

SUPPORTING INFORMATION

“NMR Investigation of the Behavior of an Organothiophosphate Pesticide, Methyl Parathion, Sorbed on Clays”

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Clay Materials.

Calcium montmorillonite, denoted STx-1 by the supplier, Source Clay Mineral Repository (University of Missouri-Columbia): traces of quartz, silica and carbonate (IR analysis); 0.57 % Fe, 0.011 % P by weight (elemental analysis). Weighed samples of 'as received' STx-1, when placed in a humidifying chamber at room temperature, sorbed water until constant weights were obtained (after about 3 months): 19.5% water (w/w). Dehydration of the 'as received' material at 100 °C and 3×10^{-3} Torr to constant weight indicates 2.1% water content by weight, as received from the supplier. The Zn(II)-, Al(III)-, and Cu(II)-exchanged montmorillonites were prepared by several washes of 'as received' Ca-montmorillonite with 1 M aqueous solutions of the corresponding metal chloride, followed by multiple washes with water until the wash solution did not precipitate AgCl(s) when added to 1 M AgNO₃(aq). The cation-exchanged montmorillonites were dried at 100 °C and 3×10^{-3} Torr to constant weight.

Methyl parathion synthesis.

Methyl Parathion was synthesized by the reaction of 310 mmol of sodium 4-nitrophenoxide dihydrate [824-78-2] with 247 mmol dimethyl chlorothiophosphate [2524-03-0] in 75 ml chlorobenzene solvent, using 1 ml triethylamine as catalyst, under reflux (95 °C) for five hours (7). The supernatant liquid containing the product was decanted from the solid sodium chloride produced by the reaction, and the solvent and catalyst were removed using a rotary evaporator (at 40 °C and 20 Torr). The crude product (an oily yellow liquid) was washed three times each with 80 ml portions of water, 5 % aqueous sodium hydroxide, 5 % aqueous HCl and finally water again. The resultant oily liquid (52 g; clear and colorless, with a faint mercaptan-like odor) was determined by ¹H and ³¹P NMR to be approximately 75 % methyl parathion. The crude methyl parathion product was purified by silica gel column chromatography, using a 50/50 ethyl acetate/hexane mixture and monitored by TLC (silica 60F and visualized by UV). The first major band off the column contained the product, and after rotary

evaporation (25 °C at 18 Torr), was determined to be 99.1 % methyl parathion by ^{31}P NMR in C_6D_6 solution (Figure SI-1). This ^{31}P NMR analysis indicates that the purified methyl parathion contains traces of the product of methoxy hydrolysis (**III**; peak at 52.6 ppm), a component generating a peak at 57.2 ppm, which is due to the bis aryl product (**XIX** in Table 1 of the main paper), and a component yielding a peak at 91.1 ppm which is tentatively assigned as an aryldimethylphosphorodithioate (**XXI** in Table 1), $(\text{ArS})(\text{MeO})_2\text{P}=\text{S}$ or $(\text{MeS})(\text{MeO})(\text{ArO})\text{P}=\text{S}$, which are reportedly common impurities in methyl parathion synthesis (6). This 99.1 % methyl parathion sample is a slightly cloudy solid, with an observed melting point range of 31 – 34 °C (literature value (1), 35 – 36 °C). Attempts were made to further purify this material (for example, by recrystallization or repeated column chromatography), with no success, so the 99.1 % material was used in this study.

^{13}C NMR spectra

The ^{13}C CP-MAS spectrum of the sample of methyl parathion on partially hydrated Al-montmorillonite (9.1 % by wt. methyl parathion, 4.5 % by wt. water), after 4 days decomposition, is shown in Figure SI-2A. The peaks are assigned, from higher to lower chemical shift (left to right) as carbon-4, carbon-1 and overlapping intensity due to carbons-2 and -3 of the aromatic ring; the methoxy carbons appear as a single peak at about 55 ppm. It is not clear from Figure SI-2 how many carbon-containing species are present in the sample. However, the ^{31}P MAS spectra in Figure 4 clearly indicate the presence of multiple phosphorus-containing structures, including both chemisorbed (i.e., strongly bound but unfragmented methyl parathion) and at least one S,O-isomerized residue. Therefore, as seen in a previously reported study on chlorpyrifos (2), ^{13}C CP-MAS NMR appears to be much less useful than ^{31}P MAS NMR to distinguish decomposition products from sorbed methyl parathion.

