EFFECTS OF PYROGALLOL ON Al_{13} TRIDECAMER FORMATION AND HUMIFICATION

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Abstract—The Al_{13} polycation is the predominant hydroxy-Al species in partially neutralized solutions. However, the existence of the Al_{13} species and the factors governing its formation in terrestrial environments still remain obscure. The objective of this study was to investigate the influence of pyrogallol, a common polyphenol in soils, on the formation of Al_{13} tridecamer. Hydroxy-Al solutions with an OH/Al molar ratio of 2.2 (pH 4.53) at pyrogallol/Al molar ratios of 0, 0.01, 0.05, 0.1 and 0.5 were prepared and mixed with 0.5 M sodium sulfate to form aluminum sulfate precipitation products. The solid-state ^{27}Al nuclear magnetic resonance (NMR) spectra of the precipitates show that the pyrogallol perturbed the formation of Al_{13} tridecamer species as indicated by the decrease in the intensity of resonance peak, observed at 62.5 ppm, with increase in the pyrogallol/Al molar ratio. The crystallization of the precipitated Al sulfates was also hampered by pyrogallol, resulting in the formation of X-ray non-crystalline products at a pyrogallol/Al molar ratio of 0.50. The absorbance at 465 and 650 nm of the hydroxy-Al-pyrogallol solutions, the C coprecipitated, the electron spin resonance and ^{13}C CPMAS-NMR spectra of the precipitates indicate the concomitant enhanced abiotic humification of pyrogallol by the X-ray amorphous Al species.

Key Words—Al_{13} tridecamer, ESR, Humification, Hydroxy-Al Sulfates, Pyrogallol, Solid-state NMR, XRD Data.

INTRODUCTION

Aluminum is released from alumino-silicate minerals into soil solution through chemical and biochemical weathering reactions. Its high reactivity leads to hydrolytic reactions as well as to strong complexation with naturally occurring organic acids (Huang, 1988; Bertsch, 1989; Vance *et al.*, 1996; Huang *et al.*, 2002; Violante *et al.*, 2002). Johansson (1960) showed that the Al_{13} polycation was the dominant hydrolyzed species formed from the hydrolysis of Al (III), at an OH/Al ratio of ~2.5, on the basis of crystallographic data for the structure of basic aluminum sulfates precipitated from Al-OH solutions. The existence of this species (Al_{13} polycation) with the idealized structure of $[AlO_4Al_{12}\cdot(OH)_{(24+n)}(H_2O)_{(12-n)}]^{(7-n)+}$, was later confirmed by ^{27}Al and ^{17}O NMR spectroscopy (Akitt *et al.*, 1972; Bottero *et al.*, 1980; Akitt and Farthing, 1981; Bertsch *et al.*, 1986a, 1986b; Bertsch, 1987; Thompson *et al.*, 1987; Akitt and Elders, 1988; Akitt, 1989). The ^{27}Al NMR resonance of the AlO_4 nucleus of the Al_{13} tridecamer is observed at 62.5 ppm in solution (Akitt and Elders, 1988) and also at an almost identical position for the sulfate crystals (Mueller *et al.*, 1981; Kunwar *et al.*, 1984).

The relative distribution of the hydrolyzed or complexed Al species is the determining factor of its mobility in soil solution leading to toxicity to aquatic and terrestrial organisms in natural ecosystems (Bertsch and Parker, 1996). The Al_{13} ion was reported to be ten times more toxic to plants than the hexaquo Al ion (Parker *et al.*, 1989). Flatten and Garruto (1992) also claimed that polynuclear Al species are more toxic to fish than monomeric Al species. This indicates the importance of the study of the formation and transformation of Al_{13} polycation. The Al_{13} polycation is also probably responsible for the decline of fish population in rivers polluted by mine drainage and acid rain (Poleo, 1995). Photochemically induced Fe(III) reduction associated with oxidation of a simple hydroxy-carboxylic acid (lactate) may promote the formation of Al_{13} polycation in natural waters (Ross *et al.*, 2001). The formation of Al_{13} is attributed to the pH rise resulting from the removal of the organic acid buffer. Mixing of mine drainage and acid waters at higher pH causes precipitation of amorphous aluminum oxyhydroxide flocs which probably form from aggregation of Al_{13} polycations because all of the flocs contain distinct $Al(O)_4$ centers similar to that of the Al_{13} nanocluster (Furrer *et al.*, 2002). These flocs move in streams as suspended solids and transport adsorbed contaminants. The chemical affinity of Al_{13} species for heavy metal cations such as Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} (Lothenbach *et al.*, 1997) suggests that dissolved Al_{13} and suspended Al oxyhydroxide flocs can transport metals downstream over considerable distances. The influence of a few organic ligands on the speciation of Al(III) was studied

