



Isolation and purification of hydrophilic fulvic acids by precipitation

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Abstract

Fulvic acids play an important role in the behavior of metals and hydrophobic organic chemicals in soil and water environments. The isolation and purification of the fulvic acids have been difficult to achieve, however, because these compounds are soluble in both alkaline and acidic solution, resulting in difficulty of dehydration and demineralization. We propose here a new procedure for isolating fulvic acids as precipitates. Our procedure includes pH-adjustment of the fulvic acid solution to weakly acidic to neutral pH range (4 to 7). In an Andisol, recoveries of the fulvic acids we prepared by precipitation at equilibrium pH of 5.0 were 86% (dissolved total organic carbon basis) and 97% (absorbance basis, 400 nm), whereas recoveries of fulvic acids adsorbed on XAD-8 resin (hydrophobic fulvic acids) were 14% and 28%, respectively. Recoveries of the fulvic acids were further increased in our procedure by adding Al. The mechanism forming the precipitates includes a complexation reaction of carboxylic groups of the fulvic acids with Al (ligand exchange reaction); this mechanism is identical to that for the retention of fulvic acids in many soils. Therefore, it is likely that our preparation procedure is appropriate for separating the fulvic acids stabilized in soils. Solid-state cross polarization and magic angle spinning ¹³C nuclear magnetic resonance spectra showed that the fulvic acids prepared by our precipitation procedure were relatively rich in *O*-alkyl carbons and poor in aromatic and alkyl carbons compared with those forms from the hydrophobic fulvic acids adsorbed on XAD-8 resin. A new scheme for preparing the hydrophobic and hydrophilic fulvic acids is also proposed here. The hydrophilic fulvic acids are likely to maintain high solubilities in water even after the formation of complexes with metals and may influence on their behavior.

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1. Introduction

Most sesquioxides and heavy metals have low solubilities in water, and they tend to persist in soil

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environments. These metals are, however, able to form soluble complexes with soil organic matters and move into groundwater systems. For the formation of the soluble complexes, the soil organic matters should have hydrophilic moieties, which increase the solubility in water. Dissolved soil organic matter can also enhance transport of hydrophobic organic chemicals of soils into groundwaters (Schwarzenbach et al., 2003). Therefore, hydrophilic soil organic matter has been considered to play an important role in the behavior of metals and hydrophobic organic chemicals in soil and water environments (Sparks, 2003).

To clarify the chemical properties of hydrophilic soil organic matter, research has been focused on soil fulvic acids, which have lower molecular weights, stronger acidities, and higher water-solubilities than humic acids. Preparation of the fulvic acids, however, has not been easy because they are soluble in both alkaline and acidic solution, resulting in difficulty of dehydration and demineralization. To isolate the fulvic acids as a solid phase, an adsorption procedure using a hydrophobic resin, XAD-8, was employed by Thurman and Malcolm (1981). This procedure has been widely accepted as a standard method for the preparation of fulvic acids and recommended by International Humic Substances Society (<http://www.ihss.gatech.edu>). However, it should be noted that the adsorbed fraction of the fulvic acids on the XAD-8 resin strictly should be called “hydrophobic fulvic acids” and that the fraction not adsorbed by the resin, which should be more hydrophilic than the adsorbed fraction, is typically discarded. Kuwatsuka et al. (1992) reported that the amounts of non-adsorbed fraction were larger than those of the adsorbed fractions for a brown forest soil and an Ando soil.

The non-adsorbed fractions on XAD-8 resin would also persist in soil environments for a long time, as well as the adsorbed fractions. The retention mechanisms of them on soils would include coordinate bonds through metals, which are called complexation or ligand exchange reactions, resulting in polymerization and adsorption on the surfaces of soil minerals (see Fig. 1A). In our study, the complexation reaction was applied to enable the fulvic acids to be isolated as precipitates, instead of using the hydrophobic interaction by XAD-8 resin. The isolated and purified fulvic acids were characterized in terms of solid-state cross

polarization and magic angle spinning (CPMAS) ^{13}C nuclear magnetic resonance (NMR) spectra and recoveries. Carbon-13 CPMAS NMR has been reported to be useful for characterizing soil organic matter under different management and environmental conditions (Mathers et al., 2000; Mathers and Xu, 2003; Ussiri and Johnson, 2003; Chen et al., 2004). Finally, a new scheme for preparing the hydrophobic and hydrophilic fulvic acids is proposed.

2. Materials and methods

2.1. Preparation of soil samples

Three soil samples from Japan were collected from surface horizons (A horizons). Selected characteristics are listed in Table 1.

2.2. Recoveries of fulvic acids prepared by precipitation procedure as influenced by equilibrium pH

Two kilograms of Ib-G5 soil were extracted with 16 L of 0.1 M NaOH in the presence of 3% NaCl overnight. Supernatant was collected by centrifugation (10,000 $\times g$, 15 min). This extraction procedure was repeated three times. The supernatant (humic acid plus fulvic acid) was acidified to pH 1.0 with 4 M HCl, allowed to stand overnight, centrifuged (10,000 $\times g$, 15 min) to remove dispersed humic acid, and then filtered through a 0.2- μm pore-sized filter membrane (cellulose nitrate, Advantec Toyo Kaisha, Ltd, Tokyo).

A 10 mL portion of the resultant filtrate (crude fulvic acid solution) was diluted with 0.1 M NaOH and distilled water to achieve variable final pH values between 1 and 13 and a final volume of 25 mL. After incubation overnight, precipitates (fulvic acid) were removed with centrifugation (6000 $\times g$, 15 min). To clarify the mechanism of the precipitate formation, similar experiments were conducted in the presence of 0.05 M phosphate and 0.05 M pyrophosphate. The non-precipitated fraction of the crude fulvic acid, which remained in the supernatant, was estimated using two different parameters: absorbance at 400 nm, as determined by a spectrophotometer (U-2010, Hitachi High-Technologies Corporation, Tokyo); and concentration of dissolved total organic carbon, as determined by a total organic carbon analyzer (TOC

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