toring of the transient tracer concentrations of GSDW will be valuable in studying the variability of deepwater formation in the Greenland Sea.

In our model calculations we assumed that the deepwater formation in the Greenland Sea operates in two modes (deepwater formation at full intensity before 1980 and slowed down deepwater formation during the 1980s). Such a simplistic view is certainly not correct. Instead, deepwater formation is a highly variable process in time and space. Whether formation of GSDW occurred continuously or sporadically in the period before 1980 cannot be derived from the tracer data because of a lack of time resolution. However, the observed tracer concentrations in GSDW between 1972 and 1979 clearly demonstrate that intensive deepwater renewal must have taken place between the appearance of the tritium bomb peak in the mid-1960s and the early 1970s. The observed tracer concentrations can be reconstructed by the model for the case of a constant deepwater renewal rate before 1980. The results demonstrate that on average formation of GSDW stopped almost completely during the 1980s. The model calculations have to be seen as a first-order approximation. Tracers are the only tool to monitor the average deepwater formation rate in the Greenland Sea on the basis of a station grid that can be realized in practical terms.

The model yields no information on the reason for the reduction of GSDW formation in the 1980s. Reduction could be connected to the appearance of the salinity anomaly observed in the northern Atlantic and the Greenland-Norwegian seas in the 1970s (21). This anomaly reached the Norwegian Current and Fram Strait in 1978 and the East Greenland Current between 1981 and 1982. This period coincides with the estimate of the start date of the cessation (1978 to 1982). A decrease in the salinity of the upper water column in the Greenland Sea can lead to the situation that the waters sinking from near-surface layers to deeper layers are, even after winter cooling, not sufficiently dense to reach the deep and bottom waters of the Greenland Sea. Such a scenario is also consistent with the observation that the temperature of GSDW increased during the 1980s (3). The deep and bottom waters would be affected first by a weakened convection. However, a further decrease of the salinity of the surface waters leading to even shallower convection depths would influence the formation of Arctic Intermediate Water. This water contributes significantly to the Denmark Strait overflow. In this way the properties of the newly formed North Atlantic Deep Water

(NADW) can be changed. Another possible process for reduction of GSDW formation could be an increase in the influence of the East Greenland Current on the surface waters of the Greenland Sea leading to a freshening of the upper water column (22). To obtain a clear link between the processes in the European Polar seas and variability in NADW requires a long-term monitoring program at key positions north and south of the Scotland-Iceland-Greenland ridges.

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24. The officers and crews of the research vessels Meteor, Knorr, and Valdivia provided logistical support during sample collection. G. Fuchs, K. P. Koltermann, J. Meincke, A. Suckow, and W. Weiss collected part of the tracer samples. G. Bader and G. Zimmek performed most of the tritium and ³He measurements. We profited from discussions with K. Aagaard, K. P. Koltermann, W. Smethie, J. Swift, and D. Wallace. This work was supported by the Deutsche Forschungsgemeinschaft and the Office of Naval Research through contract N00014-90-J-1362. L-DGO contribution no. 4749.

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Evidence for a Phytotoxic Hydroxy-Aluminum Polymer in Organic Soil Horizons

DOUGLAS HUNTER* AND DONALD S. ROSS

The toxicity of Al that has been mobilized in soil, streams, and lakes through acid deposition primarily has been attributed to mononuclear Al species. Polynuclear Al species are more toxic than mononuclear species, but they have not been considered to be significant in the environment. Aluminum-27 nuclear magnetic resonance (NMR) spectra of forested spodosol soil horizon samples show the presence of polynuclear $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$. The $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ species accounted for 30 percent of the aqueous Al observable by NMR, and this could make a significant contribution to the toxicity of the Al in these soils.

ALUMINUM IS A FUNDAMENTAL component of clay minerals in soils (1) that can be solubilized by acid deposition. The toxicity of Al to plants in acid soils and to fish in acid lakes has been

D. Hunter, Department of Botany, University of Vermont, Burlington, VT 05405.
D. S. Ross, Department of Plant and Soil Science, University of Vermont, Burlington, VT 05405.

