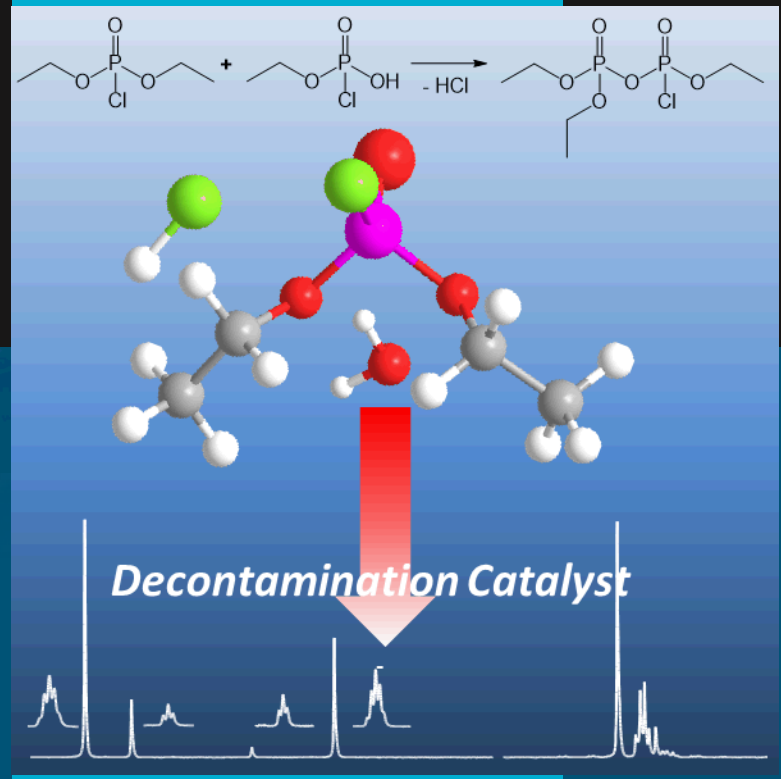
SAND2018-2086C

Multinuclear NMR Monitoring of Decontamination Chemistries of Bulk Chemical Agents and Simulants



PRESENTED BY

Todd M. Alam

Practical Applications of NMR in Industry Conference (PANIC): (Session) NMR in National Security. March 2018

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SAND2017-12286A

NNSA Laboratory - Purpose Statement

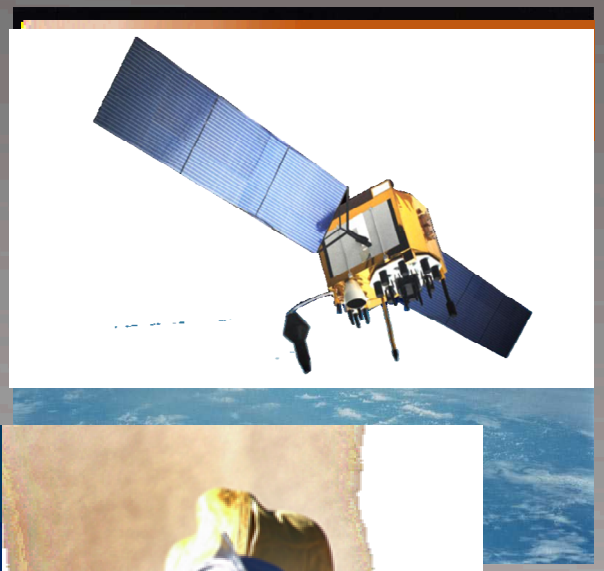
Sandia develops advanced technologies to ensure global peace

Multiple missions beyond the nuclear weapon (WP) program.

2

Global and Homeland Security

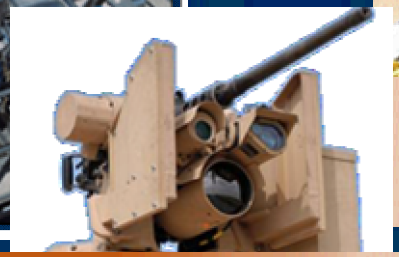
Global Security



Homeland Security Programs

WMD Counterterrorism and Response

Cyber and Infrastructure Security



Homeland Defense and Force Protection

DTRA (Defense Threat Reduction Agency)
DHS (Department of Homeland Security)

Motivation:
Control of Chemical Warfare Agents and Recent World Events

North Korea

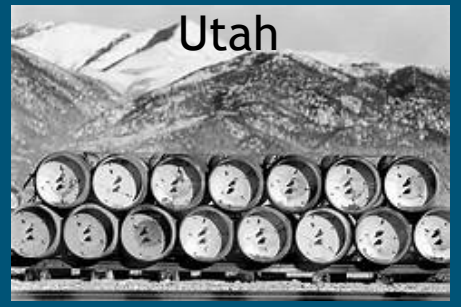
Syria/Iraq/Iran

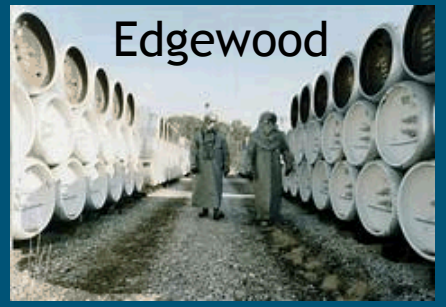
Cape Ray Ship - Destruction Processes

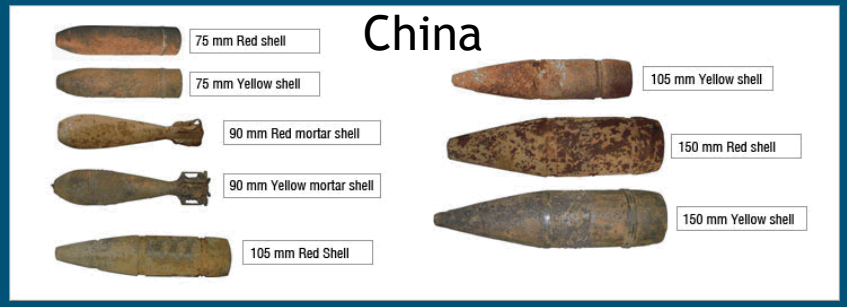
- Housed 1,038.5 tons of CWAs and precursors that Syria declared.
- Ship contained two field hydrolysis units.
- Process involves very high dilution of the agents with water (acid or basic) solutions.
- Mission took place in the Mediterranean Sea.
- Endeavor Started on July and August, 2014.

New Chemistries for Bulk Decontamination?

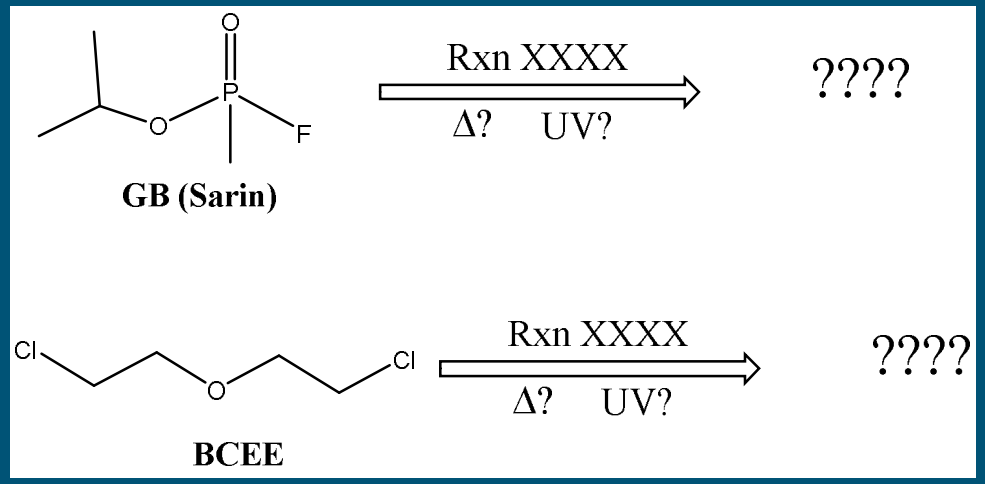
- Exploring chemistries that can be used for *"in-situ"* decontamination.
- For non-secure sites or limited time access for process.
- Should be "catalytic" and involve small amounts of the reactive chemical.
- Process does not involve dilution – must be performed on the neat (bulk) agents and precursors.
- Reactive chemicals must be cheap and readily available in obtainable amounts.
- No "exotic" materials or synthesis required.
- End Target: The CWA must either be degraded or unusable following reaction.