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by ^{27}Al NMR spectroscopy (Thomas *et al.*, 1991, 1993; Yamaguchi *et al.*, 2003) and small-angle X-ray scattering (Masion *et al.*, 1994a, 1994b, 1994c). The Al$_{13}$ tridecamer forms at pH > 4.2 and the presence of organics leads to depolymerization of Al$_{13}$ polycation into oligomers and subsequently to monomers.

Direct ^{27}Al NMR evidence of the existence of the Al$_{13}$ polycation in an acid forest soil, under natural terrestrial environment conditions was obtained by Hunter and Ross (1991). Subsequent investigations at the same site failed to prove the existence of Al$_{13}$ polycations, although it is possible that the presence of Al$_{13}$ polycations is masked by other paramagnetic metals (*e.g.* Fe, Mn) in these soils (Bertsch and Parker, 1996). The Al$_{13}$ peak at 62.5 ppm is increasingly difficult to quantify in solution samples with Al concentration <3×10^{-4} M. Shann and Bertsch (1993) demonstrated the existence of Al$_{13}$ at Al concentrations of ~10^{-5} M, as quantified by the Ferron procedure (Parker and Bertsch, 1992a,b), to be toxic to plants. The Ferron method is a $10-100$ fold improvement in sensitivity over NMR capabilities.

The occurrence of the Al$_{13}$ polycation and the factors governing its formation in soil and related environments remain obscure. Krishnamurti *et al.* (1999) reported that low-molecular-weight organic acids, such as tartaric acid, inhibit the formation of Al$_{13}$ polycation and suggested that organic acids may partially contribute to perturbation of the formation of Al$_{13}$ tridecamer species in terrestrial ecosystems.

Polyphenols are common in the decomposition products of plant and animal materials and microbial metabolites and are commonly present in soils (Hayes and Swift, 1978; Wang *et al.*, 1986; Huang and Bollag, 1999). The concentration of phenols in soil solution varies seasonally, between 10^{-3} M and 10^{-4} M, with higher concentrations encountered under plant litter and in the soil rhizosphere (McKeague *et al.*, 1986). The present report highlights the influence of pyrogallol, which is a common polyphenol in soils, in perturbing the formation of Al$_{13}$ tridecamer species and also indicates the concomitant abiotic humification of pyrogallol during hydroxy-Al transformations.

MATERIALS AND METHODS

Preparation of OH-Al solutions both in the absence and in the presence of pyrogallol

Solutions with an OH/Al molar ratio of 2.2 were prepared by titrating 100 mL of 0.1 M AlCl$_3$ solution to pH 4.53 with 0.1 M NaOH at a rate of 1 mL min^{-1}; the solution was diluted to 500 mL. The final concentration of Al in the solution was 0.02 M. Hydroxy-Al solutions titrated to pH 4.53, at pyrogallol/Al molar ratios (*R*) of 0.01, 0.05, 0.10 and 0.50 (concentration of pyrogallol ranging from 2×10^{-4} to 10^{-2} M), were also prepared as described above.

Determination of absorbance of hydroxy-Al-pyrogallol solutions

The absorbances of the OH-Al solution, after filtration (Whatman # 1) and then centrifugation at 15,000 g for 30 min, formed at a pyrogallol/Al molar ratio of 0.5, and of the pyrogallol solution in the absence of OH-Al were determined at 465 and 650 nm by visible absorption spectrophotometry using a Beckman DU 650 microprocessor-controlled absorption spectrophotometer (Beckman Instruments, Fullerton, California).

Precipitation of basic aluminum sulfates

50 mL of 0.5 M sodium sulfate were mixed with 200 mL of the OH-Al solution formed both in the absence and in the presence of pyrogallol at *R* = 0.01, 0.05, 0.10 and 0.50, and pre-aged for 5 days to make the final concentration of 0.016 M Al and 0.1 M sulfate. The precipitate of the basic aluminum sulfate, formed from the solution aged for 12 days, was collected by ultrafiltration (0.01 µm nitro-cellulose filter).

