



**Table S1.** Included articles focusing on the use of NMR spectroscopy and results of individual sources of evidences.

First Author	Atoms Studied	NMR Spectrum Acquisition Phase	Multidimensional Techniques	Study Objects <sup>1</sup>	Using the chemical shift ranges given in Table 1
Cuniasse [1]	<sup>13</sup> C	in solution and solid	1D	single SOM	no
Lodygin [2]	<sup>1</sup> H, <sup>13</sup> C	solid	1D	HA, FA	yes
Mao [3]	<sup>1</sup> H, <sup>13</sup> C, <sup>15</sup> N, <sup>31</sup> P	in solution and solid	1D, 2D	HA, lignin, OS	yes
Preston [4]	<sup>1</sup> H, <sup>13</sup> C, R	in solution	1D	HA, humin, DOM	no
Preston [13]	<sup>1</sup> H, <sup>13</sup> C, R	in solution and solid	1D	HA, humin, DOM, OS	no
Keeler [20]	<sup>13</sup> C	solid	1D	HA, FA, OS	yes
Kulikova [23]	<sup>13</sup> C, <sup>29</sup> Si	in solution	1D	HS	no
Knicker [24]	<sup>13</sup> C, <sup>15</sup> N	solid	1D	HS, OS	yes
Rennert [25]	<sup>29</sup> Si	solid	1D	MS	no
Wang [26]	<sup>1</sup> H, <sup>31</sup> P	in solution	1D, 2D	HS	no
Keshari [27]	<sup>1</sup> H, <sup>13</sup> C	in solution and solid	1D	single SOM	no
Vasilevich [28]	<sup>13</sup> C	solid	1D	HA	yes
Mao [29]	<sup>1</sup> H, <sup>13</sup> C	solid	1D, 2D	HA	yes
Luz [31]	<sup>13</sup> C	solid	1D, 2D	single SOM	no
Mitchell [25]	<sup>1</sup> H	in solution and solid	1D	DOM	no
Peuravuori [32]	<sup>13</sup> C	solid	1D	FA	yes
Klein [33]	<sup>13</sup> C	in solution	1D	HA, FA, DOM	yes
Nebiosso [34]	<sup>1</sup> H, <sup>13</sup> C	in solution and solid	1D, 2D	HA	no
Mylotte [35]	<sup>1</sup> H, <sup>13</sup> C	in solution and solid	1D, 2D	HA, humin	no
DiDonato [36]	<sup>1</sup> H, <sup>13</sup> C	in solution and solid	1D, 2D	HA	yes
Soucémarianadin [37]	<sup>1</sup> H, <sup>13</sup> C	in solution and solid	1D, 2D	OS, MS	yes
Tadini [38]	<sup>1</sup> H, <sup>13</sup> C	in solution and solid	1D, 2D	HA	yes
Polyakov [39]	<sup>1</sup> H, <sup>13</sup> C	solid	1D, 2D	HA	yes
Chen [40]	<sup>1</sup> H, <sup>13</sup> C	solid	2D	HA	yes
Cao [41]	<sup>1</sup> H, <sup>13</sup> C	solid	2D	HA, single SOM, OS	yes
Lodygin [42]	<sup>13</sup> C	solid	1D	HA, FA	yes
Preston [43]	<sup>13</sup> C, <sup>15</sup> N, <sup>31</sup> P	solid	1D, 2D	HS, OS, MS	no
Simpson [44]	<sup>1</sup> H, <sup>13</sup> C, <sup>19</sup> F	in solution and solid	1D, 2D	HA, FA, DOM, OS, MS	no
Vasilevich [45]	<sup>13</sup> C	solid	1D	HA, FA	yes
Aquino [46]	<sup>13</sup> C	solid	1D	HA, HS	yes
Harris [47]	<sup>1</sup> H, <sup>13</sup> C, <sup>15</sup> N	in solution and solid	1D	single SOM, DOM	no
Chien [48]	<sup>1</sup> H, <sup>13</sup> C, <sup>27</sup> Al, <sup>29</sup> Si, <sup>31</sup> P	solid	1D, 2D	single SOM, MS	no
Keeler [49]	<sup>13</sup> C	solid	1D	HA, FA, humin, HS, OS	yes
Kholodov [50]	<sup>13</sup> C	in solution	1D	HA	yes
Lodygin [51]	<sup>13</sup> C	solid	1D	HA, FA	yes
Ware [52]	<sup>13</sup> C	solid	1D	HA	yes
Busman [53]	<sup>13</sup> C	solid	1D	OS	yes
Tadini [54]	<sup>13</sup> C	solid	1D	HS	yes

