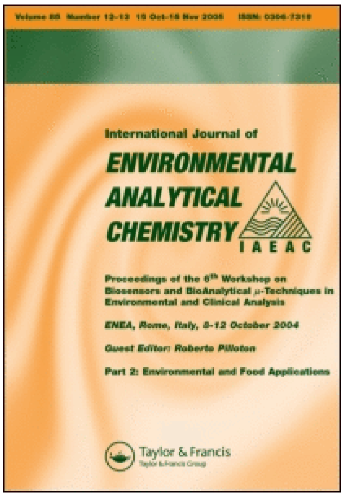

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Gupta, S. , Blatter, A. and Häni, H.(1988) 'Concentration of Ionic Copper in Soil Solution', International Journal of Environmental Analytical Chemistry, 34: 1, 45 — 50
To link to this Article: DOI: 10.1080/03067318808029920
URL: http://dx.doi.org/10.1080/03067318808029920

Intern. J. Environ. Anal. Chem., Vol. 34, pp. 45–50
Reprints available directly from the publisher
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Printed in Great Britain

Concentration of Ionic Copper in Soil Solution

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(*Received 10 December* 1987; *in final form 4 February 1988*)

The ecological relevance of heavy metals in soils cannot accurately be judged by the total metal content, although it is the best indicator for the degree of metal saturation of a given soil. However, metal concentration and metal forms in soil solution are of great significance for assessment of their impact on plants and soil microorganisms.

Soil solution has been simulated by a neutral salt extract (i.e. $NaNO_3$) of soil. Prediction of metal impact on a given plant and on the growth and activities of soil microorganisms could be made with a satisfactory accuracy irrespective of large differences in physiobiochemical properties of soils. In order to improve the accuracy of such prediction, it is very important to understand the distribution of a metal in soil solution.

With the help of analytical techniques like atomic absorption spectroscopy and ion chromatography, it is possible to differentiate three following operational forms of a metal in a given soil solution: (1) Total soluble; (2) Ionic and labile charged complexes; (3) Molecular and uncharged complexes.

The results show that the total soluble copper in fourteen investigated vineyards soils range between 0.5 to 1.85 mg/kg soil. The ionic copper as percent of the total soluble copper varied between 36 to 68 %. Because pH values of these soils were very close to each other, it is reasonable to assume that the large variation in ionic copper could be due to differences in the soluble organic ligands concentration in these soils. Further research work is needed to show the relevance of forms of copper for the growth of vineyards and soil microorganisms.

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*Presented at the 5th Symposium on Ion Chromatography, Sils Maria, Oct. 1987.

INTRODUCTION

Native and/or anthropogenic heavy metals of soils are distributed in soil-solid and soil-solution phases. The relative distribution of metals in either of the phases is the net result of several physiobiochemical reactions occuring in soils. The binding mechanisms and binding strength of heavy metals with soil solid or with soluble ligands in soil solution are manifold and quite variable.

The metal concentrations in soil-solution phase, which is usually simulated by salt solutions such as $NaNO_3$[3,4,5] or $CaCl_2$[8] or saturation extracts[1] are very important from the ecological point of view because it is the part of soil metal which is available to plant roots and soil microorganisms. In polluted soil, the metal concentration in soil solution could be larger as compared to an unpolluted soil having similar physiobiochemical characteristics.

The distribution of metal species in soil-solids or in soil-solution are regulated by the processes such as precipitation, adsorption, complex formation, ion pair formation and pH.[2] Studies of metal speciation in soil-solid are restricted due to complexity of physiobiochemical and often unknown reaction kinetics. However, there are proposals to estimate it either by fractionation[8] or by calculation using physicochemical constants.[2]

By using different analytical techniques, in contrast, the forms of metals in soil solution could be determined. In this context, ion specific electrodes have played an important role. In spite of the fact that this technique is very elegant, it has failed in soils and especially in polluted soils to determine the ionic species of a metal because of poisoning of the electrode surface. Ion chromatography technique needs to be tested for such purposes.

