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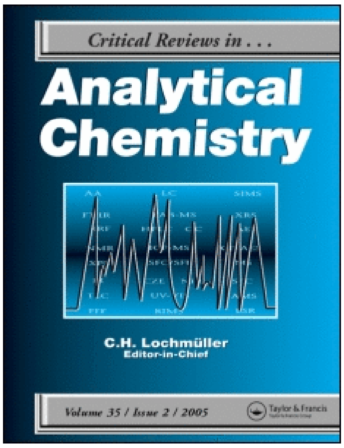

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SELECTIVE CHEMICAL EXTRACTION OF SOIL COMPONENTS AND BOUND METAL SPECIES

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I. INTRODUCTION

A. Background

Soils and sediments are basic components of our environment, as they provide nurture for living matter and serve as "sinks" for deleterious species. The composition of these materials reflects the nature of the original base rock, the degree of degradation and leaching introduced by weathering cycles, and the influence of external inputs such as plant debris or contamination introduced by human activities, and accordingly varies greatly between geographical regions or the horizon sampled.

For the purpose of this article it should suffice to describe soils and sediments as complex mixtures of mineral fragments and decomposition products, with the component particles having sizes ranging from >0.2 cm diameter (gravel) to <2 μm diameter (clays).

The ability of the soils to provide nutrients (and in some cases retain toxic materials) influences plant growth. Uptake by the plant can involve intermediate steps, such as transfer of ions or complexes into the adjacent "soil solution", and it has been a longstanding aim to devise analytical procedures which effectively simulate the natural "extraction" by plants or "distribution" processes.

The nutrients (or toxic materials) of interest can be components of mineral lattices (e.g., K^+ in micas) or be held on the surfaces of the various solid phases. Where adsorption is the more important process, plant availability can be determined, to a large extent, by the proportion of "clay-sized" material in the solid phase, since this component (composed primarily of alumino-silicate minerals, organic matter, and hydrous oxides of Fe, Al, Mn) provides an extremely large surface area per unit weight.

With both soil and waterway sediments, elements of interest can be present in several different chemical forms and be associated with a range of components. (Figure 1). The mode of bonding and ease of release into an aqueous phase are variable and subject to changes induced by chemical interactions.

This heterogeneity creates problems in any attempt to establish a simple procedure (e.g., chemical extraction), which adequately represents the ability of living matter to extract nutrients or toxic materials from different types of soil. For example, it is difficult to define the fraction(s) most appropriate to the problem under consideration. The usual practical approach is to conduct pot trials in which plant uptakes are correlated with the analytical results obtained using a range of soil analysis procedures. As shown in Section II, consistent conclusions are not necessarily derived from this approach.

Some of the variations may be attributable to incomplete understanding of the chemical processes associated with the release of nutrients or toxic materials from the various components. This area of uncertainty should shrink as more studies are made on

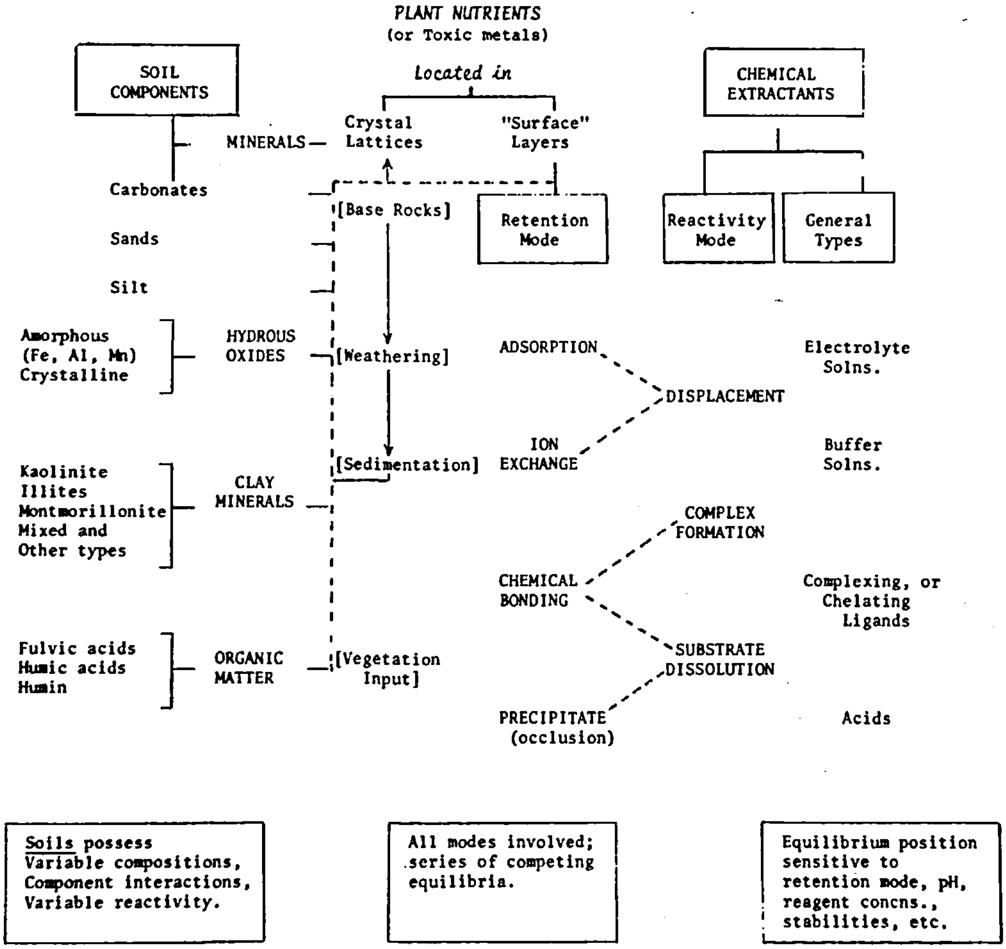


FIGURE 1. Diagrammatic representation of the relationship between retention mode of metal ions and nature of soil components, showing possible roles for chemical extractant solutions.

topics such as behavior in the root zone and factors which influence solute distributions.

In this review, discussion is centered on heavy metal distributions, partly because this is a research interest of the author; partly because it is an area of increasing interest (e.g., in pollution evaluation); and partly because the behavior of major nutrients has been previously documented, e.g., in cation exchange capacity studies.

The concept that "availability to plants" is reflected in the "exchangeable content" value possibly applies reasonably well in the case of major nutrients (K, Ca, Mg), since there is only a limited tendency to form stable complexes or insoluble precipitates under environmental conditions. The same statement cannot be applied to micronutrients such as Cu, Zn, or potential toxic materials (Cd, Pb).

B. Soil/Sediment Analysis

The diverse approaches adopted in soil/sediment studies can be explained, in part, by investigators having different specific aims.

In preceding paragraphs comment has been made on the evaluation of "available levels", a topic of interest to agricultural scientists. Other important activities in this area are classification of soil types, identification of nutrient deficient zones, and clarification of origins or weathering patterns. For many of these purposes, determination of the elemental composition using a suitable modern instrumental procedure is totally adequate. Routine processing of samples using direct reading emission spectroscopy and X-ray fluorescence is firmly established, and spark source mass spectrometry has been shown[1] recently to be applicable to the determination of over 50 elements. The elemental values are often supplemented by information on actual mineral contents, as derived from X-ray diffraction studies, electron microscopy, infrared spectroscopy, and thermal analysis. Any organic content (customarily reported in terms of percent C, H, N, etc.) can also be more specifically defined through application of physical methods such as infrared spectroscopy, pyrolysis gas chromatography, thermal analysis, etc.

Elemental analysis can also be used to identify zones possessing content levels higher than background, as sought by geochemical prospectors and environmental pollution monitors. For the identification of trends or "abnormalities", the use of "absolute" or "total values" has been judged, by some, to provide information of no greater value than the comparative results obtained using simpler procedures, for example, analysis of acid extracts using atomic absorption spectroscopy.

The analytical values obtained using acids or other extractant solutions are usually smaller than the content values derived from total sample elemental analysis, and the results vary with the actual experimental procedure adopted. This is not a surprising observation, since, as shown in Figure 1, the extractant can serve many roles. It can cause dissolution of solids, reversal of chemical reactions, formation of stable nonadsorbed complexes, and/or displacement of adsorbed or ion-exchangeable material. The choice of extractant can be based on analogy (e.g., with cation exchange capacity determinations) or on the results of comparison studies (sometimes validated with plant uptake determinations). Some approaches even appear to be totally empirical.

The need to clearly define the analytical problem and specify the object of the analysis will become increasingly important in the future. It is predicted that legal cases (dealing with, say, pollution problems) eventually will require clearer resolution of the "degree of availability" of toxic materials and possibly absolute specification of the chemical form responsible for undesirable effects. Advances in agricultural practice could place additional emphasis on the influence of chemical treatments on nutrient mobility.

It is believed that there will be much greater demand for valid analyses, that is, values for species which have direct relevance to the total problem under consideration. Species identification (as distinct from elemental values) presents many major challenges, particularly with matrices as complex and varied as soils/sediments. On the other hand, improved understanding of the underlying chemical processes should permit more critical judgments to be made (in respect to both extractant selection and data interpretation) and, in turn, it may promote the development of more "speciation" or "fractionation" procedures.

C. Chemical Environment Effects

The evaluation of the cation exchange capacity (CEC) of soil/sediment samples normally involves measuring the amount of Ca^{2+}, Mg^{2+}, K^+, Na^+, (Al^{3+}), and (Mn^{2+}) displaced on treating suspensions of the solid with a selected chemical solution. Use of a simple salt solution (e.g., M KCl or NH_4Cl) gives values for the CEC at the natural pH of the sample. The capacity at some specified pH is estimated by using an appropriate buffer solution (e.g., NH_4OAc adjusted to pH 4.8 or 7.0; $Ba(OAc)_2$ at pH 7.0 or 8.2; $BaCl_2$-triethanolamine mixtures of pH 8.2; etc.). With the buffer system approach one can also determine a total acidity value by titrating aliquots of the extracts back to the initial sediment in suspension value. As discussed later, capacity varies with pH and the acidity value is considered to provide a measure of the fraction of the total CEC which may be assigned to pH-dependent surface charges.

The many factors which can influence CEC values and the numerous procedure variants which have been adopted have been recently reviewed and assessed.[2] It was concluded that the selection of a method for a particular study should be based on the parameter sought. In other words, the analytical problem must be first defined, i.e., does the investigation require evaluation of the exchange capacity at the natural pH, or at some other pH?; is the variation with pH an important consideration?, and so on.

The determination of the CEC tends to be a regular component of sediment quality evaluations, and its inclusion can be defended readily in situations where the topic of concern is release of soluble species on contact of particles with electrolyte solutions, e.g., stream suspended matter meeting salt water in estuary regions. The data may not be completely relevant, however, because in environmental situations the aqueous phase can contain a series of natural ligands.

The amount of soluble humic material appears to be greatest in poorly drained soils,[3] and studies of the amount of Cu, Co, Fe, Mn, and Ni present in the fulvic acid fraction of one group of soils has been found[4] to be similar to that extracted from the whole soil by 0.05 *M* EDTA. In another investigation, the amount of copper extracted from some subsoils by this chelating agent (and also by diethylenetriaminepentaacetic acid [DTPA]) was found to be only slightly greater than the amount released by 0.1 *M* solution (pH 7) of the naturally occurring chelating agent, 2-ketogluconic acid.

This kind of evidence can be used to sustain the argument that extraction with chelating agents allows one to clearly distinguish between total values and "leachable" fractions. For example, an EDTA solution has been observed to release nearly all the copper presorbed on "purified" Na^+-form clay minerals,[5] 70 to 80% of the copper present in the upper horizons of soils treated with distillery wastes,[4] and about 40% of the copper content of top soils treated with Cu-rich pig slurry. (Untreated soil possessed about half as much total copper, of which only about a tenth was EDTA extractable.)

The leachable fraction does not, however, necessarily correspond to the amount available to vegetation. Much remains to be learned about the translocation of inorganic cations into plants via the root systems. In the case of metal ions, some interesting preliminary results in respect to Mn, Cu, and V uptakes have been reported.[4,6] Copper uptake from solutions containing Cu^{2+} is considered to involve initial immobilization on root surfaces, followed by the formation of soluble copper-amino acid complexes within the free space of the root. In roots held in a moist atmosphere, the concentration of complexes within the free space of the root can increase to very high levels. However, the complexes rapidly diffuse if the roots are held in an aqueous environment. This ability of root systems to remove metal ions from the soil solution should disturb the overall equilibrium, promoting, for example, dissociation of labile complexes or partial release of adsorbed ions.

