the long term (throughout the cultivation period). In this case, the apparent validity of the Michaelis-Menten uptake kinetics is probably more closely linked to the root growth than to the Cd internalization mechanisms. To take into account the resistance to the ion transport linked to crossing the root cortex, thermodynamic and diffusion formalisms had to be associated, which enabled the prediction of the Cd flux towards xylem, with $K_X = 12.48$ and a diffusion coefficient $D_{Co} = 3.44\text{E-}11$ m^2 s^{-1}. The Cd flux from xylem to aerial tissues was better predicted by modelling the sap flow due to plant transpiration. This work opens perspectives towards a relatively simple modelling of plant Cd accumulation.

1. Introduction

Cadmium is a contaminant of soils which for several decades has been the subject of much research, because of the risks generated by its transfer from soil to plants. We know that a large part of the world's population is overexposed to this toxic trace metal, because of its excessive levels in common plant foods such as cereals, tubers or vegetables. The Cd contained in vegetal foodstuffs most often comes from the soil where the plant was grown and has absorbed it through its roots [2, 3,29,31].

Research has led to progress in understanding soil Cd chemistry, which determines its availability for root uptake. Works in plant physiology and molecular biology have sought to describe the mechanisms of

Cd absorption by the roots and its subsequent translocation to the aerial parts. The processes mediating its internalization and storage in the roots, as well as its loading into the xylem are relatively well understood [24]. On the other hand, those processes behind the allocation of the metal to the various aerial tissues, in particular, to reproductive organs and fruit, are less clearly established, and are still under investigation [32].

One of the practical outcomes of this research is an integrative modelling of the Cd accumulation processes, which would make it possible to predict the concentration of the metal in the harvested part, by highlighting the main edaphic, climatic or genotypic factors that led to this. Pollutant transfer risk assessment would then be possible, which could guide cultural practices (choice of plots, fertilization or treatment

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of the soil, choice of cultivar, etc.) in order to reduce the metal content in the agricultural products. Modelling the total uptake of Cd by plants has been the subject of various studies since the '80 s and has achieved some success [12,22]. It is often based on an equation of reactive transport in the rhizosphere, which is considered as a porous medium [1]. Thanks to this approach, we are not far from being able to correctly predict the total quantity of Cd taken up by a plant during its crop cycle, which is highly dependent on the metal partition coefficient in the soil and the growth kinetics of the root system. On the other hand, it is not currently possible to correctly allocate this absorbed quantity to the different organs and tissues of the plant. Therefore, the models for predicting Cd levels in crops are most often statistical functions of soil properties which are only valid for given, often restricted, agro-climatic conditions [7,17].

Thermodynamic concepts are often briefly presented in books on the mineral nutrition of plants, as laws governing the ion movements in the plant [5,28,30]. However, the use of thermodynamics mostly remains at the level of establishing theoretical principles and more rarely at that of predicting these movements. Thellier [27] is, to our knowledge, the first to have used thermodynamics, in the field of non-equilibrium, to model the flow of absorption of ions by the roots. He compared this formalism to a very similar electrokinetic one [26] and showed that it correctly represented the root absorption fluxes of various major ions ($H_2PO_4^-$, K^+, Na^+, Cl^-, SO_4^{2-}), described in works where they were usually modelled by Michaelis-Menten kinetics. This biophysical approach was more recently recalled by Le Deunff and Malagoli [8], who confirmed its interest in modelling the absorption of NO_3^- [9,10].

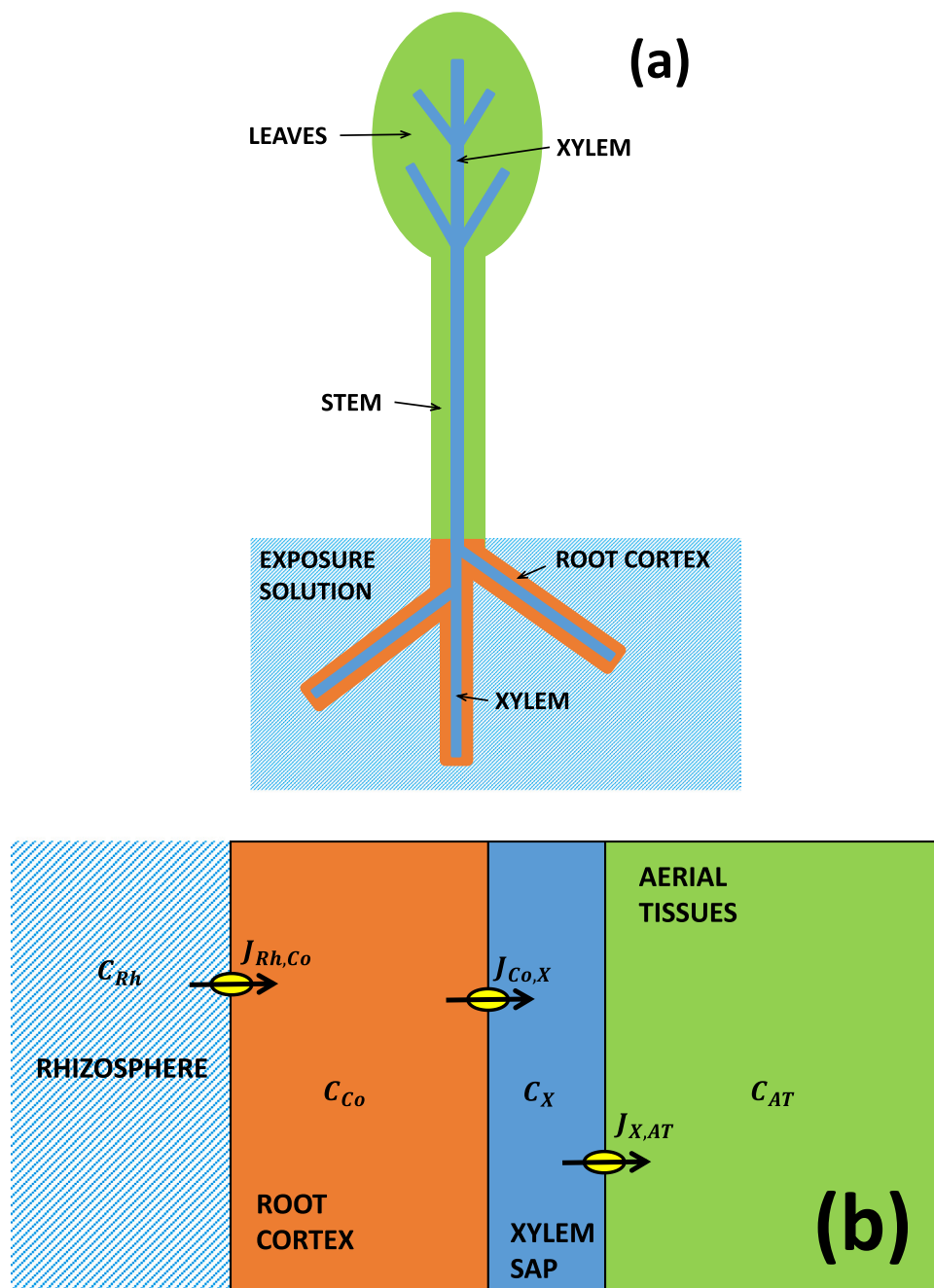Validated for its formalization of the flow between the external