First Author	Atoms Studied	NMR Spectrum Acquisition Phase	Multidimensional Techniques	Study Objects <sup>1</sup>	Using the chemical shift ranges given in Table 1
Kovaleva [55]	<sup>13</sup> C	in solution	1D	HA, lignin	yes
Duarte [56]	<sup>1</sup> H, <sup>13</sup> C	in solution	2D	DOM	yes
Brotto [57]	<sup>13</sup> C	solid	1D	lignin, OS	yes
Ryazanov [58]	<sup>13</sup> C	solid	1D	FA	yes
Liang [59]	<sup>13</sup> C	in solution	1D	DOM	yes
García [60]	<sup>13</sup> C	solid	1D	HA	yes
Dymov [61]	<sup>13</sup> C	solid	1D	HA	yes
Cervantes-Arista [62]	<sup>1</sup> H, <sup>13</sup> C	solid	1D, 2D	HA, FA	no
Prietzl [63]	<sup>13</sup> C	solid	1D	lignin, single SOM, OS, MS	yes
Chukov [64]	<sup>13</sup> C	solid	1D	HA	yes
Jafarzadeh-Haghighi [65]	<sup>13</sup> C	solid	1D	HS	yes
Zolotareva [66]	<sup>13</sup> C	solid	1D	HA	yes
Kida [67]	<sup>13</sup> C	in solution	1D	HA, FA	yes
Abakumov [68]	<sup>13</sup> C	solid	1D	HA	yes
Diniz [69]	<sup>13</sup> C	solid	1D	HA	yes
Certini [70]	<sup>13</sup> C	solid	1D	MS	yes
Bravo-Escobar [71]	<sup>1</sup> H	in solution	1D	DOM	no
Dymov [72]	<sup>13</sup> C	solid	1D	HS	yes
Dymov [73]	<sup>13</sup> C	solid	1D	OS	yes
Dymov [74]	<sup>13</sup> C	solid	1D	OS	yes
Alexis [75]	<sup>13</sup> C	solid	1D	OS	yes
Hishinuma [76]	<sup>13</sup> C	solid	1D	OS	yes
Kovaleva [77]	<sup>13</sup> C	solid	1D	HA, lignin	yes
Criquet [78]	<sup>13</sup> C	solid	1D	MS	yes
Hannam [79]	<sup>13</sup> C	solid	1D	OS	yes
Lorenz [80]	<sup>13</sup> C	solid	1D	MS	yes
Amoah-Antwi [81]	<sup>13</sup> C	solid	1D	HA	yes
Farrell [82]	<sup>13</sup> C	solid	1D	MS	yes
Zhang [83]	<sup>13</sup> C	solid	1D	HA, humin	yes
Wang [84]	<sup>13</sup> C	solid	1D	HA	yes
Suleymanov [85]	<sup>13</sup> C	solid	1D	HA	yes
Trubetskoi [86]	<sup>13</sup> C	solid	1D	HA	yes
Danchenko [87]	<sup>13</sup> C	solid	1D	HA, MS	yes
Lu [88]	<sup>1</sup> H, <sup>13</sup> C	solid	1D	HA	yes
Zhil kibayev [89]	<sup>13</sup> C	in solution	1D	humin	yes
Chabbi [90]	<sup>13</sup> C	solid	1D	HS, MS	yes
Wershaw [91]	<sup>13</sup> C	in solution	1D	DOM, OS	yes
Gehring [92]	<sup>13</sup> C	in solution and solid	1D	HS, OS	yes
Vasilevich [93]	<sup>13</sup> C	solid	1D	HA, FA	yes
Vishnyakova [94]	<sup>13</sup> C	in solution	1D	HA	yes
Polyakov [95]	<sup>13</sup> C	solid	1D	HA	yes
Fragouli [96]	<sup>1</sup> H, <sup>13</sup> C	solid	2D	HA, FA	yes
Nascimento [97]	<sup>1</sup> H	in solution	1D	HA, single SOM	no

<sup>1</sup> HA – humic acids, FA – fulvic acids, HS – unfractionated humic substances, single SOM – single soil organic substances, DOM – dissolved organic matter, OS – organic soil and MS – mineral soil.

**Table S2.** Included articles focusing on the use of EPR spectroscopy and results of individual sources of evidences.

First Author	The nature of SOM paramagnetism	Study Objects <sup>1</sup>		Parameters of the EPR spectra <sup>2</sup>
Lodygin [98]	polyconjugation systems	HA, FA	virgin and arable	FRC, gFV
Lodygin [99]	polyconjugation systems	HA	virgin	FRC, gFV
Lishtvan [100]	polyconjugation systems	HA	virgin	FRC, gFV, PPLW
Rosa [101]	isn't discussed	HS	virgin	FRC
Debska [102]	semiquinone structures	HA	virgin	FRC, gFV, SS, PPLW
Jezierski [103]	semiquinone structures	HA	virgin	FRC, gFV
Kurochkina [104]	semiquinone structures	HS	virgin	FRC, SS
Lodygin [105]	polyconjugation systems	HA, FA	virgin and arable	FRC
Lodygin [106]	polyconjugation systems	HA, FA	virgin	FRC, gFV
Jezierski [107]	semiquinone structures	HA, FA, OS, MS	virgin	FRC, gFV
Chukov [108]	isn't discussed	HA	virgin	FRC, gFV
Gonzalez-Perez [109]	isn't discussed	HA	arable	FRC, gFV
Saab [110]	semiquinone structures	HA, FA, humin, MS	virgin	FRC, SS
Barančíková [111]	isn't discussed	HA	virgin and arable	FRC
Venezia [112]	isn't discussed	HA	virgin	FRC
Sun [113]	isn't discussed	HS	arable	FRC
Tadini [114]	isn't discussed	HA	arable	FRC
Baltrėnaitė-Gedienė [115]	isn't discussed	MS	arable	FRC, gFV
Sartakov [116]	isn't discussed	HA	virgin	FRC, gFV

<sup>1</sup> HA – humic acids, FA – fulvic acids, HS – unfractionated humic substances, OS – organic soil and MS – mineral soil;

<sup>2</sup> FRC – free radical concentration, gFV – g-factor value, SS – spectral shape and PPLW – peak-to-peak line width.