Figure SI-2B shows the ^{13}C CP-MAS spectrum of crystalline sodium 4-nitrophenoxide dihydrate; note the large changes in the aromatic carbon peak positions compared to the ^{13}C CP-MAS spectrum of the sample of methyl parathion on partially hydrated Al-montmorillonite (9.1 % by wt.

methyl parathion, 4.5 % by wt. water), after 4 days decomposition, shown in Figure SI-2A. This comparison suggest that ^{13}C CP-MAS NMR may have utility to detect the product of aryl hydrolysis of methyl parathion, albeit with much lower sensitivity than by ^{31}P NMR because of the much lower isotopic abundance of carbon-13.

^{31}P Chemical Shift Assignments

Measured or predicted ^{31}P chemical shifts of possible methyl parathion decomposition products are summarized in Table 1 of the main paper. The methods employed to make those assignments were largely based on comparison with corresponding liquid-sample chemical shifts. These, in turn were made by a variety of techniques, as summarized in Table SI-3, in many cases involving the extraction of specific species from adsorption on the clay and mass spectrometric identification. The MS analyses were carried out in both positive-ion and negative-ion modes, with MS/MS identification of fragmentation patterns, using a Finnegan LCQ, Duo LC/MS instrument. Details of these liquid-sample ^{31}P chemical shift assignments, including substantial MS evidence, are included in the appendix to reference 2a.

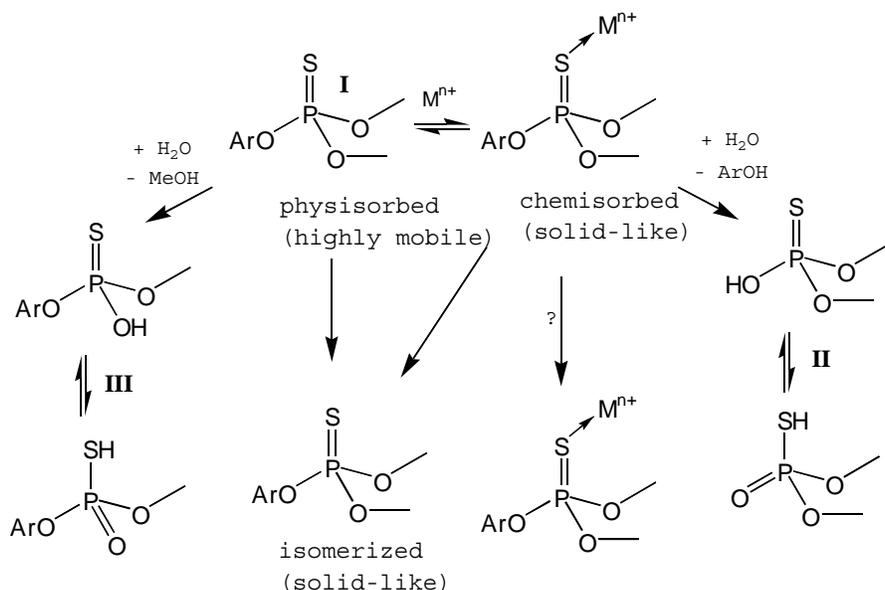
Possible role of metal ion complexation.

Scheme SI-1 shows one mechanistic picture of how complexation of methyl parathion with a metal ion (M^{n+}), presumably associated with a clay mineral, might effect the decomposition of the pesticide (4).

The 58 ppm peak in methyl parathion/Cu-montmorillonite.