The correlation studies summarized in Section II may be interpreted as supporting the view that available metal ion consists of the ion exchangeable, the fraction sorbed on inorganic surfaces, and (possibly) the organically bound fractions. However, a different relationship may need to be proposed if the portion of the plant used as the marker system was more specifically defined (e.g., roots, stems, leaves, grain, etc.). For example, in one recent study[7] four species of seed plants were grown for 2.5 months on soils to which metal salts had been added. All species were found to take up Cd, Cr, Cu, Ni, and Pb into their root systems, with linear correlations between root and soil concentrations. Cd, and to a lesser extent Cu and Ni, were translocated from the roots to the tops, whereas Pb and Cr were retained in the roots. The ratios of the contents found in the various parts of plants are not necessarily consistent, as shown[8] by quoted analyses for wheat grown in two different types of soil, each having been spiked with 0.5 ppm Cd (as $^{115}CdSO_4$). The lower values (in parentheses) were obtained using the soil preclassified as suitable for wheat cultivation — Cd concentration (ppm) in: dry straw, 3.0 (0.33); chaff, 2.9 (0.15); bran, 2.8 (0.2); whole grains, 1.1 (0.1); and flour, 0.55 (0.07).

D. Analytical Specifications

It would seem appropriate to repeat the theme introduced in Section I.B. For the production of relevant data, each system under review needs to be carefully considered, the analytical problem defined, and alternative approaches listed. Selection of the most appropriate procedure may then be made after critical appraisal of all aspects.

The requirements for many projects may be simple to define. For example, if it is accepted that total content determinations provide suitable information for survey purposes, factors such as speed, convenience, volume of samples to be handled, or equipment available will tend to determine whether an emission technique (involving a solid sample) should be utilized, in preference to total dissolution of the solid followed by elemental analysis (e.g., by atomic absorption spectroscopy, spectrophotometric analysis, etc.). In the latter case, the merits of different modes of dissolution need to be considered.

To ascertain the contribution of human activities to the total, it has been proposed that one should monitor only the nondetrital component of sediments. In this case, the mode of attack should not cause decomposition of the mineral fragments present in the sample, but it should ensure release of all the species of interest from other components (e.g., organic matter, hydrous oxides, clay surfaces). It has been claimed that extraction with a dilute acid (e.g., 0.5 *M* HCl) achieves this aim.

Extraction with a similar type of chemical solution would be the obvious approach if the question to be answered had the form "what will be released if this sediment becomes exposed to acid inputs (e.g., accidental industrial discharges), synthetic ligand inputs (e.g., "builders" present in domestic and industrial detergents), or natural ligand inputs (e.g., sewerage)?".

Not so obvious are the approaches worthy of consideration for the determination of availability to plants or biota, and as shown in the next section, many alternatives have been proposed. While past work provides guidance, each soil/plant system may require individual investigation. Adoption of a standard procedure may provide numbers that can be compared with data accumulated in past studies, but the relevance of the approach to any new system should always be critically assessed.

For basic studies on mobility effects or distributions within a sediment bed, etc., partition of the species of interest between the various solid components could be judged to be the more important aspect to be examined. For this purpose series or sequential fractionation procedures have been proposed. (cf. Section III). These vary in format and can provide slightly different types of information.

The aim of the following sections is to summarize the various approaches which have been adopted and to emphasize the chemical interactions which should be considered in any fundamental approach to the analytical problem.

II. RELATIONSHIPS BETWEEN SOIL EXTRACT VALUES AND PLANT UPTAKE

By comparing the amount of metal ion extracted from soils/sediments by a series of different reagents, it is possible to assess the effectiveness of systems in releasing part, or all, of the total content. If conducted in conjunction with plant studies, one may also identify some favorable correlations between extract values and plant uptakes.

However, as shown by the summaries which follow, the publications of different authors are not necessarily directly comparable, because of variations in the nature of the soils used, the sources of metal ion (e.g., natural content, sludge addition, added metal salt, etc.), and the growth patterns of different species of plants. The listing is intended to be indicative of variable response, rather than comprehensive. Thus, some elements receive more citations than others, and no attempt has been made to summarize observations related to other nutrients such as Fe, Co, alkaline earths, etc.

A. Extractable Manganese

The uptake of manganese by soya bean plants, grown on 12 different soils containing added $MnSO_4$, has been recently examined,[9] and correlation between uptake and the extractable Mn value was found to decrease in the following order: 0.1 *N* $H_3PO_4 >$ steam, $NH_4OAc >$ 1.5 *M* $NH_4H_2PO_4 >$ 0.1 *M* HCl > 1 *M* $NH_4OAc >$ 0.005 *M* DTPA. Consideration of the different soil characteristics indicated that MnO fractions explained two thirds of the variations in Mn uptake; inclusion of pH, base ratio, and total Mn accounted for over 80% of the observed variations.

In an earlier study[10] using soils of different pH value, it was concluded that with soils of pH 5.8 and 6.8, DTPA extraction provided the best measure of Mn available to soya beans or wheat plants. For soils of pH 4.8, water was the extractant of choice. Double acid NH_4OAc and EDDHA (ethylenediamine-N,N′-di-hydroxy phenylacetic acid) were intermediate in their ability to predict Mn concentrations in plants. For example, correlations between Mn extracted with water or NH_4OAc and wheat plant Mn were high over the entire range. However, with soya beans, only water extracts correlated well at pH 4.8, while with the soils of higher pH both DTPA and double acid usages gave good correlations.

B. Lead Studies

In one examination of the extractability of lead from soils,[11] 12 different extractants were used. Almost complete recovery of the initial total level was obtained on extraction with 6 *M* HNO_3, and large fractions (~80%) were released by chelating agents such as DTPA and EDTA. Relatively small amounts were displaced by electrolyte solutions such as 1 *M* NH_4OAc (1 to 10%), 0.5 *M* $BaCl_2$ (0.1 to 4%), or 0.05 *M* $CaCl_2$ (traces). Of the reagents tested in another investigation,[12] NH_4OAc proved to be the least effective extractant, while Grigg's reagent (acidified ammonium oxalate) was classified as the best, since it gave higher recovery yields and there was a high degree of correlation between these values and the concentration of Pb in wheat plants grown in the soil.

With soils in which metal contents had been augmented by incubation with sewage sludge, extraction with 1 *M* HNO_3 was found to dissolve most of the Pb, Cu, Cd, and Zn content. A smaller proportion (~25%) was removed by DTPA solutions, with the actual amount increasing with increased time of extraction. Treatment with 1 *M* KNO_3 displaced very little of the metal species.[13]

C. Cadmium Extraction

Some soil survey bodies employ a double acid extraction mixture (0.05 *N* HCl, 0.025 *N* H_2SO_4) for routine trace metal studies. As in the preceding example, the acid treatment extracts a higher proportion of the total metal content than DTPA solutions, but a significant correlation between two sets of results was noted[14] using soils whose levels had been augmented by the addition of sulfate salts. Good correlations were reported between each set of data and the Cd, Cu, or Zn contents of corn plants grown on the contaminated soils.

Many procedures besides the two mentioned above have been proposed for the assessment of Cd levels. These include treatment with boiling $HClO_4$, extraction with acids such as HNO_3 (1 or 2 *M*), 0.1 *M* HCl, or HOAc (0.5 or 0.8 *M*), and displacement by 1 *M* NH_4Cl or NH_4OAc. Other methods, such as treatment of the solids with HF or boiling HNO_3, or extractions with 1 *M* HCl, 5% HOAc, 1 *M* HOAc/NH_4OAc, 0.05 *M* EDTA, and 1 *M* NH_4NO_3, were assessed by adding cadmium salt solutions to several soils, and subsequently seeking correlations between the analytical values obtained using this series of reactants, and the observed Cd levels in radish plants grown in the same soils.[15] Extraction with ammonium nitrate proved to be the most sensitive index of potential plant uptake, using this particular marker species.

D. Copper Extraction

In one bid to ascertain the best estimate of available copper in soils, nine extractants were compared.[16] As in Pb comparison studies, Grigg's reagent was deemed to be superior to others, with a distinct relationship between the experimental extraction values and the uptake of copper by wheat plants being discerned.

The amount of copper extracted by 0.1 *M* HCl from seven silt loams and two gravel soils was found[17] to bear no relationship to the copper content (or yield) of oat kernels grown in these soils. A later study[18] showed that a positive correlation ($r = 0.76$) between the copper content of corn plants and 1 *M* extractable values could be obtained if one simultaneously considered the organic content of the soil.

In a study[19] involving over 400 different soils, it was found that the fraction of the total metal ion extracted by 0.1 *M* HCl varied with soil type and generally represented only 1 to 20% of the total. The clay content appeared to strongly affect Cu, Mn, Zn, Co, and Fe values, while the soil pH influenced the amounts of Zn, Mn, Fe, and Co retrieved.

For millet plants grown on 34 different acid, to near neutral, silt loams, the uptake of copper was found[20] to correlate positively with both EDTA extractable ($r = 0.57$) and dithizone extractable ($r = 0.62$) values.

Extraction with DTPA has been accepted by many as an appropriate method for evaluating the trace metal content of soils (cf. Reference 14). However, others[21] have demonstrated that with Ontario soils, DTPA extraction values are poor predictors of plant Cu levels. The difficulty, in part, arises from the fact that the amount of metal ion released can be increased by increasing the shaking time,[13,22] extractant concentration,[22] solution pH (4.8 to 8.5),[22] or the duration of the initial sample grinding period.[14]

These factors were kept in mind during the development of a revised DTPA soil test for the four micronutrients Cu, Zn, Fe, and Mn.[23] The recommended extractant consists of 0.005 *M* DTPA, buffered with 0.1 *M* triethanolamine at pH of 7.3. $CaCl_2$ (0.01 *M*) is also included in the reagent to ensure that when the soil (10 g) is shaken (2 h) with the extractant (20 cm^3), dissolution of $CaCO_3$ should be minimal, and release of occluded nutrients, which are not normally available to plants, avoided.

E. Zinc Recovery Studies

Zinc uptake by corn plants grown on a series of Ontario[21] and Californian[24] soils have been shown to be closely related to DTPA extraction values, while others[14,25] have observed good correlations with acid extractable zinc values.

A direct relationship between 0.1 *M* HCl extractable zinc and the zinc supplying power of soils of similar texture and pH has been reported.[26-28] On soils that differed widely in respect to these properties, neither 0.1 *M* HCl nor dithizone extractable zinc was found to give a reliable estimate of plant availability.[18,29-33] In several cases, however, the extraction values were shown to serve as a satisfactory measure, provided that one also took soil pH into account.[29,30,33]

The type of soil involved is obviously quite important. It would seem that the metal ions associated with different components may respond in diverse ways to both extractants and plant root systems. For example, it has been noted[34] that both total zinc content and extractable zinc levels tend to increase with increasing soil acidity, finer texture, and increasing organic content. Positive correlations between organic carbon content and zinc extracted (by four different reagents) have been established.[35] Others have observed that both extractable zinc values and plant uptake decrease with increasing soil pH.

The zinc content of the above-ground parts of oats plants has been found[36] to be positively correlated with the amount of metal ion extracted from the soil by NH_4OAc solutions of pH 4.8. The same extractant (as well as EDTA and DTPA) has also yielded readings which correlated well with zinc levels in maize and mung bean plants.[37] With fine sandy soils, DTPA solutions tended to remove less Zn (and Cu or Mn), but more Fe than EDTA extractant solutions.[22] A favorable relationship between DTPA extraction values and zinc uptakes by both corn and wheat plants has been established using a series of alkaline soils.[38] Longer, or more vigorous grinding was observed to increase the amount extracted.[39]

Since plant availability can be profoundly affected by the reactivity of soil components, it has been suggested[26] that the most desirable extractant is one which maintains the normal soil pH (e.g., a neutral salt such as 2 N $MgCl_2$). This hypothesis was supported by a series of studies in which the zinc content of over 40 different Wisconsin soils was augmented by the addition of sulfate salt. The correlation between the metal content of Japanese millet plants grown in these soils and the $MgCl_2$ extract values were quite good ($r = 0.93$) and far superior to that observed using either 0.1 M HCl or dithizone as extractant. The amount of zinc taken up by corn plants grown on 20 Virginian soils which differed in pH, organic matter, and clay contents, was also found[18] to be more closely related to $MgCl_2$ extraction values ($r = 0.66$) than to acid extract values. Prediction ability was not improved by including soil variables in the correlation analysis.

