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Role of biologically-mediated boundary reactions in the bioavailability of Cd to freshwater phytoplankton

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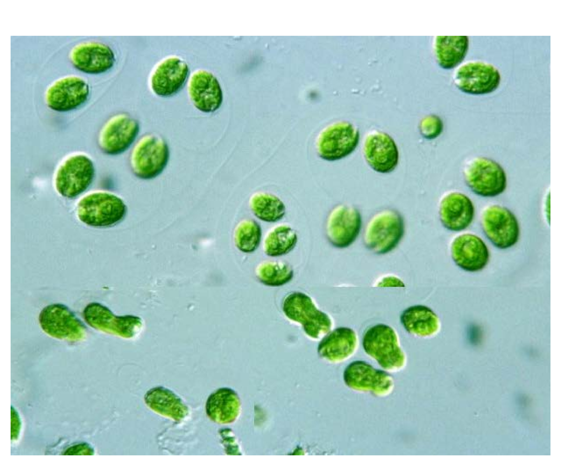
Abstract

We show that at a given constant free Cd^{2+} concentration in ambient well-buffered water, the bioavailability of dissolved Cd decreased or increased due to biologically-mediated chemical changes in the boundary layer of planktonic cells under different physiological conditions. For instance, decreased Cd bioavailability can result from a decrease in the free Cd^{2+} concentration in the boundary layer, resulting from de-protonation of metal-binding ligands induced by local pH enhancement as a consequence of algal release of HO^-. The observations of increased Cd bioavailability were probably due to an enhancement of the free Cd^{2+} concentration in the boundary layer, resulting from chemical oxidation of metal-binding ligands (e.g., cysteine) by oxidants released by the algal cells. Note that there is no uptake of intact cysteine-Cd complexes. The results highlight the importance of biologically-mediated surface processes (e.g., redox and pH changes), in addition to other well-known abiotic processes, in determining metal bioavailability.

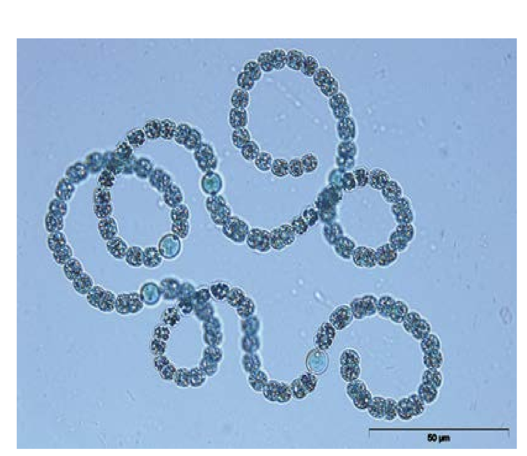
Methods

One-hour Cd uptake rates were investigated in two green algae (*Chlamydomonas reinhardtii* CC1690 and CPCC11 and *Pseudokirchneriella subcapitata*), and a cyanobacterium (*Anabaena flos-aquae*) in media with a constant concentration of free Cd^{2+} (e.g., 0.1 nM) buffered by NTA or cysteine.