Fig. 1. Diagrams of the modelled system.

solution and the root compartment, non-equilibrium thermodynamics have never been tested for the prediction of ion fluxes between internal compartments of the plant. Neither has it been applied to Cd. This is why we undertook to test this formalism in the representation of the flows of this metal between the soil solution, the root, the xylem and the aerial parts. This article presents the results of an experimental test of the thermodynamic formalisms and the alternative modelling proposed in case of failure of the initial formalism.

2. Materials and methods
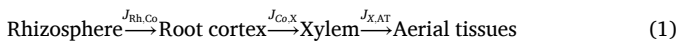
2.1. Theory

2.1.1. The system

The plant is at the vegetative stage, composed of a root system and a stem bearing leaves (shoot) (Fig. 1a). It includes three compartments: the root cortex, the aerial tissues and the xylem. What is designated by 'root cortex' here includes all root tissues with the exclusion of the xylem, while what is called aerial tissues are the shoot tissues with the exclusion of the xylem. The xylem is considered as a network of vessels full of an aqueous solution (sap), that continuously extends into roots and shoot. It is separated from the cortex and the aerial tissues by a semi-permeable membrane, which have the properties of the cell membrane. Other compartments that may play a role in Cd distribution are neglected, in particular the apoplast, the cytosols, the vacuoles and the phloem. The phloem is considered to have a negligible role in the distribution of Cd at the vegetative stage, while the apoplast, the cytosols and the vacuoles are confused with root cortex and aerial tissues. The soil solution is regarded as a fourth external compartment, in contact with root cortex by the intermediate of a semi-permeable membrane.

Distribution of Cd in the different compartments of the plant is driven by the difference in electrochemical potential of the element between each compartment. Metal moves from one compartment to another *via* transport proteins (Fig. 1b). The ions taken up by the roots enter the root cortex, are poured into the xylem sap and are transported to the leaves by convection, resulting from plant transpiration. It is initially considered that the convection due to transpiration is fast enough so that at each instant, the concentration of solute in the xylem sap is homogeneous. There is no direct passage of Cd from the cortex to the aerial tissues.

2.1.2. The formalism

The Cd fluxes in the plant can be schematized as follows:

$$\text{Rhizosphere} \xrightarrow{J_{\text{Rh,Co}}} \text{Root cortex} \xrightarrow{J_{\text{Co,X}}} \text{Xylem} \xrightarrow{J_{\text{X,AT}}} \text{Aerial tissues} \quad (1)$$

The Cd concentrations in each compartment are given by:

$$\text{Rhizosphere}: \quad C_{\text{Rh}} = K_{\text{Rh}}c_{\text{Rh}} = c_{\text{Rh}}, \text{ as } K_{\text{Rh}} = 1 \quad (2)$$

$$\text{Root cortex}: \quad C_{\text{Co}} = K_{\text{Co}}c_{\text{Co}} \quad (3)$$

$$\text{Xylem}: \quad C_{\text{X}} = K_{\text{X}}c_{\text{X}} \quad (4)$$

$$\text{Aerial tissues}: \quad C_{\text{AT}} = K_{\text{AT}}c_{\text{AT}} \quad (5)$$

where c is the bulk concentration, i.e. the concentration in equilibrium in an aqueous Cd solution. For the sake of simplicity and because the concentrations are low, the relationships are considered linear.

$J_{\text{A,B}}$ is the Cd flux from compartment A to compartment B, subscripts Rh, Co, X and AT representing respectively rhizosphere solution, root cortex, xylem and aerial tissues as defined above. C_{A} is the total Cd concentration in compartment A and c_{A} the concentration of free hydrated Cd in the liquid phase, in equilibrium with compartment A at the concentration C_{A}, the corresponding equilibrium constants being K_{A}.

According to non-equilibrium thermodynamics [27], provided the reaction is not too far from equilibrium, $J_{\text{Rh,Co}}$ (mol m^{-2} s^{-1}) can be

considered as a linear function of the difference in electrochemical potentials (μ_{Cd}, J mol^{-1}) between the two compartments:

$$J_{\text{Rh,Co}} = \frac{\beta_{\text{Rh,Co}}}{RT}\left(\mu_{\text{Cd}_{\text{Rh}}} - \mu_{\text{Cd}_{\text{Co}}}\right) \quad (6)$$

$\beta_{\text{Rh,Co}}$ being a transfer coefficient (mol m^{-2} s^{-1}) between rhizosphere and root cortex, R is the molar gas constant (J K^{-1} mol^{-1}), T the temperature (K). Neglecting the diffusion resistance in the liquid phase at the rhizosphere-root interface, where the Cd concentration $c|_{\text{interface}} = c_{\text{Rh}}$, it becomes:

$$\mu_{\text{Cd}_{\text{Rh}}} = \mu^* + RT\ln(c_{\text{Rh}}) \quad (7)$$

$$\mu_{\text{Cd}_{\text{Co}}} = \mu^* + RT\ln(C_{\text{Co}}) + \Phi_{\text{Co}} = \mu^* + RT\ln\left(\frac{C_{\text{Co}}}{K_{\text{Co}}}\right) = \mu^* + RT\ln(c_{\text{Co}}) \quad (8)$$

$$J_{\text{Rh,Co}} = \beta_{\text{Rh,Co}}\ln\left(\frac{c_{\text{Rh}}}{c_{\text{Co}}}\right) = \beta_{\text{Rh,Co}}\ln\left(\frac{K_{\text{Co}}C_{\text{Rh}}}{C_{\text{Co}}}\right) \quad (9)$$

μ^* is a reference potential and Φ_{Co} the assumed constant potential (for instance electrical) which applies to Cd ions in the root cortex.

