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Publisher *Taylor & Francis*

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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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P. Del Castilho^a; I. Rix^b

^a DLO-Institute for Soil Fertility Research, Haren, RA, The Netherlands ^b Laboratory of the Government Chemist, Teddington, United Kingdom

To cite this Article Castilho, P. Del and Rix, I.(1993) 'Ammonium Acetate Extraction for Soil Heavy Metal Speciation; Model Aided Soil Test Interpretation', International Journal of Environmental Analytical Chemistry, 51: 1, 59 – 64

To link to this Article: DOI: 10.1080/03067319308027611

URL: <http://dx.doi.org/10.1080/03067319308027611>

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AMMONIUM ACETATE EXTRACTION FOR SOIL HEAVY METAL SPECIATION; MODEL AIDED SOIL TEST INTERPRETATION

P. DEL CASTILHO

*DLO-Institute for Soil Fertility Research, P.O.B. 30003, 9750 RA Haren, The
Netherlands*

I. RIX

*Laboratory of the Government Chemist, Queens Road, Teddington TW11 0LY, United
Kingdom*

(Received in final form, 17 July 1992)

The availability of cations in soil is a function of their solubilities and dissolution rate as they affect ionic activities in the soil solution over time. In practice this is time consuming to measure and a simpler approach focussed on exchangeable metals is chosen. It is believed that exchangeable metals in soil are most available to plants. Ammonium acetate extraction of soil and subsequent determination of extracted cation concentrations has been used widely to extract "exchangeable" ions. In the following review the suitability of this extraction method to predict heavy metal availability is discussed. It is recommended that extraction methods be supported with theory originating from soil chemistry and physics.

KEY WORDS: Soil, cation exchange, ammonium acetate, soil testing, heavy metals, modelling.

INTRODUCTION

Much agricultural land is polluted to a lesser or greater extent and it is necessary to be able to predict the availability of heavy metals for plant uptake. Two approaches exist to resolve this problem in modern soil science; the design of soil tests and (thermodynamic) models which include kinetic considerations.

The design of a soil test is based on concepts. It is usually postulated that the metal is divided over several different pools, *not* interacting with each other. The metal bond strengths from the pools vary between fractions defined as "water soluble", "exchangeable", "strongly sorbed", "occluded by or coprecipitated by metal oxides, carbonates and phosphates" and "residual" (crystal lattice bound in primary minerals). The possible ways that heavy metals may be retained by soil sites and in soil components are summarised in Table 1.

Table 1 Summary of different ways of retention of cations in soils. The process to release the cation in the soil solution is indicated.

<i>RETENTION MODE</i>	<i>PROCESS</i>
ION EXCHANGE	$S^-M^{2+} + N^{2+} \leftrightarrow S^-N^{2+} + M^{2+}$
CRYSTAL LATTICE	$+ HF \rightarrow M^{2+}$
(CO-)PRECIPITATE	Carbonate/hydroxide, acid dissolution
ADSORPTION	$S.M^{2+} \leftrightarrow S. + M^{2+}$

Water soluble and exchangeable bound heavy metals in soil deserve special attention because they are assumed to be readily available for plant roots.

The applicability of a soil test is proven empirically. The criterium is an acceptable correlation between soil test results and plant response (greenhouse, field plots). The use of a particular test is usually restricted to a certain soil type, heavy metal and type of crop.

Much work has been carried out on the development of quick soil tests to measure the soluble/exchangeable metal concentration.

Several factors govern the exchangeable trace element concentrations for soils. For one particular soil, a test result for "exchangeable" trace metals will depend on pH, ionic strength, redox potential, type of cations and anions in the extraction suspension. Also factors as the degree of acid precipitation, fertilizer treatment, manuring, decomposition state of plant roots, etc. will influence the exchangeable metal levels. Between different soils there may be a variation in kinetic controlled reactions having an effect on the "exchangeable" trace metal concentrations. One must pay attention to the possibility that soils from the same region may differ from each other as to their behaviour in a given soil test. Soils from different regions may differ so much (e.g. loam, sand, and clay with large differences in e.g. effective diffusion rates) that different extractants and procedures might be needed to obtain acceptable correlation with plant uptake.

Finally plant response itself, apart from differences amongst types of plants, is a complicating factor: it includes yearly variation in rooting depth, local variations in physical circumstances such as water table, and biological circumstances in the rhizosphere (bacterial and fungal action).