*Present address: Division of Biogeochemistry, The University of Georgia, Savannah River Ecology Laboratory, Drawer E, Aiken, SC 29802.

observed to increase from pH 3 to pH 5.4 (2, 3). This phenomenon has been attributed to mononuclear hydroxy-aluminum species on the basis of equilibrium thermodynamic models. Aluminum can also polymerize to form polynuclear species at these higher pHs. Recently, a soluble polymer of Al, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (hereafter referred to as Al₁₃), has been shown to inhibit the growth of several plant species at one-tenth the concentration of Al^{3+} (4). Solutions containing polynuclear

Al species at pH 6 have been shown to be toxic to brook trout fry at levels of 1 μM of rapidly reactive Al (5, 6). The use of ^{27}Al nuclear magnetic resonance (NMR) spectroscopy is the only definitive means of identifying the Al_{13} species in solution. Although many ^{27}Al NMR studies have shown that Al_{13} can persist at low solution pH (7–9), there have been objections that Al_{13} is not of general significance in acid soils (4, 10). We present ^{27}Al NMR spectra of organic soil fractions that show that a major fraction of spectroscopically visible Al is present as Al_{13}.

There have been two major limitations to the application of ^{27}Al NMR to biological and soil systems. First, the large quadrupole moment of the ^{27}Al nucleus ($I = 5/2$) permits the easy observation of only those Al complexes for which there is a small electric-field gradient across the nucleus. This condition is met when complexing ligands are in a highly symmetric octahedral or tetrahedral coordination about the Al atom (11). Second, the concentration of aqueous Al in soil or biological systems is typically less than 100 μM, which is difficult to detect with ^{27}Al NMR.

Samples from the forested spodosol soil horizon were collected from Camel's Hump State Forest, Duxbury, Vermont, and stored moist at 4°C. Samples were formed into plugs and inserted into 10-mm NMR tubes. We performed routine ^{27}Al NMR experiments in which 50,000 transients were collected over a 5-hour period on samples from three soil profiles. We were able to detect aqueous Al in two of three organic surface horizons (samples 1 and 2 in Table 1). We were unable to detect Al in any of the lower mineral fractions from the three profiles sampled. The data collection time was increased to 40 hours (500,000 transients) for the two soil samples where Al was detected.

Several broad overlapping peaks in the ^{27}Al NMR spectra of two organic horizon samples were observed between −9 and 12 ppm (Fig. 1). Peaks in this part of the spectrum are indicative of octahedral Al (11), and in consideration of the high organic content of these samples (Table 1), the Al is most likely complexed to organic acids and humic substances. It is unlikely that we could detect small quantities of solid Al present in mineral phases under the conditions of our NMR experiments. The complexity and heterogeneity of organic acids and humic substances in soils prohibits assignment of specific Al complexes to any of these peaks.

A single peak of line width 120 Hz was observed at 63.5 ppm. A peak at 62.5 ± 2 ppm is indicative of Al_{13} (7–10, 12); we thus interpret the peak at 63.5 ppm as Al_{13}.

Spiking samples 1 and 2 (Table 1) with 1.0 mmol of Al per gram of soil improved the signal of the peak at 63.5 ppm. The increase in the Al_{13} species may represent the formation of new Al species or mobilization of preexisting species, including Al_{13}, from the solid phase. Aluminum still could not be detected in soil sample 3, after spiking with the same amount of Al.

The hydrolysis and polymerization reactions of $Al(H_2O)_6^{3+}$ at increasing pH is complex. The Al_{13} polymer has been shown to predominate in many partially neutralized Al solutions (4). The structure of the Al_{13} polymer consists of a central Al tetrahedron surrounded by 12 Al octahedra (12). In simple aqueous solutions, the ^{27}Al NMR spectra of Al_{13} consists of a sharp peak of 6-Hz line width at 62.5 ppm that arises from the central tetrahedral Al. The 12 octahedral Al atoms produce a broad resonance that is observable only at extremely high concentrations of Al_{13}. The line width of 120 Hz observed for Al_{13} in the soil samples versus 6 Hz in more concentrated aqueous solutions reported by others (9) may be attributed to hindered rotation of the molecule if it were loosely adsorbed to soil particles. Bertsch has found a similar increase in the line width of Al_{13} when it was associated with chelex resin or purified cell wall material (13).