K_{Co} is given by:

$$\ln(K_{\text{Co}}) = -\frac{\Phi_{\text{Co}}}{RT} \quad (10)$$

The Cd potential in xylem is given by:

$$\mu_{\text{Cd}_{\text{X}}} = \mu^* + RT\ln(C_{\text{X}}) + \Phi_{\text{X}} = \mu^* + RT\ln\left(\frac{C_{\text{X}}}{K_{\text{X}}}\right) = \mu^* + RT\ln(c_{\text{X}}) \quad (11)$$

Therefore, the Cd flow between root cortex and xylem can be written:

$$J_{\text{Co,X}} = \beta_{\text{Co,X}}\ln\left(\frac{c_{\text{Co}}}{c_{\text{X}}}\right) = \beta_{\text{Co,X}}\ln\left(\frac{K_{\text{X}}C_{\text{Co}}}{K_{\text{Co}}C_{\text{X}}}\right) \quad (12)$$

Similarly, the flow between xylem and aerial tissues is given by:

$$J_{\text{X,AT}} = \beta_{\text{X,AT}}\ln\left(\frac{c_{\text{X}}}{c_{\text{AT}}}\right) = \beta_{\text{X,AT}}\ln\left(\frac{K_{\text{AT}}C_{\text{X}}}{K_{\text{X}}C_{\text{AT}}}\right) \quad (13)$$

2.2. Experiment

2.2.1. Principle

Maize plants were grown in hydroponics, in a growth chamber, for 24 days (including 3 days of germination), with no Cd in the hydroponic solution. At the end of the cultivation, the roots were exposed for 0.5 h, 1 h, 1.5 h, 2 h, 3 h, 4 h, 6 h and 8 h to a nutrient solution containing Cd at a constant concentration of 0.5 μM. The exposure was limited to 8 h so that any plant growth could be neglected. At the end of the exposure, the shoot was excised and the xylem sap was collected. Root surface, as well as the mass of xylem sap, roots and shoots were recorded. Cadmium concentration was measured in xylem sap, as well as in roots and shoots. There were 4 replicate plants per exposure time.

2.2.2. Maize cultivation

Germination of the INRAE MB862 cultivar was carried out in petri dishes, on moistened filter papers, placed in the dark. Hydroponic cultivation was carried out in PVC pots containing 1.2 L of nutrient solution. The plants were supported by a polystyrene float pierced with a conical hole and later staked by means of a stake fixed to the pot and plastic-coated wire. A capillary tube used to aerate the nutrient solution by bubbling air was placed in each pot. Seedlings were transplanted into the hole of the float and cultivated for 21 days in a growth chamber, with 16 h of light at 25°C and 8 h of darkness at 20°C, and 70 % relative humidity. The photon flux density (PAR) was 350 μmol photons m^{-2} s^{-1}. The composition of the nutrient solution was as follows, in μM: Ca (NO$_3$)$_2$: 1000; KNO$_3$: 1000; KCl: 50; MgSO$_4$: 500; KH$_2$PO$_4$: 100; H$_3$BO$_3$: 10; MnCl$_2$: 1; ZnSO$_4$: 10; NaFe(III)EDTA: 40; CuSO$_4$: 0.2; Na$_2$MoO$_4$: 0.2;

NiSO$_4$: 0.7; MES: 2000. The pH was adjusted to 5.7 by adding 0.1 M KOH. The nutrient solution was renewed twice a week.

2.2.3. Exposure to cadmium and xylem sap collection

The exposure and sap collection were carried out in the growth chamber, in the daylight conditions. At the start of the exposure, all the plants were simultaneously placed in 3 L pots containing the nutrient solution plus 0.5 µM Cd(NO$_3$)$_2$. The exposure solution was renewed every hour. At exposure time minus 15 min, the shoot was excised with a razor blade, about 5 mm above the adventitious roots. The xylem sap collection was started just after shoot removal and stopped 15 min after the exposure time, to last 30 min. The stem section at the crown was briefly blotted and the flowing sap was continuously sucked with a 250 µL micropipette, then transferred into an Eppendorf™ vial.

2.2.4. Measurements

The xylem sap was weighed, acidified with a known volume of concentrated HNO$_3$ and analysed for Cd content with electro-thermal atomic absorption spectrometry (ETAAS, SpectraAA Zeeman 220, Varian, Australia). Roots were gently blotted, weighed and scanned so their total surface and volume could be measured using RhizoVision Explorer software [20]. They were then oven-dried at 70 °C, weighed and milled for analysis. Fresh and dry weight was also recorded for all shoots, before they were milled for analysis.

Roots and shoots were analysed for Cd determination as follows. A test portion of 0.5 g was digested with a mixture of 2.5 mL HNO$_3$ (14.65 M) and 5 mL H$_2$O$_2$ (12.7 M), progressively heated to 95 °C for 3 h, using a heating block system (DigiPREP, SCP Science, QC, Canada). The final extract was filtered at 0.45 µm and adjusted to 25 mL with water. Cadmium was determined in the extracts using inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP PRO, Thermo Scientific, England) or ETAAS, when Cd concentration in the extracts was below the detection limits of ICP-OES. Control plant samples with a known composition as well as certified solutions (EU-H-4, SCP Science, Courtaboeuf, France) were included as quality control.

2.3. Data processing

Based on Eq. 9, the Cd flux from exposure (rhizosphere) solution to the root cortex ($J_{Rh,Co}$) can be written

$$J_{Rh,Co} = \beta_{Rh,Co}\ln(K_{Co}) + \beta_{Rh,Co}\ln\left(\frac{C_{Rh}}{C_{Co}}\right) \tag{14}$$

$c_{Rh} = C_{Rh}$ is fixed (5 10^{-7} mol L^{-1}) and C_{Co} (mol (kg FW)$^{-1}$) is measured experimentally as follows:

$$C_{Co}(t) = \frac{FW_R(t)C_R(t) - FW_{RX}(t)C_X(t)}{FW_R(t) - FW_{RX}(t)} \tag{15}$$

where FW designates the compartment fresh weight and the subscripts R, X and RX designate the root, xylem sap and root xylem sap compartments. FW_{RX}, the mass of xylem sap in the roots is calculated considering that xylem sap represents 12.3 % of the maize root volume [25] and has a density of 1. This proportion of xylem was extrapolated to the whole plant.