F. General Comments

Extraction procedures which yield high recovery rates do not consistently exhibit a favorable correlation with plant uptakes, but their widespread use may be justified on the grounds that quoting upper limits compensates (at least partially) for variable effects introduced by changes in soil type or plant growth patterns.

The influence of soil type on extraction behavior could arise, *inter alia,* from pH effects on the reactivity of natural ligands (e.g., fulvic and humic acids) present in the various samples. The introduction of an extractant solution having a pH >7 provides an environment in which organo-metal components tend to be more soluble. Conversely, retention of metal ions by insoluble humic acids tends to peak in weakly acid media (cf. Figure 3).

The effectiveness of isolated fulvic or humic acids in releasing Zn, Fe, Mn, and Cd from soils has been found[40] to be less than that of synthetic chelating agents (e.g., EDTA or EDDHA), but where the soils are in contact with an extractant of limited complexing power, particularly with suspension pH values of > 7, the contribution of these natural ligands to the total solution values could be highly significant. Its influence on plant uptake correlation values will then tend to depend on whether the living matter can utilize complexed nutrient. It has been proposed[48] that plants may have access to the organically bound reservoir through the existence of multiple equilibria such as: Cu (exchangeable) $\rightleftharpoons$ Cu (weakly adsorbed) $\rightleftharpoons$ Cu (organically bound).

Other important components whose relative proportions will vary with soil type include those having high surface areas per unit weight, such as clay particles and colloidal hydrous oxides. The mode of bonding of metal ions to these solids can vary with pH, ranging from electrostatic attraction (ion exchange) to strong retention in the form of polymeric metal hydroxy species. Retention behavior differs between clay minerals, hence the significance of "clay content" on uptake may depend more on the type present than on total value. Similar remarks would apply to hydrous oxide segments, since these possess varying proportions of iron, aluminum, and manganese, Some of these aspects are taken up in later sections.

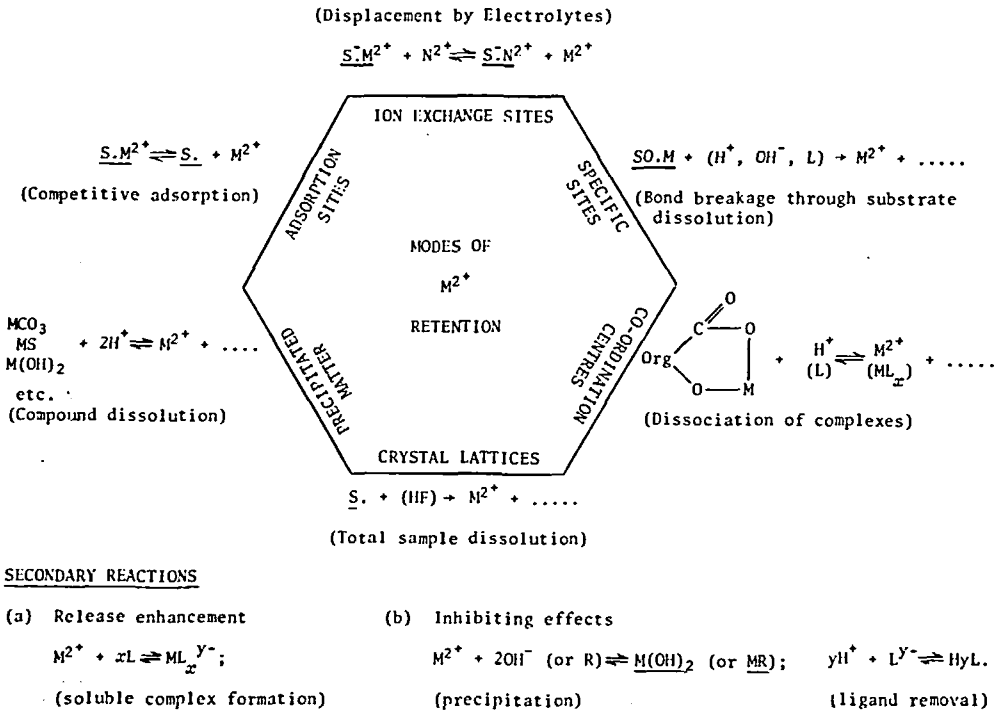


FIGURE 2. Summary of potential modes of M^{2+} retention in soils, with an indication of the chemical processes required to release the cation into an aqueous phase (symbol S = soil component).

III. SELECTIVE EXTRACTION OF A SOIL COMPONENT OR METAL IONS BOUND IN DIFFERENT FORMS

As indicated in Figure 1, the metal content of a soil or sediment can be distributed between a number of component phases which range in nature from fragments of the initial base rock (minerals, carbonates, sands) to accumulations of weathering products (hydrous oxides, clay minerals, organic matter). The metal may be bound to the various components by a range of chemical processes (e.g., ion exchange, adsorption, compound formation, etc.). Figure 2 records some of these modes of attachment and indicates the types of chemical reactions which may facilitate release of the various fractions.

It may be concluded from simplified summaries such as these that by careful selection of reagent type, one should be able to release the various fractions of the total in successive order. This principle has been adopted by a number of investigators (as discussed in Section III.C.), but it will become apparent from the subsequent reports that selectivity is not easy to achieve.

Where the bonding of metal ion to a soil component is strong, release may require selective dissolution of that particular substrate, and in most cases a number of alternatives are available.

A. Dissolution of Sample Components

The large surface areas and reactivity of the poorly ordered hydrous oxides of aluminum, iron, and manganese can result in the retention of large amounts of metal ions by such species,[41-44] particularly if the initial abstraction from solution occurs at $pH > 5$. The hydrous oxides also play a major role in the adsorption and release of fertilizer anions such as phosphate and sulfate. Accordingly evaluation of the amount of poorly ordered hydrous oxide in a soil is a useful quality-assessment procedure.

For this particular determination, the recommended extractants include sodium carbonate solutions, sodium fluoride, and sodium dithionite/potassium pyrophosphate mixtures, and these alternatives have been recently compared and assessed.[4] Poorly ordered hydrated gels containing mainly silica and alumina have a greater solubility in alkaline solutions than do crystalline clay minerals, and treatment with cold Na_2CO_3 (~5% w/v) has been shown[45] to extract the most reactive gel components without altering materials such as imogolite and allophane gels. The amount of aluminum released by NaF solutions compares well with the amount extracted by Na_2CO_3 at room temperature,[46] but application of this reagent is limited by the fact that carbonate must first be removed from carbonate-bearing soils, and the procedure is not suitable for surface soils because of interference by organic matter.

Treatment of sediment with Na- or K-pyrophosphate solutions releases organically bound iron and aluminum, but is reported[47,48] to have little effect on amorphous or crystalline inorganic Fe and Al substances. At pH 10, however, this reagent can peptize finely divided amorphous hydrous oxides as well as organic matter.[49]

Dissolution of the amorphous (or "poorly ordered") inorganic phase can be promoted by reducing the iron and manganese to lower valency states, e.g., through reaction with either oxalate ions or dithionite ions. A mixture of pyrophosphate and dithionite was found[47] to remove some iron from crystalline oxides as well as from amorphous organic and inorganic forms. Oxalate treatment did not appear to attack the crystalline material, but it has been shown[50] that the degree of interaction varies with illumination. When sediments were treated with an NH_4Ox/HOx mixture (pH 3.2) in the dark, only amorphous oxides dissolved. In sunlight crystalline portions of recent origins also tended to dissolve, while exposure to ultraviolet light promoted attack on fossil formations.

Combination of the reducing power of the dithionite ion with the complexing ability of citrate ions, in a solution buffered to pH 7.3 (with HCO_3^-), was shown[51] to effectively remove free iron oxide from soil fractions with less damage to iron-bearing base exchange materials than may be occasioned by oxalate methods in acid media. Another comparison study[52] led to the converse view. After examination of the Fe and Al content of extracts derived from a wide range of soils, plus several oxide and silicate minerals, as well as amorphous preparations, it was proposed that oxalate extraction dissolved much of the Fe and Al from the amorphous components, but little from crystalline oxide phases. The dithionite reagent dissolved a large part of both materials.

The dithionite/citrate mixture has been used widely to release the trace metals bound to the Fe, Mn oxides present in soils and particulate matter.[53-57] Other investigators[48,58,71] have opted to use acidified ammonium oxalate.

An acetic acid solution (25%), 1 *M* in hydroxylamine, has been examined[59-61] as an alternative. This reagent appears to satisfactorily dissolve ferro-manganese oxides and carbonates,[59,60] and its potential value in sediment studies was evaluated[61] by comparing it against dithionite/citrate mixtures of differing pH (3 and 7), and against 0.3 *M* HCl. Organic matter in the sediments was first destroyed through oxidation with H_2O_2, and this step released 10 to 20% of the total metal ion retrieved by the two more "efficient" extractants, namely 0.3 *M* HCl and pH 3 dithionite/citrate solution. These two extractants released similar amounts of Cu, Ni, and Pb, but the mineral acid recovered more Zn and less Cd, Cr, and Co. Repeated acid extraction yielded more solute on each occasion, and analysis for Fe, Mn, Al, and Si indicated that solution of the trace metal followed Fe and Mn increments more closely than structural components such as Si and Al. The amounts of those last two elements were sufficiently small for it to be concluded that the acid procedures caused minimal structural degradation. Extraction with pH 7 dithionite/citrate or hydroxylamine/acetic acid retrieved much smaller amounts of metal ion. This could be due, in part, to a more selective reaction, i.e., less attack on crystalline material.

The organic matter in sediments and soils consists of nonhumic substances (e.g., carbohydrates, proteins, peptides, amino acids, fats, waxes, resins) and the complex polymeric material known as humic acid. If desired, the first grouping can be isolated through extraction with organic solvents.[62] The humic component is soluble in dilute alkali, with the yield depending on the concentration and type used. Isolation of this component by alkaline extraction has some critics, since it is claimed that reagents like NaOH promote hydrolysis reactions, including precipitation of any metal ions released. The latter may be lost during separation of the extractant solutions from residual solids, or become partitioned into the fulvic acid fraction when extracts are acidified to pH 1 to reprecipitate the humic acids. Soils and sediments with high exchangeable Ca values, or containing bases such as $CaCO_3$, are often pretreated with dilute acid prior to extraction, and this process also tends to release metal ions associated with the organic phase.

Extraction with 1% NaF or dilute $Na_4P_2O_7$ (e.g., 0.1 *M*, pH 7) gives similar type products, and while the overall yield is usually less than that obtained using NaOH, their use ameliorates the problem of decalcifying the soil or sediment.[63] The $Na_4P_2O_7$ procedure was classified as the most satisfactory of 25 reagents tested on seven different soils. The solvent power of neutral salts depends on their ability to react with the Ca, Fe, Al, etc. associated with the various functional groups present in the organic structures, e.g.,

$$Na_4P_2O_7 + R(COO)_4Ca_2 \rightarrow R(COONa)_4 + Ca_2P_2O_7 \qquad (1)$$

Pyrophosphate solutions also extract metal ions bound in other ways, hence the isolated organic component tends to have a high ash value.

Ion exchange resins have also proved useful for isolating fulvic and humic acids.[64] In one recent study[65] five extractant procedures were compared. NaF and $Na_4B_2O_7$ extractions were found to be the least efficient (in terms of yield), the NaOH approach gave lower ash products (attributed to precipitation of heavy metals at the higher pH), while treatment with the chelating resin Chelex 100® was assessed as a useful, gentle approach to organic component retrieval.

For the determination of the total amount of metal ion associated with organic material, total destruction of the organic material appears to be highly desirable. The reagent most commonly used is hydrogen peroxide, but a number of problems have been identified. For example, the extract needs to be acidified to prevent the scavenging of metal ions by any iron (III) hydroxy precipitates formed at higher pH values. Similarly, while peroxidation may make soils incapable of chelating metal ions (e.g., zinc[66]), all the organic matter is not necessarily destroyed.[67] The major product identified[67] on treating soil organics with peroxide was oxalic acid, and this compound can attack the hydrous oxide component (see above), or interact with calcium ions. Both calcium oxalate[130] and Fe and Al oxalates[68] have been observed in samples predigested with hydrogen peroxide. At pH <5, H_2O_2 can react with MnO_2, and as a result soils/sediments containing this material tend to yield erroneously high Mn levels in the organic fraction,[69] with simultaneous release of any micronutrients held by this component. Other procedures for destroying the organic component include oxidation with NaOCl,[55] Br_2, or acids such as HNO_3 and $HClO_4$.