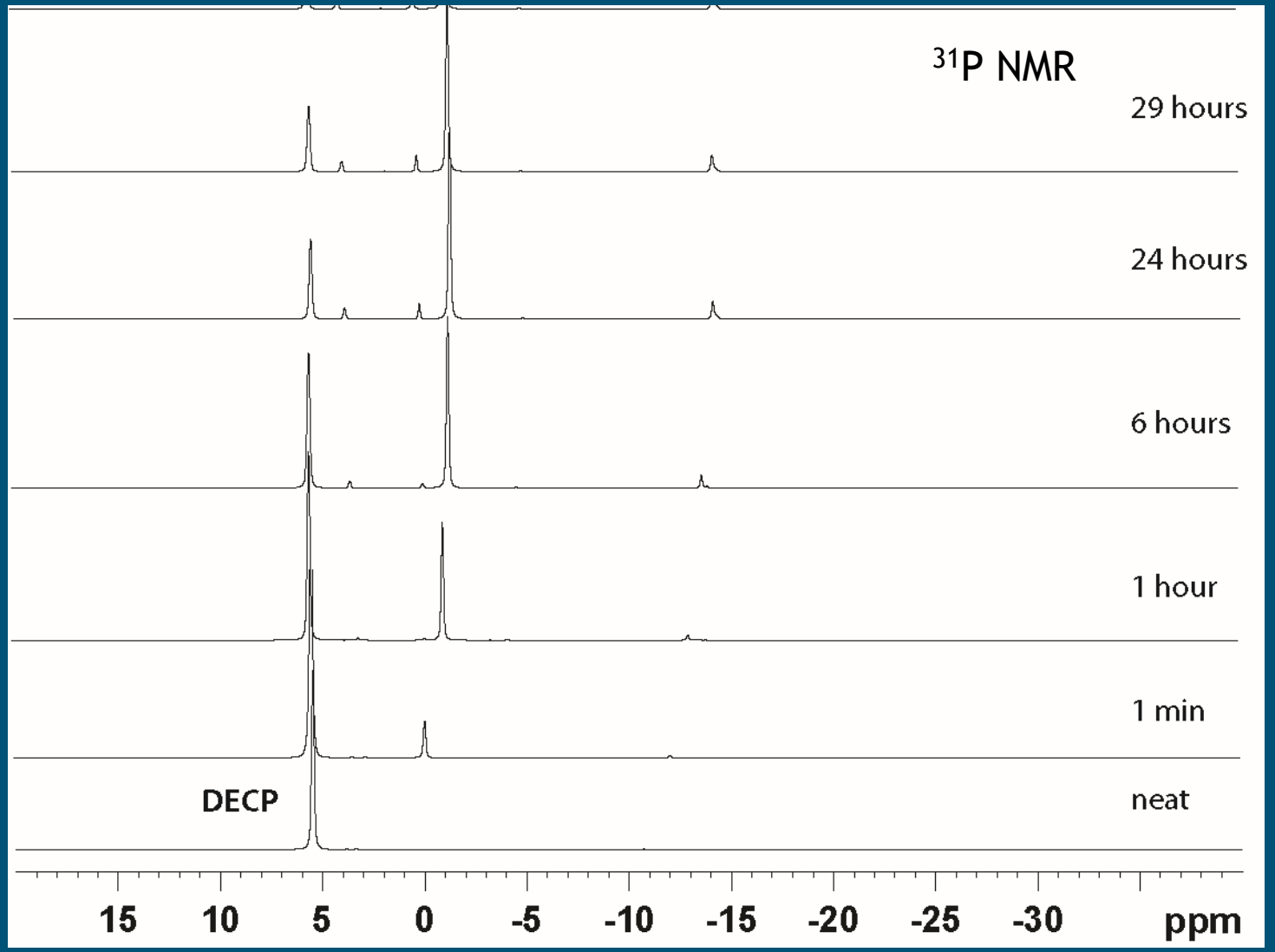


Using NMR to Following Decomposition Kinetics

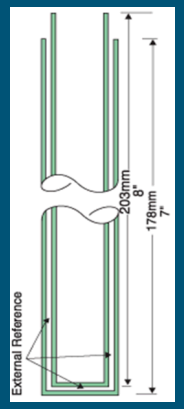


- Kinetics via ^{31}P (**), ^{13}C, ^{1}H and ^{19}F NMR.
- 2D correlation experiments used for assignments.
- Simplest is usually the best.
- Easy…. Neat!

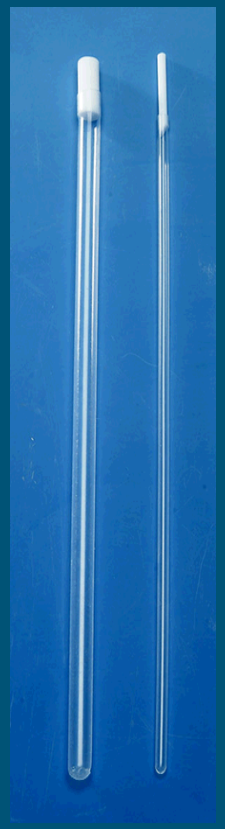
- XXXX – Reaction conditions (details may not be given.



Sample Handling for Neat Simulant Reactions

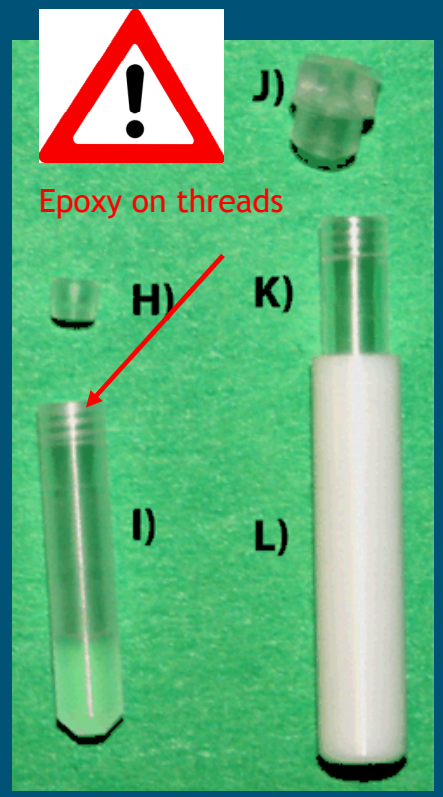


5 mm sealed Teflon inserts ($$)



5 mm Teflon liners (unsealed)

