

## Article Addendum

# What role does cell membrane surface potential play in ion-plant interactions

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Almost all cell membrane surfaces (CMS) are intrinsically negatively charged. These negative charges create a surface electrical potential ( $\psi_0$ ) which affects ion concentrations at the CMS and consequently affects the phytotoxicity of metallic cations and metalloid anions in different ways. The  $\psi_0$  is also controlled by the ionic composition of the bulk-phase medium (BM). Common cations, especially  $H^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ , can reduce the negativity of  $\psi_0$  by ionic screening and binding. Treatments that reduce the negativity of  $\psi_0$  would reduce the surface activity of  $Cu^{2+}$  ( $\{Cu^{2+}\}_0$ ) and increase the surface activity of arsenate ( $\{As(V)\}_0$ ) at the CMS, and consequently alleviation of  $Cu^{2+}$  toxicity but aggravation As toxicity would be expected. It is the  $\psi_0$ , rather than site-specific competition, that plays the principal role in ionic interactions and biotic effects.

## Introduction

The common ions  $Ca^{2+}$ ,  $Mg^{2+}$  and  $H^+$  have been known to reduce the uptake and alleviate biotic effectiveness of toxic cations to organisms<sup>1-4</sup> but to have the opposite effects upon anions.<sup>4,5</sup> Toxicologists and environmentalists commonly interpret the interactions between toxic cations (commonly heavy metals) and ameliorative cations as competitions for binding sites at a cell membrane surface (CMS) ligand.<sup>6,7</sup> This view is also incorporated in the biotic ligand model (BLM), which has gained increasing attention from both academic scientists and regulators and has been incorporated into its regulatory framework by the U.S. Environmental Protection Agency (EPA). The attribution of alleviative effect by coexistent cations to competitions between ions may be arbitrary. Generally neglected is

the significant role of cell membrane electrical features, especially the CMS electrical potential ( $\psi_0$ ).<sup>8</sup>

## Cell Membrane Surface Potential

Almost all cell surfaces are intrinsically negatively charged. These negative charges create negative potentials at the CMS ( $\psi_0$ ), which play important roles in ion-plant interactions.<sup>4,9</sup> The  $\psi_0$  controls ion distribution between the CMS and bulk-phase medium (BM): increase the surface activity of cations and decrease the surface activity of anions at the CMS. It is also controlled by the ionic composition in the BM. Common cations, especially  $H^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ , reduce the negativity of  $\psi_0$  by ionic screening and binding.<sup>4,5,10</sup>

The  $\psi_0$  is very difficult to directly measure. However, a Gouy-Chapman-Stern (G-C-S) model is available at present to calculate the  $\psi_0$  of plant cell membranes in response to the solution ionic environment.<sup>4,11</sup> The applicability of the G-C-S model has been verified by the measured  $\zeta$  potentials, which reflect the electrical potential at the hydrodynamic plane of shear at a small distance from the CMS.<sup>4</sup>

Based on the  $\psi_0$ , the activity of ion  $I^Z$  at the PM-surface ( $\{I^Z\}_0$ ) was computed from the activity of  $I^Z$  in the BM ( $\{I^Z\}_b$ ) according to the Nernst equation:

$$\{I^Z\}_0 = \{I^Z\}_b \exp[-ZF\psi_0/(RT)],$$

where  $F$ ,  $R$ ,  $T$  are the Faraday constant, the gas constant and temperature, respectively.

## Effects of Common Cations on Ion Toxicities

In the studies assessing Ca-Cu and Ca-As interactions, with the increase of  $Ca^{2+}$  activity in the BM ( $\{Ca^{2+}\}_b$ ), the surface activity of  $Ca^{2+}$  at CMS ( $\{Ca^{2+}\}_0$ ) increased initially and then reached a plateau, and at the same time the negativity of  $\psi_0$  decreased from -50.9 to -5.9 mV (Fig. 1A). As a result, the enrichment factor of  $Cu^{2+}$  activity ( $\{Cu^{2+}\}_0/\{Cu^{2+}\}_b$ ) decreased from 51 to 1.6, whereas the depletion factor of arsenate ion activity ( $\{As(v)\}_0/\{As(v)\}_b$ ) increased from 0.17 to 0.45; accordingly, alleviation of  $Cu^{2+}$  toxicity (inhibition of root elongation, denoted as relative root elongation) but aggravation of As toxicity were observed (Fig. 1B and C).