$Q_P(t)$ (mol m^{-2}), the amount of Cd in the plant at time t was calculated as:

$$Q_P(t) = \frac{FW_R(t)C_R(t) + FW_S(t)C_S(t)}{S_{Co}} \tag{16}$$

where S_{Co} is the root surface area (m^2) and subscript S designates the shoot compartment. Division by the measured value of S_{Co} enables a correction of the differences in plant size. A logarithmic function was adjusted to the experimental measurements of $Q_P(t)$ and the Cd flux between rhizosphere and root cortex can be estimated by deriving $Q_P(t)$ over time:

$$J_{Rh,Co}(t) = \frac{dQ_P(t)}{dt} \tag{17}$$

If the theory is valid, the experimental relationship

$$J_{Rh,Co}(t) = a\ln\left(\frac{C_{Rh}}{C_{Co}(t)}\right) + b \tag{18}$$

can be adjusted with a linear function whose slope is, according to Eq. 9,

$$a = \beta_{Rh,Co} \tag{19}$$

and the y intercept is given by

$$b = \beta_{Rh,Co}\ln(K_{Co}) = a\ln(K_{Co}) \tag{20}$$

Similarly, the Cd flux from the root cortex to the xylem sap can be written

$$J_{Co,X} = \beta_{Co,X}\ln(\beta_{Co,X}) + \beta_{Co,X}\ln\left(\frac{C_{Co}}{C_X}\right) \tag{21}$$

The experiment gives $C_{Co}(t)$, $C_{RX}(t)$ and $C_S(t)$. Q_{XR+S} is the amount of Cd in the root xylem and in the shoot:

$$Q_{XR+S}(t) = \frac{FW_{XR}(t)C_{XR}(t) + FW_S(t)C_S(t)}{(0.123)^{\frac{1}{2}} \, S_{Co}} \tag{22}$$

$J_{Co,X}$ can be calculated by deriving $Q_{RX+S}(t)$ over time, after adjusting a logarithmic function $Q_{RX+S} = g(t)$ to the experimental values. $\beta_{Co,X}$ and $\beta_{Co,X}$ can be determined in a similar way as that used to determine $\beta_{Rh,Co}$ and K_{Co}.

Finally, a similar approach can be used to measure $\beta_{X,AT}$ and K_{AT}, the parameters of the Cd transfer reaction between xylem sap and the aerial tissues.

3. Results and discussion

After 8 h of exposure to Cd, the mean concentrations (in mol (kg FW)$^{-1}$) in the four compartments can be ranked as follows: C_{Co} (2.63E-05) > C_X (1.92E-06) > C_{Rh} (5.00E-07) > C_{AT} (1.28E-07) (Table 1). It appears that the root cortex strongly concentrates the Cd from the rhizosphere solution, by a factor of 53, while the concentration in xylem sap is 14 times lower than that in the root cortex, where the metal comes from. Similarly, the Cd concentration in the aerial tissues is reduced by factor 15 compared to that in the xylem sap, and about 4 times compared to the exposure solution. The root cortex and the xylem sap are enriched in Cd compared to the exposure solution, while the shoot is impoverished. This ranking is consistent with the fact that maize concentrates more Cd in roots than in shoots [4,13,14]. As shown below, these differences are due to equilibrium constants but also to the delay due to transport in the cortex and from the xylem towards the aerial parts.

3.1. From exposure solution to root cortex

The Cd concentration in cortex (C_{Co}) rapidly increased with time (Table 1), from 10 (after 0.5 h) to 53 (after 8 h) times higher than the exposure solution (C_{Rh}). The relationship $Q_P(t) = f(t)$ was modelled by a logarithmic function with R^2 = 0.96 (Fig. 2a). The relationship between $J_{Rh,Co}$ and $\ln(\frac{C_{Rh}}{C_{Co}})$ could be modelled by an increasing exponential function with R^2 = 0.98 (Fig. 2b), suggesting that Eq. 9, i.e. the model is not valid. This is due to the fact that the reaction is too far from equilibrium, the concentrations in both compartments varying too much with time. Therefore, we selected the last four exposure times (3 h, 4 h, 6 h and 8 h), when the system is closer to equilibrium (Fig. 2b), in order to adjust a linear function (R^2 = 0.82), in agreement with Eq. 9. $\beta_{Rh,Co}$ and K_{Co} could be calculated according to Eqs. 19 and 20. These were respectively 8.7E-11 mol m^{-2} s^{-1} and 73.

Another modelling approach, based on a continuity equation, was

Table 1

Evolution of Cd concentration in the four maize compartments. C_{Rh}: Concentration in rhizosphere solution; C_{Co}: In root cortex; C_X: In xylem sap; C_{AT}: In aerial tissues. Concentrations are mean values of 4 replicates.

| Time	C_{Rh}	C_{Co}	C_X	C_{AT}	C_X/C_{Rh}	C_{Co}/C_{Rh}	C_{Co}/C_X	C_{AT}/C_X
h	mol L^{-1}	mol (kg FW)$^{-1}$	mol L^{-1}	mol (kg FW)$^{-1}$				
0.5	5.00E-07	4.98E-06	7.27E-09	1.42E-08	1.45E-02	10	685	1.9
1.0	5.00E-07	8.34E-06	5.42E-09	1.49E-08	1.08E-02	17	1539	2.8
1.5	5.00E-07	1.05E-05	5.55E-09	2.76E-08	1.11E-02	21	1892	5.0
2.0	5.00E-07	1.22E-05	1.91E-08	2.32E-08	3.83E-02	24	639	1.2
3.0	5.00E-07	1.80E-05	1.98E-07	2.52E-08	3.96E-01	36	91	0.13
4.0	5.00E-07	1.74E-05	4.73E-07	4.49E-08	9.45E-01	35	37	0.09
6.0	5.00E-07	2.41E-05	1.06E-06	3.51E-08	2.11E+00	48	23	0.03
8.0	5.00E-07	2.63E-05	1.92E-06	1.28E-07	3.83E+00	53	14	0.07
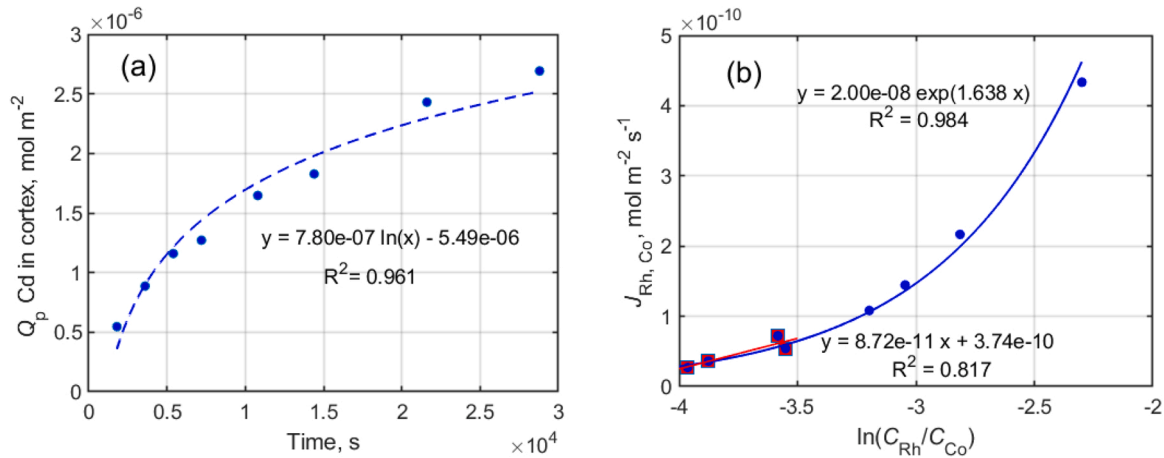
Fig. 2. Transfer of Cd from rhizosphere solution to root cortex of maize. (a): Kinetics; (b): Relationship between Cd flux and $\ln(C_{Rh}/C_{Co})$.