The above discussion supports the statement that a soil test is merely an operationally defined procedure which use is accepted if sufficient correlation with plant response is obtained.

The thermodynamic chemical potential of a trace metal ion through season should be known by measurement and/or calculation¹. The measurement by ion-selective electrodes is hampered by the often low ion activities. The model calculation is possible after defining the system, however this definition is also hampered by the fact that metals may be in partial equilibrium between different compounds in the solid and soil solution phase. Complete equilibrium is not reached when thermodynamically favorable reactions are blocked or proceed very slowly. A further complicating factor is that the necessary stability constants are not always precisely known. However knowledge is increasing making this approach more valid.

It is proposed to soil chemists that a more indepth and theoretical support for soil testing

based on modern soil science is needed. The ammonium acetate extraction will be discussed as a specific example of a soil test.

Heavy metals in the soil solution, and soil extracts

A soil extract obtained in the laboratory can be regarded as a soil solution under special field conditions: the special conditions are governed by the choice of a given test. The measurement of trace metals in the soil solution from the field, in laboratory soil extracts, and the use of models, including model aided soil test interpretation (MASTI) to predict heavy metal availability for plants will be discussed.

1. *Soil solution heavy metals.* The concentration of trace metals in the soil solution at one moment can approximatively be estimated by using thermodynamic or sorption models including relevant soil and soil solution data, and by direct measurement^{2,3}. In these studies soil solution was obtained by centrifugation of field moist soil samples over a paper filter and collection of the centrifugates. A hundred-fold variation in Cd and Zn soil solution concentration (centrifugate) was observed in an acid loamy sand soil during one season. Dissolved organic carbon (DOC) and pH in the soil solution were the most important parameters influencing soil solution trace metal concentrations. Only one sampling and heavy metal determination of the soil solution is insufficient to assess availability of trace metals to plants; the availability is more likely an integration of successive soil solution trace metal concentrations combined with a plant response function.

The availability for plants of trace metals in soils depends on concentration in, and translocation velocity over the soil solution-plant root interface. The uptake may have a negative effect on the crops quality, and/or growth. Translocation velocity may depend on the type of metal, percentage of pore water saturation, size of pores, growth stage of the plant, etc. Plant roots excrete acids, bases, including complexing substances regulating the ion activity of necessary nutrients and micropollutants by interaction with the soil solid phase. The most readily reacting part of the soil solid phase is the exchanger phase. Low soil organic matter levels are sufficient to exceed the exchange capacity from mineral matter. Metal solubility is regulated together with relevant soil solution parameters (pH, DOC and electrical conductivity as gross parameters).

Although the measurement of soil solution parameters at different times in a season combined with a model interpretation, may lead to acceptable predictions, a quicker approach may be desirable employing extraction and measurement of trace metals, using well defined pH, DOC, redox and EC conditions; eventually followed by MASTI.

2. *Soil extract for exchangeable heavy metals.* The previous discussion confirms that it makes sense to design a test aimed at the determination of "exchangeable" trace metals. This can be achieved by shaking a soil sample with a solution containing exchanging cations (e.g. ammonium, or calcium ions) and measuring the displaced ions in the extraction solution obtained.

Some practical aspects of soil tests for the determination of "exchangeable" trace metals should be considered. First of all one could try to make an inventory of the exchanger phases

present. Often this can be done considering available knowledge from past soil surveys. In the great majority of the cases it is concluded that study of the fine particulate matter with its extremely large relative surface (and exchanger site density) is sufficient (e.g. < 50 or $< 16 \mu\text{m}$). So it is proposed that the coarser material is separated from this fine matter before running a test. This approach removes the need to consider the arguments posed by soil grinding.

The contact time of an exchange experiment must be established. Ion exchange is a fast process (ms or μs), so diffusion from the soil pores, or the soil surface diffusion layer is the rate determining process.

Even at high stirring rates the time scale of diffusion-controlled ion exchange is in the order of 1 second or longer. Batch experiments with a solid exchanger needed 3 hours to study the displacement from solutions to a solid exchanger phase⁴.

Ammonium acetate extraction

The following discussion examines why ammonium acetate might be used and which selectivity problems arise.