C. reinhardtii
(Photo from Protist Information Server)

P. subcapitata
(Photo from the Algal Web)



A. flos-aquae
(Photo from http://toxinology.nilu.no/)

Results

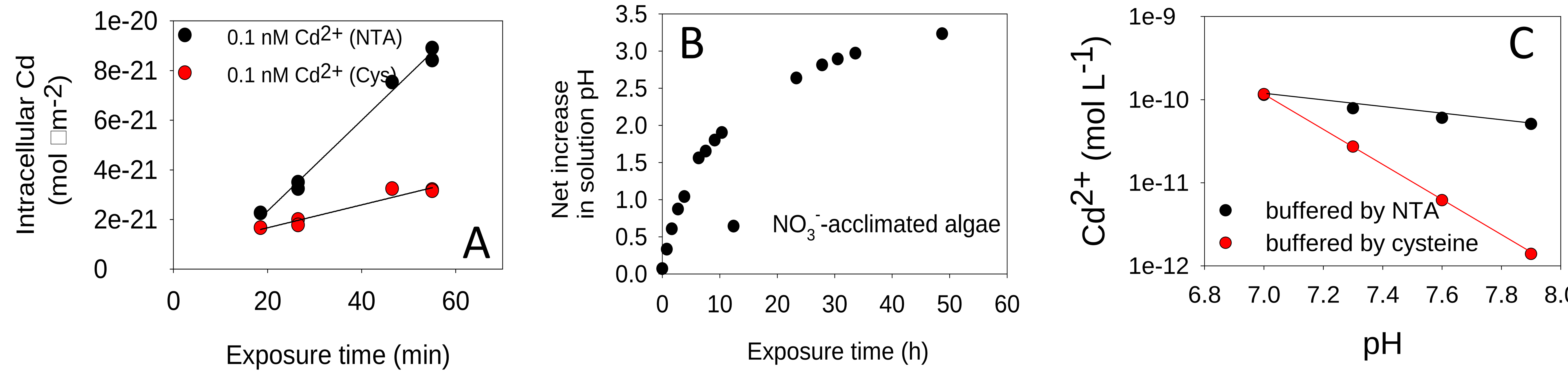


Figure 1. Cd uptake in NTA- (black dots) or cysteine- (red dots) buffered media (pH buffered at 7.0 with 10 mM MOPS) at the same free [Cd^{2+}] by NO_3^--acclimated *C. reinhardtii* (CC1690) (**A**), pH change in bulk solution (no pH buffer addition, in order to detect short-term pH changes) containing NO_3^--acclimated *C. reinhardtii* (CC1690) (**B**); and simulation of Cd speciation (total Cd = 20 nM) in NTA- or cysteine-buffered media at different pH (**C**).

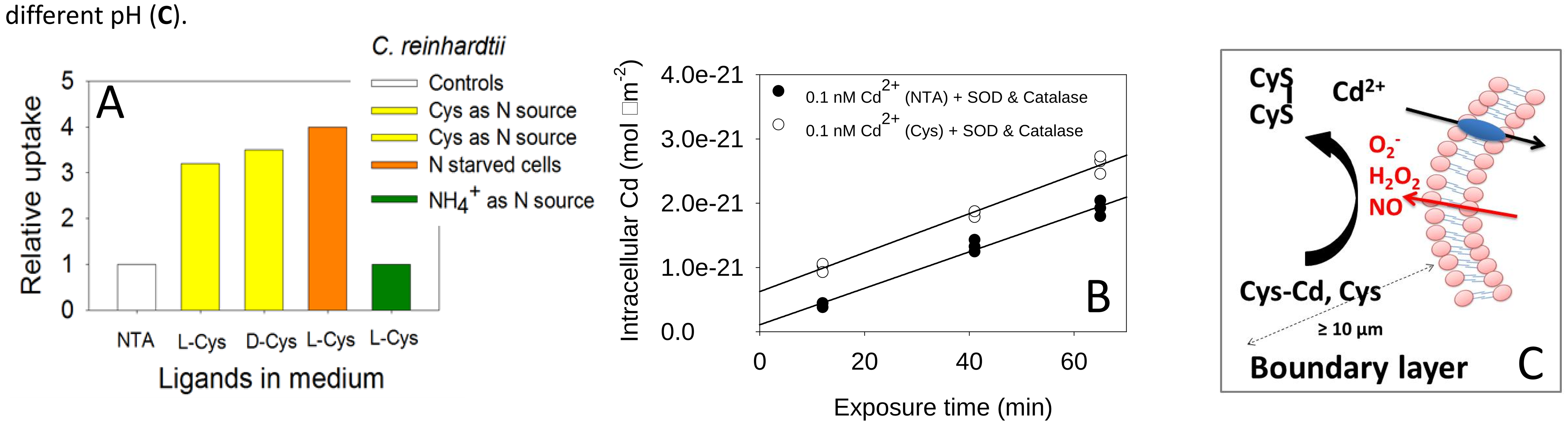


Figure 2. Relative Cd uptake rate by *C. reinhardtii* CPCC11 acclimated with different N sources in the presence of Cys in comparison with their respective controls (i.e., the same algal batches but exposed to media buffered by NTA) at the same free [Cd^{2+}] (**A**); Cd uptake (n = 3, some dots overlap) at the same Cd^{2+} concentration in the presence of 5.6 kU•L^{-1} Cu/Zn-superoxide dismutase (SOD) and 3.2 mg•L^{-1} catalase by N-starved *C. reinhardtii* CPCC11 (**B**); and the hypothetical 'oxidation of cysteine or Cys-Cd complexes in the boundary layer' (**C**).