The processes discussed above for the isolation or destruction of a particular component are clearly identifiable in the procedures used for evaluating the distribution of elements between different soil components.

B. Selective Release of Fractions Bound in Different Modes or Associated with Specific Soil Components

The groupings used in descriptions of distribution patterns are somewhat arbitrary, but the fractions most commonly considered appear to be the ion exchangeable, the weakly adsorbed, organic-bound, hydrous oxide segment, and lattice component material. The latter segment has been termed the detrital or residual component, with the sum of the other fractions then being the nonresidual fraction. Views differ on the type of reagent required for the release of specific types of fractions.

For evaluation of the ion exchangeable (or available) component the extractants used have included 0.1 M HCl,[26] NH_4Cl (5 M, pH 8),[54] 1 M NH_4OAc,[53] 1 M NaOAc,[57] 0.05 M $CaCl_2$,[48] and 1 M $MgCl_2$.[18,32,55,71] The latter reagent was preferred[55] over NH_4OAc for the determination of exchangeable Mn and Cu, because the acetate appeared to dissolve some hydrous oxide coatings.

To release metal ions weakly bound to specific inorganic sites (e.g., on carbonates) extraction with 0.4 M HOAc,[48] HOAc/NaOAc (pH 5),[57] or complexing agents (of moderate ligand strength)[65] has been recommended. The weak chelating agents investigated[65] were found to be somewhat specific for particular metal ions, e.g., tartrate for Fe, glutamate for Cu. It was also noted that the amount of copper extracted by acetic acid increased with decreasing sample size. This was attributed to a greater degree of oxide dissolution and desorption from organic sites.

As indicated in Section III.C., total retrieval of the fraction associated with organic matter has been sought through oxidation of this component with NaOCl[55] or H_2O_2,[71] by dissolving the segment using $Na_4P_2O_7$,[48] through proton displacement (with 0.5 M HCl), or by chemical competition (e.g., using 0.05 N EDTA).[72] For the release of copper from organic matter, one investigation[48] used potassium pyrophosphate in preference to EDTA because it was considered to dissolve less oxide material. The EDTA solutions had higher metal ion contents and a statistical study showed a distinct relationship between the free Fe and Mn contents of the soils and the differences between the copper contents of the two extract solutions. At the same time, it was noted that the proportion of Cu in the pyrophosphate extract was not itself solely dependent on organic content; best correlation was obtained against the ratio, organic matter/free Mn.

The apparent ability of both EDTA and HCl to release metal ions associated with both organic and oxide phases has led to these being used as extractants for the evaluation of the total nondetrital segment.[72] It was found that 0.05 N EDTA (pH 4.8) extracted slightly lower concentrations of trace metals than 0.5 M HCl, while 1 M NH_2OH/25% HOAc solutions appeared to release little of the copper associated with the organic material.

Determination of the fraction present in the detrital or lattice-bound component is usually based on the difference between total values and the sum of the various extraction values (i.e., the nondetrital segment). As mentioned in Section I, the total analyses may be based on the use of an appropriate instrumental technique (e.g., X-ray emission spectroscopy) or involve complete dissolution of the solid samples.

For the latter purpose a combination of acids has usually been used. Inclusion of H_2SO_4 in the mixture introduces the possibility of partial loss of those elements capable of forming sparingly soluble sulfates. Nitric acid promotes destruction of organic matter, but when used alone or in conjunction with HCl or $HClO_4$, the procedure does not completely dissolve some types of silicate minerals. In a similar vein, attack by $HClO_4$ alone has been shown[73] to incompletely solvate the Cu and Zn content of soil samples.

Acid mixtures appear to release a high proportion of the total content (by effectively dissolving precipitated components, releasing adsorbed and complexed material, etc.), but leaching from silicate lattices tends to be partial, and for maximum recovery HF has to be included in the mixture. As shown in one fairly recent study,[72] the differences between hot acid extract values and dissolutions using acid plus HF (in a PTFE bomb) can be quite marked.

Destruction of the mineral components can also be achieved using fusion techniques. For example, residues have been fluxed with lithium metaborate,[55] and fusion with Na_2CO_3 has been used in the determination of total Cu and Zn.[73] The relative efficiencies of Na_2CO_3 fusion and extraction with HF solution or $HNO_3/H_2SO_4/HClO_4$ mixtures have been examined[74] by analyzing two "artificial" soils spiked with Pb, Cu, and Cd. The acid methods proved to be the more reliable; the carbonate fusion procedure yielded low and erratic results.

It can be gathered from the preceding discussion that reagents are not narrowly specific in their action, and competitive equilibrium effects could lead to variable release values. To fully evaluate the significance of overlapping effects, more needs to be known about basic adsorption mechanisms and retention processes (cf. Section IV). Thus, fractionation procedures, such as outlined in the next subsection, usually involve some compromises or assumptions. On the other hand, systematic subdivision into smaller categories is a desirable aim and a laudible advance on "total level" surveys or empirical extraction data.

C. Sequential Extraction Procedures

In geochemical and environmental studies, maximum contrast between anomolous and background values is needed, and in many situations this aim can be met by using a fractionation procedure which distinguishes between nonresidual and lattice-held material.

As indicated in the preceding subsection, this may be achieved by subjecting finely ground samples to extraction with cold 0.5 *M* HCl (or EDTA) and subtracting the derived values from the total contents. With a Lake Ontario sediment the percentage of total metal present in the nonresidual segment varied between elements,[72] with values ranging from 65% (Cu) to 5% (Cd) (Pb, ~55%; Zn, ~50%; Mn, ~15%). In a study involving nearshore marine sediments,[53] the trace metal content increased with decreasing sand content, and the lattice-held character decreased in the order Cu > Mn > Fe > Cr > Ni > Pb > Zn > Cd. The ion-exchangeable fraction of the nonresidual material decreased in the order Fe > Mn > Zn > Ni > Cr > Pb > Cd = Cu. With these samples the percentage of Cu, Cd, Pb, and Zn in the organic and precipitated segments was distinctly related to the sulfide concentration.

Variations in the order of predominance in detrital fractions drawn from different regions is predictable, since these primarily reflect the nature of the bedrock in the catchment area. In the course of pedological weathering, some elements are mobilized, and these become extractable by relatively weak reagents (e.g., NH_4OAc or dil. HOAc, for exchangeable and acid-soluble fractions or EDTA [when chelated]).

Soil profile studies[70] have shown clearly that distribution patterns vary between horizons (i.e., the clearly defined strata zones observed at different depths). This investigation considered over 20 elements, and the strength of adsorption (or difficulty of replacement) was observed to vary between elements and with the nature of the exchange-reactive matrix. In freely drained soils the extractable content of most trace elements fell steadily from the surface downwards, and was generally no more than 1 to 5% of the total content. With poorly drained soils, extraction values up to 20% of total were not uncommon.

In a study[55] of the distribution of metal ions in some sediments taken from the Amazon and Yukon rivers, some general similarities were observed. Exchangeable ions were displaced with $MgCl_2$, the hydrous oxide coatings were removed by dithionite/citrate solutions, organic matter was destroyed with NaOCl, and the residue was fused with

$Li_2B_2O_7$ before dissolution in nitric acid. The percentage of total metal ion present in the residual matter varied from >70% (Cu, Cr) to ~50% (Fe, Co) and ~30% (Mn, Ni). In the hydrous oxide fraction, the amount present decreased in the order Fe, Mn, Ni (~45%) > Co >> Cu, Cr (~5%), while the amounts associated with organic matter decreased from ~15% (Ni, Co) to ~5% (Cr, Fe > Mn, Cu).

In an investigation of the distribution of copper in soils,[48] 20 g samples were treated with 0.05 M $CaCl_2$ to release the exchangeable Cu fraction, and were subsequently mixed with 0.4 M, HOAc to displace any metal ion weakly bound to inorganic sites. These segments were found to account for only 1 to 2% of the total, and the proportion decreased with increasing sample pH. To bring organically bound copper into solution, a much smaller weight of sample was extracted with 1 M $Na_4P_2O_7$. This treatment released (on an average) about 30% of the total copper content. The fraction occluded in hydrous oxide coatings and particles was next retrieved by treating the residual solids with acidified ammonium oxalate (pH 3.25) while exposed to UV light. Another 15% (on average) was usually found in this fraction. Finally, the residue was ignited and portion dissolved in hydrofluoric acid to release the residual Cu held in mineral lattices. In most cases, over half the total was found in this acid solution.

In a more recent study[71] of the distribution of Cu, Zn, and Mn in soil fractions, successive extraction steps were utilized to solvate the metal ion present in exchangeable sites (1 M $MgCl_2$), held by organic matter (destroyed with H_2O_2 and system re-extracted with $MgCl_2$), and associated with the iron oxide fractions (removed by 0.2 M NH_4Ox/HOx, pH 3). The residue was separated into sand, silt, and clay fractions, and these, along with whole soil samples, were totally dissolved ($HCl/HNO_3/HF$) and analyzed for Zn, Mn, and Cu. The amount of each element present in an exchangeable form was found to be relatively small (< 7%), and the distribution pattern among the other components varied with the element considered.

The greater part of the zinc was found in the colloidal fractions (~40% in the clay), a similar observation to that made in an earlier study.[26] The proportion present in the organic and sand fractions was similar to the silt figure (~12%), and twice as much was associated with the hydrous oxide materials. The fraction located in the latter phase was smaller than values reported previously[54] (viz. 30 to 60%). With these other soils, 1 to 7% of the zinc was found to be exchangeable, 10 to 40% was associated with organic matter, and 20 to 45% was present in mineral lattice form.

The copper distribution pattern[71] indicated that retention by the clay and organic fractions predominated (30 to 40% each) with silt carrying about half this size loading. The amount found in the hydrous oxide fraction (~10%) differed from the results obtained in another study,[58] where very high amounts of Cu and Mn were found in the iron oxide fraction.

In this latest investigation,[71] most of the Mn (~45%) was found in the organic fraction, significant amounts were held by the sand and silt, and smaller proportions (~10%) in the clay and iron oxide fractions. The sum of the data for individual fractions agreed well with the total soil analyses (for Zn, Cu, Mn), but the extraction scheme has been classified by the author as preliminary, since he considers that (1) the possible dissolution of MnO_2 by H_2O_2 must be resolved, (2) better purification of the extraction salts may be required, and (3) in future studies it could be preferable to isolate two iron oxide fractions, i.e., initially the amorphous segment, with a subsequent attack on the more crystalline forms.

In another fractionation (i.e., sequential extraction) procedure for particulate samples which was proposed recently,[57] the fraction present as exchangeable trace metals was released through shaking with 1 M $MgCl_2$ (pH 7) or 1 M NaOAc (pH 8.2). Leaching with an acetate buffer solution of pH 5 (1 M) was used to displace the fraction bound to carbonates, and extraction with a dithionite/citrate/bicarbonate mixture released the metal ions bound to the Fe, Mn oxide component. After dissolution of this material, the trace metals bound to the organic components were released by destroying the organic matter with successive hot nitric acid/hydrogen peroxide attacks. Any residual metal ion was freed finally by digesting the particulate matter with $HF/HClO_4$.

It has been shown[75] that the heavy metal content of river sediments is related to the surface area, that is, the finer sediments generally contain more heavy metal than the coarser material. This general conclusion was confirmed in a study[65] in which sized fractions were individually subjected to a series of extraction steps. Metal ions present in nondetrital matter was released by overnight shaking with 0.5 *M* HCl, and total dissolution of the solids was achieved using a $HNO_3/HCl/HF$ attack. The cation exchangeable component of the various sized fractions was evaluated by shaking with 1 *M* $CaCl_2$, and weakly bound metals were released by using 1 *M* tartrate, citrate, or glutamate solutions. The amount of metal ion extracted by $NH_2OH/HOAc$ was also determined. To isolate the fraction associated with humic material admixture with Na^+-form Chelex 100 resin was utilized. No metal ions were detected in the nonhumic organic material extracted by benzene/methylene dichloride/methanol mixtures. With the other fractions, distribution patterns varied with the particle size.

As shown by the preceding examples, many combinations of reagents can be proposed for both sequential procedures and studies in which a series of extractions using different reagents are performed. It can be predicted that many new modifications will be investigated in the coming decade as interest in speciation increases. Several authors have commented on apparent limitations in their approach, and careful contemplation of Figure 2 shows that many of the chemical extractants used in soil/sediment studies are capable of fully, or partially, releasing cations retained in several of the different basic bonding modes. Proton transfer is involved in many of the chemical processes, hence pH control is obviously an important consideration. The response of a sample system to an imposed chemical environment must also be strongly influenced by soil composition, since this determines the relative proportions of the various retention modes. In view of this, it was considered desirable to briefly review our knowledge of the factors which influence adsorption/desorption behavior, before attempting to reassess the chemical role of extractant solutions.