Analysis of the aluminum sulfate precipitates

Solid state nuclear magnetic resonance (NMR) spectroscopy. High-resolution solid-state ^{27}Al NMR spectra of the basic aluminum sulfates formed at pyrogallol/Al molar ratios of 0, 0.01, 0.05, 0.10 and 0.50 were obtained at ambient temperature (~23ºC) on a Bruker AM360WB spectrometer with cross polarization magic angle spinning (CPMAS) accessory using 80 Hz line broadening, with a 90º pulse of 6.5 µs and recycle delay of 1 s, and a spinning speed of 4 kHz, with AlCl$_3$ chemical as a reference.

High-resolution solid-state ^{13}C CPMAS NMR spectra were also obtained for the basic aluminum sulfate precipitates, formed at a pyrogallol/Al molar ratio of 0.50, at ambient temperature (~23ºC) on a Bruker AM360WB spectrometer with CP/MAS.AU accessory at 90.561 MHz using 80 Hz line broadening, with a 90º pulse of 6.5 µs, a recycle delay of 1 s, and a spinning speed of 4 kHz. Tetramethylsilane (TMS) was used as a reference.

X-ray diffraction (XRD). The basic aluminum sulfate precipitation products, formed at pyrogallol/Al molar ratios of 0, 0.01, 0.05, 0.10 and 0.50, were examined by powder XRD using FeKα radiation on a Rigaku Rotaflex 2000 X-ray diffractometer equipped with graphite monochromator, operating at 40 kV and 130 mA at a step-scan rate of 0.01º2θ s^{-1}.

Electron spin resonance (ESR) spectroscopy. The ESR spectra of the basic aluminum sulfate precipitates formed at a pyrogallol/Al molar ratio of 0.50 were recorded at ambient temperature (23ºC) on a Bruker ESP 300 spectrometer, employing 100 kHz modulation and a nominal frequency of 9.38 GHz. Line widths and

g values were calculated according to standard methods (Wertz and Bolton, 1972).

Organic C analysis. The organic C content of the basic aluminum sulfate precipitation products formed in the presence of pyrogallol at various concentrations was determined with a Leco CR 12C analyzer (Wang and Anderson, 1998).

RESULTS AND DISCUSSION

The solution ^{27}Al NMR spectrum of the OH-Al solutions formed in the absence of pyrogallol shows only one sharp or intense resonance peak at 62.5 ppm indicating that Al was present predominantly as Al_{13} tridecamer species in the OH-Al solution (data not shown). The Al_{13} tridecamer $[AlO_4Al_{12}.(OH)_{24}(H_2O)_{12}]^{7+}$ gives two resonances, a sharp one at 62.5 ppm from the AlO_4 nucleus and which is always visible, and a very broad one at ~12 ppm from the 12 octahedrally coordinated Al atoms (Akitt, 1989). At room temperature, only the AlO_4 resonance at 62.5 ppm is seen, and the octahedral component is only visible if the solution is heated (Akitt and Farthing, 1981).

The ^{27}Al NMR resonance of the AlO_4 nucleus of the Al_{13} tridecamer was also observed at 62.5 ppm in solution by Akitt and Elders (1988) and at an almost identical position for the sulfate crystals (Mueller *et al.*, 1981; Kunwar *et al.*, 1984). The effect of pyrogallol on the formation and transformation of the Al_{13} tridecamer species was carried out using the sulfate precipitates in the present study. No attempt was made to quantify the Al_{13} tridecamer species in the supernatant liquids using solution ^{27}Al NMR spectroscopy, as most of the Al_{13} tridecamer species must have precipitated as sulfate, and the concentration of the Al_{13} tridecamer species in supernatant liquids would be much below the detection limit of ^{27}Al NMR spectroscopy.

Al_{13} tridecamer species formed in the absence of pyrogallol

The ^{27}Al NMR spectrum of the sulfate precipitates formed in the absence of pyrogallol ($R = 0$) shows a strong resonance peak at 62.5 ppm (Figure 1a). The presence of a single peak at a chemical shift of 62.5 ppm indicates that the precipitates were dominated by the Al_{13} tridecamer (Figure 1a).

