Phosphorus forms in forest soil colloids as revealed by liquid-state ^{31}P-NMR

Supplementary Material

Author list

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1) Method development: Impact of re-dissolving of lyophilized EDTA + NaOH soil extracts

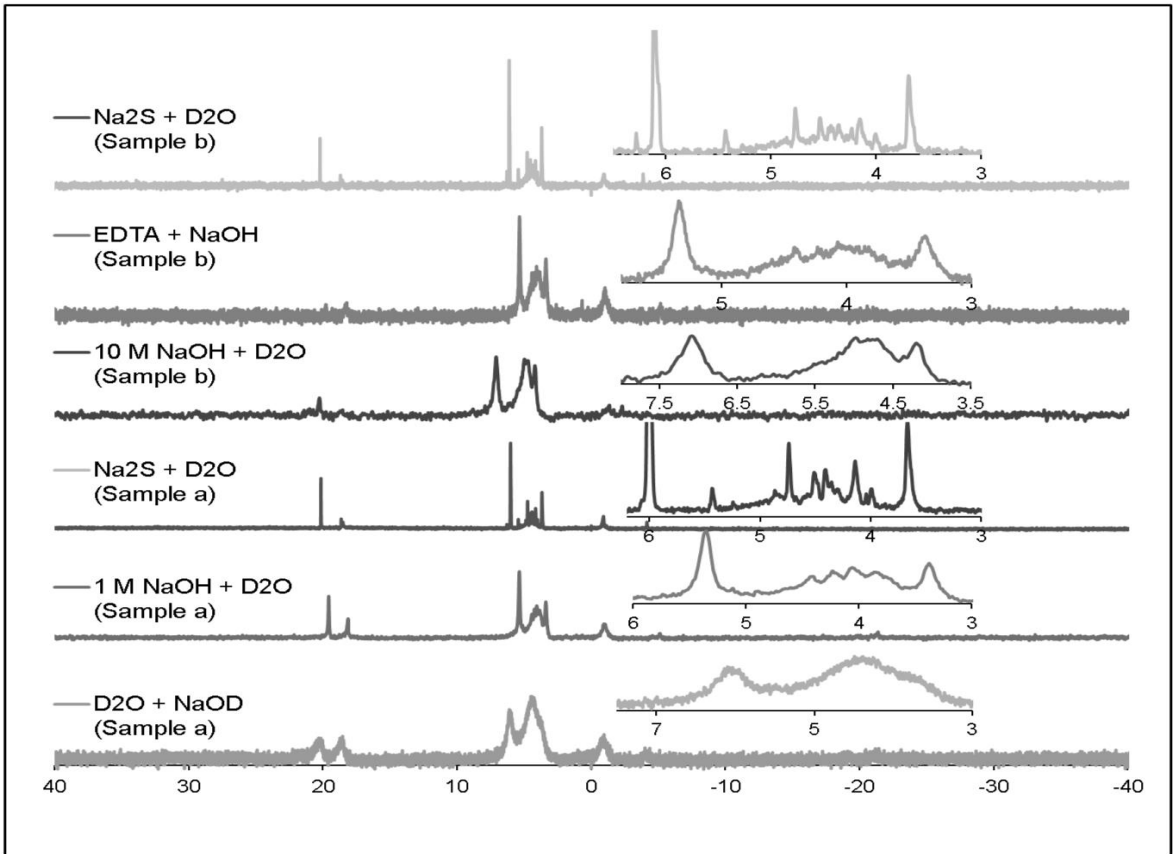

Figure S1: Comparison of re-dissolving tests for the acidic forest bulk soil samples. Two different samples were used (sample a: of an Oh-horizon and sample b: of an Ah-horizon).
Sample a: The spectra below showed the sample re-dissolved in 1.5 mL D_2O and 100 µL NaOD. The second sample was re-dissolved in 1 mL of 1 M NaOH + 100 µL D_2O. The third spectra shows the result of the re-dissolving as performed for the samples in the manuscript, with 1.5 mL of 5 M Na_2S (in D_2O) and 10 µL NaOD.
Sample b: The fourth samples was dissolved in 10 M NaOH + 200 µL D_2O. The fifth spectra is of a sample dissolved in 1 M NaOH + 0.1 M EDTA + 200 µL D_2O. To compare the signal quality the y-axes intensity was adjusted. The upper spectra is from sample b dissolved in 1.5 mL of 5 M Na_2S (in D_2O) and 10 µL NaOD.

