

Mobility of copper in greenhouse soils

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Abstract

The mobility of copper (Cu) was studied in 13 soil samples from greenhouses in Falasarna, northwestern Crete, Greece. The spatial variability of Cu concentration in greenhouse soils and their physicochemical characteristics were examined. The results showed that the concentrations varied considerably, between 15 and 4900 ppb. Sorption and leaching experiments – kinetic and equilibrium – were conducted in uncontaminated and contaminated soils, respectively. Both leaching and sorption equilibrium experiments were performed as a function of pH. The leaching experiment results indicated that the total dissolved Cu concentration was between 10 and 15 ppb at a pH of 7.5, which is below the drinking water standards. The results suggest that the kinetics of Cu leaching were fast and the leachate concentration was relatively low, whereas Cu sorption kinetics were rapid and the sorbed concentrations were significant.

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1. Introduction

The fate and transport of Cu was examined in 13 greenhouse soils in the area of Falasarna, northwestern Crete. Falasarna (Fig. 1) is one of the most renowned beaches in Europe for its water quality and its biodiversity, both from the touristic and the ecological point of view. The area is part of NATURA 2000, a European Union environmental protection project and is used for recreational and agricultural purposes. Unfortunately, during the last decade, its ecological quality has deteriorated due to the intensive greenhouse agricultural practices that utilize agrochemicals, thus creating non-point pollution of metals and organics. Cu-based foliar sprays used in the cultivation of tomatoes have been applied extensively in the area. Depending on the soil properties and the applied concentrations, a substantial amount of Cu may leach out of the soil during rain or irrigation and eventually reach the groundwater [1].

Cu is an essential micronutrient for human, animal and plant life. However, both Cu deficiency and over-exposure may cause serious health disorders to humans [2]. The concentration upper limit of Cu in drinking water is 2 ppm and 2500 ppb in the soil [3]. The toxicity limits for a number of aquatic organisms are extremely low, in the order of 5 ppb [3]; therefore, any Cu concentrations above 5 ppb in groundwater may be responsible for

toxicity effects to aquatic life [4]. The bioavailable and therefore toxic form of Cu is its free divalent ion (Cu^{2+}). The sorbed and organically complexed forms of Cu do not pose a toxic threat to environmental quality. For acute toxicity estimation (LC50), *Daphnia pulex* has been used as the test organism [3].

The fate of Cu in soil is greatly affected by numerous parameters such as the soil type, pH, organic matter content (OM), cation exchange capacity (CEC) and the quantity of iron and aluminium hydroxides [5]. Cu creates complexes with organic matter, a process that is greatly affected by pH [3]. The presence of carbonates effectively immobilizes Cu^{2+} by buffering the soil pH [6].

The sorption of metals onto soil can be modeled using the Langmuir and Freundlich isotherms. Models that incorporate sorption on iron oxides have been developed, such as the Diffuse Layer Model (DLM), the Constant Capacitance Model and the Triple Layer Model. Additionally, metal sorption onto organic matter has been studied intensively and many mathematical models have been developed. The NICCA-Donnan model was used to simulate Cu and Cd binding in a mountain lake and in two sandy soils [7]. MINEQL+ [8], an interactive data management system for chemical equilibrium modeling, has been used in this study to model sorption of heavy metals.

The objective of this research was to determine the fate and transport of Cu in greenhouse soils. More specifically:

- to examine the spatial variability of Cu concentrations in greenhouse soil,

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Fig. 1. Aerial view of the greenhouses at Falasarna, Crete.

- to study the adsorption and leaching behaviour of Cu in soil and
- to identify the main mechanisms that control Cu mobility in soil and reduce its toxicity risk.

2. Materials and methods

2.1. Sampling protocol

Surface soil samples were collected from 13 greenhouses – one sample per greenhouse – to measure Cu concentrations. In all greenhouses tested, the main crop cultivated was tomato and Cu was used as a fungicide; KOCIDE® 2000 [57% Cu(OH)₂] was used in dilution [0.5 kg/200 L H₂O] and was applied as a spray every 10 days.