The powder XRD pattern of the precipitate of crystals with tetrahedral habit obtained in the present study is presented in Figure 2a. The *d* spacings calculated from the powder pattern were distinctly different from the powder XRD patterns of other synthetic and natural forms of basic aluminum sulfates reported (Table 1) (Bassett and Goodwin, 1949; Bersillon *et al.*, 1980; Tsai and Hsu, 1984). It is possible that the XRD patterns reported in those earlier studies might be from a

composite powder pattern of crystals conforming to more than two different symmetries.

The powder XRD pattern of the tetrahedral crystals was indexed following the method outlined by Azaroff and Buerger (1958) and the unit-cell dimensions were refined using the nonlinear least-squares refinement program UNITCELL (Holland and Redfern, 1997). The crystals conform to cubic symmetry ($a_o = 17.75\pm0.01$ Å) and a space group of $P4_232$ was assigned to the crystal based on the systematic conditions for reflections observed in the powder XRD pattern (Figure 2a). There was good agreement between the spacing calculated from the unit-cell dimensions and those observed in the powder XRD pattern (Table 1). The unit-cell dimension of 17.75 Å is in good agreement with that reported for tetrahedral single crystals of basic aluminum sulfates obtained from Al-OH solutions with an OH/Al molar ratio of 2.5, using X-ray Weissenberg photographs ($a_o = 17.9$ Å, Johansson *et al.*, 1960).
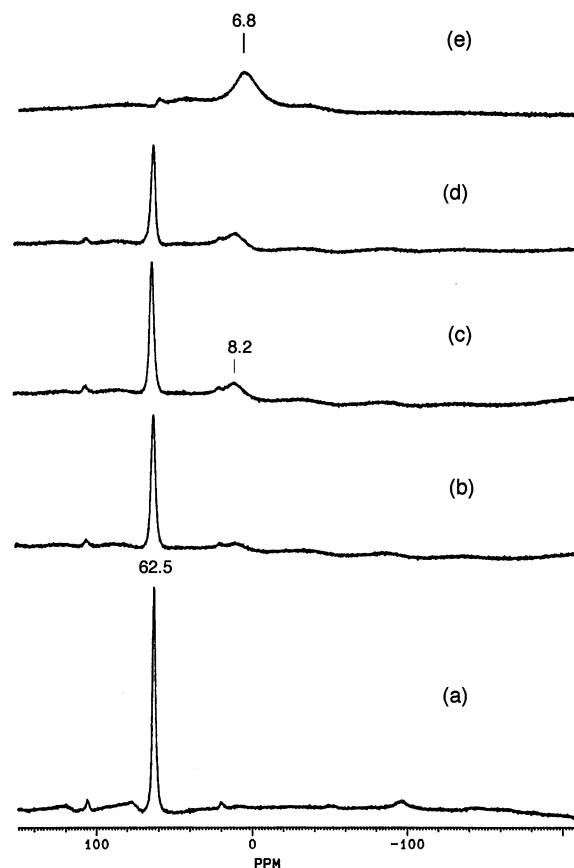

Figure 1. ^{27}Al CPMAS-NMR spectra of the basic aluminum sulfate precipitation products after 12 days of ageing, from 5-day aged OH-Al solutions formed at pH 4.53 and different pyrogallol/Al molar ratios (R). (a) control at $R = 0$; (b) sample at $R = 0.01$; (c) sample at $R = 0.05$; (d) sample at $R = 0.10$; and (e) sample at $R = 0.50$.
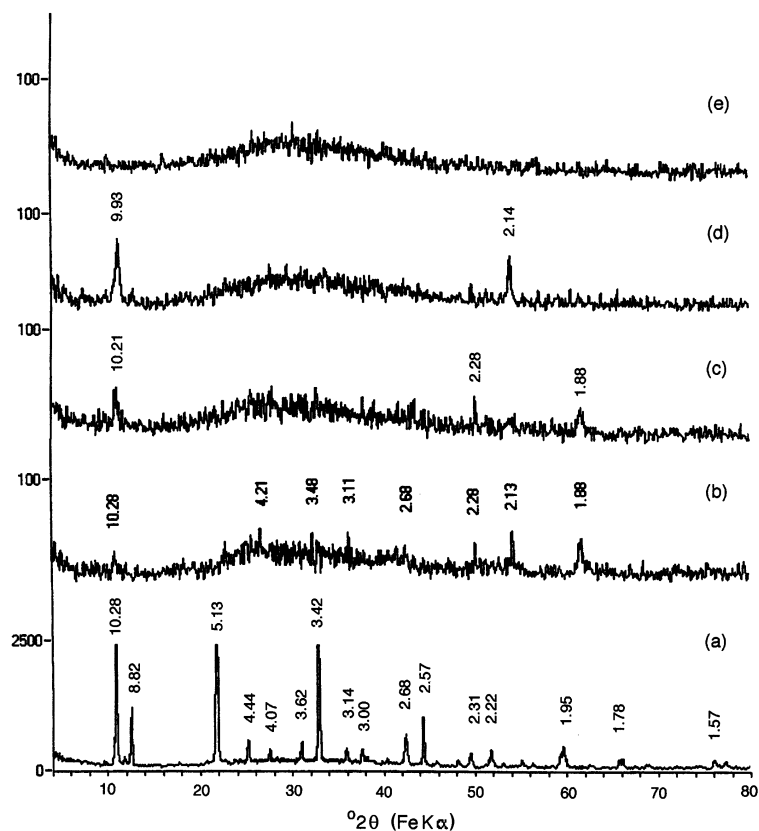
Figure 2. XRD patterns of the basic aluminum sulfate precipitation products after 12 days of ageing, from 5-day aged OH-Al solutions formed at pH 4.53 and different pyrogallol/Al molar ratios (R). (a) control at $R = 0$; (b) sample at $R = 0.01$; (c) sample at $R = 0.05$; (d) sample at $R = 0.10$; and (e) sample at $R = 0.50$.