Table S1: Relative proportion P compound classes for the three spectra shown in Figure 1. The proportions were calculated by the integration of the signal shapes. The sample extracted with D2O and NaOD does not show quantitative results because the signal to noise ratio was too low.

	Phosphonate 1	Phosphonate 2	Ortho-P	Monoester-P	Diester-P	Pyro-P	Poly-P
sample	---------- % ----------						
b) 5 M Na2S in D2O & NaOD	4	3	23	60	9	1	0
b) 10 M NaOH & D2O	1	3	21	59	14	2	0
b) 1 M NaOH+ 0.1 M EDTA + D2O	3	0	29	63	5	0	0
a) 5 M Na2S in D2O & NaOD	6	5	20	56	11	1	1
a) 1 M NaOH & D2O	8	6	23	51	10	1	1
a) D2O & NaOD	8	6	21	53	9	1	2

Table S2: Control of the P, Fe and Mn concentrations of the NMR samples redissolved in three different ways. Firstly, in the same way the samples (of this work) were treated: 1 mL of 5 M Na_2S (in D_2O) and 10 µL NaOD;secondly, the same samples were redissolved in 10 M NaOH + 200 µL D_2O, and thirdly exemplary the bulk soil samples were redissolved in 1 M NaOH + 0.1 M EDTA + 200 µL D_2O. The concentrations show that the Na_2S mostly increased the P concentrations in the sampled but reduce the Fe and Mn concentrations. STD means standard deviation.

			P mg/g sample	STD mg/g sample	Fe mg/g sample	STD mg/g sample	Mn mg/g sample	STD mg/g sample	P/(Fe+Mn)
Redissolved in 5 M Na2S in D2O + 10 µl NaOD	Conventwald	Oh Elec	0.06	0.003	0.01	0.002	0.005	0.000	5.23
		Oh Col	0.25	0.02	0.03	0.003	0.001	0.000	9.43
		Oh Soil	0.93	0.42	0.14	0.085	0.001	0.000	6.84
		Ah Elec	0.07	0.002	0.01	0.000	0.017	0.001	3.10
		Ah Col	0.09	0.002	0.01	0.001	0.004	0.000	6.51
		Ah Soil	0.38	0.02	0.05	0.003	0.001	0.000	7.38
	Wüstebach	Oh Elec	0.03	0.00	0.00	0.001	0.000	0.000	6.03
		Oh Col	0.33	0.01	0.04	0.001	0.001	0.000	8.63
		Oh Soil	0.57	0.07	1.09	0.538	0.034	0.002	0.51
		Ah Elec	0.03	0.00	0.01	0.001	0.000	0.000	4.77
		Ah Col	0.25	0.01	0.03	0.001	0.000	0.000	8.09
		Ah Soil	0.33	0.02	0.61	0.179	0.211	0.002	0.40
Redissolved in 10 M NaOH	Conventwald	Oh Elec	0.03	0.001	0.21	0.004	0.009	0.000	0.16
		Oh Col	0.17	0.01	1.38	0.102	0.018	0.002	0.12
		Oh Soil	0.73	0.02	1.41	0.398	0.052	0.002	0.50
		Ah Elec	0.05	0.002	0.20	0.008	0.025	0.002	0.23
		Ah Col	0.08	0.01	0.24	0.015	0.010	0.001	0.32
		Ah Soil	0.28	0.01	2.00	0.110	0.024	0.002	0.14
	Wüstebach	Oh Elec	0.03	0.01	0.13	0.004	0.002	0.000	0.22
		Oh Col	0.25	0.02	0.55	0.042	0.007	0.000	0.44
		Oh Soil	0.66	0.52	2.95	0.052	0.021	0.010	0.22
		Ah Elec	0.01	0.001	0.04	0.001	0.001	0.000	0.33
		Ah Col	0.16	0.005	0.16	0.007	0.003	0.000	0.97
		Ah Soil	0.44	0.02	0.70	0.028	0.210	0.004	0.48
Redissolved in 1M NaOH + 0.1 M EDTA	CW	Oh Soil	0.05	0.002	0.06	0.001	0.005	0.000	0.71
		Ah Soil	0.46	0.02	7.94	0.196	0.047	0.001	0.06
	Wu	Oh Soil	1.02	0.55	6.54	0.157	0.039	0.016	0.16
		Ah soil	0.36	0.03	1.27	0.318	0.121	0.013	0.26