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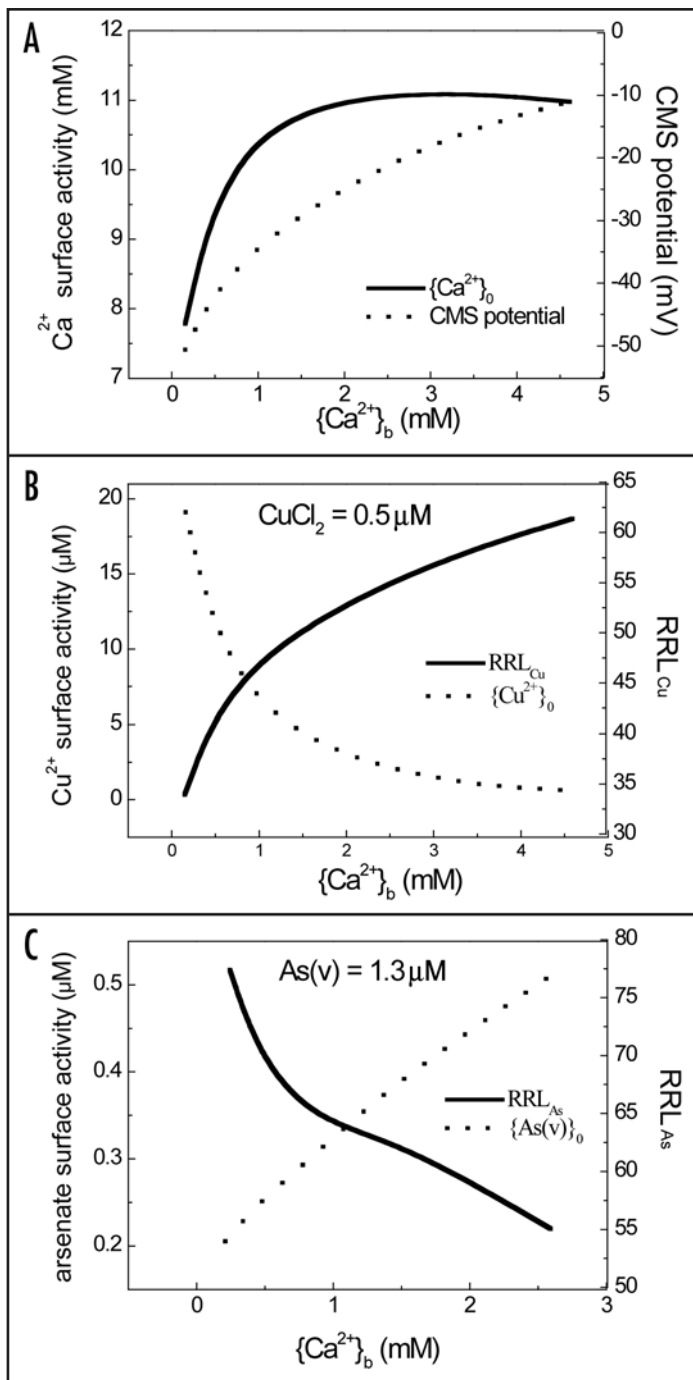


Figure 1. Calculated CMS potentials and ion ( $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  and arsenate ion) activities at CMS in response to  $\text{Ca}^{2+}$ . The bulk medium contained 0.25 mM  $\text{MgCl}_2$ , 1.0 mM  $\text{NaCl}$ , 0.5 mM  $\text{KCl}$ , 0.5  $\mu\text{M}$   $\text{CuCl}_2$  or 1.3  $\mu\text{M}$   $\text{NaH}_2\text{AsO}_4$  and variable  $\text{CaCl}_2$  at pH 6.0. The values of relative root elongation ( $\text{RRL}_{\text{Cu}}$  or  $\text{RRL}_{\text{As}}$ ) were the responses of wheat roots to  $\text{Cu}^{2+}$  and arsenate ions.

## The Mechanisms for Ion-Plant Interactions

The mechanism for the alleviation of  $\text{Cu}^{2+}$  toxicity by  $\text{Ca}^{2+}$  cannot be arbitrarily attributed to a site-specific competition among  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  at the CMS (invoked by the BLM) because the surface activity of  $\text{Ca}^{2+}$  does not increase all along (Fig. 1A). The results in present study and previous studies indicate several mechanisms for ion-toxicant interactions. The mechanism of electrostatic interactions is the principal mechanism considered in our study. The cationic components of salts commonly cause reductions in the negativity of CMS electrical potentials ( $\psi_0$ ). The depolarizing effectiveness of some common cations follows the order  $\text{Al}^{3+} > \text{H}^+ > \text{Ca}^{2+} \approx \text{Mg}^{2+} > \text{Na}^+ \approx \text{K}^+$ , depending upon the charge and strength of binding to the CMS. The reduced negativity of  $\psi_0$  causes reductions at the CMS of cationic toxicants and increases of anionic toxicants. In some cases, these effects appear to account almost entirely for ion-toxicant interactions.<sup>4,8,12</sup>

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