If the 58 ppm peak in Figure 5 is indeed due to unreacted methyl parathion, sorption onto Cu(II)-montmorillonite causes a greater increase in the isotropic ^{31}P shielding (about 9 ppm relative to the pesticide in DMSO solution) than was seen with the other forms of montmorillonite encountered above (0 - 3 ppm increase in shielding upon sorption). It is possible that the manner of methyl parathion adsorption is significantly stronger for partially hydrated Cu(II)-montmorillonite than for the other cation-exchanged forms. For example, perhaps methyl parathion may strongly coordinate to Cu^{2+} via

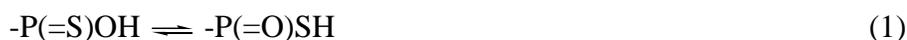
Scheme SI-1. A possible role for metal ion (M^{n+}) complexation in pesticide decomposition



the thiophosphate sulfur, slowing atomic-level motion or chemical exchange of the pesticide to other (similar or different) adsorption sites. Other possible assignments for the 58 ppm peak in Figure 5 are structures **II** and **III**, the hydrolysis products of methyl parathion. If this assignment is correct, then this hydrolysis reaction is much more rapid than in the other samples discussed above, such as chlorpyrifos sorbed onto a similar partially hydrated Cu(II)-montmorillonite (2).

The 10.6 ppm peak in the liquid-solution DMSO- d_6 extract of the 11-day methyl parathion/kaolinite sample.

The breadth of the 10.6 ppm peak in Figure SI-5A, at least twice the breadth of other peaks in that spectrum, suggests the possibility that the observed species undergoes tautomerization (18) (Eq.1). Thus, the 10.6 ppm peak may be due to some type of thiophosphoric acid, possibly as the



monomethyl ester, although no supporting evidence for this interpretation could be found. The ^{31}P chemical shift of unsubstituted thiophosphoric acid ($\text{S}=\text{P}(\text{OH})_3 \rightleftharpoons \text{O}=\text{P}(\text{OH})_2(\text{SH})$, structure **VIII** in Table 1) is reportedly 34 to 32 ppm (12, 13). Another possible explanation for the linewidth of the 10.6 ppm peak in Figure SI-5A could be some other chemical exchange process. No conclusions can be

made now on the origin of the 10.6 ppm peak, which was not observed in the ^{31}P spectra of any other DMSO- d_6 extract. Figure SI-5A also shows a peak at 91.4 ppm, attributed to O,O,S-dimethylarylphosphorodithioate, $(\text{ArS})(\text{MeO})_2\text{P}=\text{S}$ (**XXI**), an impurity present in the purified (99.1%) methyl parathion starting material (2).

Table SI-1. ^{31}P NMR relaxation times of methyl parathion and its decomposition products adsorbed on partially hydrated clays.

clay	methyl parathion content % by wt.	H ₂ O content % by wt.	peak (ppm) ^a	^{31}P T ₁ (s)	^1H T ₁ (s)	T _{HP} ^b (ms)	^1H T _{1p} ^b (ms)
kaolin	1.4 %	1.1 %	64	< 2	< 1	0.75	10.5
			27			0.39	7.7
			17			0.32	5.0
			-11			0.25	5.5
Ca-mont.				< 2	< 1		
Zn-mont.	8.5 %	4.5 %		< 2	< 1		
Al-mont.	8.8 %	0.2 % (est.)	29	< 2	< 1	0.37 (.45 to .30)	5.6 (6.3 to 5.1)
Al-mont.	9.1 %	4.5 %	65	< 2	< 1	0.52	6.3
			30			0.71	6.8
Cu-mont.	8.5 %	4.8 %	61	< 2	< 1	0.34	1.8
			30			0.42	1.8
			-13			0.23	3.6

^a ^{31}P chemical shift relative to 85 % H₃PO₄.

^b 95 % confidence limits are shown in parentheses.

Table SI-2. ³¹P chemical shifts^a of DMSO-d₆ extracts of methyl parathion, and its decomposition products sorbed on partially hydrated clays.^b