It has been argued that during synthesis, the Al_{13} polymer forms around the central tetrahedral Al (8). Because tetrahedral $Al(OH)_4^-$ does not form in appreciable quantities at a pH of less than 8, Bertsch (10) suggested that Al_{13} forms in partially neutralized solutions as a result of inhomogeneous pH conditions at the point of base injection. This notion has cast doubts on whether Al_{13} would form in significant amounts in natural acidic weathering environments. However, lactic acid has been shown to facilitate the formation of Al_{13} under acidic conditions (14). Humified polymers of soil organics likely can induce the formation of Al_{13} in soils. The area of

the peak at 63.5 ppm in the spectra that was scaled to account for all 13 Al in the polymer (9), indicates that Al_{13} constituted 30% of the spectroscopically visible Al in these samples.

The aqueous Al concentrations of 40 μM or less in the organic horizons studied (Table 1) are roughly 1/10th to 1/50th of the sensitivity of ^{27}Al NMR. The quantity of exchangeable Al (Table 1), when expressed as a molar concentration, was between 1 and 10 mM. This amount of Al is well within the sensitivity of NMR, if the species of ex-
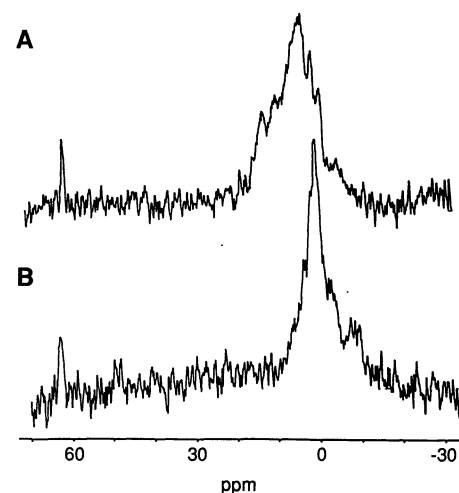

Fig. 1. ^{27}Al NMR spectra of two organic soil horizons; (A) sample 1; (B) sample 2 (Table 1). Several broad resonances occur between −9.0 and 12.0 ppm with respect to an externally referenced sample of 1.5 M $AlNO_3$. A relatively sharp peak with a line width of 120 Hz is also observed at 63.5 ppm. This peak is assigned to the Al_{13} polymer. The spectrum was recorded on a Bruker W.M. 250-MHz spectrometer operating in standard Fourier transform mode with a broadband probe tuned to 65.17 MHz. Parameters included a 16-μs (60°) pulse width and 0.274-s acquisition time. In all, 500,000 transients were recorded at 31°C in 40 hours. An artifact of ^{27}Al NMR of dilute solutions is a hump in the base line, which has been attributed to solid Al in the probe (17). This hump was suppressed with a 250-μs preacquisition delay. The final base line was flattened with the computer base line correction program.

Table 1. Analysis of the organic soil horizons tested by ^{27}Al NMR. Aluminum could be detected with ^{27}Al NMR for only samples 1 and 2 for 5-hour collection times. When Al was detected the collection time was increased to 40 hours.

Analysis	Sample		
	1	2	3
Organic matter* (g kg^{-1})	854	840	332
Soil solution pH†	3.5	3.6	3.7
Soil solution total Al‡ (μM)	24	5	40
Soil solution moderately reactive Al§ (μM)	13	1.8	36
Exchangeable Al‖ (cmol$_c$ kg^{-1})	13.8	2.1	7.2

*Determined by weight loss on ignition at 400°C.   †Solutions were extracted in the field by the method of Ross *et al.* (16).   ‡Determined by graphite furnace after passing through a 0.2-μm filter (6).   §Determined by the rate of reaction with catechol violet (15).   ‖Extractable with 0.1 M $BaCl_2$.

changeable Al were spectroscopically visible, as we suggest.

The ^{27}Al NMR data have shown that Al$_{13}$ can occur in soils although it cannot be predicted when soil Al will be spectroscopically visible. Changes in the physical properties of the samples during the time to acquire the ^{27}Al spectra is a concern, but little change in the aqueous Al concentration and soil pH is expected (15). The presence of Al$_{13}$ in acid soils will require a reevaluation of current thermodynamic models in which aluminum toxicity is attributed to mononuclear Al species.

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The Greenhouse Effect in Central North America: If Not Now, When?