Influence of pyrogallol on Al$_{13}$ tridecamer formation

The ^{27}Al NMR spectra of the sulfate precipitates formed in the presence of pyrogallol are presented in Figure 1. A decrease in the height of the resonance peak at 62.5 ppm (due to Al$_{13}$ tridecamer) with a concomitant increase in the intensity of a broad peak around 6.8–8.2 ppm (apparently due to complexes of octahedral Al-pyrogallol transformation species) was observed with the increase of the pyrogallol/Al molar ratio. The data show that the presence of pyrogallol perturbed the formation of Al$_{13}$ tridecamer species. The almost complete disappearance of the resonance peak at 62.5 ppm together with an additional broad peak at 6.8 ppm observed at $R = 0.50$ (concentration of pyrogallol = 10^{-2} M) (Figure 1e) indicated the inhibition of the formation of Al$_{13}$ tridecamer species. The XRD data of the precipitation products (Figure 2) showed that the crystallization processes of the precipitated aluminum sulfates were also increasingly perturbed with increase in the pyrogallol/Al molar ratio. At a pyrogallol/Al molar ratio of 0.50, the crystallization of the Al tridecamer species was completely perturbed resulting in the formation of X-ray amorphous Al precipitates (Figure 2e).

Effect of poorly ordered Al species on pyrogallol transformation

The absorbances of the pyrogallol-OH-Al solution (at pyrogallol/Al molar ratio of 0.50), and of the pyrogallol solution in the absence of OH-Al were determined at 465 and 650 nm by visible absorption spectrophotometry to assess the extent of the Al-OH species in catalysis of humification of pyrogallol. Such measurements were used to study abiotic formation of humic substances from polyphenols by catalysis of mineral colloids (Shindo and Huang, 1982, 1984; Wang *et al.*, 1986; Huang, 1990; Stevenson, 1994). The absorbances at 465 and 650 nm of the hydroxy Al-pyrogallol solution formed at $R = 0.50$ were 38.9 and 100 times higher, respectively, than that of the pyrogallol system in the absence of hydroxy-Al ions (Table 2). Further, the proportion of organic C co-precipitated in the aluminum sulfate precipitation products also increased with the increase in the concentration of pyrogallol (Table 3). This indicates that OH-Al species catalyzed humification of pyrogallol.

The ESR spectrum of the basic aluminum sulfate precipitate formed at $R = 0.50$ showed a single symmetrical line devoid of any fine splitting

Table 1. Data from the XRD pattern of the tetrahedral basic aluminum sulfate crystals formed from hydroxy-Al solutions (pH 4.53), together with the data from earlier reports.