applied in order to consider all the experimental data, and not only the last four exposure times. Neglecting the small amount of Cd transported from cortex to xylem, this can be written:

$$V_{Co}\frac{dC_{Co}}{dt} = \beta_{Rh,Co}S_{Co}\ln\left(\frac{K_{Co}c_{Rh}}{C_{Co}}\right) \tag{23}$$

where V_{Co} is the volume of the root cortex (m^3). It becomes:

$$\frac{dC^*}{dt} = \frac{\beta_{Rh,Co}S_{Co}}{K_{Co}c_{Rh}V_{Co}}\ln(C^*) = -\kappa\ln(C^*) \tag{24}$$

considering that c_{Rh} is constant, $C^* = \frac{C_{Co}}{K_{Co}c_{Rh}}$ ($C^* < 1$) and $\kappa = \frac{\beta_{Rh,Co}S_{Co}}{K_{Co}c_{Rh}V_{Co}}$.

Integration of Eq. 24 (as described in Supplementary Material) with an initial null value of the concentration gives:

$$\int_{-\ln C^*}^{+\infty} \frac{\exp(-v)}{v}dv = E_1(-\ln(C^*)) = \kappa t \tag{25}$$

where $E_1(z)$ is the exponential integral. The two parameters (κ, K_{Co}) problem was solved numerically using *lsqcurvefit* from MATLAB®. The fit according to this modelling had R^2 = 0.99 (Fig. 3), slightly higher than that modelled by a logarithmic function (R^2 = 0.95). In this case, $K_{Co} = 78.2$ and $\kappa = 2.54$E-05 s^{-1}, which gave $\beta_{Rh,Co} = 1.29$E-10 mol m^{-2} s^{-1} taking $V_{Co} = 1.81$E-05 m^3 and $S_{Co} = 1.39$E-01 m^2, the average measured values. The two modelling methods gave close values for K_{Co} and $\beta_{Rh,Co}$.

The electrochemical potential of Cd in the root cortex is lower than that in the rhizosphere solution (Eq. 6, Table 2). The high value of K_{Co} indicates that the equilibrium value of Cd in the cortex is linked to the equality of the electrochemical potential and not to that of the Cd concentration (see Eq. 8). This is consistent with the negative electrical potential of the root cell cytoplasm resulting from the excretion of
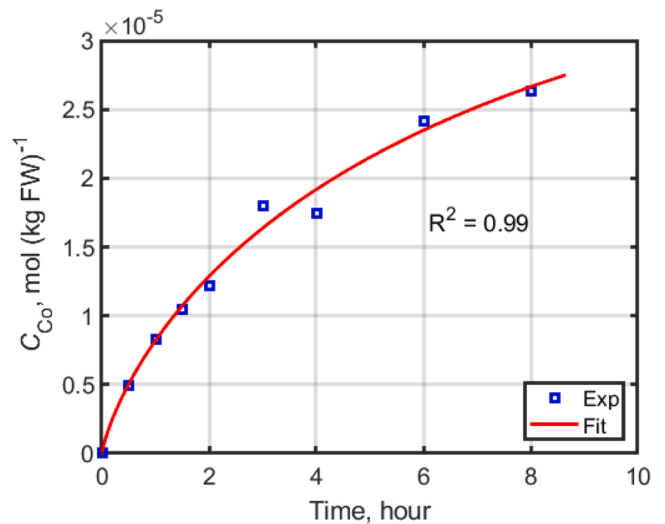

Fig. 3. Kinetics of Cd accumulation in root cortex of maize. Experimental results and model evaluation.

protons from the cell, driven by H$^+$-ATPases [30]. Another possibility to explain the increase in the total concentration of Cd in the cortex is the production of various structures responsible for the deactivation of Cd^{2+}, for instance ligands, which complex the metal ions or the vacuoles which sequestrate them. Therefore, the root cortex could be considered as an aqueous compartment containing a virtual ligand L_{Co}^{vir} representing all the Cd^{2+} ligands which average stability constant would be:

Table 2

Evolution of the measured root absorption flux of Cd and of the electrochemical potentials in the different compartments. For abbreviations, see text.

Time	$J_{\mathrm{Rh,Co}}^{mes}$	$RT\ln(C_{\mathrm{Rh}}/K_{\mathrm{Rh}})$	$RT\ln(C_{\mathrm{Co}}/K_{\mathrm{Co}})$	$RT\ln(C_{\mathrm{X}}/K_{\mathrm{X}})$	$\mu_{\mathrm{Cd_{Co}}} - \mu_{\mathrm{Cd_{Rh}}}$	$\mu_{\mathrm{Cd_X}} - \mu_{\mathrm{Cd_{Co}}}$
h	mol m^{-2} s^{-1}	J mol^{-1}				
0.5	3.03E-10	-3.60E+04	-4.09E+04	-5.27E+04	-4.94E+03	-1.18E+04
1.0	2.46E-10	-3.60E+04	-3.96E+04	-5.34E+04	-3.66E+03	-1.38E+04
1.5	2.15E-10	-3.60E+04	-3.91E+04	-5.34E+04	-3.09E+03	-1.43E+04
2.0	1.77E-10	-3.60E+04	-3.87E+04	-5.03E+04	-2.71E+03	-1.16E+04
3.0	1.52E-10	-3.60E+04	-3.77E+04	-4.45E+04	-1.75E+03	-6.80E+03
4.0	1.27E-10	-3.60E+04	-3.78E+04	-4.24E+04	-1.83E+03	-4.57E+03
6.0	1.13E-10	-3.60E+04	-3.70E+04	-4.04E+04	-1.03E+03	-3.38E+03
8.0	9.35E-11	-3.60E+04	-3.68E+04	-3.89E+04	-8.10E+02	-2.12E+03

$$K_{\mathrm{L_{Co}}} = \frac{[\mathrm{CdL_{Co}^{vir}}]}{[\mathrm{Cd^{2+}}][\mathrm{L_{Co}^{vir}}]} = \frac{[\mathrm{CdL_{Co}^{vir}}]}{c_{\mathrm{Co}}[\mathrm{L_{Co}^{vir}}]} \quad (26)$$

