

^{31}P NMR Studies Of Humic Acids From Different Soils

Vera D. Tikhova, Makhmut M. Shakirov, Valentina P. Fadeeva, Marya I. Dergacheva

Institute of Organic Chemistry, SB RAN, Novosibirsk

Institute of Soil Sciences and Agrochemistry, SB RAN, Novosibirsk

A different distribution of organic and inorganic phosphorus species in soils is stipulated by mineral and chemical composition of soil-forming rocks and quantity of soil organic substances.

Traditional determination of this distribution in humic acids (HA) by wet chemical methods consists of many stages, requires long time to carry out and is not so informative as we need. ^{31}P NMR method gives real illustration of different phosphorus bonds with HA, as well as it permits to estimate both full quantity of phosphorus and quantitative proportions between their different forms.

HA were derived from humus accumulative horizon (A_1) from south step chernozem of Altay region (1), different tundra soils of Komi Republic (2,3,4), grey forest soil (5) and fossil soil - Kazantsev interglacial period (6). Phosphorus was determined spectrophotometrically in samples ignited in retort with oxygen. The ^{31}P NMR spectra were obtained with Bruker DRX-500 spectrometer, and samples were soluted in 0.5M NaOD.

number of sample	1	2	3	4	5	6
% P (elemental analyses)	1.30	1.25	1.35	1.10	0.60	0.90
% P (^{31}P NMR data)	1.10	1.25	1.29	1.04	0.69	0.92

The ^{31}P NMR spectra identify mineral orthophosphate (5.9 ppm) in all samples of HA, and in grey forest HA there are pyrophosphate (-5.2 ppm) and polyphosphate (-19 ppm). HA of tundra soils have in ^{31}P NMR spectra wide nonstructural peak near 5 ppm common to orthophosphate and phosphate monoester. These spectra are similar to the spectrum of fossil soil HA. According to ^{31}P NMR there are many different organic phosphorous species in HA of south chernozem, such as inositol hexaphosphate (4.35 ppm), phosphate monoester (3.95 ppm), aromatic phosphate diester (2.1 and 0.5 ppm), phosphate diester (-0.3 ppm) .

IR spectra of all samples studied show strong sygnal at 1020-1040 cm^{-1} , which characterises P-O-Aryl bond and confirms real phosphate bond to aromatic part of HA macromolecule.

^{31}P NMR data well illustrate variety of phosphorous compounds in HA even when it contains 1-2 % P. And there is good correspondence between quantitative analyses by ^{31}P NMR and elemental analyses.