2.2. Physicochemical analysis

All soil samples were homogenised, sieved and air-dried; only the fraction <2 mm was used for the leaching and sorption experiments. Samples were analysed for the following parameters: dry bulk density and porosity [9], soil moisture (D2216-ASTM), particle size distribution (DIN ISO 11277, edition 2002-08), pH (9045A, EPA, using Orion, 9107 pH meter), redox potential, specific surface area (BET method, using a Nova 2200 Quanta Chrom analyser), chemical composition (XRF, using SRS 303) and organic matter (OM) (as Ash Free Dry Mass), organic carbon (OC), total carbon (TC) and total nitrogen (TN) (CHN analyser). The soil samples were digested using Microwave 3000 (method 3051 EPA) in order to measure the total Cu concentration. Ten milliliters of HNO₃⁻ was used for the digestion of the soil samples, after which the samples were filtered through 0.45 µm membrane filters and the pH was increased to 4.5–9.0. Anodic Stripping Voltammetry (ASV) – Trace Detect Nanoband Explorer – was then used to analyse the digested samples. The detection limit of this method for Cu is 4 µg/L. For each analysis one replicate has been used for each sample.

2.3. Quality Assurance/Quality Control

Strict Quality Assurance/Quality Control (QA-QC) guidelines were followed for the analysis of Cu by ASV. ASV was calibrated daily. A preparation blank was analyzed for every 20 samples run. A matrix matched deionized water sample was analyzed after the initial calibration, after every 10 samples and upon

completion of the analytical run. Every 10 samples, a laboratory duplicate analysis was performed. The acceptance criterion for the laboratory duplicate was 20% relative difference. Matrix spike samples were analyzed every 20 samples in order to monitor, assess and control bias resulting from sample matrix on sample digestion (if applicable to analysis type) and analysis procedures. The acceptance criterion for the matrix spike sample was 75–125% recovery.

2.4. Leaching kinetic experiments in contaminated soils

The purpose of these experiments was to study the rate of release of Cu from the soil. The experiments were conducted using the soil sample with the highest concentration (D1). Five grams of soil was added in 100 mL flasks that were then filled up to 100 mL with 0.1N NaNO₃—1:20 solid to solution ratio. All samples were placed on a shaking table for 4 days and the pH was maintained at 7.5, by adding HCl 3.7% v/v or NaOH 0.1N. The samples were centrifuged (4000 rpm) for 15 min and the supernatant was collected. The supernatant was filtered through a 0.45 µm Nylon filter and analyzed at 1, 3, 6, 10, 25, 32, 48, 56, 73 and 80 h.

2.5. Effect of pH on Cu leaching from contaminated soils

The purpose of these experiments was to evaluate the effect of pH on Cu release from the soil. Leaching experiments were performed using again the soil sample with the highest Cu concentration (D1) in order to evaluate the potential of soil to release sorbed Cu. For the experiments 5g of soil were added in 100 mL flasks that were then filled up to 100 mL with 0.1N NaNO₃. The experiments were conducted at four different pH values 5.5, 6.5, 7.5 and 8.5 at room temperature (25 °C). Each sample was run in triplicate in order to assess the experimental variability. The samples were placed on a shaking table for 4 consecutive days and analyzed.

2.6. Sorption kinetic experiments in uncontaminated soils

Sorption experiments were conducted in order to study the kinetics of Cu sorption in the soil. The sample with the lowest concentration was used (D2). The experiments were performed using the same solid to solution ratio as in the leaching experiments; the initial aqueous Cu concentration was 5 mg/L. The sampling and analysis procedure was the same as in the leaching kinetic experiment.