		tentative assignments and peaks observed (ppm)													
sample	age	MeP content (% by wt. or mol %)	H ₂ O content (% by wt.)	?	XXI	XX	I	XIX	III	II or III	V	?	?	various phosphates ?	VI
impure MeP	NA	ca. 75 mol% P	0	115.7 s	91.4 vs	74.0 vs	66.8 vl		53.5 s		27.5 m	12.2 vs		2.4 vs 1.4 vs	-4.4 m -5.3 s
purified MeP	NA	99 mol% P	0	115.4 vs	91.1 vs		66.8 vl	57.2 vs	52.6 vs						
MeP aged in DMSO	6 mos.	initially 99 mol% P	0				66.8 s				28.3 vs				-4.5 m -5.3 m
MeP on kaolin	11 days	1.4 %	1.1 %		91.4 s		66.8 l			32.5 s	28.2 l		10.6 vs		
MeP on Ca-mont.	> 3 yr.	9.2 %	1.9 %							31.3 s					
MeP on Zn-mont.	1 day	8.5 %	4.5 %		91.5 s		66.8 l		52.3 s	32.6 s	28.3 m				
MeP on Zn-mont	> 3 yr.	8.5 %	4.5 %				66.8 s								
MeP on Al-mont.	10 days	9.1 %	4.5 %			71 vs	66.8 m			32.7 s	28.4 l	12.8 vs			
MeP on Cu-mont.	> 3 yr	8.5 %	4.8 %												-3.6 s

^a relative to 85 % H₃PO₄.

^b Qualitative peak intensities: vl = very large, l = large, m = medium, s = small, vs = very small.

Table SI-3. Summary of confirming evidence for the ^{31}P chemical shift assignments of liquid-solution samples of solvent-extractable species of methyl parathion sorbed on clay.

structure no.	structure	assignment method ^a	reference
I (pesticide)	$(\text{ArO})(\text{RO})_2\text{P}=\text{S}$	1, 2, 3, 4	3, 6, 10, 11
II (desaryl)	$(\text{HO})(\text{RO})_2\text{P}=\text{S}$	1, 3, 4, 5, 6	6, 13
III (desalkyl)	$(\text{ArO})(\text{RO})(\text{HO})\text{P}=\text{S}$	4, 5, 6	14, 15
IV (S-aryl)	$(\text{ArS})(\text{RO})_2\text{P}=\text{O}$	4, 5	13
V (S-alkyl)	$(\text{ArO})(\text{RO})(\text{RS})\text{P}=\text{O}$	4, 5	3, 6
VI (oxon)	$(\text{ArO})(\text{RO})_2\text{P}=\text{O}$	1, 3, 4	7, 16

^aAssignment methods:

1. Confirmed by 'spiking' with (or comparison to) an authentic sample.
2. Confirmed by MS detection of the molecular ion.
3. Consistent with assignments made by ^1H liquids NMR.
4. In agreement with literature values for that compound.
5. Consistent with literature values for similar compounds.
6. Consistent with MS results, but not confirmed.

FIGURE CAPTIONS

Figure SI-1 A) 242.9 MHz liquid-sample ^{31}P NMR spectrum of 99.1 % methyl parathion in C_6D_6 .

B) Same as Figure SI-1A, except the spectrum is vertically expanded by a factor of 8.

Figure SI-2 50 MHz ^{13}C CP-MAS spectrum of the sample shown in Figure 5, containing 9.1 % by wt. methyl parathion sorbed on a partially hydrated Al-montmorillonite with 4.5 % by wt. water content, after 4 days, 31333 scans.

Figure SI-3 60.7 MHz ^{31}P DP-MAS spectra (each 1000 scans) during the first 43 hours of decomposition of the sample shown in Figures 2-16 (8.5 % by wt. methyl parathion sorbed on Cu(II)-montmorillonite containing 4.8 % water by wt.).

Figure SI-4 60.7 MHz ^{31}P DP-MAS and CP-MAS spectra of a sample containing 8.8 % by wt. methyl parathion sorbed on a Al-montmorillonite with less than 0.2 % by wt. water content: A) DP-MAS after 1 day, 400 scans. B) DP-MAS after 1 day (1000 scans). C). DP-MAS after 4 days (1000 scans). D) CP-MAS after 4 days (1000 scans). E) DP-MAS after 19 days (1000 scans). F) CP-MAS after 19 days (1000 scans). G). DP-MAS after 2.0 years (1000 scans). H) CP-MAS after 2.0 years (1000 scans). Asterisks indicate spinning sidebands.