2) Method development: ^{31}P-NMR Measurement parameters

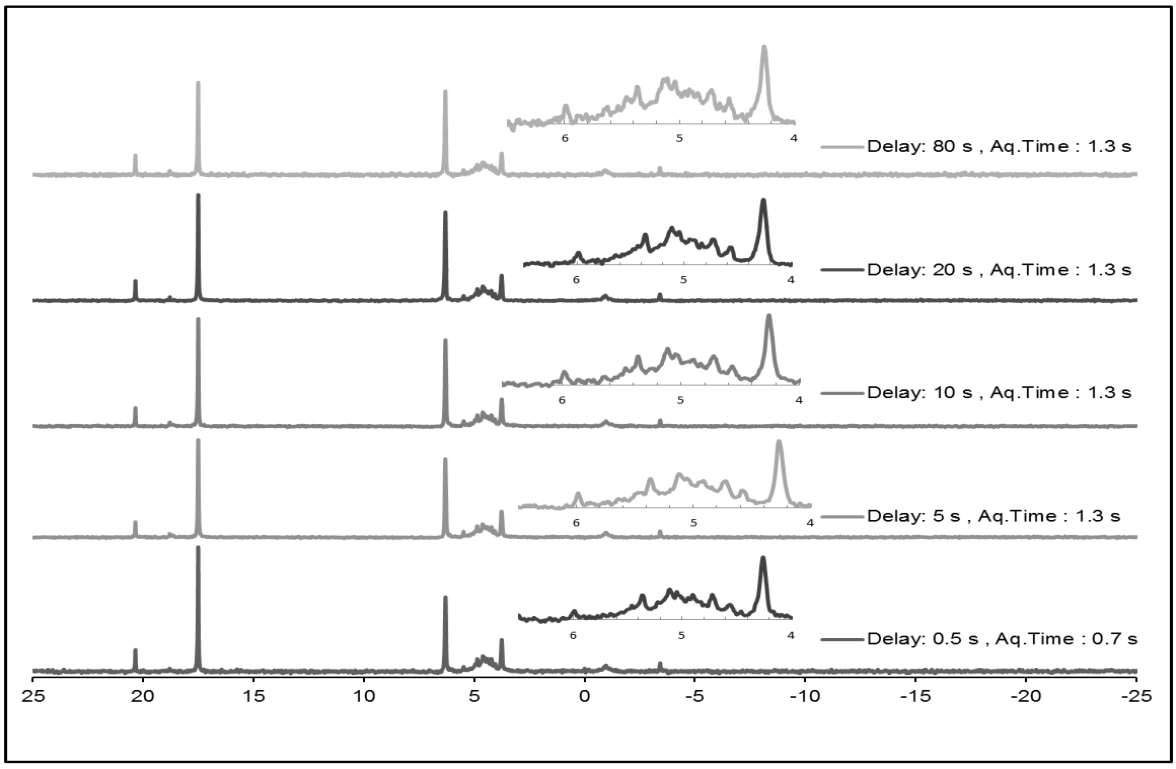

Figure S2: Spectra measured at different 31P-NMR measurement parameters. The under most spectra demonstrates the experimental parameters used in the paper. An Oh-horizon sample was used for the measurement.

Table S3: Relative proportion P compound classes for the five spectra shown in Figure 2. The proportions were calculated by the integration of the signal shapes.

		Phosphonates	MDPA	Ortho-P	Monoester	Diester	Pyro- & Poly-P
		----------%----------					
Delay Time, Aq. Time	80 s, 1.3 s	5	20	25	43	2	5
	20 s, 1.3 s	4	21	25	43	2	5
	10 s, 1.3 s	5	21	23	44	1	6
	5 s, 1.3 s	5	21	23	45	1	5
	0.5 s, 0.7 s	4	22	20	46	2	6