IV. THE ROLES OF SOIL COMPONENTS AND CHEMICAL EQUILIBRIA IN RETENTION PROCESSES

As noted previously, soils consist of mineral fragments, inorganic materials of differing degrees of stoichiometry and crystallinity, and organic matter of poorly definable nature, with divisions within each of the main categories. Thus in the inorganic segment, distinctive mineral types can be identified, or the material can be extremely fine and associated with products of variable composition. Besides causing decomposition of primary minerals, weathering can lead to the coating of particles with layers of hydrous oxides (e.g., of iron, aluminum, or manganese), which on aging, may yield distinct species such as goethite, hematite, or gibbsite. The less ordered hydroxy species and other components of the clay-sized fraction (such as alumino-silicate weathering products) possess large surface areas per unit weight, and are thus capable of retaining significant amounts of any species (such as metal ions) having a special affinity for their surface sites. The organic component of soils, introduced by plant decay, can consist of polysaccharides (thought to help bind soil products into aggregates[76,77]), polymeric carboxylic acids (soluble in alkaline solutions), and other insoluble material called humin. The fulvic (acid soluble) and humic acid fractions can possess other functional groups besides -COOH (e.g., -OH, $-NH_2$) and can react with polyvalent cations to form salts and/or chelates. The solubility of the salt/chelate compounds tends to be a function of matrix composition, element involved and solution pH (being greatest in alkaline media, see

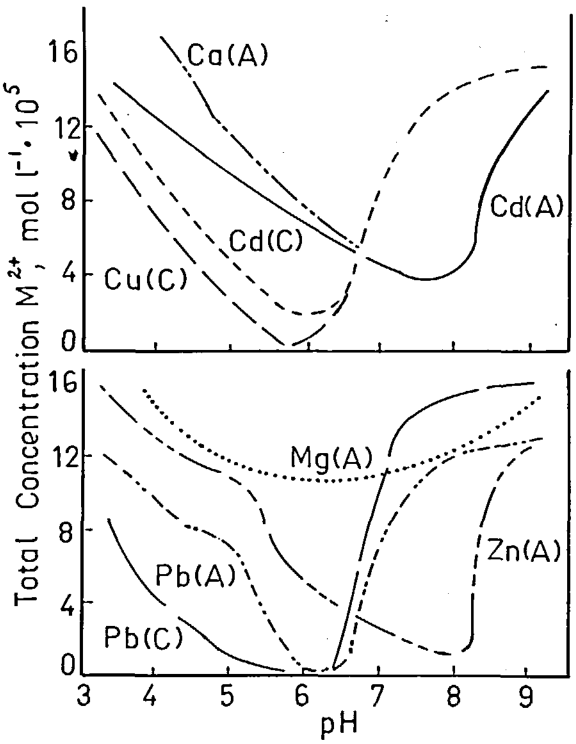


FIGURE 3. Diagram showing the effect of pH on the amount of M^{2+} observed in 30 cm^3 of solution containing 3 mg humic acid. A — Fluka reagent; C — forest soil extract. (Based on data from Reference 92.)

Figure 3). The acidic properties, adsorption (or reactivity) capacity and chemical form of the organic components of soils, are a function of the plants from which they are derived, the degree of decomposition,[3] etc. Lower molecular weight fractions appear to have greater complexing power than higher molecular weight material.[78]

Interactions can occur between the organic and inorganic components of the systems, leading to partial decomposition of minerals (e.g., K^+ release from micas[79]), coatings on clays, leaching of cations through formation of soluble "complexes", or dispersion of aggregated colloidal material.

A. Cation Exchange Capacity — pH Effect

It has been noted by many authors[80-84] that the cation exchange capacity of soils increases with pH. These studies have led to the view[2] that the CEC consists of two main components: a constant, or permanent, negative surface charge (generated by partial isomorphous substitution within the lattices of clay-size layer silicates), and regions of pH dependent charge, in which exchange sites are generated through dissociation of hydroxyl groups (located at the edges of layer silicate crystals or on the surfaces of hydroxy alumino-silicate gels), or by dissociation of Al or Fe complexes formed with the phenolic and carboxylic acid functional groupings present in some of the organic matter.[81,85-89]

The pH dependent charge on crystalline Fe and Al hydrous oxides appears to be small, but it has been demonstrated that kaolinite, halloysite, imogolite, and allophane could contribute to the reversible component of the pH-dependent CEC.[90]

When the organic content of a soil is high (e.g., surface soils), a major part of the variable charge may be attributable to displacement from functional groupings.[91] This process is quite sensitive to pH (cf. Figure 3), and recent studies[92] using four isolated humic acids have shown that the pH effect can vary with the nature (or source) of the humic material and the cation being adsorbed (or displaced). One consequence of different affinities and pH effects is an apparent marked variation in the adsorption capacities for different divalent cations, when measurements are made at some selected pH value. For example, Langmuir isotherm studies made at pH 5 yielded capacity values which varied from ~400 mmol kg^{-1} (Ca^{2+}, Mg^{2+}) to ~900 mmol kg^{-1} (Pb^{2+}, Cu^{2+}).

The adsorption of aluminum species is considered to play an important role in determining the pH dependence of the exchange capacity of the clay component of soils. Polynuclear hydroxy-Al species have been shown[93] to behave like normal exchangeable cation. With suspensions of acid soils, for example, the concentration of these Al-hydroxy species in solution increases with increasing external electrolyte concentration and increasing valency of the desorbing cation (e.g., KCl, $CaCl_2$). It is interesting to note at this point that proton release on hydrolysis of Al^{3+} displaced by the addition of unbuffered electrolyte solutions accounts for the observed pH of many acidic soil suspensions.[94]

For the estimation of the potentially reactive aluminum pool in acid soils, extraction with $CuCl_2$ has been examined[95] as an alternative to KCl displacement. With acid surface soils (pH <5) the amount of Al extracted by 1 *N* $CuCl_2$ was found to be generally twice that released by 1 *N* KCl, which suggests that the metal ion solution also extracted Al bound by organic matter. Both solutions were equally effective in extracting exchangeable Al from Al-saturated montmorillonite, but the $CuCl_2$ solution released almost twice as much Al from aluminum saturated vermiculite, which also contains a hydroxy-aluminum layer.

The view has been expressed[2] that some of the "permanent" negative charge associated with clay minerals may be blocked at lower pH values through the strong adsorption at nearby sites of hydroxy-aluminum cations. At more elevated pH, these cations should precipitate (as hydrous aluminum oxide), and in this way the newly exposed negative sites could then become free to participate in cation exchange reactions.

By preextracting the solid with KCl[88] or with a dithionite/citrate/bicarbonate mixture,[96] the magnitude of the pH-dependent component of the cation exchange capacity can be reduced. In studies using peroxidized clay separates isolated from a group of Irish soils, the CEC at pH 8.2 and the pH-dependent CEC were highly correlated with the citrate-dithionite extractable aluminum. The CEC at pH 4.8 was negatively correlated with this parameter, which suggests that hydrous oxides reduce CEC at lower pH values. The mean pH-dependent CEC could be further reduced by subsequent extraction with NaOH.

As with humic acids, the total capacity of clay suspensions has been observed[97] to vary with the nature of the divalent cation being taken up. Previous workers[98] have also reported variations in the apparent capacity when using displacing ions of different valency. These differences were attributed to the adsorption, at pH > 7, of hydroxy cations such as $CaOH^+$ and $MgOH^+$. With metal ions, the formation of monovalent hydroxy species occurs in discernible amounts at lower solution pH values, and it was proposed[99,100] that uptake by clays in acid media could involve species such as $CuOH^+$, $ZnOH^+$, $ZnCl^+$, etc.

The behavior of Cu, Pb, Cd, and Zn solutions in contact with three different types of clay suspensions ($-Na^+$ form) has been extensively examined, and in all cases studied[101-103] the metal ions were totally precipitated at pH values lower than those calculated to be required for significant degrees of MOH^+ formation in the solution phase. On the other hand, there was some evidence[104] to suggest that with increasing pH the first abrupt increase in metal ion uptake (Figure 4) coincides with the formation of

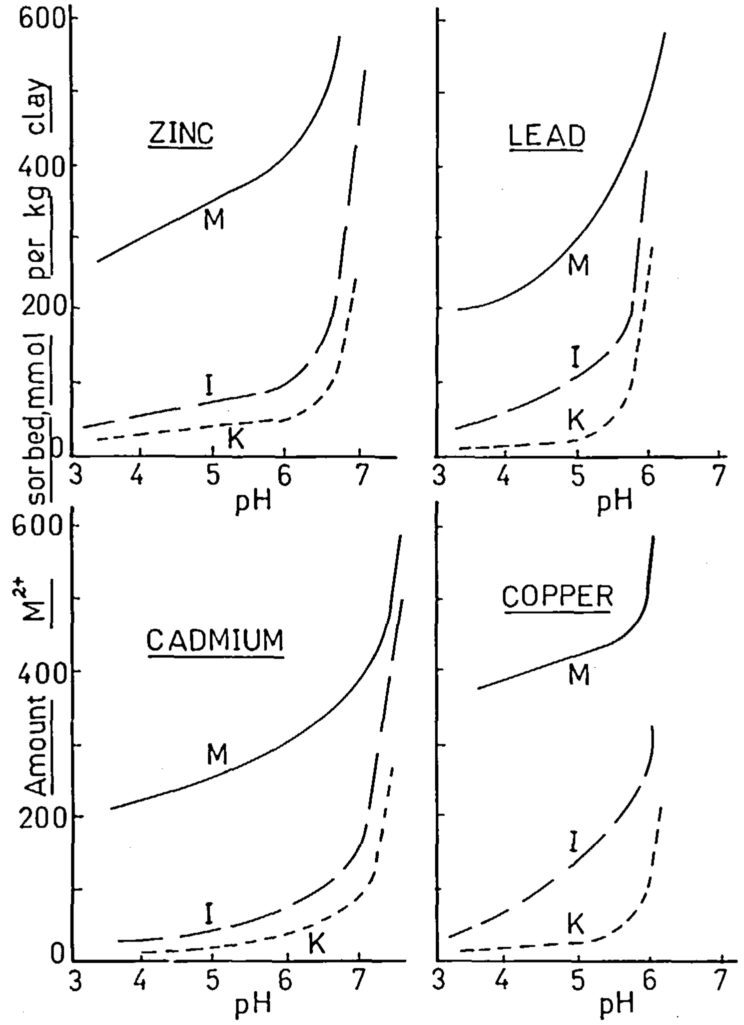


FIGURE 4. Diagram showing the effect of pH on the amount of metal ion sorbed by clays from a $1.7 \cdot 10^{-4}$ *M* M^{2+} solution. Vertical segments mark onset of hydroxy species precipitation. M = montmorillonite; I = illite; K = kaolinite (all in Na^+-form). (Based on data from References 101 to 103.)

polymers having the general formula $(M\ OH)_x$. The degree of hydroxylation increases at higher pH values, i.e., regions of total precipitation. Prior to precipitation as hydroxy species, the amount of metal ion adsorbed increased with increasing pH (Figure 4), and this has been attributed to the creation of new surface sites.

Extension of these observations to soils causes one to surmise that the presence of metal ions could lead to further variations in the magnitude of CEC readings determined by traditional procedures. Using standard displacing agents (e.g., NH_4^+ or Ba^{2+}) and pH values (7 or 8.2) may lead to higher or lower values, depending on whether hydroxy polymer formation exposes sites (as suggested for Al) or forms a coherent coating.

Uptake of metal ions could involve displacement of aluminum hydroxy species from both clays and organic components. Fractionation studies[71] have indicated, for example, that the highest proportion of Cu in soils occurs in the organic matter and clay fractions, while manganese is found mainly in the exchangeable and organic fractions. The capacity of soils to immobilize Pb is considered[105] to be caused principally by reactions involving essentially insoluble organic materials. (Sorption by hydrous oxides or precipitation by carbonate appear to be of secondary importance.)