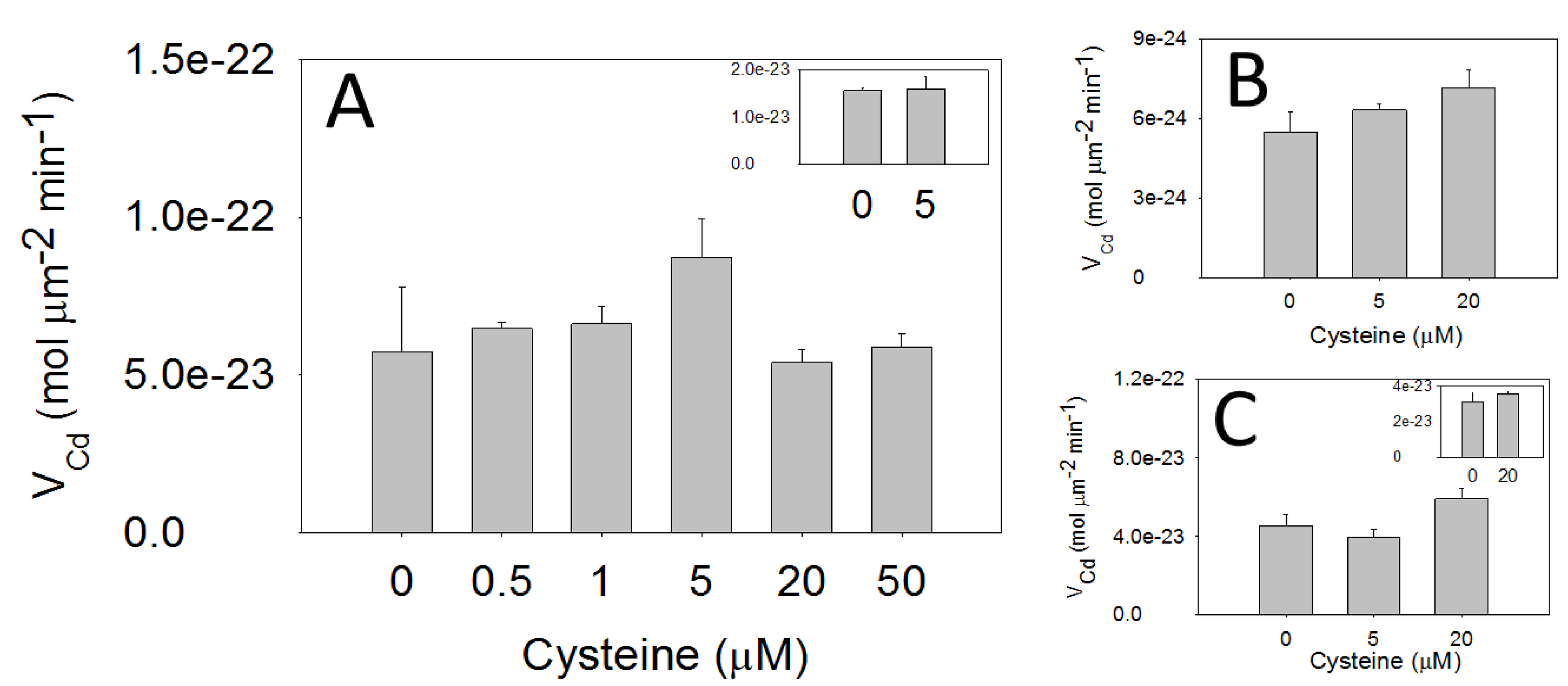


Figure 3. One-hour Cd uptake rates by *C. reinhardtii* CPCC11 (**A**), *P. subcapitata* (**B**), and *A. flos-aquae* (**C**) in media with 0.1 nM free Cd^{2+} and increasing concentrations of Cd-cysteine complexes (n = 3-4, mean ± SD). Data for each panel were from a single test (i.e., the same algal batch), and inserts in panels A and C show one independent repeated test.

Conclusions

1. Cd bioavailability is determined by the concentration of free Cd^{2+} in the boundary layer, which can be different from that in the surrounding waters and might be regulated by the metabolism of these microorganisms. **2.** Uptake of other trace metals (e.g., Cu, Zn, Hg, etc.) by phytoplankton will also be sensitive to the proposed 'boundary layer effect'.

Acknowledgements

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