Figure SI-5 242.9 MHz liquid-sample ^{31}P spectra of the DMSO-d_6 extracts of methyl parathion sorbed on various clays: A) methyl parathion (1.4 % by wt.) sorbed on kaolinite (1.1 % water by wt.) after 11 days, 8864 scans; spectrum is vertically expanded such that largest peak is 16 times larger than shown. B) methyl parathion (9.2 % by wt.) sorbed on Ca-montmorillonite (1.9 % water by wt.) after 3 years, 2080 scans. C) methyl parathion (8.5 % by wt.) sorbed on Zn-montmorillonite (4.5 % water by wt.) after 1 day, 7232 scans; spectrum is vertically expanded such that largest peak is 4 times larger than shown. D) methyl parathion (8.6 % by wt.) sorbed on Zn-montmorillonite (5.3 % water by wt.)

after 3 years, 2760 scans. E) methyl parathion (9.1% by wt.) sorbed on Al-montmorillonite (4.5 % water by wt.) after 10 days, 6632 scans. F) methyl parathion (9.1% by wt.) sorbed on Al-montmorillonite (4.5 % water by wt.) after 2.0 years, 5930 scans. G) methyl parathion (8.8 % by wt.) sorbed on Al-montmorillonite (<0.2 % water by wt.) after 2.0 years, 19220 scans. H) methyl parathion (8.5 % by wt.) sorbed on Cu-montmorillonite (4.8 % water by wt.) after 3 years, 17988 scans.