B. Adsorption Equilibria

The levels of inorganic micronutrients and toxins in soil solutions are rarely likely to be of sufficient magnitude to saturate the substrate totally, hence the affinity of different species for soils are possibly best evaluated from adsorption isotherm studies. The uptake of many species by soils have been found to conform to isotherm relationships such as the Freundlich (i.e., amount sorbed α $[M]^x$ where $x < 1$) or Langmuir equations. The Langmuir approach has the advantage that one may use the derived constants to compare bonding strengths and estimate total capacities. On the other hand, many soil adsorption studies have yielded multiple segment Langmuir plots, an observation often attributed to the heterogeneity of the substrate being used. Recently, it has been demonstrated[106] that a single linear plot can be attained over a wider range of concentrations if one uses the competitive form of the Langmuir equation, that is, all displaced ions should be assumed to be competing for the available adsorption sites. This implies that one adsorbent (or component) probably dominates in many systems, and it provides an insight into the factors which should be considered in extraction procedures (i.e., desorptions) based on the addition of electrolyte solutions.

If (A) is the species to be displaced, then the amount retained per unit weight $[(x/m)_A]$ should be reduced to a minimum, that is, the fractional term in the equation

$$(x/m)_A = (\text{ads. capacity}) \cdot \{k_1[A]/1 + k_1[A] + k_2[B] + k_3[C] + \ldots\} \qquad (2)$$

should be $<<1$. This aim may be readily met if the bonding constants (k_2, k_3) for all competing species, (B), (C), etc. (e.g., added Ba^{2+} or H^+), are of a similar order of magnitude to that of the prime adsorbant A (i.e., k_1). Where $k_1 >> k_2$, k_3, then the difference must be redressed by either increasing the concentration of extractant (i.e., [B], [C] or greatly reducing [A] through complex formation.

It has been noted,[107] for example, that while hydrated copper ions tend to be strongly retained by soils, anionic complexes such as $[Cu(P_2O_7)_n]^{2-4n}$ and $[Cu\ edta]^{2-}$ are only partially sorbed. With zinc the sorption of complex ions decreased in the order $[Zn(P_3O_{10})_n]^{2-5n} \geq [Zn(P_2O_7)_n]^{2-4n} > [Zn\ edta]^{2-}$, or expressed in another way, the presence of sodium salts of these ligands decreased zinc sorption by soils, whereas KNO_3, NH_4OH, and CSN_2H_4 had no effect. It has also been shown that conversion of metal ions into stable anionic complexes (e.g., using appropriate excesses of, say, EDTA, NTA, or citrate at suitable pH values) virtually eliminates uptake of metal species by clay minerals[101-103] or some isolated humic acids.[92]

However, should the primary interest be the evaluation of the amount likely to be made "available" through "displacement" by cations, then the introduction of ligands could lead to positive errors.

Much of the element of interest is likely to be held on the highly reactive surfaces of the poorly-ordered, clay-sized aluminosilicate (or allophane) segment of the soil. As mentioned in a previous section, this material is soluble in cold alkali and in complexing reagents such as acid ammonium oxalate,[50,109] pyrophosphate,[47,49] and citrate.[110] Even dilute acids have been shown[111] to be capable of removing poorly ordered material, although the degree of attack may be partial, e.g., 0.5 *M* $CaCl_2$ at pH 1.5 appears to extract the Al component but little Si or Fe.[112]

The adsorption aspect is further complicated by the observation that with clays[97] and humic acids,[92] bonding constants for divalent cations tend to vary less in magnitude than the apparent capacity for each species. With mixed adsorbent systems, as in soils, interactions between the various components is probable and could modify the overall behavior.

C. Adsorbent Interactions

The extent to which fulvic and humic acids are themselves adsorbed by clays has been demonstrated to depend on the concentration and molecular weight of the organic polymer,[113-117] the clay mineral type,[113,118] the nature of the clay counter ions,[117-120] and pH.[121, 122] The adsorption of low molecular weight fractions appears to be preferred,[113,115] with the amount taken up, (y), varying with equilibrium solution concentration, (x), in accordance with an equation having the form $y = a \cdot x^b$, where the coefficient b may have a value of unity (e.g., on montmorillonites[117] at pH ~7) or less than one (e.g., on kaolinite, vermiculite, or muscovite[113]). The affinity of a humic acid for a montmorillonite charged with different counter ions has been measured[117] in terms of the logarithm of the slope, (a), and this yielded sequences such as $Na^+ < K^+ < Cs^+$; $Ba^{2+} < Ca^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+}$; $La^{3+} < Al^{3+} < Fe^{3+}$. Other studies[118,119] have bridged valency series, e.g., $K^+ < Na^+ < Ca^{2+} < Mg^{2+}$ and $Ca^{2+} < H^+ < Fe^{3+}$.

The amount sorbed by montmorillonitic clays has been found[113] to exceed that taken up by quartz, muscovite, biotite, vermiculite, or Ca-kaolinite (with soil preceding this group), while another investigation[118] yielded the series illite > chlorite > kaolinite > marine sediment.

The bonding between humic acid and clay can be quite strong, particularly when polymerized iron or aluminum forms an intermediate surface cover.[123] For example, repeated washing,[118] or even exposure to sodium pyrophosphate or hydroxide,[119] has been found to remove only a fraction of the total uptake.

This latter observation is significant in relation to extraction studies, since it could result in modification of the behavior observed with isolated organic matter or clay minerals, e.g., a high pH normally solubilizes metal-humate complexes. An investigation[124] of the effect of pH on the retention of heavy metal ions by Na^+ form clay-humic acid mixtures has confirmed the existence of an interaction effect. It was found that the amount of metal ion present in a soluble form (i.e., true solution or dispersed colloid) at pH >7 varied with the nature of the metal ion, the type of humic acid used, and clay structure, but in all cases it was a fraction of the total content. In acid media, interaction between illite or kaolinite and the organic acid was apparently minimal since observed adsorption values were similar to the sum of the two individual effects. With montmorillonite, the amount adsorbed exceeded individual retention values, but the total was less than the sum of the two. A similar intermediate adsorption effect was observed in a study of Co^{2+}, Ni^{2+}, and Mn^{2+} uptake by a magnesium-clay, humic acid complex.[125]

In natural systems, the retention of organic matter and hydrous oxides can sometimes virtually mask the adsorptive capacity of the base clay. For example, when much of the organic content of some island surface muds was destroyed by peroxide treatment, uptake of copper and zinc ions (as function of pH) was found to increase.[126]

As noted above, surface coatings of polymerized iron or aluminum hydroxides can promote firmer bonding of organic matter to clay surfaces, and so moderate the distribution of metal species between aqueous and solid phases. Significant changes in clay behavior can also be induced in the absence of organic matter. It has been demonstrated,[127,128] for example, that the addition of hydroxy-M(III) cations to clay systems alters properties such as surface area, surface acidity, and cation exchange capacity. The polymeric hydroxy species, formed through hydrolysis of solutions containing Fe(III), Al(III), or Cr(III), were shown to interact strongly with the surfaces of kaolinite, illite, and bentonite, with the amount sorbed varying with solution pH and $OH^-/M(III)$ ratio.

One effect of a hydrous oxide coating on clays can be a marked reduction in the pH required for precipitation of heavy metal ions, and the oxides may exert a chemical activity effect which is out of proportion to the amount present. The hydrous oxides are considered[69] to be important components of any aquatic environment, because their formation and dissolution can be induced by changes in acidity or oxidation potential or by the presence of complexing agents.

The removal of hydrous iron oxides from some soil clays previously treated with peroxide to destroy organic matter has been found[129] to enhance the exchange capacity of the samples, yet it had nearly the opposite effect in respect to zinc adsorption values. The iron removal effect was so variable that it is difficult to decide whether the iron component initially caused some aggregation of the clay particles, blocked exchange sites, or acted as an independent adsorbent.

Zinc is adsorbed by both Fe, Al oxides,[43] and clays,[129] with the relative degree of retention varying with the type of clay present. Very little specific adsorption of zinc was observed[131] using natural soil samples (except where halloysite was present), but with calcium saturated samples significant amounts of specific retention were detected, with the degree varying with the nature of the cation exchange material present. Over 40% of the total cation exchange sites in soils containing allophane, imogolite, and halloysite had high selectivity constant values. Samples with low to moderate selectivities tended to be montmorillonitic, vermiculitic, and humic soils.

The use of extracting solutions which are capable of wholly or partially stripping coatings off clay minerals may accordingly yield variable recoveries of metal ions, the equilibrium position being determined by the affinity of residual surfaces for the cationic species present in the extracting solution.

D. Ion Exchange

The practice of determining and quoting cation exchange capacities tends to imply that the dominant chemical process in soil systems is ion exchange, i.e.,

$$\underline{S}.M^{2+} + N^{2+} \rightleftharpoons \underline{S}.N^{2+} + M^{2+} \qquad (3)$$

In an ideal exchange system, displacement proceeds in a stoichiometric manner, with the ratio of $S.N^{2+}/S.M^{2+}$ being directly proportional to the solution concentration ratio, $[N^{2+}]/[M^{2+}]$. The proportionality constant or selectivity coefficient can have values $>$, $=$, $<$ unity. Using this model, displacement of M^{2+} should be maximized by increasing the concentration of added reagent, N^{2+}, and selecting a species with a high affinity for the solid substrate, $\underline{S}$.. In ideal systems (e.g., synthetic organic exchangers) using dilute aqueous solutions, the relative affinities can be predicted in terms of some simple general rules, e.g., affinity increases with increasing valency; or with constant valency, affinity increases with decreasing radius of the hydrated cation. Replacement of M^{2+} by N^{2+} would also be facilitated by the removal of M^{2+}, e.g., through selective interaction with a complexing agent, leading to the formation of an anionic species.

However, while some interactions between clay (e.g., montmorillonite) or soils and electrolyte solutions (e.g., alkaline earth cations) display behavior which approximates to a direct exchange of ions, there is an equally large body of evidence in respect to nonstoichiometry and anomolous behavior. The position of equilibrium, using natural exchangers, is often better described by an adsorption isotherm, or a variation of same, rather than in terms of a selectivity coefficient. With metal ion exchange by clay systems, coefficient values have been found to be a function of several parameters including pH,[132-134] temperature,[133,134] and relative concentration levels.[132,134] Some changes with conditions correspond to a reversal in selectivity order (e.g., 0.9 at pH 3.5, 1.3 at pH 5.2). Such reversals are considered to be a characteristic of heterogeneous systems, that is, surfaces which possess several types of sites, each having a different affinity for ions.

The concept of "specific adsorption sites" has been invoked to explain the observation[135] that metal ion sorption occurs from 5.10^{-6} M solutions, even in the presence of a large excess of other electrolytes (e.g., 0.05 M $CaCl_2$). The creation of new sites through sorption of silicate ions is believed[136] to contribute to the specific adsorption process, while other workers consider that traces of organic matter are responsible for some specific adsorptions. Other explanations involve migration of dehydrated ions into holes in the crystal lattice, physical entrapment in clay lattice wedge zones, and precipitation as hydroxy species.

The observed variation of exchange capacity with pH, the varied behavior observed with metal ions, and the lack of reversibility noted with displacements involving the ions of the alkali, or alkaline earth groups, all serve to warn that the designation "ion exchange" should not be used too rigorously when dealing with environmental samples.

E. Precipitation and Dissolution

The accumulation of some micronutrients in soils can involve a precipitation reaction, and recovery of this segment in an extraction stage requires dissolution of an "aged" form of the deposited material. For ionic solids having limited solubility, the main equilibrium relationship of interest is the solubility product equation, i.e.

$$yA^{x+} + xB^{y-} \rightleftharpoons A_yB_x;\ K_{so} = (A^{x+})^y(B^{y-})^x \qquad (4)$$

Formation of the species A_yB_x should occur whenever the activity products term exceeds the value of the thermodynamic constant, K_{sp}, and with a heterogeneous system, one has to remember that the activity level of the precipitant (B^{y-}) is likely to be higher at the interface (due to adsorption) than in bulk solution. Thus precipitation of zinc silicate on clay surfaces has been noted[136] when solution levels did not exceed the tabulated K_{sp} requirements. Similarly, hydroxy metal species precipitate on clays and other substrates (e.g., hydrous oxides, cellulose) at pH values lower than those required in the absence of suspended matter.[42,101-103,137-139]

On standing or aging, the precipitated material can change in structural form, resulting in a marked decrease in the magnitude of the appropriate K_{sp} value.