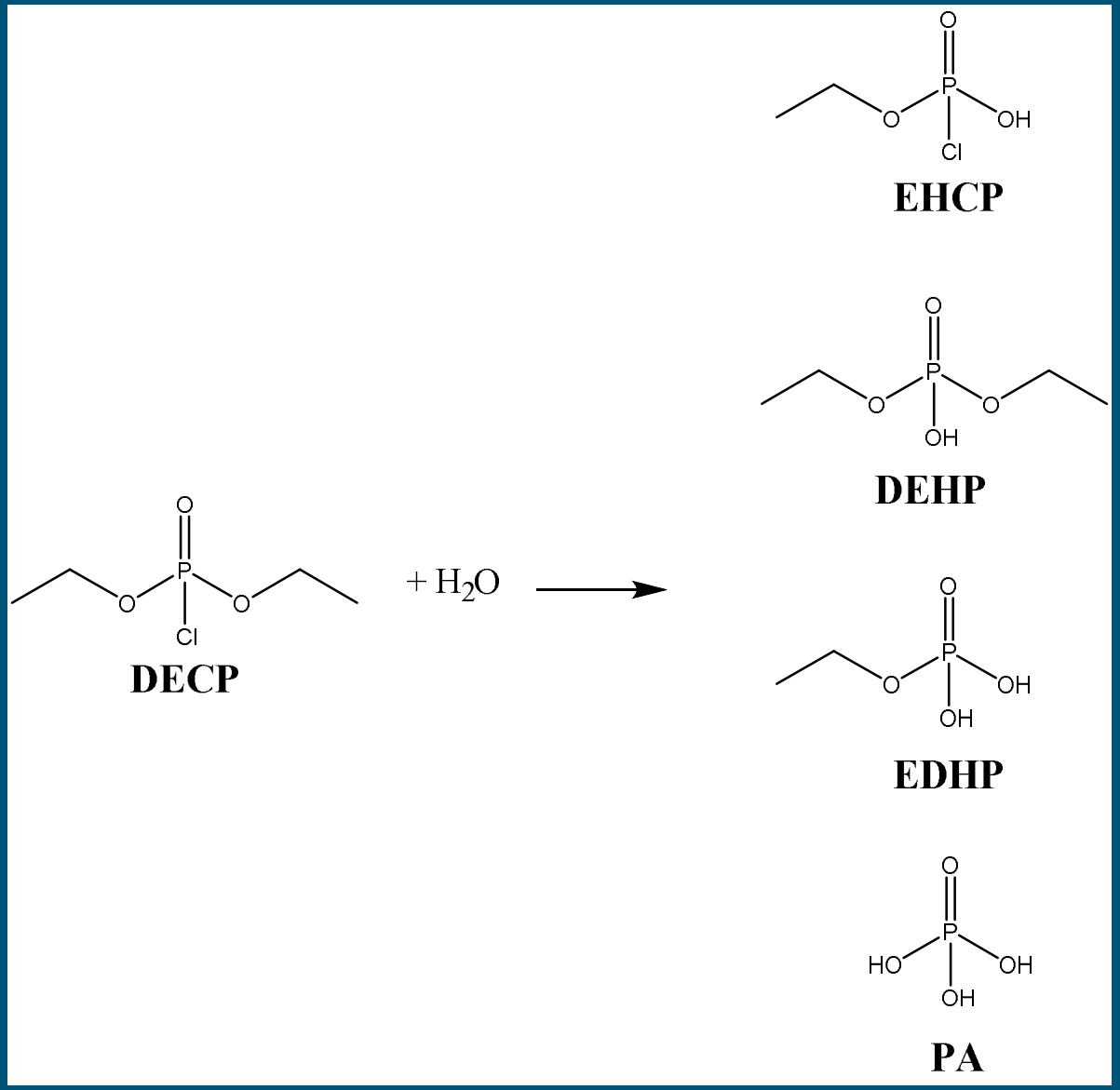
Concentric tubes (capped)

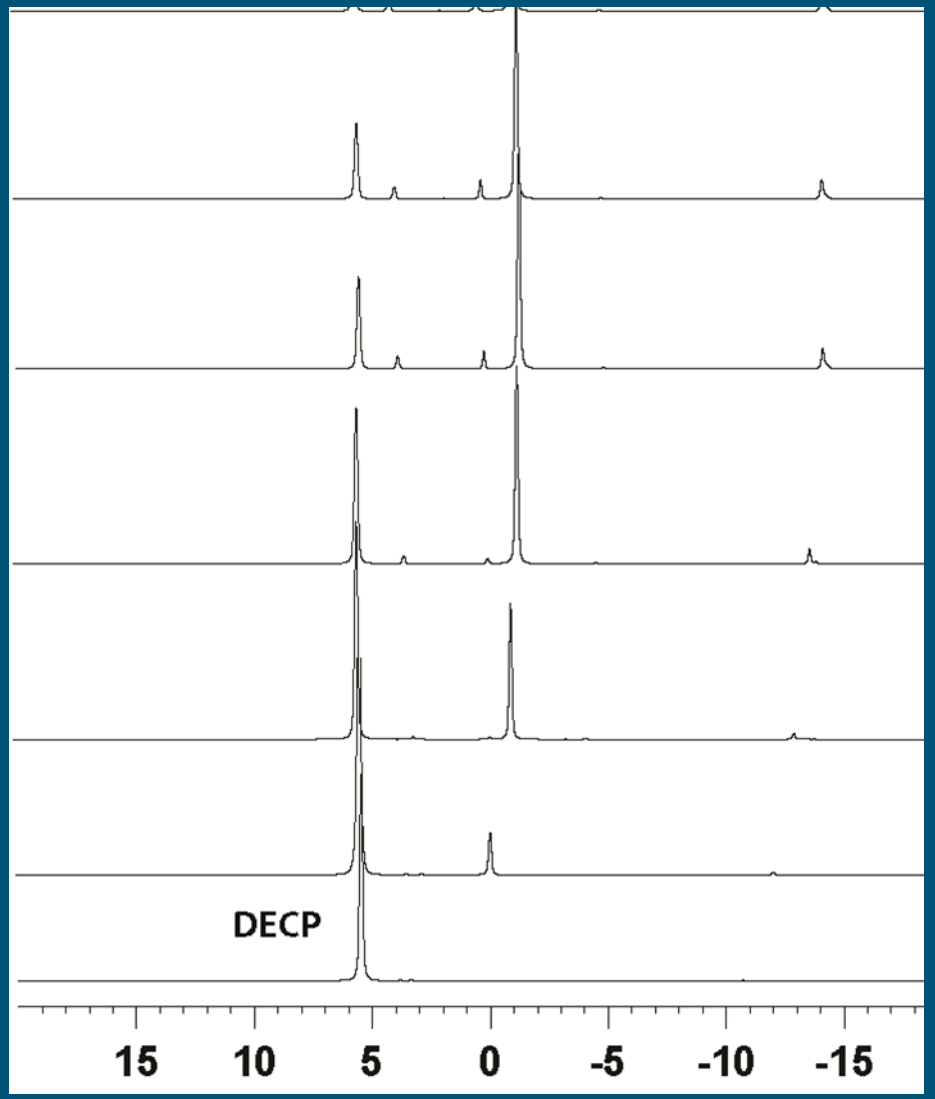


HRMAS Inserts Epoxy seal

- ES&H concerns over handling of 1 ml reaction volumes of neat simulants. (DFP LD50 2 mg/kg)
- All reactions tested in vials before repeat analysis for kinetic NMR studies (*i.e.* violent).
- "Nastier Simulants" restricted to controlled NMR facility with restricted access.
- Decontamination solutions available.
- Reduce possibility of exposure using double containment with tube configuration.
- Explored a variety of different possibilities.
- Still no perfect solution for HRMAS inserts – "dry" sample only.