As C_{Co} represents the total Cd content in the root cortex ($[\mathrm{CdL_{Co}^{vir}}] + [\mathrm{Cd^{2+}}]$),

$$[\mathrm{Cd^{2+}}] = c_{\mathrm{Co}} = \frac{C_{\mathrm{Co}}}{1 + K_{\mathrm{L_{Co}}}[\mathrm{L_{Co}^{vir}}]} \quad (27)$$

and if $[\mathrm{L_{Co}^{vir}}]$ is considered as a constant during the root exposure to Cd,

$$K_{\mathrm{Co}} = 1 + K_{\mathrm{L_{Co}}}[\mathrm{L_{Co}^{vir}}] \quad (28)$$

It is not excluded that after longer exposure times, because of the production of ligands, such as phytochelatins [6,19], K_{Co} would not be constant and would increase with time, as well as with the storage capacity of the root cortex.

After 8 h of exposure, the equilibrium between the rhizosphere solution and the root cortex is not far from being reached, as $C_{\mathrm{Co}}/C_{\mathrm{Rh}} = 53$, which is about 3/4 of the estimated equilibrium value. This is consistent with the relatively low difference in potential between rhizosphere solution and root cortex $(\mu_{\mathrm{Cd_{Co}}} - \mu_{\mathrm{Cd_{Rh}}})$ (Table 2). The thermodynamic conception of the root absorption, as well as the decrease of $(\mu_{\mathrm{Cd_{Co}}} - \mu_{\mathrm{Cd_{Rh}}})$ with time demonstrate that the root influx of Cd should also decrease with time, as the root concentration increases, the outside concentration being constant. This is confirmed by the measured root influx ($J_{\mathrm{Rh,Co}}^{mes}$), calculated from the total Cd uptake, the measured root surface and the exposure time, which was reduced more than threefold after 8 h of exposure (Table 2). It can be noted that the value of Cd influx after 1 h exposure (2.46E-10 mol Cd m^{-2} s^{-1}) is very close to that calculated for the same maize cultivar with the $I_{\max}$ and K_m measured by Redjala et al. [15] (2.48E-10 mol Cd m^{-2} s^{-1}), thereby confirming the consistency of the influx measured in the present experiment. This observation calls into question the use of a Michaelis-Menten influx function as an inner boundary condition in the Barber-Nye-Tinker model [1,18,28], which is used to simulate root uptake of nutrients and trace metals. This boundary conditions is:

$$J_{\mathrm{Rh,Co}} = \frac{I_{\max}C_{\mathrm{Rh}}}{K_m + C_{\mathrm{Rh}}} \quad (29)$$

where $I_{\max}$ is the maximum root net influx and K_m the Michaelis-Menten affinity constant for the solute.

This can be compared to the thermodynamic expression of the root influx:

$$\frac{I_{\max}C_{\mathrm{Rh}}}{K_m + C_{\mathrm{Rh}}} = \beta_{\mathrm{Rh,Co}}\ln(K_{\mathrm{Co}}\frac{C_{\mathrm{Rh}}}{C_{\mathrm{Co}}}) \quad (30)$$

If $C_{\mathrm{Co}}/K_{\mathrm{Co}}$ is considered as constant, and taking $C_{\mathrm{Rh}}^* = C_{\mathrm{Rh}}/K_m$, Eq. 30 becomes:

$$\frac{C_{\mathrm{Rh}}^*}{1 + C_{\mathrm{Rh}}^*} = \frac{\beta_{\mathrm{Rh,Co}}}{I_{\max}}\ln(K_{\mathrm{Co}}\frac{C_{\mathrm{Rh}}^*}{C_{\mathrm{Co}}K_m}) \quad (31)$$

Using *lsqcurvefit* from MATLAB® and taking $0.01 < C_{\mathrm{Rh}}^* < 5$, $C_{\mathrm{Co}}/K_{\mathrm{Co}}$

$= 0.0710K_m$ and $\beta_{\mathrm{Rh,Co}}/I_{\max} = 0.1969$, the root influx according to the thermodynamic model is close to that simulated with the Michaelis-Menten function (Fig. 4). This means that when considering that the root Cd content does not increase significantly, the thermodynamic influx law is confused with the Michaelis-Menten one. This is the case when measuring solute influx during a very short time exposure (20–60 min), as done to assess $I_{\max}$ and K_m. In this case, the increase in solute content in the root cortex can be considered negligible and the Michaelis-Menten function fits the data points as well as the thermodynamic one, as found by Thellier [26]. However, this situation does not appear realistic for longer exposure times, as the solute content increases in the root cortex. This is particularly the case for non-essential and toxic trace elements like Cd which accumulate in the roots and are poorly translocated towards the shoot. For plants exposed for several days or weeks, the root Cd influx should be lower than that estimated using the Michaelis-Menten kinetics. Such a difference was observed with the zinc hyperaccumulator *Noccaea caerulescens* [11,21]. At the other extreme, when used for long periods (vegetation period), the Michaelis-Menten seems to be more closely related to root growth than to enzymatic kinetics. If the equilibrium value of the cortex with the rhizosphere concentration can be described by a Langmuir relation, the mole quantity absorbed during time dt is given by

$$2\pi r_0 J_{\mathrm{Rh,Co}}Ldt = A_{\mathrm{Co}}C_{\mathrm{Co}}^{\max}\frac{c_{\mathrm{Rh}}}{K + c_{\mathrm{Rh}}}dL \quad (32)$$