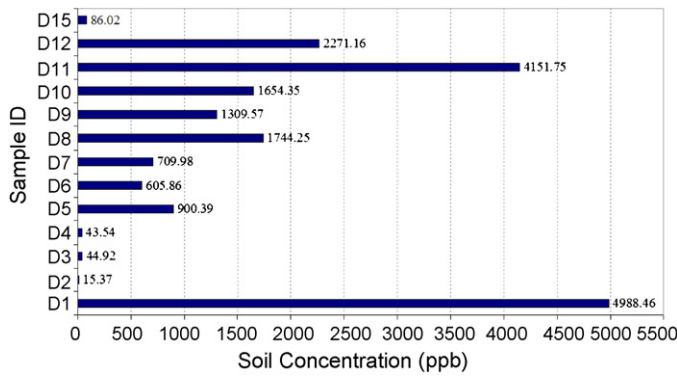


Fig. 2. Cu concentrations in soil samples.

2.7. Sorption equilibrium experiments at different pH levels in uncontaminated soils

Sorption equilibrium experiments were performed in order to estimate Cu sorption capacity of the soil. The sample with the lowest concentration was used (D2). The experiments were conducted using the same solid to solution ratio as in all the above experiments, at three different pH values – 6.5, 7.5 and 8.5 – and with initial aqueous Cu concentrations of 0.5, 1, 5, 10, 20, 30, 50, 80 and 100 mg/L. All samples were analyzed in duplicates.

3. Results

3.1. Experimental results

The total Cu concentration of the soil samples varied significantly—from 15.4 ppb (D2) to 4988.5 ppb (D1) (Fig. 2). This variability could not be correlated either with the soil physicochemical properties or with the duration of crop cultivation. More specifically, the pH of D1 and D2 were 7.4 and 7.2, respectively. For samples D1 and D2, porosities were both measured to be 40%, the soil moistures 5.1 and 5.6% and the dry bulk densities were 1.24 and 1.44 g cm⁻³, respectively. The D1 and D2 inorganic carbon content was 5.11 and 4.33% and the organic carbon content was 1.82 and 0.98%, respectively. Sample D1 had higher CaO, Fe₂O₃ and Al₂O₃ concentrations (Table 1). The higher oxide concentrations suggest higher number of surface sites for sorption.

Fig. 3 presents the results of the leaching kinetic experiment. During the first 8 h of the experiment, Cu concentration was below the ASV detection limit and after that it was fluctuating from 10 to 14 ppb. The equilibrium concentration was relatively low (12 ppb); only 0.24% of the soil Cu was leached out at pH 7.5. The equilibrium leaching experiment indicated

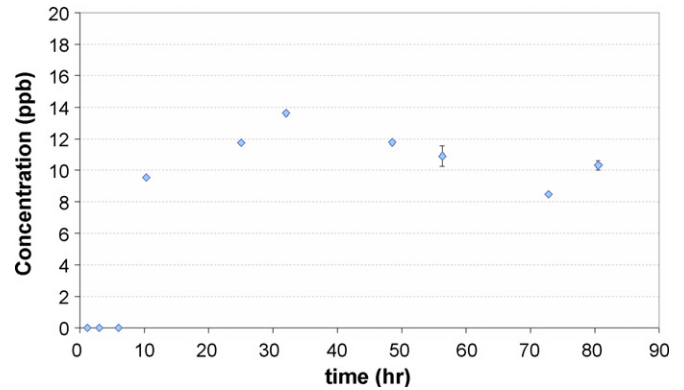


Fig. 3. Leaching kinetic experimental results.

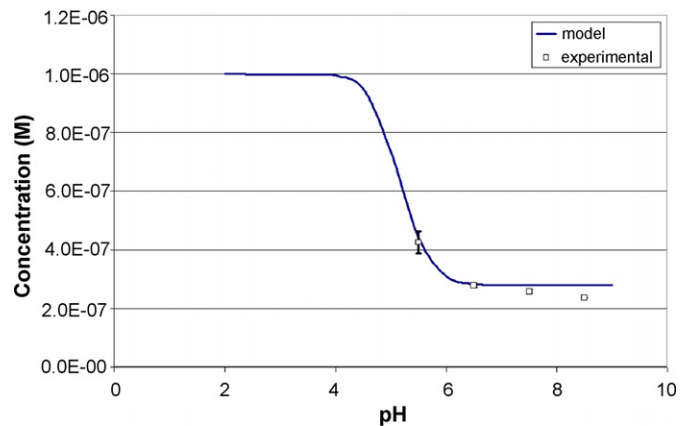


Fig. 4. Effect of pH on Cu leaching from contaminated soil and modeling results.

that leachate concentrations decrease substantially with increasing pH (Fig. 4). Desorbed Cu increased as pH decreased due to the increase of positively charged sorption sites [10].