DECP Reaction followed by ^{31}P NMR



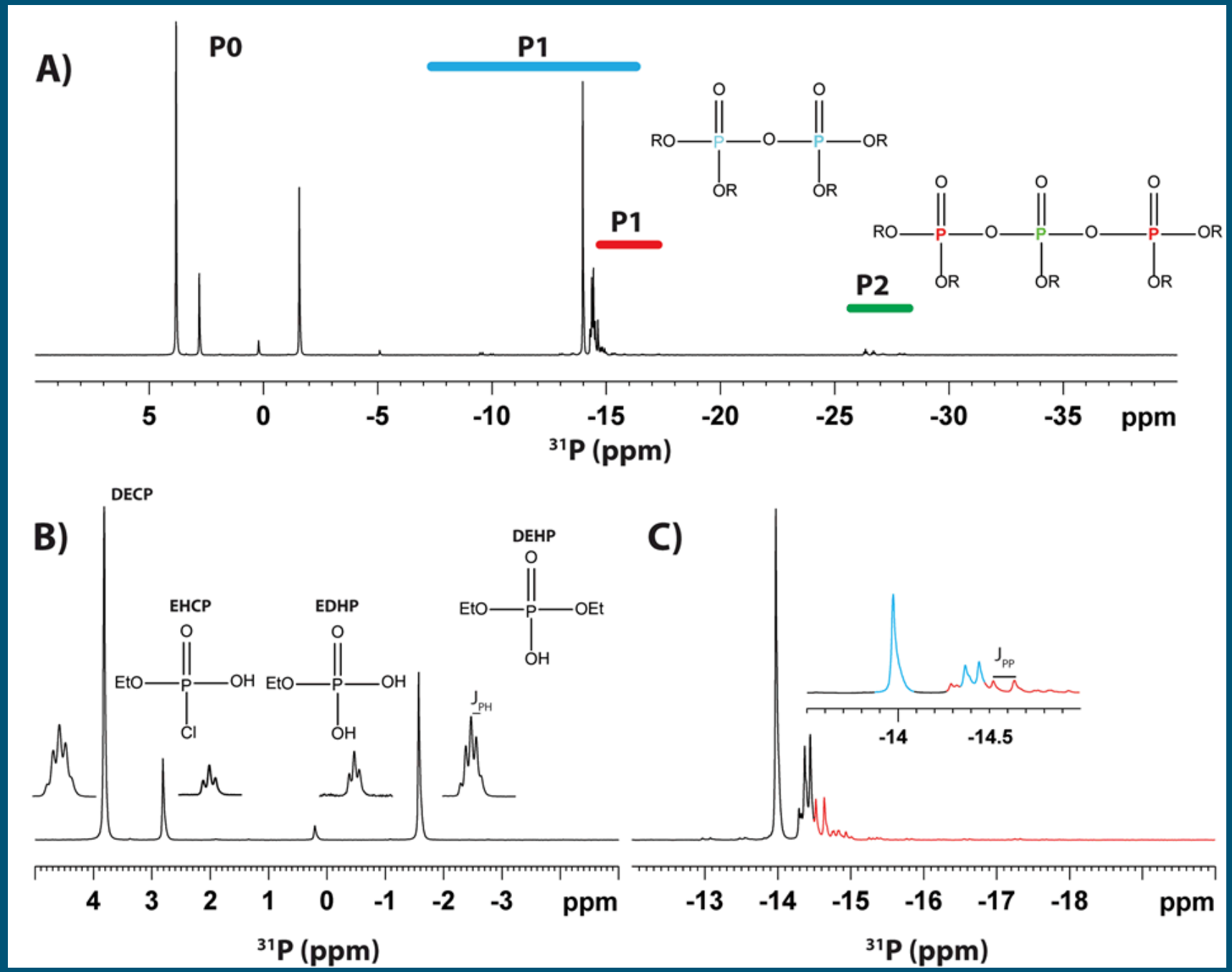


DECP

Monomer degradation species identified based on P-H J couplings.

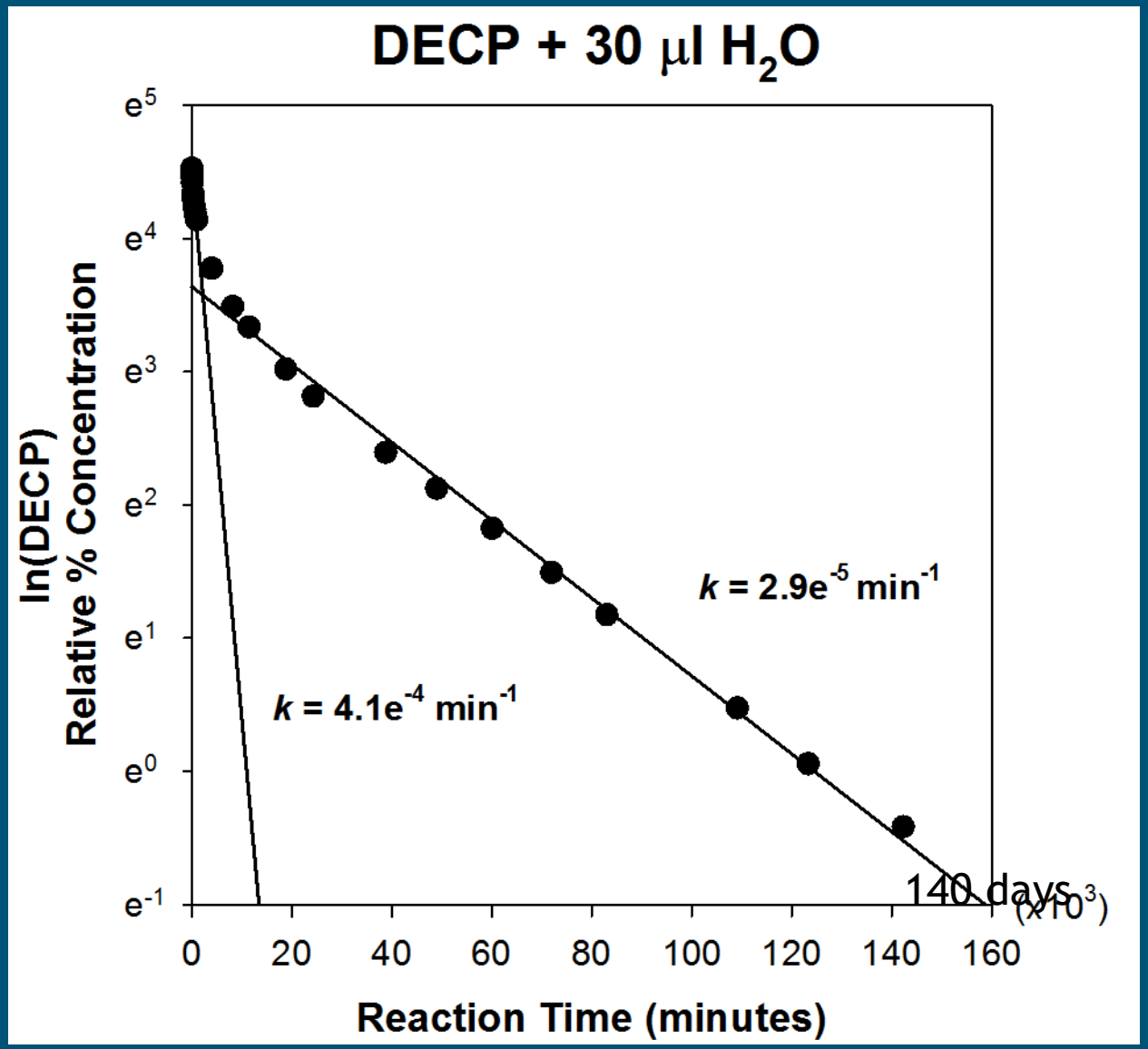
Condensation to form polyphosphates is actually a dominant reaction.