Figure SI-1

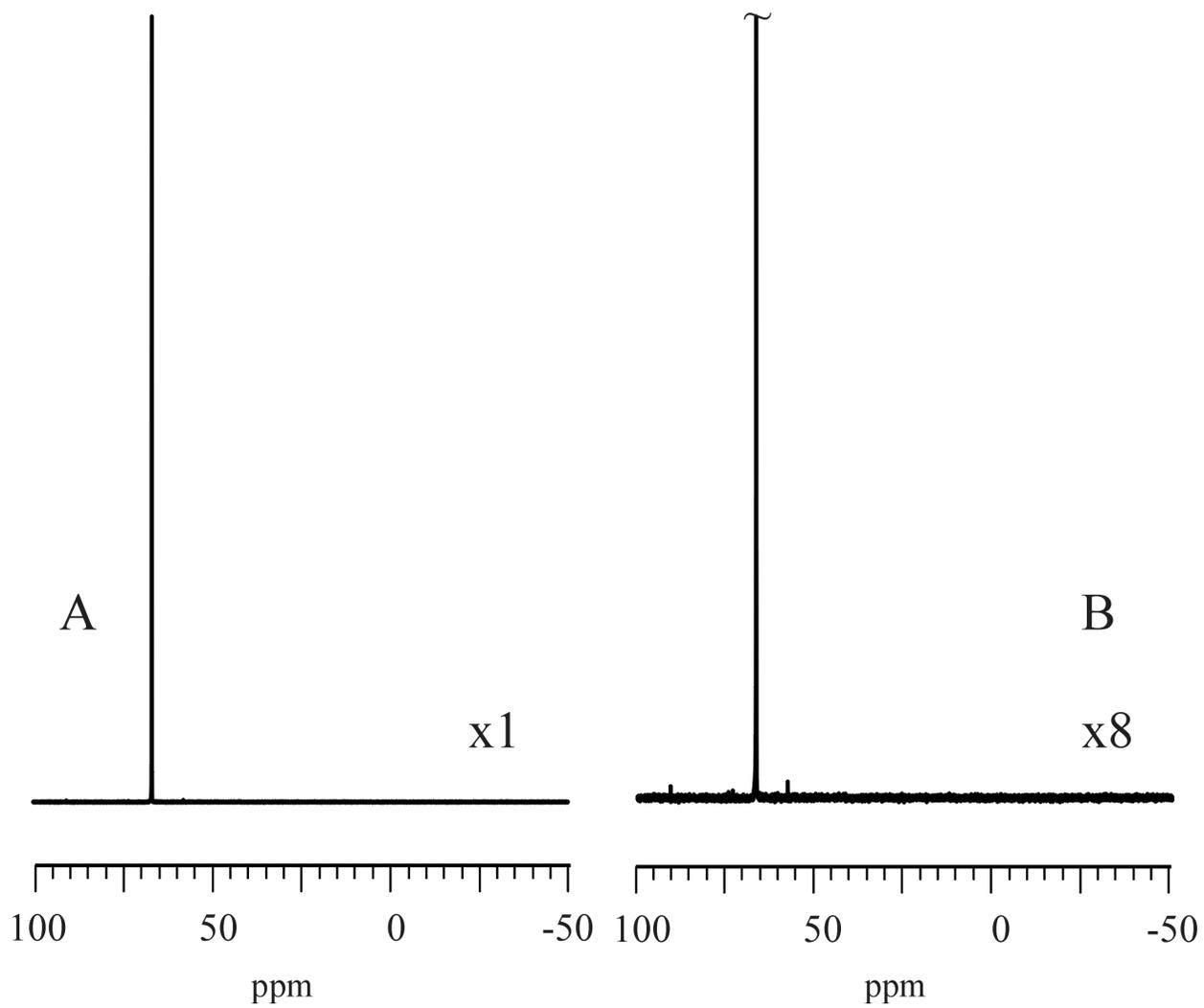


Figure SI-2