Sorption equilibrium was reached within 70 h (Fig. 5). The equilibrium concentration was 200 ppb; only 4% of the initial concentration remained in solution. The kinetic sorption experiment was modeled using a first-order decay kinetic. The rate constant was found to be 0.029 h⁻¹ and the equation that described Cu concentration (*C*) in solution with time was $C = 2097.5 e^{-0.029t}$. The fitting of the data satisfies the R^2 ($R^2 > 0.9$). The Student's *t*-test also shows that the results are within the 90% confidence intervals for 9 degrees of freedom. Therefore, the exponential decline equation simulates adequately the experimental data. The results of the equilibrium sorption isotherm experiments are presented in Fig. 6. More specifically *q*, the sorbed concentration of Cu per mass of soil versus aqueous Cu concentration is shown. Cu sorption onto the soil increases with increasing pH, due to the increase of negatively charged adsorption sites, to the reduction of competition

Table 1
Chemical composition (%) (XRF analysis) of soil samples

| | MgO | K ₂ O | CaO | TiO ₂ | MnO | Fe ₂ O ₃ | Al ₂ O ₃ | SiO ₂ | P ₂ O ₅ | LOI |
|----|------|------------------|------|------------------|------|--------------------------------|--------------------------------|------------------|-------------------------------|------|
| D1 | 0.67 | 0.23 | 5.70 | 0.07 | 0.02 | 0.63 | 1.71 | 9.72 | 0.03 | 2.09 |
| D4 | 0.35 | 0.23 | 3.15 | 0.05 | 0.02 | 0.51 | 1.42 | 9.56 | 0.02 | 1.48 |

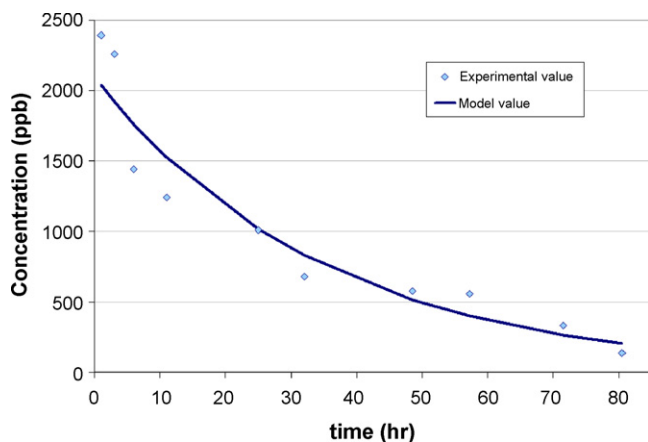


Fig. 5. Sorption kinetic experimental and modeling results.

with H^+ ions and to the changes in Cu hydrolysis in solutions [11,12].

3.2. Modeling copper leaching

MINEQL+ [8] was used to simulate the leaching of Cu from the soil at different pH levels. MINEQL+ utilizes surface complexation processes to model the adsorption of metals onto both iron oxide coatings and soil organic matter. The Triple Layer Model surface complexation formulation was used. The parameters affecting Cu leaching from soil were calibrated to fit the experimental data. The model simulation is presented in Fig. 4. The root mean square error (RMSE) was estimated to be 2.59×10^{-8} M and the R^2 was 0.9.