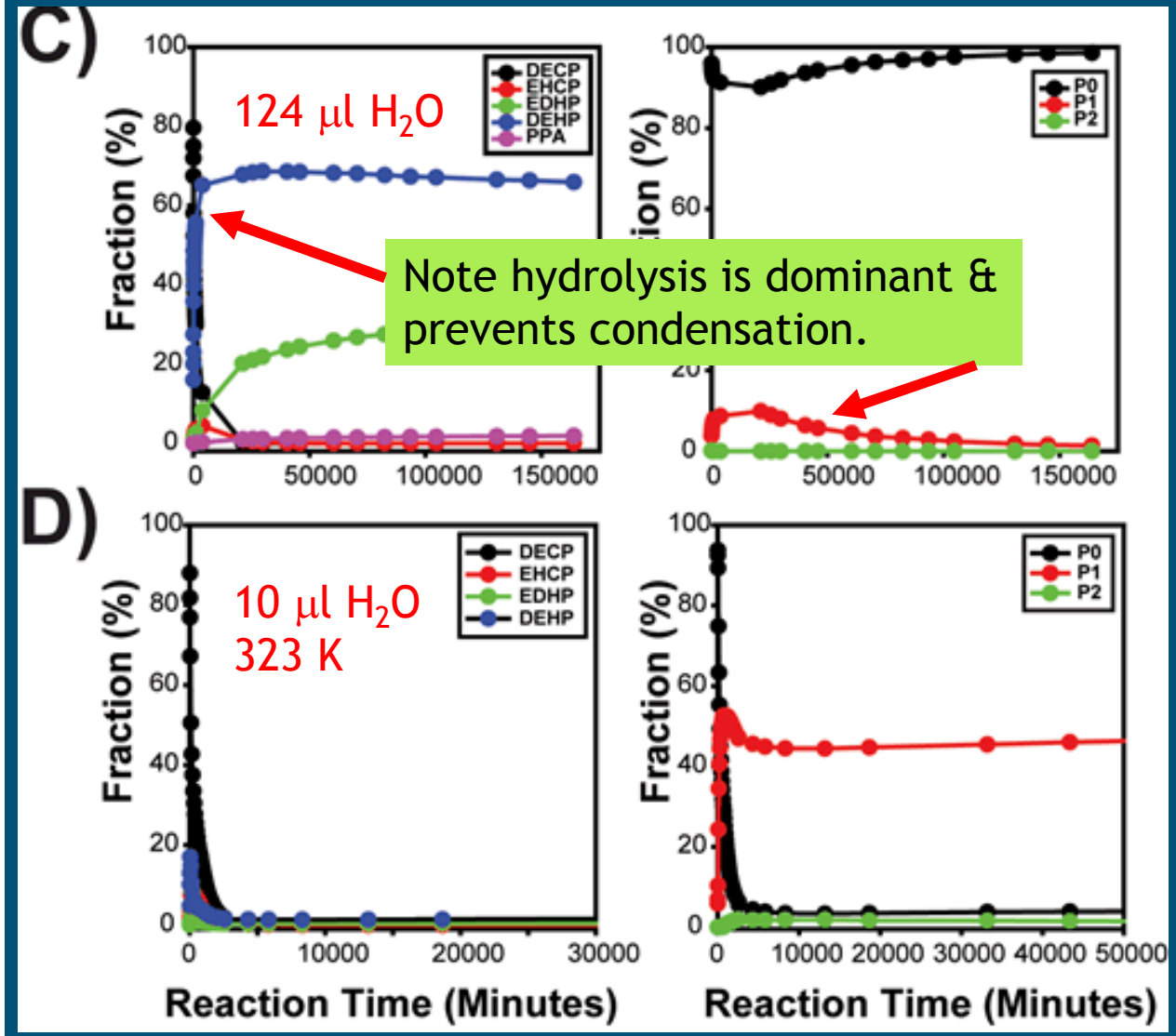
P_n
n = # of P-O-P bonds



Todd M. Alam, Mark K. Kinnan, Brendan W. Wilson, and David R. Wheeler, "Sub-Equimolar Hydrolysis and Condensation of Organophosphates", Chemistry Select, 1, 2698-2705 (2016).

DECP Reaction Kinetics by ^{31}P NMR



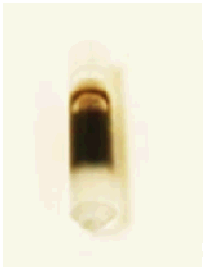


Todd M. Alam, Mark K. Kinnan, Brendan W. Wilson, and David R. Wheeler, "Sub-Equimolar Hydrolysis and Condensation of Organophosphates", Chemistry Select, 1, 2698-2705 (2016).

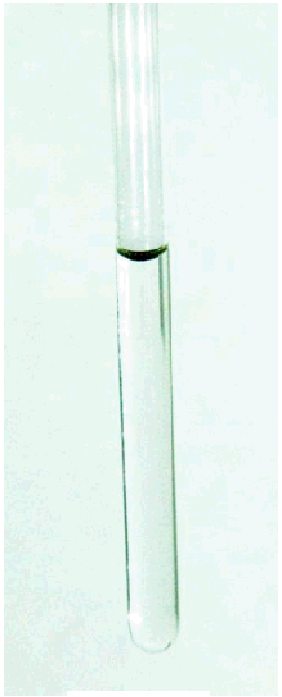
DECP Reactions

DECP + 124 µl H_2O

DECP + 30 µl H_2O



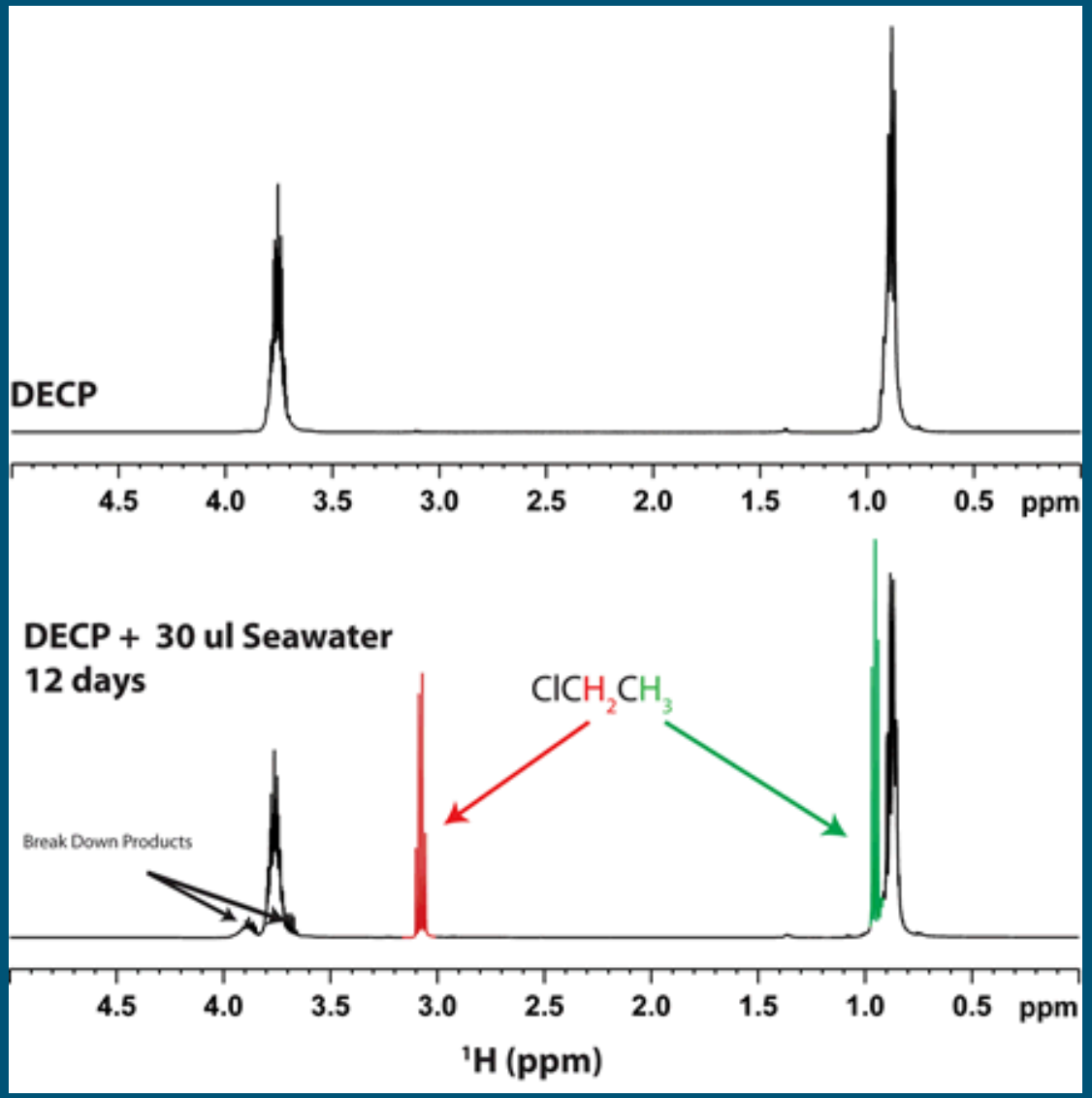
DECP + 30 µl H_2O (Seawater)