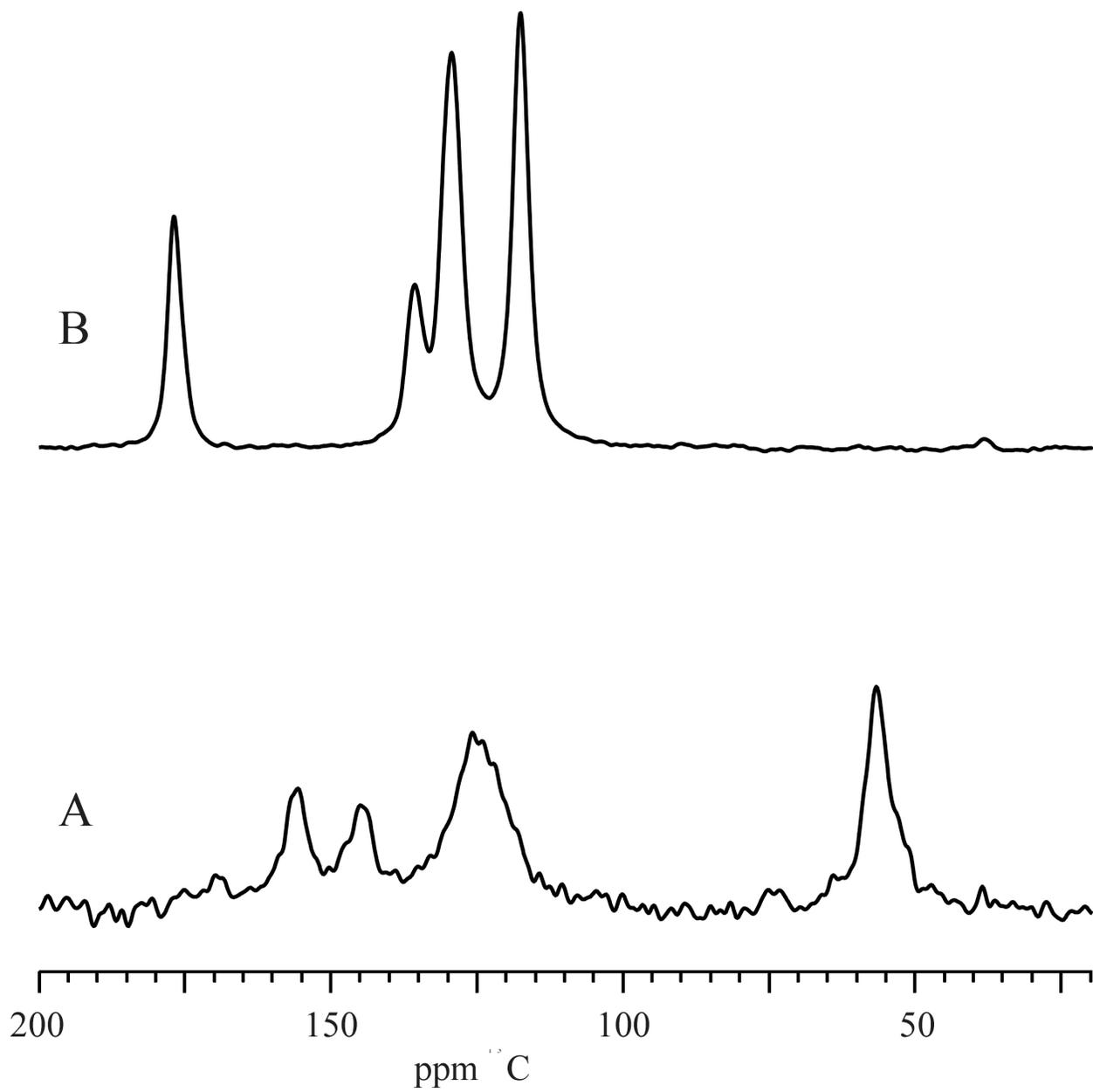


Figure SI-3

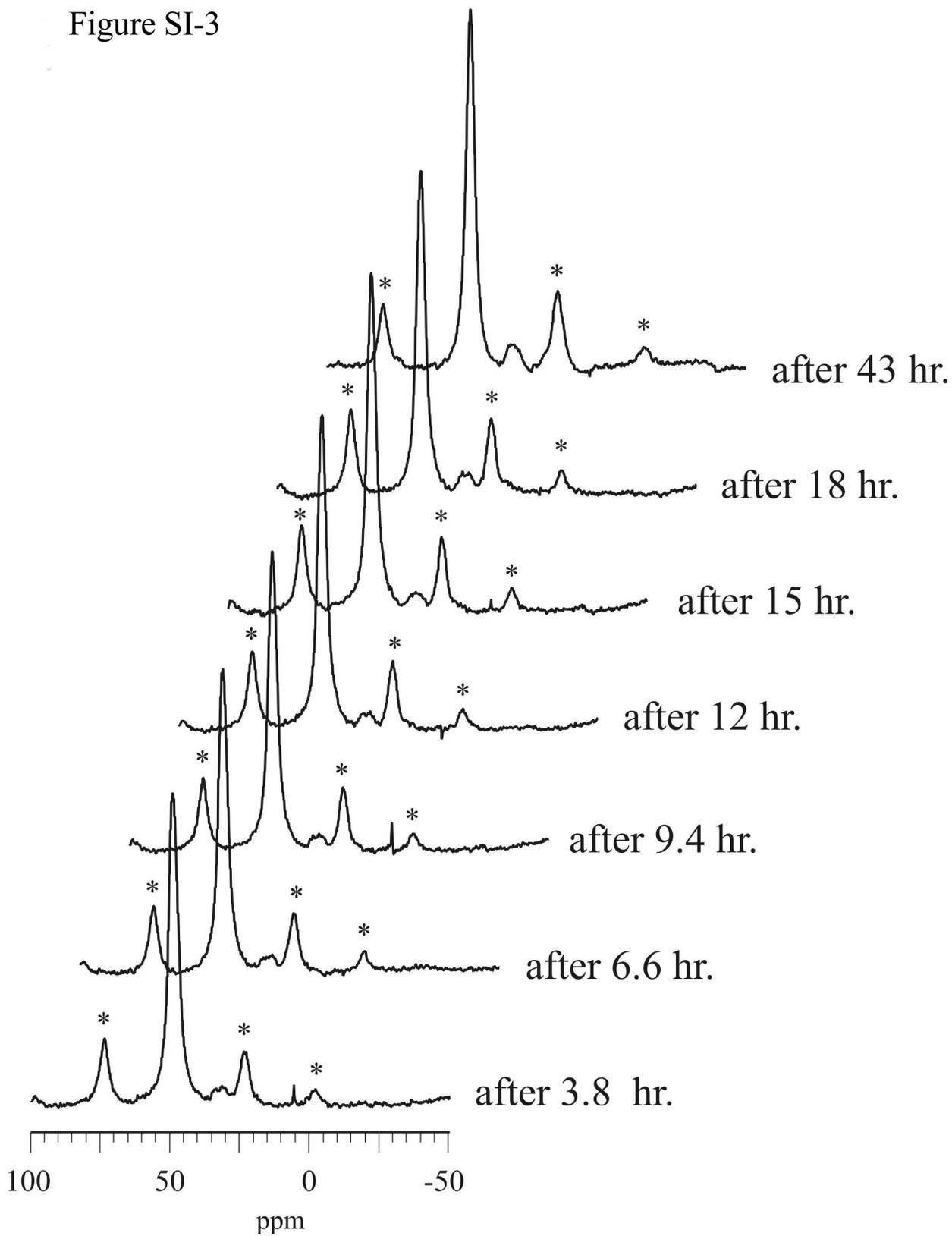