For dissolution (or extraction) the process has to be reversed. That is, the solution activities of A^{x+} or B^{y-}, or both, have to be reduced to extremely small values to encourage further dissociation of the solid. The introduction of electrolyte solutions can increase the solubility slightly (by reducing activity coefficient values), but marked changes require secondary chemical processes such as the formation of stable complexes by the cations (e.g., $M^{2+} + EDTA \rightleftharpoons [M.edta]^{2-}$) or removal of anions through protonation reactions (e.g., $C_2O_4^{2-} + 2H^+ \rightleftharpoons H_2C_2O_4$, $CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$, etc.). The solubility of compounds of some transition group elements (e.g., Fe, Mn) can be increased by reducing the solution potential. (The electron transfer process which follows the addition of excess reductant may be considered to remove A^{x+} by producing an ion of lower valency. A good example would be the use of dithionite[51] to dissolve hydrous iron oxides.)

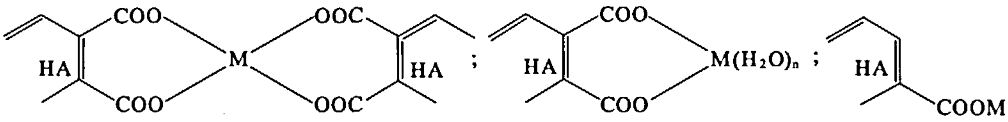
However, dissolution can be a kinetically controlled process. The slowest step may be diffusion of reactant (or product) through any surface coatings (e.g., of organic matter), across surface diffusion layers, or into structural pores. The speed of such processes can be accelerated by using increased temperature, increased reagent concentration, more vigorous mixing, and finer particles. Smaller particles also provide a larger surface area per unit weight on which reagent may be adsorbed.

The surface activity at defect centers, surface irregularities, etc. tends to ensure most rapid attack at these points. With some materials, the concentration of active sites can be increased during sample preparation (e.g., by grinding); other soil components are naturally disordered. Accordingly, it is not surprising to find references in the literature which indicate that the degree of extraction of some species increased with increased grinding time,[14,39] finer soil texture,[34] mode of soil preparation,[140] and shaking time.[13,22] Similarly, in Section II, the quoted examples of selective dissolution of poorly-ordered hydrous oxides of alumino-silicates rely on the principle that less-structured materials dissolve more readily than structured compounds.

Much remains to be learned about the factors which influence dissolution processes and the mechanism of heterogeneous reactions (as discussed in a review of oxidation processes[141]), but it seems highly probable that sparingly soluble components of soils would contribute varying amounts of ionic components to extract solutions, depending on the experimental parameters used.

F. Chemical Interactions

It has been noted previously that bonding between humic acid and clays can be particularly strong, with affinity varying with the nature of the clay counter-ion. Chemical interaction between organic soil components and soil solution solutes can also lead to retention of nutrient species by the solid phase. Proposed[142] reaction modes include chelation and salt formation, e.g.,



The stability of the humate complexes is considered to be a function of the nature of the bound cation, the binding energy of the ligand functional groups, and environmental factors such as pH and E_h. The relative order in which cations may be retained has been evaluated[143] and the order derived was $Fe^{3+} > Al^{3+} >> Fe^{2+} > Cu^{2+} >> Zn^{2+} > Co^{2+} > Pb^{2+} \geqslant Ca^{2+} \geqslant Mn^{2+} \geqslant Mg^{2+}$.

To extract material coordinated to organic material (or other components) in this type of manner obviously requires either the destruction of the ligand species (e.g., oxidation of organic matter) or the addition of a competing ligand (L) which forms a more stable complex with the cation of interest, i.e.

$$R_xM + yL^{z-} \rightleftharpoons ML_y^{(yz-2)-} + R_x^{2-} \qquad (5)$$

Since both ligands, R and L, are prone to protonation, the position at equilibrium is determined by the solution pH, the acid dissociation constants for R and L, and the thermodynamic stability of the complexes R_xM and $ML_y^{(yz-2)-}$.

While compilations of stability constant data may provide all the desired information for added ligand L, the corresponding information for the natural soil reactant R is just not available. As mentioned earlier, the composition of the organic component varies with source and prehistory. Accordingly, in extractions with solutions containing monodentate ligands (e.g., Cl^-, F^-) or synthetic chelating agents (e.g., EDTA, DTPA), one can only assume that the release reaction is proceeding predominantly in the desired direction.

The acidity of soil reactant functional groups can vary between samples, and the actual mode of bonding can be a function of R/M ratios. The equilibrium concentration of competing ligand can also be reduced by the buffering action of the soil and interaction with other cations capable of forming complexes and chelates (e.g., present as exchangeable or adsorbed species).

Many of these effects are predictable. For example, recently constructed metal stability diagrams[144] show the effect of pH and redox potential on many heavy metal-chelate equilibria in soils. The reactions considered included the interaction of the cations H^+, Fe^{3+}, Fe^{2+}, Al^{3+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, and Ni^{2+}, with synthetic chelating agent such as DTPA, EDTA, CDTA, EGTA, and HEDTA. In the absence of Ni, either Cd or Pb ligand species tend to dominate in alkaline media, while in acid systems Cu, Pb, Fe, and Zn are the major chelated species. Nickel complexes tend to be the predominant species in acid media, if one assumes this element to be present at the 10^{-5} to 10^{-7} M level. It was concluded that for acid soils, reagents such as EDTA, EGTA, and HEDTA deserve further study as extractants. At the same time, the equilibrium calculations show that there is sound theoretical support for the DTPA test procedure proposed previously[23] for the evaluation of plant available Pb, Cd, and Ni in soils.

Formation of chelates is not necessarily instantaneous, hence once again, the time allowed for the achievement of equilibrium could influence the magnitude of extract values.

The amount of soil component capable of forming coordination compounds, which is present in a sample, may be quite small, so that errors introduced by partial dissociation may be regarded as unimportant. There is also some experimental evidence[92] to support the view that appropriate excesses of EDTA, or alkaline citrate ion, etc. can ensure retention of metal ions, at least, in the solution phase.

The alternative mode of dealing with coordinated material, namely destruction of the substrate, can also be criticized on the basis that the efficiency of the destruction process may be debatable. For example, peroxide oxidation only destroys part of the total organic content, vigorous conditions can be required to break up metal-organo chelates, and so on.

In summary, the components of a soil act as a reservoir for the chemical species utilized in plant growth. The nutrients (and inorganic toxic species) are stored in many different ways. Some are readily available (e.g., ion exchange counter ions, weakly adsorbed), some may be released by chemical reaction (e.g., slow dissolution by soil or plant acids), and part can be totally inaccessible. The task in selecting extractants is to understand the bonding modes and choose a reactant which specifically isolates the most appropriate segment of the "store house".

V. THE CHEMICAL ROLE AND APPARENT EFFICIENCY OF EXTRACTANT SOLUTIONS

It can be seen from the discussion in Section II that views on the "best" extractant differ greatly. With processes as complex as plant growth and nutrient transmission, involving materials as complex as soils and living matter of many diverse types, one must expect varied observations and occasional contradictory responses. On the other hand, it can be proposed that collection of much information of doubtful value could be avoided if the role of various chemical solutions was better understood, and if the analytical problem was more specifically defined.

A. Chemical Reactivity and Kinetic Effects

In this section, the interaction modes of different categories of extractants are considered briefly.

Discussion is based on chemical reactivity and assumes that equilibrium is achieved during the time of contact. However, as noted earlier, many factors can influence the rate of heterogeneous processes, and differences between samples may arise from variations in physical characteristics, as well as from different distribution patterns between components. The use of standard conditions hopefully ensures that in comparison studies reactions proceed to the same extent, so that observed variations are attributable to composition effects rather than to kinetic artifacts. Theoretically, if equilibrium has been reached, further extraction with the same reagent will either retrieve no more of the species sought (i.e., extraction 100% efficient) or it will release a fairly constant fraction of the residual sample component to each successive volume of extractant. This method of checking efficiency may fail if material is released slowly from another component of the soil, or if the time of shaking used is insufficient to ensure achievement of an equilibrium state in the chemical interaction of interest. One has to recognize that in some circumstances kinetic effects may aid selectivity. For example, with short contact times an extracting solution may come to equilibrium with one group of sites (e.g., exchange positions), but release very little from other centers (e.g., components which dissolve slowly).

1. Acids

Extraction of a soil or sediment with cold, nonoxidizing acid solution should, in theory, release exchangeable and adsorbed cations (particularly from sites having a high affinity for protons), reverse reactions involving proton transfer (e.g., promote dissociation of metal-humate complexes), dissolve disordered or non-aged hydroxy species and carbonate minerals, partially dissolve some silicate minerals and minor sample components, and precipitate some sparingly soluble species (e.g., humic acid).

Some of the residual solid components (e.g., colloidal silica, clays, humic acids) retain adsorptive powers (albeit with reduced capacity), and reduction of losses from this source requires the introduction of further chemical steps. For example, dehydration of silica through evaporation to dryness or to fumes; destruction of organic matter by treatment with hot HNO_3 or by addition of H_2O_2 or Br_2, exposure to ultraviolet light, etc. The use of filtration to separate the phases can also lead to losses, since filter media (cellulose papers, sintered glass supports) have been shown to be capable of removing trace metals from solution.[139,145,146]

Variations in the extent of the partial dissolution segment introduces another area of uncertainty. The use of a weaker acid (e.g., acetic) should ensure minimum attack on crystalline components, but at the same time, dissolution of disordered hydrous oxides may also become partial and both clays and humic acids can retain measureable amounts of metal ions at pH ~3. As an indication of the difference in recovery levels, one may quote the data obtained in comparison studies using Cd-spiked soils.[15] The average Cd level detected in strong acid solutions (HF, hot HNO_3, 1 *M* HCl) was around 70 mgℓ^{-1}; with weak acid (5% HOAc) the value was half this, while an acidic electrolyte solution (1 *M* NH_4OAc, HOAc, pH 4.8) yielded solution concentrations of *circa* 40 mg ℓ^{-1}.

Another acidic electrolyte solution, namely ammonium oxalate adjusted to pH 3.2, has been reported[12-16] to be the best extractant for Pb and Cu in soils. Conversely, adsorption of Pb, Cu, Cd, or Zn by both clays[101-108] and humic acids[92] has been shown to be minimal in the presence of oxalate solutions of pH <4. Such solutions also retrieved[5] virtually all the metal ion sorbed by clay samples when preexposed to high concentrations (10^{-4} *M*) of metal salt solutions. The effectiveness of this reagent appears to arise from a combination of effects. The ability of oxalate ions to coordinate and form moderately stable complexes in weakly acid solution leads to the stripping of disordered hydrous oxide layers, preferred adsorption of protonated ligand on clay surfaces, and the formation of anionic metal complexes which have little affinity for negative adsorption sites. The inclusion of ammonium ions assists by adding another competitor for exchange and adsorption sites. Adjustment of the solution to a pH around 3 prevents complications such as partial precipitation of oxalate salts (e.g., of Fe, Ca), while retaining a medium which is possibly too weakly acidic to attack silicates and other minerals or carbonate compounds effectively.

At the other extreme, one can aim to ensure maximum release by promoting near total dissolution of the solids. For example, comparison of the trace metal results obtained using hot aqua regia digests, with values obtained by emission spectroscopy (i.e., total solid), has shown[4] that this mode of acid treatment dissolves a large proportion of the total amounts of many potentially toxic elements present in waste sludge treated soils. The use of hydrofluoric acid promotes dissolution of the silicate minerals and hydrous oxides (aided by the formation of anionic complexes such as AlF_6^{3-}, FeF_6^{3-}), but may cause the loss of some species (e.g., Ca^{2+}) due to the sparing solubility of the flouride salt.

For the determination of total levels by "wet methods", it can prove necessary to fuse the residues left after an acid attack, or initially to destory mineral structure by means of an alkaline fusion step. As noted in the introduction, however, total levels are now usually evaluated instrumentally, and this requires a different mode of sample preparation.

2. *Electrolyte Solutions*

Exposure of soils or sediments to salt solutions (e.g., of K^+, Na^+, Ca^{2+}, Ba^{2+}, NH_4^+) of concentrations of 0.1 to 1 *M* should promote displacement of other cations from accessible ion exchange sites and weakly bonding adsorption sites. Having no buffer capacity, the extractant solutions tend to adopt the pH of the soil suspension, and while displacement of aluminum species may cause[94] a slight lowering in pH, this change is unlikely to release material through dissolution of hydrous oxides or carbonates. However, it has been pointed out in previous sections that the exchange capacity (i.e., amount of cation displaced) varies with the pH used and displacing ion selected.