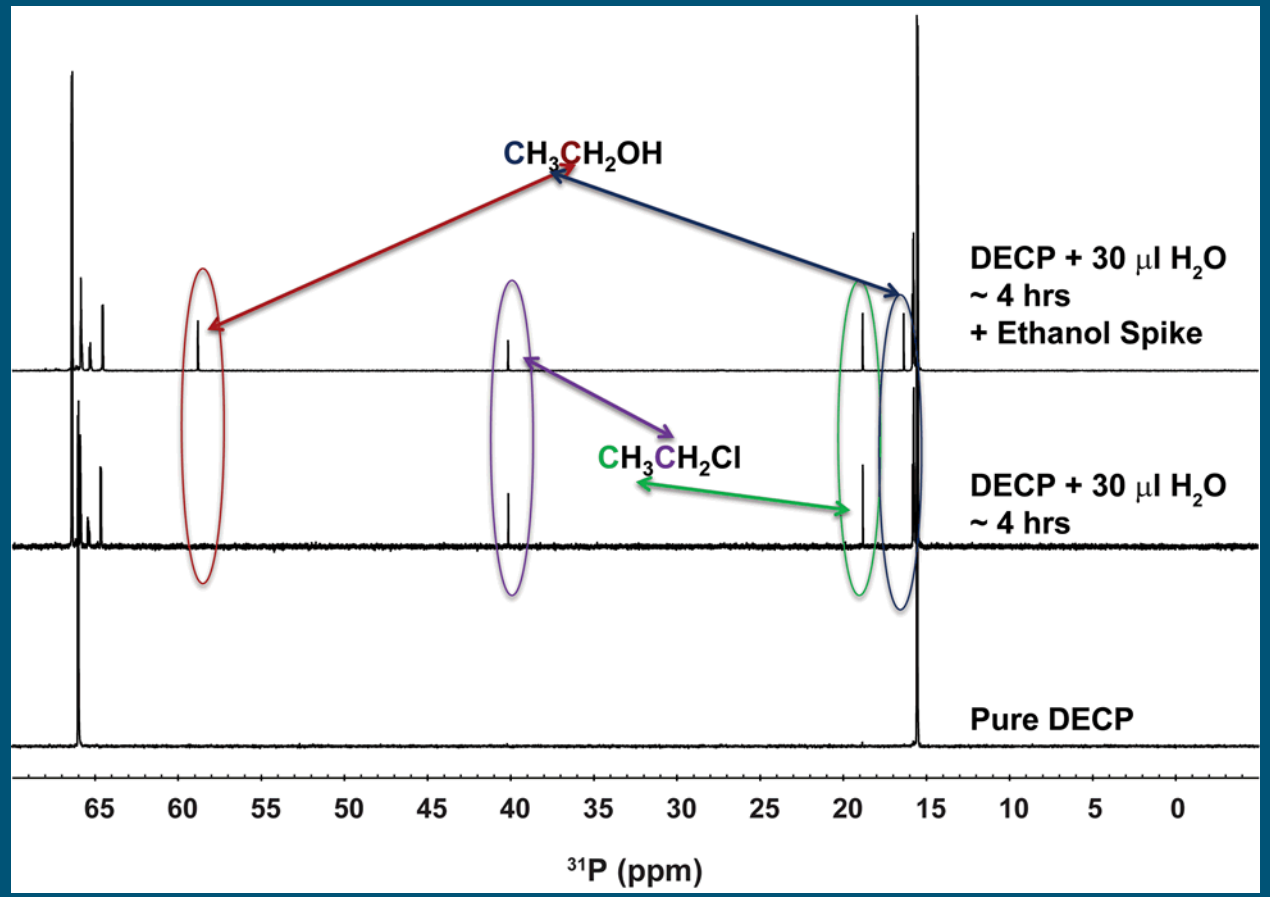


DECP

DECP + 30 µl H_2O

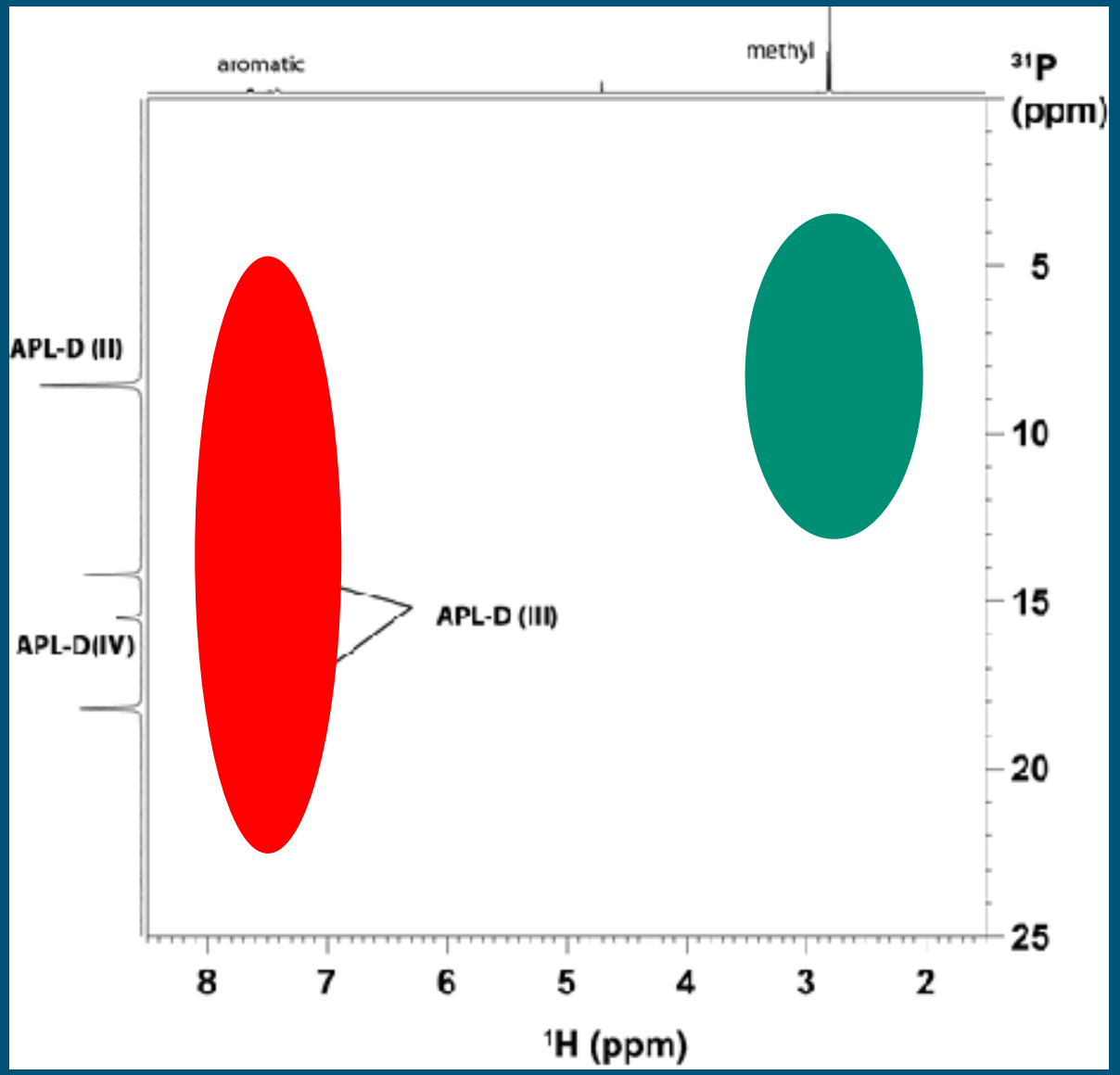
^{1}H NMR DECP Reactions





^{31}P 2D HMBC NMR

- 2D HMBC experiments not as powerful as desired.
- ^{1}H chemical shift separation not as resolved as the ^{31}P chemical shifts.