Assuming an exponential growth of the roots $L = L_0\exp(kt)$, the flux at the root is similar to the classical Michaelis-Menten form, but with a very different meaning of the parameters:

$$J_{\mathrm{Rh,Co}} = \frac{kA_{\mathrm{Co}}}{2\pi r_0}C_{\mathrm{Co}}^{\max}\frac{c_{\mathrm{Rh}}}{K + c_{\mathrm{Rh}}} \quad (33)$$
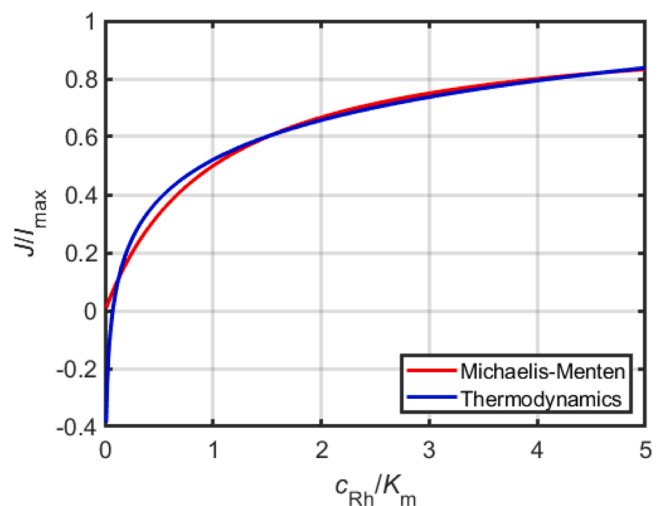

Fig. 4. Comparison of the Michaelis-Menten and the thermodynamic models for root Cd absorption flux.

where A_{Co} is the cortex transversal area. This corresponds to the fact that root growth provides at an exponential rate new roots not containing Cd and whose instantaneous absorption according to the thermodynamic law can be confused with Michaelis-Menten kinetics. This is valid as long as the growth of the roots is exponential, so that at any moment there are more very young roots containing little Cd than old roots having absorbed more metal.

3.2. From root cortex to xylem sap and aerial tissues

The Cd concentration in xylem sap remained very low and steady during the 1.5 first hours of exposure and started to increase after that duration (Table 1). Moreover, during the first three exposure times (up to 1.5 h), the concentration factor (C_{Co}/C_X) increased from 685 to 1892, before decreasing to 639 after 2 h, and then more strongly from 91 after 3 h to 14 at the end of exposure (8 h). This suggests that during the first two exposure hours, there was no significant transfer of Cd between cortex and xylem sap. Before symplastically reaching the stele and finally the xylem vessels, the Cd ions have to move from the external cell layers towards the centre of the root and to cross the exodermis and then the endodermis [16]. Moreover, at the beginning of the internalisation, Cd is transferred into the root cell vacuoles, which favours its retention in the root cortex [2]. It therefore takes some time before a sufficient Cd concentration is reached in the root cortex close to the xylem sap.

As a consequence, the relationship $Q_{XR+S}(t) = g(t)$ (Fig. 5) could not be modelled by a logarithmic function. Another model was developed, supposing that the resistance to transfer into xylem is mainly due to the diffusion through the root cortex and not to membrane crossing. The root cortex was designed as a cylinder of radius r_{Co}, in which the xylem is another parallel cylinder centrally inserted, which radius is r_X. The Cd concentration in xylem was considered spatially uniform because of uniform root absorption along the root and of the sap movement. Cadmium diffuses through the root cortex for $r_X < r < r_{Co}$:

$$K_{Co}\frac{\partial c_{Co}}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{Co}\frac{\partial c_{Co}}{\partial r}\right) \tag{34}$$

The initial condition is:

$$t = 0, \quad c_{Co} = 0 \tag{35}$$

At the root surface, the Cd concentration is fixed:

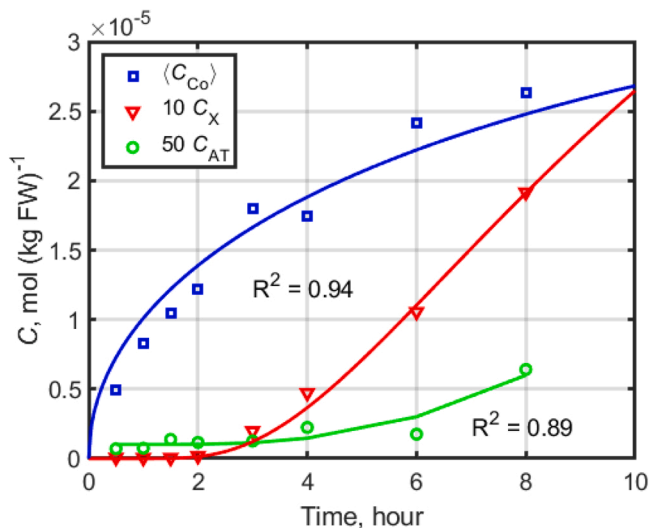$$r = r_{Co}, \quad c_{Co} = c_{Rh} \tag{36}$$

Fig. 5. Kinetics of the transfer of Cd from rhizosphere solution to root cortex, xylem and aerial tissues of maize. Comparison of modelling with experimental results.

At the xylem surface:

$$r = r_X, \quad c_{Co} = c_X \tag{37}$$

and the metal is accumulated in the xylem neglecting the translocation towards the aerial tissues (as justified below):

$$\pi r_X^2 K_X \frac{\partial c_X}{\partial t} = 2\pi r_X D_{Co}\frac{\partial c_{Co}}{\partial r}\bigg|_{r=r_X} \tag{38}$$

The detailed solution is given in Supplementary Material. The problem has three parameters: K_{Co}, K_X and D_{Co} (diffusion coefficient in root cortex). It was solved using the sub-program *lsqcurvefit* from MATLAB®.

Identification takes place simultaneously on the average value in the cortex and on the value in the xylem. With $K_{Co} = 73.14$, $K_X = 12.48$ and $D_{Co} = 3.44E\text{-}11$ m^2 s^{-1}, it was possible to fit both the average concentration into the cortex $<C_{Co}> = f(t)$ and the uniform value into the xylem and $C_X = g(t)$ ($R^2 = 0.94$) (Fig. 5). The value of D_{Co} is consistent with that found for Cd transport in porous media like soil [23]. That of K_{Co} is close to those previously found when modelling only the transfer of Cd from rhizosphere solution to root cortex. The difference of potential between root cortex and xylem sap $(\mu_{Cd_X} - \mu_{Cd_{Co}})$ after 8 h is clearly higher than that between rhizosphere solution and root cortex $(\mu_{Cd_{Co}} - \mu_{Cd_{Rh}})$ (Table 2), indicating root cortex and xylem sap are farther from equilibrium than root cortex and rhizosphere solution. The ratio $K_{Co}/K_{Rh} = 73.14$ is much higher than $K_X/K_{Co} = 0.1706$, showing that the Cd concentration in root cortex will be higher than in the rhizosphere solution and in the xylem sap, as at equilibrium ($J_{Rh,Co} = J_{Co,X} = 0$), $C_{Co} = 73.14\ C_{Rh}$ and $C_X = 0.1706\ C_{Co} = 12.48\ C_{Rh}$. This high value of $K_X = 12.48$ is consistent with the hypothesis that part of the Cd stored in the root cortex is released in the xylem sap by a specific transport system, of the HMA ATPase type, acting as a Cd pump using the energy stored in ATP (Mills et al., 2005; Verret et al., 2004). As Cd is unessential and toxic for the plant, in particular perturbating its photosynthesis (Küpper and Andresen 2016), its transfer to xylem would be due to the fact that Cd^{2+} hijacks HMA transport systems activated for the translocation of nutrients like Zn.

