Reactions between aqueous zinc, aluminium and iron with increasing solution pH

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ABSTRACT

Solutions of zinc, aluminium and/or iron, as chlorides in NaCl of ionic strength 0.13 mol/l at pH 3, were mixed to give initial concentrations of 0-5, 5-50 and 10-100 mg/ml, respectively. Sodium hydroxide was then added to increase the pH in a range up to 7. Turbidity was measured and equilibrium concentrations were determined after filtration (< 0.1 µm). Decrease in pH on mixing suggested an immediate reaction, with the release of protons. At all pH values Zn concentration decreased with increasing initial concentrations of Fe and Al. Adsorption and/or nucleation of Zn with Fe and Al was highly pH dependent and increased markedly with increasing pH. The particle size of the products increased with increasing pH and initial concentration of the elements. Increasing Al concentration decreased the size of Fe nucleates at a given Fe concentration. The results suggest that co-precipitation may be involved as well as adsorption. This has important consequences for the availability of Zn to plants, especially in Zn-deficient soils, and is of relevance to the products of mixing acid drainage waters with streams and lakes.

INTRODUCTION

Reports of Zn deficiency in crops grown on a wide variety of soils continue to increase with the greater use of more sophisticated methods of analysis and under the demands of intensive agriculture, especially in less well-developed countries. Recent examples are citrus trees in India (Chauhan et al., 1984), maize and rice in Egypt (El-Fouly et al., 1984), wheat in India (Khamparia et al., 1984), apple trees in the USSR (Naumov et al., 1984), avocado trees in the Canary Islands (Barroso et al., 1985) and navy beans in Australia (Wade and Bath, 1985).

Deficiency often occurs despite relatively high total soil Zn contents and much attention has been paid to the mechanisms by which Zn is rendered unavailable to plants. It has been concluded that specific adsorption by metal oxide and hydroxide minerals is the principal mechanism of Zn retention over a wide pH range. The minerals involved are mainly oxides of Al, Fe and Mn (Jenne, 1968; Brummer et al., 1983; Micera et al., 1986).

Clay minerals have also been shown to retain Zn (Bingham et al., 1964; Reddy and Perkins, 1974), but adsorption by the soil clay fraction is usually attributed mainly to its oxide content (Shuman, 1976; Wada and Abd-Elfattah, 1978; Cavallaro and McBride, 1984). There are conflicting reports on the significance of soil organic matter in Zn adsorption (Brummer et al., 1983; Cavallaro and McBride, 1984), but soluble or dispersed organic complexes may make Zn apparently more available at higher pH values (Trehan and Sekhon, 1977; Jahiruddin et al., 1985).

As shown by the reviews of Pickering (1980) and Kinniburgh and Jackson (1981), by far the greatest emphasis has been placed on adsorption as the method of Zn retention in soils. However, it must be recognised that as soil pH is increased on liming, precipitation of many aqueous metal species will occur. This may result in complex co-precipitation products and Zn will behave very differently from a surface-adsorbed complex. This work was undertaken to observe the relationships between aqueous Al, Fe and Zn in acid solutions as the pH is raised, in order to help understand better Zn retention mechanisms in soils.

MATERIALS AND METHODS

Stock solutions of Al, Fe and Zn were prepared from the respective analytical reagent grade chlorides in 0.1305 M NaCl solution, acidified to pH 3 as necessary with 0.1305 M HCl, thus giving a Na concentration of ~ 3,000 mg/ml and a standard ionic strength. Mixing of solutions, pH control and titrations were carried out in a Radiometer titration unit comprising: a TTA 80 titration assembly; two ABU 80 autoburettes and two TTT 80 titrators, one set for acid and one set for base titrations; an REA 80 pH-stat unit; an REA 160 titrograph module; and a Servograph REC flat-bed recorder.

Volumes of Al and/or Fe stock solution were measured into the titration vessel and diluted with 0.1305 M NaCl (pH 3) solution to 18 ml or 20 ml, then finally adjusted to pH 3 with 0.1305 M HCl or 0.1305 M NaOH. A 2-ml portion of solution containing the required quantity of Zn, also at pH 3, was then added with the titrator in
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Figure 1 Turbidity versus pH curves Fe-Zn (A,B) and Al-Zn (C) solutions. Initial concentrations: Al, 5 and 50 μg/ml (Al₁, Al₂); Fe, 10 and 100 μg/ml (Fe₁, Fe₂); Zn, 0, 1 and 5 μg/ml (Zn₀, Zn₁, Zn₂).

pH-stat mode. Various mixtures were prepared with final concentrations of Al close to 5 or 50 μg/ml, of Fe close to 10 or 100 μg/ml and of Zn at 0 or close to 1 or 5 μg/ml.

Duplicate sets were titrated to pH values in the range 3 to 6 at half pH-unit intervals and to pH 7 for Al-Zn and Fe-Zn mixtures, and in the range 3 to 7 at full pH-unit intervals for Al-Fe-Zn mixtures. Titration was continued in pH-stat mode until reaction had essentially ceased. This took from 5 to 30 minutes depending on the metal concentrations. The final solution volume was used in all subsequent calculations.

Samples were transferred to sealed containers, allowed to stand for 24 hours at 20 ± 1°C and solution pH was measured. After vigorous shaking, absorbance of the suspension at 300 nm was measured on a Cecil CE 505 double-beam UV spectrophotometer. The values were translated into arbitrary "turbidity units", the difference between the sample and a 0.1305 M NaCl solution blank. Suspensions were filtered through 0.1 μm Nucleopore membrane filters. Turbidity values for the filtrates were insignificant in all cases. Filtrates were analysed for Al by flame emission spectrophotometry, and for Fe and Zn by atomic absorption spectrophotometry using matrix-matched standards. All results presented are means of duplicates.