- Occasionally get additional structural information.

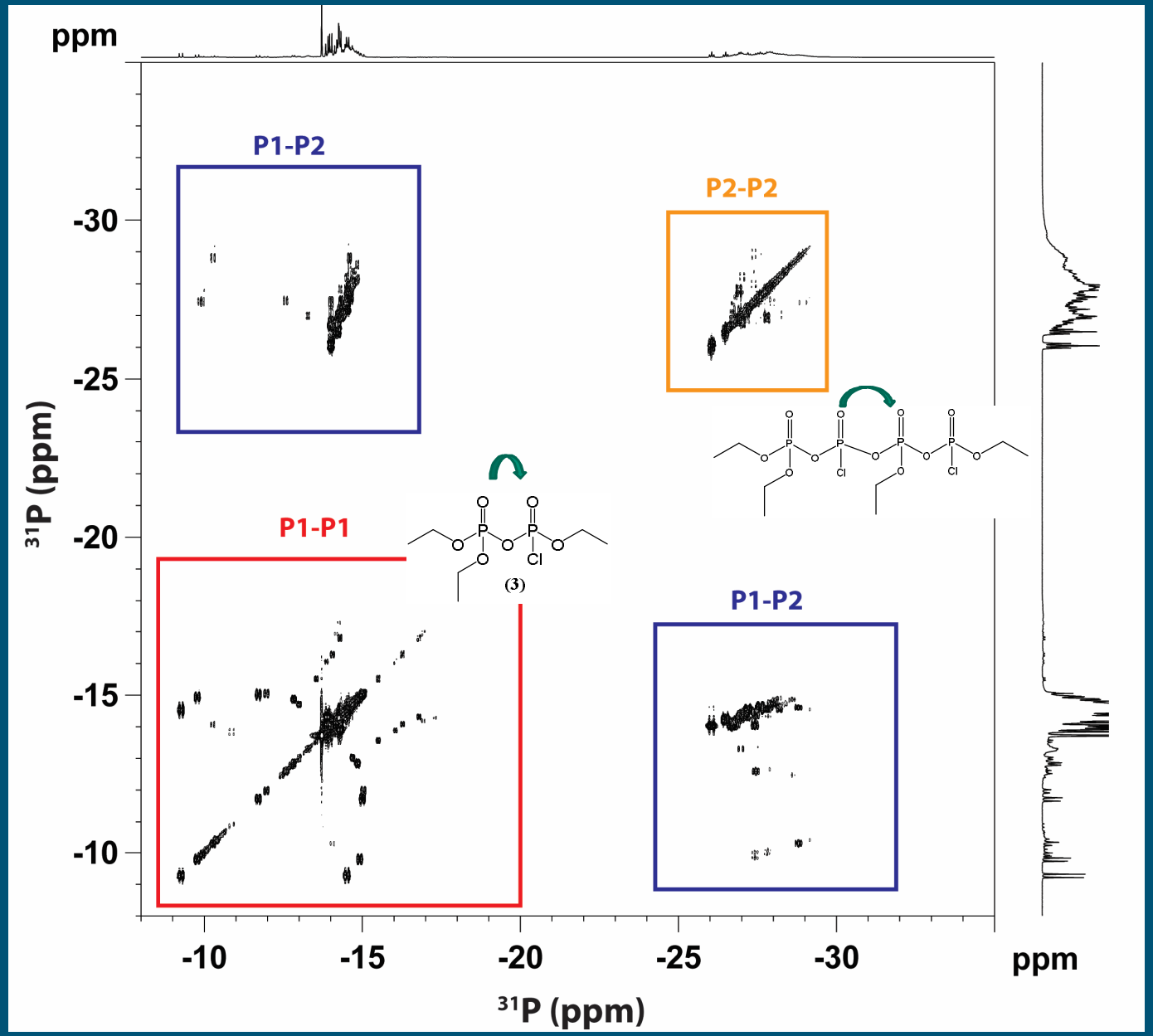


2D ^{31}P-^{31}P COSY NMR of DECP Reaction

Can directly monitor chain growth (condensation)….

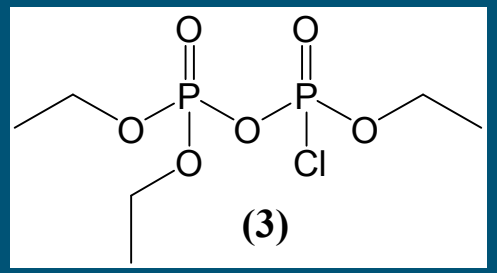
P1 = end groups
P2 = intrachain groups
P3 = Crosslinks