During the first two hours, the concentration in the aerial tissues C_{AT} was very low ($\sim$1E-8 mol Cd (kg FW)$^{-1}$) but greater than that in the xylem (Table 1), thereby indicating that Cd in the shoot was accumulated before the exposure to 0.5 mM Cd, during the three-week precultivation. This is consistent with the fact inferred above, that during the first two exposure hours, there was no significant transfer of Cd between root cortex and xylem sap. The Cd accumulation during precultivation would be due to Cd in the reagents used for the nutrient solution and also the metal contained in the seed. The Cd content started to slightly increase from the fourth hour of exposure, but it was not possible to model the relationship $C_{AT} = h(t)$ using a logarithmic function. The exposure time was too short for sufficiently transfer Cd to the xylem sap so there could be a retroaction from the aerial tissues and the thermodynamic conditions are not satisfied. Transport of Cd in the shoot is dominated mass flow caused by plant transpiration. Therefore, a model based on plant transpiration can be proposed to simulate the Cd flux to the aerial tissues. Knowing the total transpiration of the plant (assumed constant), $q_w = 2\pi r_0 Lv$, where v is the water velocity at the root surface, the concentration of Cd in the aerial parts (assuming an initial concentration C_{AT}^0) is simply given by

$$q_w \int_0^t C_X dt = m_{AT}(C_{AT} - C_{AT}^0) \tag{39}$$

where m_{AT} is the mass of aerial tissues. Using the same previous identification technique, the two unknown parameters are determined: $v = 2.31E\text{-}09$ m s^{-1} and $C_{AT}^0 = 2.02E\text{-}08$ mol (kg FW)$^{-1}$ ($R^2 = 0.89$). Cd in aerial tissues can thus be reasonably well predicted (Fig. 5).

3.3. Practical interest of the thermodynamic model

If plant roots are exposed to a constant Cd concentration from the beginning of their growth, considering that the metal transfer from one compartment to the other is faster than the plant growth (compartment expansion), the plant compartments are in equilibrium concerning the Cd concentrations and the flux between compartments is nil. Therefore

$$\ln(K_{\text{Co}}) = -\ln\left(\frac{C_{\text{Rh}}}{C_{\text{Co}}}\right) \tag{40}$$

$$K_{\text{Co}} = \frac{C_{\text{Co}}}{C_{\text{Rh}}} \tag{41}$$

and similarly

$$K_{\text{X}} = \frac{C_{\text{X}}}{C_{\text{Co}}} \tag{42}$$

$$K_{\text{AT}} = \frac{C_{\text{AT}}}{C_{\text{X}}} \tag{43}$$

and therefore

$$\frac{C_{\text{AT}}}{C_{\text{Co}}} = K_{\text{X}}K_{\text{AT}} \tag{44}$$

$$\frac{C_{\text{AT}}}{C_{\text{Rh}}} = K_{\text{Co}}K_{\text{X}}K_{\text{AT}} \tag{45}$$

Eqs. 44 – 45 indicate that the Cd concentration ratios between the different plant compartments are constant, once the system is at equilibrium. This is consistent with the results of Lovy et al. [11], who showed a constant ratio between the Cd levels in the root and the aerial parts or between these the plant parts and the rhizospheric solution, for three different Cd exposure levels. These equations plead in favour of a constant Cd ratio between plant organs, for a given plant genotype, at a given development stage. Measuring these ratios would help in predicting Cd concentration in plant organs from the simulation of the total plant uptake, which can be achieved using Barber-Nye-Tinker model [22].

4. Conclusions

The thermodynamic formalism $J_{\text{A,B}} = \beta_{\text{A,B}}\ln(K_{\text{B}}C_{\text{A}}/K_{\text{A}}C_{\text{B}})$ made it possible to describe the flow of Cd from the rhizosphere to the root cortex. This means that the root Cd uptake flux decreases as the metal accumulates in the root cortex. This contradicts the Michaelis-Menten kinetics usually used to formalize root uptake of ions, as this modelling considers that the influx never decreases and only depends on the external concentration. When considering that the root Cd content does not increase significantly, i.e. for short duration uptake, as done for the measurement of the Michaelis-Menten parameters (in 20–60 min), the thermodynamic influx law is confused with the Michaelis-Menten one. For longer durations, corresponding to the cultivation time, the Michaelis-Menten formalism seems linked to the exponential growth of the roots. In this way, roots containing little Cd dominate and the metal uptake kinetics resemble the Michaelis-Menten law, but with a very different meaning for the parameters.

The thermodynamic formalism could not be used in its initial expression to predict the passage of Cd from the root cortex to the xylem. Indeed, the ion is delayed in its movement towards the xylem sap by transport in the apoplast and the symplast, and even diverted by storage in the vacuoles of the cortical cells. To consider this resistance, the thermodynamic formalism had to be associated with a diffusion one, which correctly predicted the Cd flux towards xylem, taking $K_{\text{X}} = 12.48$. These results are consistent with the existence of proton pumps (H$^+$-ATPases) which strongly reduce the electrochemical potential of cortical

cells, favouring the internalization of Cd^{2+} through passive transport systems, but also with complexation in solution and vacuolization of the metal once in the cytosol of cortical cells. They also support the hypothesis that other ATPases, of the HMA type, further lower the potential of the xylem sap, so that Cd^{2+} can be released there.

The transport of Cd from xylem to aerial tissues is simply a convective motion according to the sap flow. The simulation of the Cd mass flow resulting from plant transpiration was found to be reasonable in describing the increase in the metal content in the aerial parts. To evaluate the thermodynamic model for the accumulation of Cd in the aerial parts (leaves), it would be necessary to extend the exposure time beyond several days, which would require biomass growth to be taken into account in the modelling.

CRediT authorship contribution statement

Christian Moyne: Conceptualization, methodology, software, validation, formal analysis, data curation, writing (review & editing), visualisation. **Pierre Leglize**: investigation, writing (review & editing). **Thibault Sterckeman**: Conceptualization, methodology, validation, formal analysis, investigation, ressources, data curation, writing (original draft, review & editing), visualisation, supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

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