## Measurement of Cupric Ion Activity in Soil Solutions to Evaluate Site-Specific Copper Bioavailability

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The potential bioavailability of copper in soils surrounding a copper mining, milling and smelting facility in the southwestern U.S. was evaluated to support an ecological risk assessment. In most ecotoxicological studies, the phytotoxicity of copper in soil is related to the total concentration or some operationally defined extractable fraction. That approach is not generally reliable because both the total copper content and the readily extractable fraction include forms of copper that are not bioavailable, and the actual portion of total or extracted copper that contributes to soil phytotoxicity is dependent on numerous site-specific factors that may be difficult or expensive to measure. Previous work by Suave et al. indicated that copper phytotoxicity may be best predicted by cupric ion activity (as  $pCu^{2+}$ ) in the soil solution, which can be easily measured using a copper-ion selective electrode. To test this approach, 34 soils from the site with total copper concentrations that ranged from 30 to 1,100 ppm and pH from 3.9 to 8 were used for a series of laboratory phytotoxicity tests and to obtain soil solutions for total copper, free cupric ion activity and pH measurements. The free cupric ion activity in soil solutions was measured using an ion selective electrode in accordance with methods developed by Suave. Multiple-regression analyses demonstrate that (1)  $pCu^{2+}$ is strongly correlated with soil paste pH, total copper and, to a lesser extent, soil organic matter ( $R^2 = 0.9$ , p<0.05); and (2) the regression equation is site specific as it differs from those defined by soils from less mesic sites. In addition, 5 of the 9 phytotoxicity endpoints measured vary significantly as a function of pCu<sup>2+</sup>. These data are used as part of the ecological risk assessment process to identify the total copper and pH conditions associated with soil phytotoxicity.