THOMAS R. KARL, RICHARD R. HEIM, JR., ROBERT G. QUAYLE

Climate models with enhanced greenhouse gas concentrations have projected temperature increases of 2° to 4°C, winter precipitation increases of up to 15 percent, and summer precipitation decreases of 5 to 10 percent in the central United States by the year 2030. An analysis of the climate record over the past 95 years for this region was undertaken in order to evaluate these projections. Results indicate that temperature has increased and precipitation decreased both during winter and summer, and that the ratio of winter-to-summer precipitation has decreased. The signs of some trends are consistent with the projections whereas others are not, but none of the changes is statistically significant except for maximum and minimum temperatures, which were not among the parameters predicted by the models. Statistical models indicate that the greenhouse winter and summer precipitation signal could have been masked by natural climate variability, whereas the increase in the ratio of winter-to-summer precipitation and the higher rates of temperature change probably should have already been detected. If the models are correct it will likely take at least another 40 years before statistically significant precipitation changes are detected and another decade or two to detect the projected changes of temperature.

ADEQUATE SUPPLIES OF WATER FOR crops and livestock are of primary importance to the central North America region (1). Severe droughts of the 20th century have affected both the biophysical and socioeconomic systems of the region (2). One of the more ominous scenarios that has been suggested on the basis of several climate model simulations in an en-

hanced greenhouse world is the decrease of summertime precipitation and an increase of temperature across central North America (3). The model predictions admittedly suffer from potentially significant limitations. For example, some regional phenomena such as the El Niño–Southern Oscillation (ENSO) are not adequately simulated by these models, but do appear to have linkages with regional surface temperature and precipitation variations in the United States (4). Nonetheless, if the projected climate occurs, it would certainly have a deleterious impact, and the region would have a difficult time

adapting. In this report, we use observational records and purely statistical methods to review temperature and precipitation trends over the past century and assess the likelihood that climate projections will be verified by current climate monitoring techniques if contemporary climate model predictions are basically correct.

Areally averaged seasonal mean temperature and precipitation over the IPCC Central region (Fig. 1A) bounded by the latitudes 35° to 50°N and longitudes 80° to 105°W (less a small part of land over the Canadian Provinces) were used to determine past changes (5). This is one of the regions where projections of temperature and precipitation change have been issued (3). The data are derived from the climate division averages of temperature and precipitation (6). A slightly different region referred to as "Central" (Fig. 1B) was used to examine past changes in the seasonal mean daily maximum and minimum temperatures (7, 8), for which projections were not made by the IPCC. The seasonal mean daily maximum and minimum temperatures are area averages over the period 1901 to 1987 derived from 147 stations (8).

We analyzed changes of seasonal mean temperature and precipitation over the IPCC Central region using tests of significance of linear trends, the nonparametric Wilcoxon sign-rank test, and the two-phase regression test described by Solow (9). The two-phase regression can be used to test for a change point in the linear trends. Use of the two-phase regression helps ensure against undetected nonlinear trends. Similar tests were also applied for changes of the seasonal mean daily maximum and minimum temperatures.
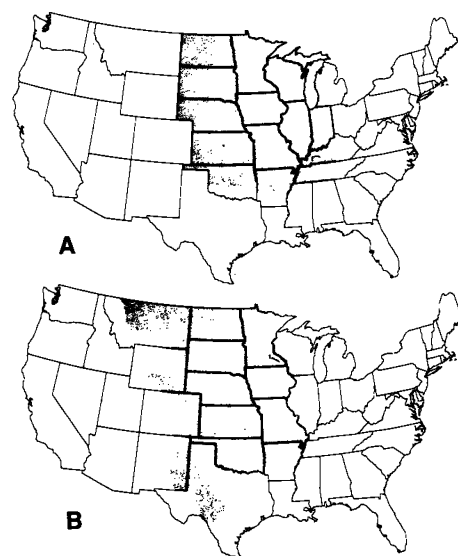

Fig. 1. (A) The "IPCC Central" North American region; (B) the "Central" United States region.

Global Climate Laboratory, National Climatic Data Center, National Environmental Satellite, Data, and Information Service, National Oceanic and Atmospheric Administration, Department of Commerce, Federal Building, Asheville, NC 28801.