Ammonium acetate solutions regrettably do not act merely as an ion exchanger but also promote dissolution of solid phases, however much less than the more aggressive media. It has been suggested that ammonium acetate removes chromium and zinc from sites on organic matter but also from iron oxides⁵; this extractant can also dissolve oxide coatings in the hydrous oxide fraction⁶, and ammonium chloride or acetate can dissolve or complex transition metals from coatings on sediment grains^{7,8}. It has also been added to other, stronger extractants to block the undesired re-adsorption of the trace metals released by the stronger extractants^{9,10}.

Ammonium acetate and other ammonium salt solution extractions at pH 7 are carried out in batch¹¹ (USA) or column^{6,7,8} and are widely used to measure soil cation-exchange capacity (CEC), or exchangeable ions. These extraction solutions are chosen because they are well buffered, the ammonium ion blocks the slow release of interlamellar cations from the weathered periphery of clay lamellae¹², it gives a sharp CEC; and because excess ammonium acetate can be disposed of relatively easily by oxidation or ignition (e.g. Aqua Regia or Schöniger flasks). Acid 1 M ammonium acetate (pH 2.5) has been used to measure "ion-exchangeable" trace metals⁹, and, at pH 6.7 or pH 7, to measure "exchangeable", "exchangeable non-specific" or "ion-exchangeable" trace metals^{5,9,13-17}; 5 M ammonium chloride at pH 8 has been used to measure "exchangeable" cations⁶, and 0.5 M calcium acetate to measure "exchangeable" copper¹⁸. According to Cottenie and Verloo¹⁹ the use of 1 M ammonium acetate at pH 7 is only suitable for investigation of very polluted soils owing to the lack of sensitive measurement technique for the determination of low trace element content (excepted for zinc). However the use of stronger extractants and lower pH bringing more trace elements into solution may change the soil conditions greatly and dissolve soil minerals to such extent that the extracted metal concentrations have little relationship with the amount removed by plants²⁰.

In The Netherlands many agricultural soils have a nearly neutral pH_{KCl} , by natural composition or by the widely used practice of adding Ca/Mg carbonates to adjust the pH to

6.2 $< \text{pH}_{\text{KCl}} < 7$. Under these circumstances a well buffered salt solution appears to be attractive to extract soil by the action of ion-exchange without pH change. Nitrate, chloride or acetate salts all seem suitable for the purpose. Ammonium acetate is a main component²¹ of pig slurry liquid and pig slurry is frequently used in The Netherlands as a fertilizer. Thus an ammonium acetate extraction simulates the first effects of such manuring practice on the dissolution/exchange of heavy metals from soil surfaces. It has the advantage, compared with low ionic strength extractions (e.g. 0.01 — 0.1 M CaCl_2), that owing to the high ionic strength (1 mole L^{-1}) readsorption is not likely to occur.

Model aided soil test interpretation (MASTI)

If one intends to simulate the results of a soil test using a chemical model, a 1 M ammonium acetate solution has the advantage over combined extractants (e.g. salt with pH-buffer and strong complexant) that only a single salt is introduced. The test results should be more easily modelled in this simple case.

Modelling may help to interpret soil test results. Instead of relying on one test result and considering it as the final answer, one might consider the following thoughts: would not MASTI lead to better results than the result of soil tests alone? We have to admit that in practice soil scientists will give an advice on fertilization using their knowledge and the test, not the test result only. In fact this “knowledge” should always be incorporated in the interpretation of a test result. In soil chemistry a soil is considered as a chemical reactor and so an extraction experiment shows the result of a chemical reaction between soil and the selected extractant. To build a chemical model information is needed (based on measurements, or on knowledge of soil characteristics). It is recommended that a set of consecutive tests (e.g. same extractant at different pH but with same ionic strength) be performed at the early stage of MASTI. Modelling is improving. Successful predictions for heavy metal solubility have been achieved already and models are still being improved. Therefore we recommend to investigate further the possibilities offered which are promising.

CONCLUSION

The availability of a micronutrient for a plant is difficult to establish. It depends on the plant life's integrated thermodynamic potential of relevant micro and macronutrient chemical species in a biological active soil rhizosphere. From a chemists point of view there are at least 3 alternative ways to estimate availability: 1) a validated model calculation of the integrated micronutrient chemical potential, 2) a validated soil test, and 3) a hybrid approach where a model is used to better understand the soil test results. For the development of the last approach combined chemical soil testing and modelling studies results should be conducted.

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