In this paper, we have attempted to measure and define three operational forms, which are measurable with the help of atomic absorption spectroscopy and ion chromatography of copper in $NaNO_3$-extracts of vineyard soils. Usefulness of such analysis for better interpretation of heavy metal guidelines, which are based on metal concentration in $NaNO_3$-extracts are also discussed.

EXPERIMENTAL

Fourteen selected vineyard soil samples are analysed for $NaNO_3$-soluble copper concentration with the help of atomic absorption and ion chromatography. A 20 g dry soil sample is mixed with 50 ml 0.1 M $NaNO_3$ solution. Shaken for 2 hours and filtered through a membrane filter paper (0.45 μ). Detection limit is 0.5 mg Cu/kg dry soil.

Perkin Elmer 420 was used for atomic absorption studies. Dionex 2010i with separator column HPIC-CS5 and concentrator column HPICCG2 was employed for ion chromatography. Oxalic acid (0.05 M, pH 4.8) (adjusted with LiOH) was used as eluent. Flow rate was maintained to 1 ml per minute and PAR-reagent was used for color development. Dry soil (0.1 mg of Cu/kg) could be analyzed by this technique.

The Cu determined by atomic absorption spectroscopy is operationally termed as *total soluble copper*. Whereas, Cu determined by ion chromatography is termed as *ionic and part of the labile charged complexes*. The difference between these two measured values is termed as *molecular and uncharged complex*.

RESULTS AND DISCUSSION

The copper concentration in fourteen soil solutions ($NaNO_3$-extracts) measured by two analytical techniques, are reported in Table 1. In spite of the limitations of atomic absorption spectroscopy and ion chromatography, the determined concentrations have been classified in three operational groups (Table 1 and Figure 1):

1) Total soluble metal (atomic absorption).
2) Ionic and part of the labile charged complexes (ion chromatography).
3) Molecular and uncharged complexes (difference between atomic absorption and ion chromatography).

The total soluble copper concentration measured by atomic absorption ranged between 0.5 to 1.8 mg Cu/kg dry soil. The ionic copper (as % of the total Cu) in investigated soils varied in the range of 36 to 68%. It has to be noted that except in few soils the copper contents in soil solution do not exceed 1.4 mg Cu/kg dry soil, which has been reported to be critical for the growth of red clover

Table 1 Distribution of native and anthropogenic copper in soil solutions ($NaNO_3$-extracts) of fourteen different vineyards