Figure SI-4

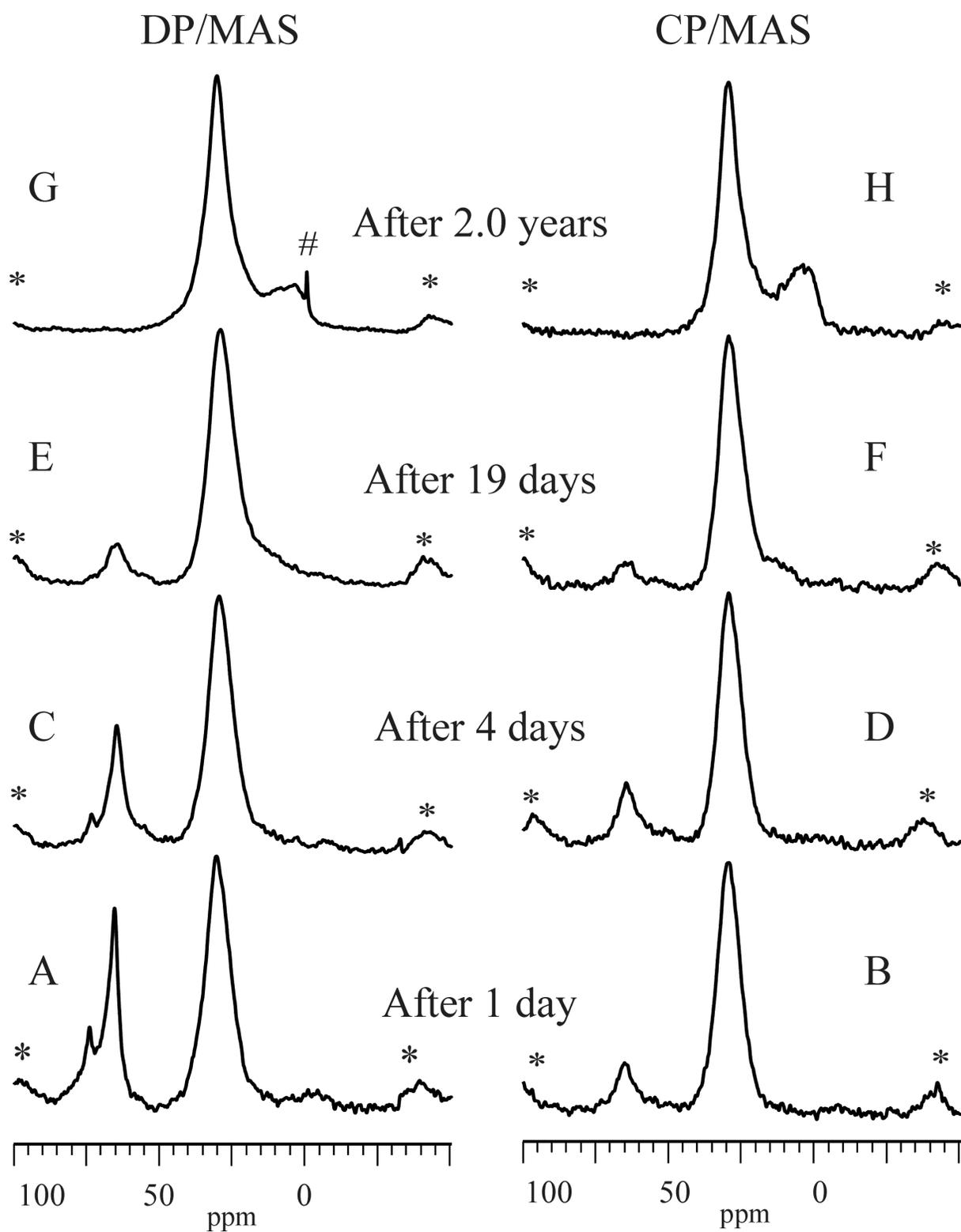


Figure SI-5