3.3. Modeling copper sorption

The Freundlich and Langmuir isotherms could not simulate adequately the experimental data; neither did the Triple Layer Model (TLM) surface complexation formulation. Interestingly, the Langmuir isotherm was able to simulate sorption at low metal concentrations where monolayer adsorption was still taking place. As the concentration increased, sorption followed

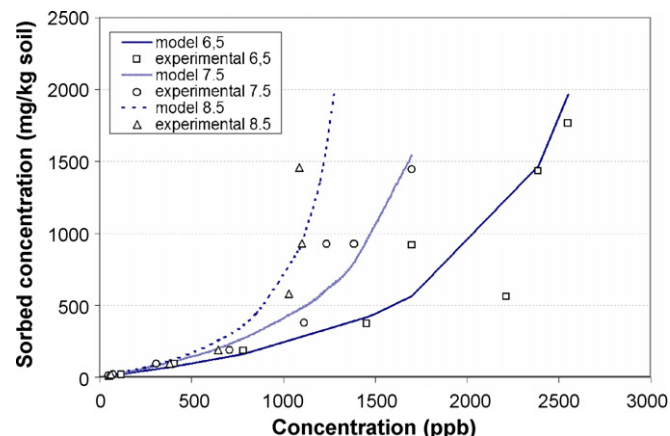


Fig. 6. Sorption equilibrium experimental and modeling results at three pH levels.

a Freundlich isotherm and as metal concentration was further increased, metal precipitation dominated the sorption process. The surface complexation model could not simulate sorption and surface precipitation. To overcome this problem adsorption reactions and surface precipitation were considered in multiple layers. This was accomplished by considering surface complexation reactions and surface precipitation at a constant pH [13], which resulted in the linearized form of the BET isotherm (Eq. (1)):

$$\frac{c_{eq}}{(c_s - c_{eq})q} = \frac{1}{Bb} + \left(\frac{B-1}{Bb} \right) \left(\frac{c_{eq}}{c_s} \right) \quad (1)$$

where q is the mg of sorbed Cu per kg of soil, C_{eq} the sorbed Cu concentration (ppb), B the constant which relates to the interaction energy with the surface, constant b the maximum monolayer sorbed coverage and C_s is the saturation concentration (ppb).

The BET model did simulate the transition between the sorption and surface precipitation of Cu on the soil. Using the BET equation, the first step was the calibration of C_s by fitting the model to the experimental data. Then the least square method was used to estimate the constants B and b . C_s ranged from 480 to 1600 ppm for pH 8.5 and 6.5, respectively; B ranged from -499 to -299 and constant b from $-501,002$ to $-334,448$. There was a decreasing linear relation between C_s and pH. The BET isotherm simulated adequately the experimental results ($R^2 > 0.8$) (Fig. 6). Under acidic conditions, Cu was adsorbed in the exchangeable form, while at higher pH, surface precipitation was occurring [14].

According to the Cu solubility diagram as a function of pH [15], for total Cu concentration of 0.01 M and for pH greater than 5, Cu precipitates in the form of tenorite (CuO). The sorption equilibrium experiments were conducted using even lower initial total dissolved Cu concentration (7.46×10^{-6} to 1.16×10^{-3} M) and pH varied within 6.5–8.5. Therefore, according to the Cu solubility diagram as a function of pH tenorite constituted the main precipitated Cu species.

4. Conclusions

The concentrations of Cu in the analyzed soil samples were considerably very high. Forty-three percent of the samples had Cu concentration above 1000 ppb which is greater than the upper limits for urban areas for direct exposure according to the work of Boulanger and Nikolaidis [3] and concentrations similar to industrialized areas in Greece such as Lavrion. Leaching experiments indicated that the total dissolved Cu concentration leached was between 10 and 15 ppb at pH 7.5, which was below the drinking water standards. Cu leaching from the soil was limited and its kinetics was fast. Cu sorbed rapidly and to great extent on uncontaminated soils. Cu sorption/precipitation was successfully modeled using the BET isotherm. At high aqueous concentrations, the main removal mechanism was surface precipitation and the precipitated mineral was primarily tenorite.

Acknowledgements

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