Present work d spacing (Å)	Int.	Calculated[1] d spacing (Å)	Indices	Bassett and Goodwin (1949) d spacing (Å)	Int.	Bersillon et al. (1980) d spacing (Å)	Int.	Tsai and Hsu (1984) d spacing (Å)	Int.
				12.15	10	12.30	10	12.20	2
10.24	6	10.25	111			10.00	6	10.40	10
				9.89	9				
						9.61	1		
8.87	3	8.87	200	8.77	6	8.85	2	8.93	7
				7.00	3	6.93	2		
								6.53	1
				5.58	4	5.83	1		
5.13	10	5.13	222	5.25	3			5.17	10
						4.58	3		
4.44	2	4.44	400	4.45	7	4.37	3	4.47	3
						4.17	3		
4.07	1	4.07	331	4.12	6	4.06	2	4.10	2
				3.80	5	3.83	1		
3.62	2	3.62	422						
				3.56	5	3.53	1		
3.42	6	3.42	333,511					3.44	10
				3.29	5	3.33	1		
						3.24	1		
3.14	2	3.14	440	3.15	2				
3.00	2	3.00	531	3.01	4	3.00	1	3.02	3
				2.86	3	2.86	1	2.82	1
2.68	2	2.68	622			2.65	2	2.69	6
2.56	3	2.56	444					2.57	4
				2.43	2	2.39	1	2.38	1
2.31	1	2.31	731			2.30	1	2.32	2
2.22	2	2.22	800			2.20	1	2.23	3
2.09	1	2.09	822			2.12	2	2.10	1
1.95	2	1.95	911,753			1.92	2	1.96	3
1.78	1	1.78	771						

[1] a_o = 17.75 Å, deduced from the XRD pattern following the method of Azaroff and Buerger (1958)

(Figure 3), indicating the presence of free radicals. The free radicals have a g value of 2.0031 with line width of 7.2 G, indicative of semiquinones, the major free radicals normally observed in the humic acid fractions of soil organic matter (Schnitzer, 1978). The g value and the line width are close to the values reported for the humic acids produced from phenols (Schnitzer *et al.*, 1984).

The ^{13}C CPMAS-NMR spectrum of the precipitate formed at R = 0.5 shows major aliphatic C signals containing OH groups at 61 and 74 ppm, strong resonances at 106, 120, 138 and 149 ppm indicative of aromatic C, resonance at 164 ppm indicative of phenolic C and resonance peaks at 173 and 193 ppm indicative of carboxyl C (Figure 4). Pyrogallol is a polyphenol which

Table 2. Absorbance of the pyrogallol and hydroxy Al-pyrogallol solutions.

System	Absorbance	
	465 nm	650 nm
Pyrogallol (0.01 M)	0.54	0.05
Hydroxy Al-pyrogallol[1]	21.00	5.00

[1] At 0.01 M pyrogallol and a pyrogallol/Al molar ratio = 0.50
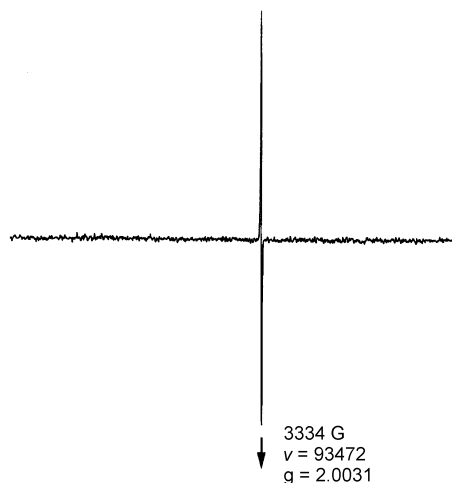

3334 G
v = 93472
g = 2.0031

Figure 3. ESR spectrum of the basic aluminum sulfate precipitation products after 12 days of ageing, from 5-day aged OH-Al solutions formed at pH 4.53 at a pyrogallol/Al molar ratio (R) = 0.50.

Table 3. Organic C precipitated together with aluminum sulfates in the presence of pyrogallol.

Concentration of pyrogallol (M)	Organic C in the precipitates (mg)	Proportion of organic C coprecipitated (%)
0	0	NA[1]
2×10^{-4}	3.6	72.0
1×10^{-3}	23.1	91.7
2×10^{-3}	47.4	94.0
1×10^{-2}	237.3	94.1

[1] NA − not applicable

does not consist of aliphatic C and carboxyl C groups. The solid-state ^{13}C CPMAS-NMR spectrum of pure pyrogallol shows only the resonances due to aromatic C at 145, 131, 121 and 110 ppm. The aliphatic and carboxyl C in the Al precipitation products formed in the presence of pyrogallol evidently resulted from the ring cleavage of pyrogallol catalyzed by hydroxy-Al ions. The origin of aliphaticity of natural humic substances is not very clear (Schnitzer, 1978). The effect of polyphenols such as pyrogallol on Al_{13} tridecamer formation (Figure 1) and on the crystallization of basic aluminum sulfates (Figure 2) and simultaneous abiotic humification of pyrogallol catalyzed by Al species (Tables 2, 3, Figures 3, 4) may, in part, account for the high aliphaticity of natural humic substances (Wilson and Goh, 1977; Hatcher *et al.*, 1981).