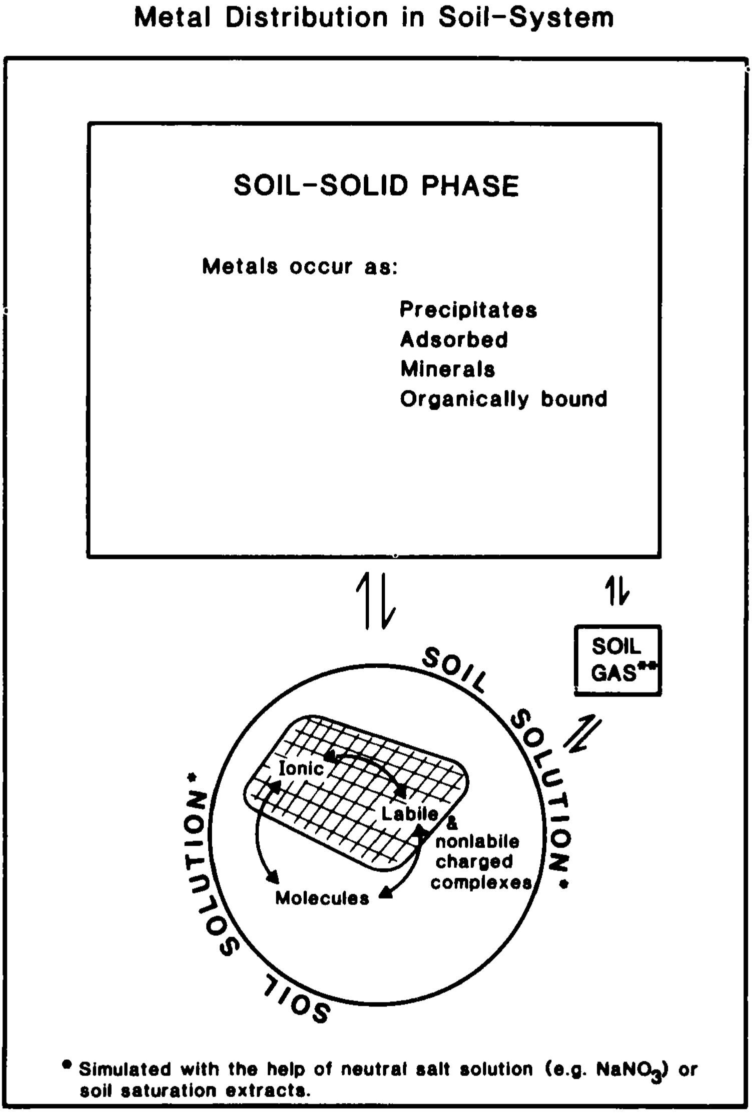
Soil characteristics			*$NaNO_3$-soluble metals (mg/kg soil)* *Copper*			*Ionic copper*[b] *(as % of the total soluble copper)*
No.	*pH*	*Type*	*Soluble*[a] *(total)*	*Ions*[b]	*Molecular*[c]	
1.	7.0	Loamy	0.87	0.52	0.35	60
2.	7.2	Loamy	0.50	0.31	0.19	62
3.	7.0	Loamy	1.07	0.73	0.34	68
4.	7.2	Loamy	1.52	1.0	0.52	66
5.	7.0	Sandy loam	0.77	0.45	0.32	58
6.	7.3	Sandy loam	1.07	0.65	0.42	61
7.	7.3	Sandy loam	0.82	0.53	0.29	65
8.	7.2	Sandy loam	1.72	0.88	0.84	51
9.	7.2	Sandy loam	1.37	0.72	0.65	53
10.	7.3	Sandy loam	1.37	0.74	0.63	54
11.	7.5	Sandy loam	0.67	0.39	0.28	58
12.	7.3	Sandy loam	1.77	0.63	1.14	36
13.	7.4	Sandy loam	1.87	0.74	1.13	39
14.	7.6	Sandy loam	0.57	0.36	0.21	63

[a] Soluble (total) measured through atomic absorption spectroscopy.

[b] Ionic and partly labile charged complexes measured through ion chromatography.

[c] Molecular and uncharged complexes is the difference between soluble (total) and ionic and partly labile charged complexes.

plants.[4,6] The ionic and part of the labile charged complexes of copper measured by ion chromatography are lower than the total soluble metal content (Table 1). Results show that a part of the copper is bound with organic ligands which are non-labile and thus could not be measured by ion chromatography (Table 1). The ionic copper concentration in soil solution varies significantly among soils, which could depend upon the amount and forms of organic ligands in soil extracts. It is the best indicator for copper intensity. Further, it has been reported that free ion concentration of copper is better correlated with the growth of American Oyster compared to the total copper content.[7] In case of cadmium, it has been reported that its ionic concentration in soil solution is better related with the



* Simulated with the help of neutral salt solution (e.g. $NaNO_3$) or soil saturation extracts.

** A small portion of total Hg and Se is exceptionally found in gaseous phase of soil.

Figure 1 Metal distribution in soil system.

growth and activities of microorganisms[4,5] than total Cd concentration in soil solution.

SIGNIFICANCE OF THE RESULTS

Total metal concentration either in salt extracts of soils or saturation extracts, probably allows the best estimate of the deleterious effects of metals on soil microorganisms and plants.[1,2,4,5,7–9] In case of some metals like copper, the prediction of deleterious effect could be improved with the knowledge about forms of metals in soil solution. Such knowledge would also help in better understanding of competetive relationships of metal in contaminated soils and their consequences on soil microorganisms and plants grown on them.[4–6]

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