The affinity of monovalent cations (and Ca^{2+}, Ba^{2+}) for humic acids appears to be relatively weak, and accordingly they are unlikely to release any cations (e.g., metal ions) retained by chelation. As noted in Section IV, displacement of this segment can be promoted by complex formation, but few of the anions introduced with electrolyte extractant solutions (e.g., Cl^-, NO_3^-) form particularly stable complexes with, say, metal ions. It is thus not surprising to find that the amount of metal ion released by simple salt solutions is very much smaller than that released by acidic solutions or synthetic chelating agents. For example, 1 *M* NH_4NO_3 was found to displace about one sixth of the amount of Cd displaced from soil by strong acids.[15] In some studies of Pb in soils,[11] 0.05 *M* $CaCl_2$ displaced traces, 0.5 *M* $BaCl_2$ released 0.1 to 4%, and 1 *M* NH_4OAc extracted 1 to 10% of the total. In comparison studies using organic matter free, Na^+ form clays, electrolyte solutions were found[5] to displace only small amounts of Cu, Pb, Cd, or Zn.

3. *Synthetic Chelating Agents*

As explained in section IV, conversion of cations into stable anionic complexes or chelates should promote their release from many components of soils.

The reaction involved on addition of a ligand containing solution may be represented as

$$A^{n+} + yHL \rightleftharpoons AL_y^{(y-n)-} + yH^+ \qquad (6)$$

and the extent to which complex formation proceeds thus depends on the stability of the complex species and the basicity of the ligand, L^-. With proton transfer involved in the process, the position at equilibrium is obviously sensitive to pH. (The equation quoted is a gross simplification, for most reagents used are polybasic and some react with cations to form a sequence of complexes.) Increasing the pH should increase the degree of interaction, but where the stability of the complex ion is only moderate, there is an upper limit which can be used, since in alkaline media hydroxyl ions also complete for coordination sites. For example, even in the presence of excess oxalate, metal-oxalato complexes tend to be increasingly converted into hydrous oxide compounds as the pH is increased beyond 7 (particularly in the presence of clay particles[101-103]).

In extraction studies the pH of the added reagent solution may be modified by the presence of the solid suspension, with the degree of change induced depending on the buffer capacity of the solid.

Synthetic chelating agents, such as EDTA and DTPA, have been widely used as extractants (Section II), due in large part to their ability to form very stable, water-soluble complexes with a wide range of polyvalent cations. The same property requires that the concentration used be sufficient to react with all releasable di- and trivalent cations, for in mixed systems reactions proceed in accordance with the effective stabilities of the individual systems at the equilibrium pH.

Chelating solutions possess the ability to dissolve some sparingly soluble solids, but the rate of attack varies markedly with the degree of crystallinity or "aging". Time, particle size of the solid, nature of the chemical compounds, pH and concentration of the reagent, and effective stability of the chelate all serve to control the extent of such dissolution processes.

As explained in Section IV, the effective stability of the chelate of interest also influences the extent to which a selected cation can be retrieved from the organic component of the soil.

While published stability constant data can be used to predict the mole fractions of different species present, with varying solution conditions, it is difficult to allow adequately for the competing processes introduced by having solids present. Distribution diagrams have been prepared[147] for EDTA and DTPA interactions with soils containing ions such as Ca^{2+}, Fe^{3+}, Zn^{2+}, and H^{+}, and a modification of this approach was used[148] to establish the solubility relationships of native forms of Cu, Zn, Mn, and Fe in some alkaline, calcareous soils. It was found that the solution levels were affected by soil pH and organic content, and the values did not conform to the solubility products of known sparingly soluble compounds or minerals. It may be appropriate here to recall that the ability of EDTA and DTPA to remove elements such as Zn, Cu, Mn, and Fe was observed to improve if one increased shaking time, solution pH, and reagent concentration.

While it is difficult to define positively the sources of cation that contribute to final values, it seems reasonable to propose that chelating agent extractions provide a comparative measure of the sum of the exchangeable or displaceable adsorbate plus organically bound.

B. Comparative Extraction Studies

The differences noted when soil samples were subjected to a series of different extractants (Section II) are, in general, consistent with the ideas outlined in preceding sections.

As outlined in Section III, a succession of extractants can be used to isolate different fractions of an element present in soils. Some steps involve exchange and displacement, others seek to dissolve, in a selective manner, soil components. Hopefully other procedures will be developed in the future, and an associated challenge is the development of methods for validating assumed bonding modes or extractant action.

Few experimental approaches suitable for judging the potential efficiency of such processes have yet been developed.

If one "spikes" natural soils or sediments with salt solutions, preferential uptake by some component sites can occur, and the degree of saturation for different sites will be concentration dependent (in accordance with appropriate adsorption isotherms). Comparison or recovery tests accordingly will tend to measure the ability of reagents to displace cations held on these more attractive or accessible positions. The bonding of this added material may bear little relation to that of native constituents, since these could have become incorporated under entirely different environmental conditions (e.g., in terms of pH, presence of precipitating anions, e.g., CO_3^{2-} or S^-, etc.).

The significance of deposition conditions was clearly discernible in a study[5] in which Na^+-form clays were treated with metal solutions adjusted to pH 5 or 7. The salt concentration used was sufficient to ensure saturation at pH 5 of most available exchange or adsorption sites. The amount taken up at pH 7 was much greater, due to the formation of sparingly soluble hydroxy species, part of which became firmly bonded to clay particles.

After isolation, the metal-ion contaminated clays were subjected to extraction, using a range of chemical solutions. The fraction retrieved by any selected reagent varied greatly between systems, being sensitive to type of clay, pH of deposition, and nature of metal ion. For example, using samples where the initial uptake occurred at pH 5, 0.1 *M* nitric acid released most of the Pb and Zn (held on kaolin), Cd (on illite), and Cu and Cd (held on montmorillonite). Only slightly more than half of the other metal ions held on these different clays was displaced by this reagent. The ability of the acid to dissolve freshly precipitated metal hydroxides was expected to ensure better percentage recoveries using the pH 7 adsorption samples, but in fact, recoveries remained quite low for Cd (kaolin, illite), Zn (illite), and Pb (montmorillonite). Oxalic acid (0.1 *M* pH 3.2), however, totally displaced Cu, Cd, and Zn from all three clays (and Pb adsorbed by kaolin and illite at pH 5). This reagent removed much smaller amounts of Pb when it was presorbed at pH 7. EDTA (0.001 *M* pH 7) extracted virtually all of each of the four metal ions, from all test samples. Simple electrolyte solutions (e.g., NH_4NO_3, $CaCl_2$) of pH <6 appeared to be capable of displacing the majority of Zn^+ retained on kaolin, Cd^{2+} held on illite, and Cu^{2+}, Cd^{2+}, and Zn^{2+} present on montmorillonite. With other metal ions on the different clays, or using clays treated at the higher pH, recoveries were often as low as 25%.

The patterns of behavior reported can only be described as somewhat inconsistent and partially predictable, but they do serve to emphasize that much more remains to be learned about basic interactions before extraction data can be confidently explained.

VI. GENERAL DISCUSSION

In past decades, the analytical problems associated with trace element analysis have been ascribable to aspects such as lack of sensitivity of techniques, interference effects, etc. A high proportion of these difficulties has been overcome, and many extensive surveys of element distributions in different types of environmental samples have been completed. Developments in interdisciplinary areas are creating new challenges, however, and some may be solved by the judicious application of selective extraction procedures. The limitations of this approach have been considered in preceding sections, and summary diagrams such as Figure 5 tend to imply that extraction procedures may only crudely differentiate between the different forms of selected species present in sedimentary material.

In this review an attempt has been made to assess the current situation and to provide some indication of the chemical processes involved. It would seem that a distinct gap

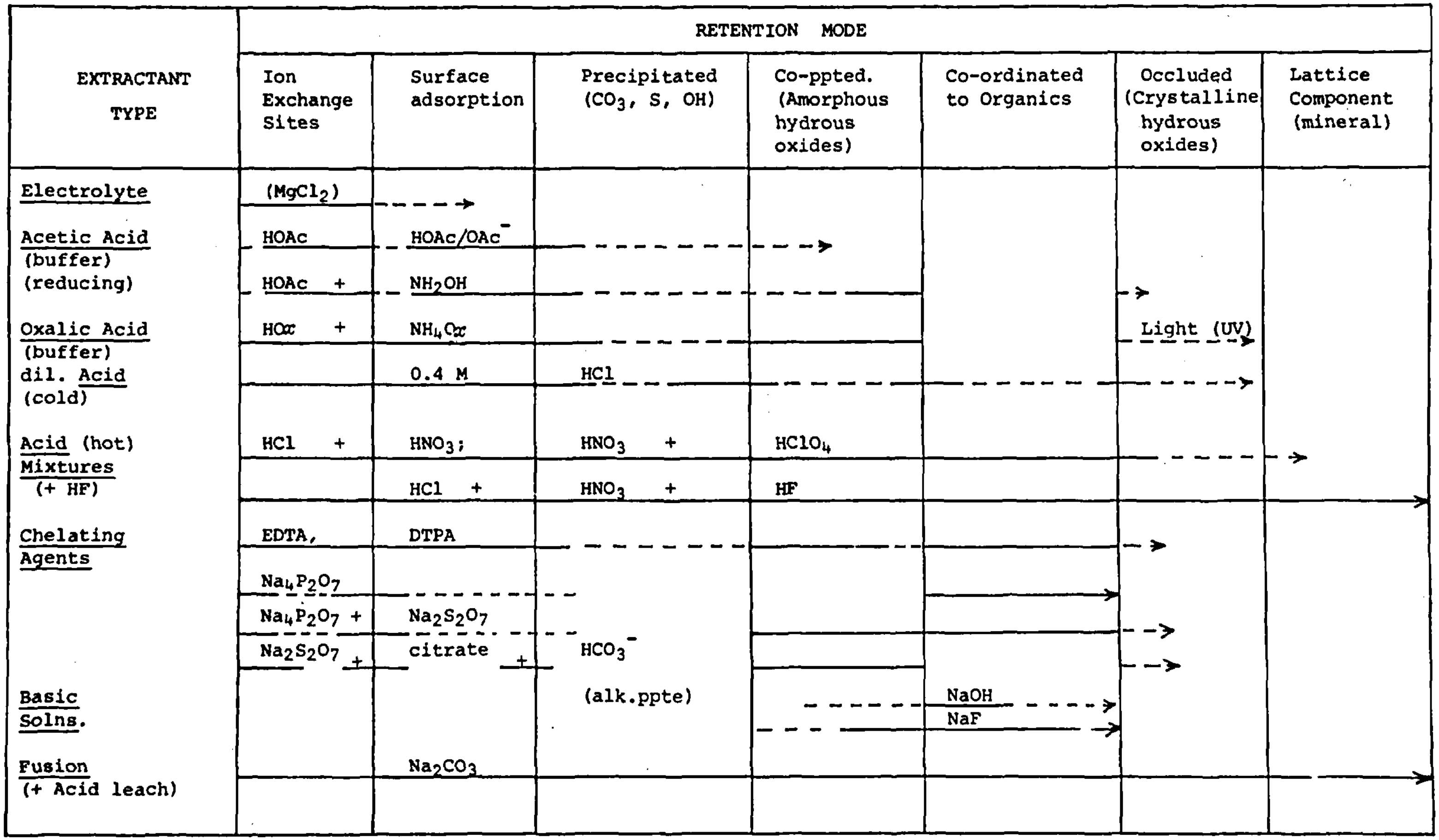


FIGURE 5. Schematic representation of the ability of different extractant solutions to release metal ions retained in different modes or associated with specific soil fractions. Dashed segments indicate areas of uncertainty.

between basic studies and applications to real systems still exists, and the influence of many experimental parameters need to be clarified. Thus the effect of grinding, particle size, time of shaking, concentration of reagent, temperature, etc. needs to be investigated further. Greater recognition must be paid to adsorption equilibria effects (soil mass/extractant volume relationships, efficiency of extraction, pH effects), and appropriate testing procedures need to be devised.

Calibration based on additions to soil/sediment samples is a compromise which could yield false conclusions, due to the unknown mode of bonding of the added material. Standards based on natural materials will be difficult to prepare, since it presupposes that the efficiency of the separation procedures initially adopted can be validated. The range of standards required could also prove to be extremely large. An initial first step might be further extraction studies on impurity loaded isolated components, with follow up studies on synthetic mixed systems.

If speciation does become a future demand, refined extraction procedures have the potential to yield the simple approach sought for routine operations. Careless usage of this technique, without an appreciation of its pitfalls and limitations, must, however, lead to further generation of erroneous or misleading data.

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