CONCLUSIONS

A close genetic link between Al_{13} species and solid Al hydroxides has been postulated (Bottero *et al.*, 1987; Hunter and Ross, 1991; Bertsch and Parker, 1996; Huang

Figure 4. ^{13}C CPMAS-NMR spectra of the basic aluminum sulfates precipitation products after 12 days of ageing, from 5-day aged OH-Al solutions formed at pH 4.53 at a pyrogallol/Al molar ratio (*R*) = 0.50.

et al., 2002). Mixing of acidic effluent from old mines and acid soils into waters with a higher pH causes precipitation of amorphous Al hydroxide flocs that probably form from aggregation of the ε-Keggin Al_{13} polyoxocation species (Furrer *et al.*, 2002). Furthermore, it has been demonstrated that the Al_{13} species forms by photochemically induced Fe(III) reduction associated with the oxidation of a hydroxy-carboxylic acid (lactate) (Ross *et al.*, 2001). The potential for photochemically induced synthesis of Al_{13} is present in the environment, but the exact conditions may be too restrictive. The Al_{13} species is difficult to observe in nature partially because the pH window between formation and aggregation is small and because condensation of Al_{13} molecules and subsequent aggregation at pH >5 are usually rapid and episodic.

The present study clearly demonstrated that polyphenols, such as pyrogallol, perturb the formation of Al_{13} tridecamer species resulting in the formation of X-ray amorphous Al species (Figures 1, 2). Besides sulfates (Kerven *et al.*, 1995), silicic acid (*e.g.* Larsen *et al.*, 1995; Hiradate *et al.*, 1998) and low-molecular-weight organic acids (*e.g.* Krishnamurti *et al.*, 1999; Yamaguchi *et al.*, 2003), polyphenols, as illustrated by pyrogallol, play a role in perturbing the formation of Al_{13} tridecamer species and hampering crystallization of Al hydroxides. The Al_{13} tridecamer, the predominant hydroxy Al species in partially neutralized solutions, is often below detection limits in natural environments; this is at least partially due to the perturbation of its formation by polyphenols present in terrestrial ecosystems.

The characteristics of polyphenol-derived polymers formed by catalysis of metal oxides have been reported (Wang and Huang, 2000) but pyrogallol transformations in relation to the formation of Al_{13} tridecamer remain obscure. The present study reports that perturbation of the formation of Al_{13} tridecamer by pyrogallol has resulted not only in the formation of poorly ordered Al phases, but also the concomitant catalyzed ring cleavage and humification of pyrogallol. Therefore, the data indicate that the formation of poorly ordered Al hydroxides through the perturbation of the formation of Al_{13} by polyphenols and the abiotic humification of polyphenols may be coupled. This information is of fundamental significance in understanding mechanisms
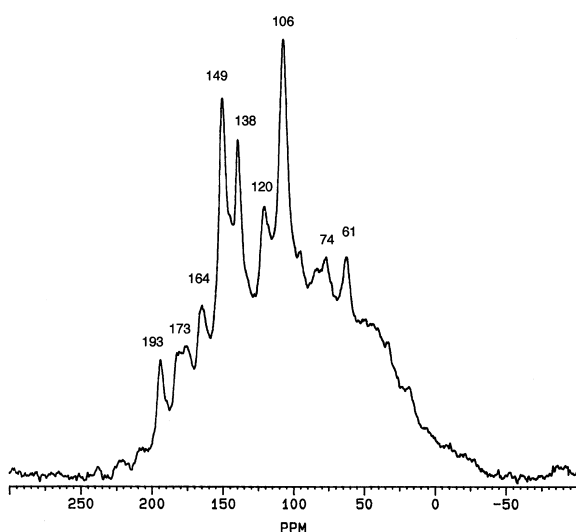
of formation and transformation of Al hydrolysis products and their role in abiotic catalysis in humification of organic substances in aquatic and terrestrial ecosystems.

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