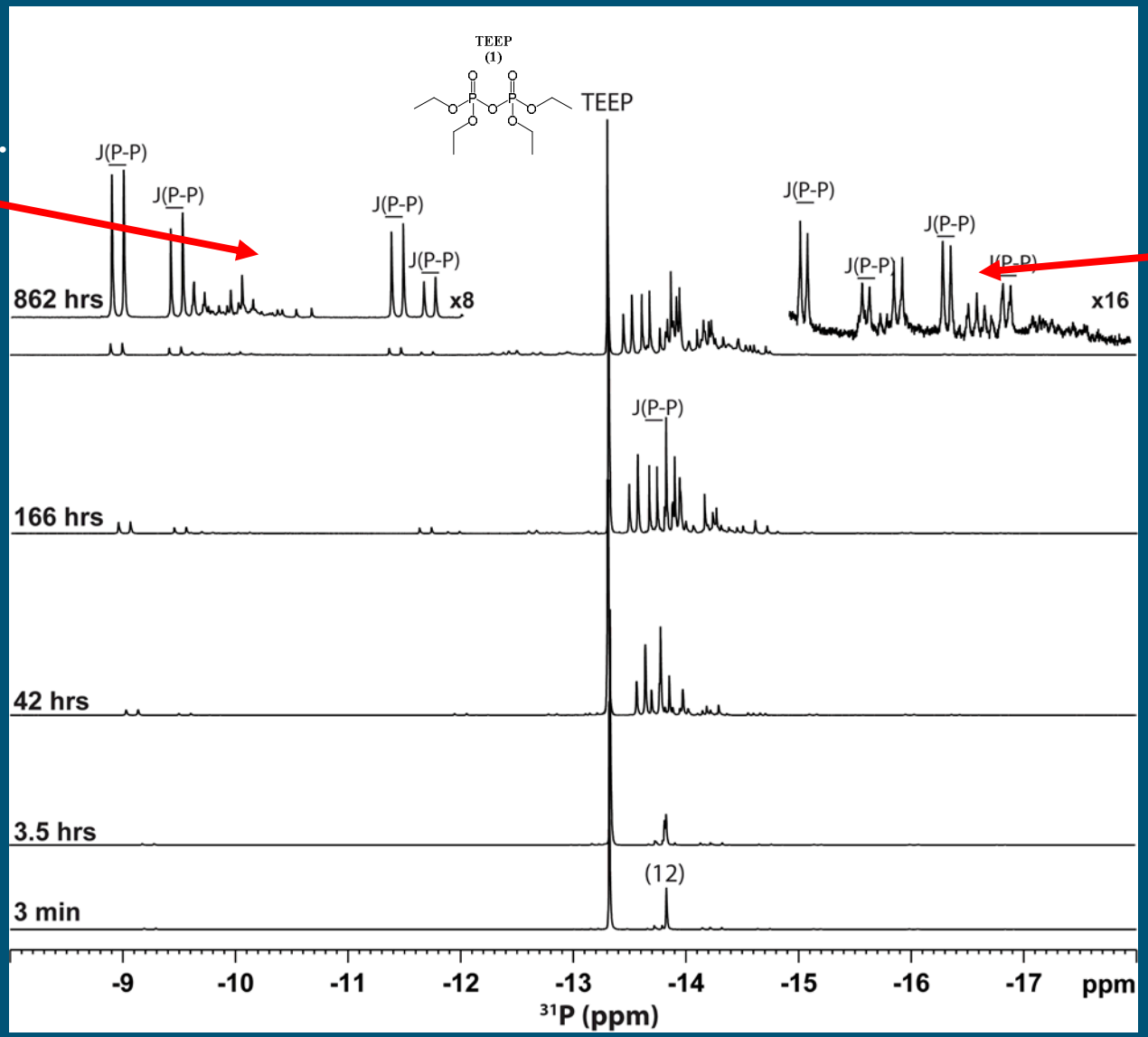
2D COSY from a almost complete reaction.



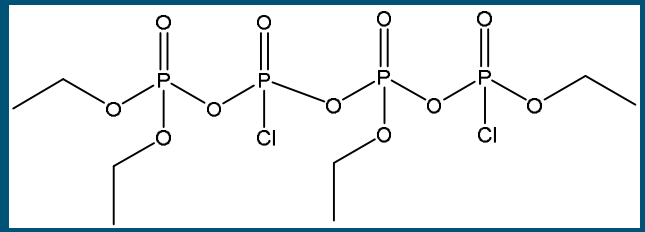
P1 Region pf ^{31}P-^{31}P COSY

P-P J coupling results from asymmetric dimers.

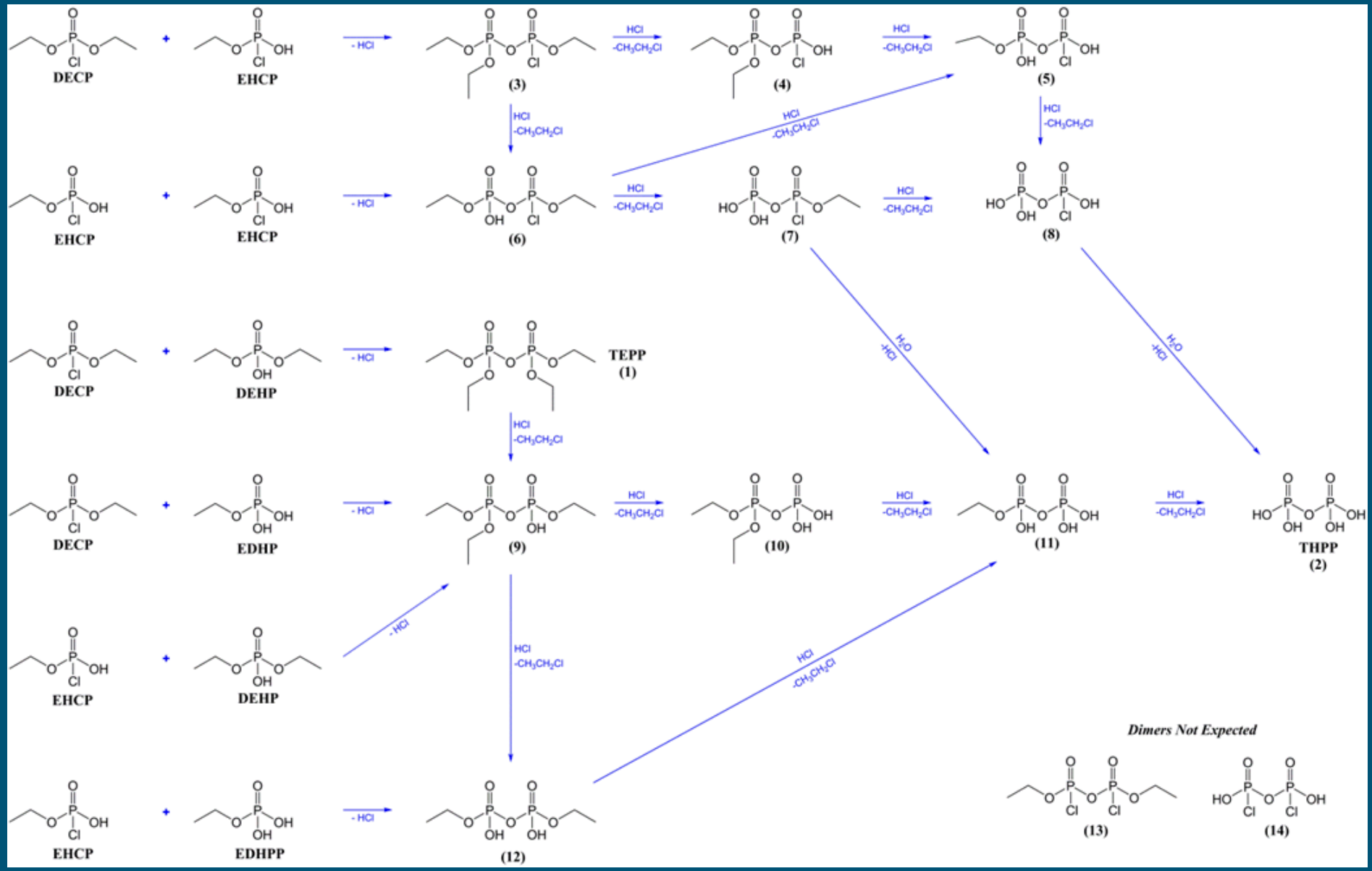




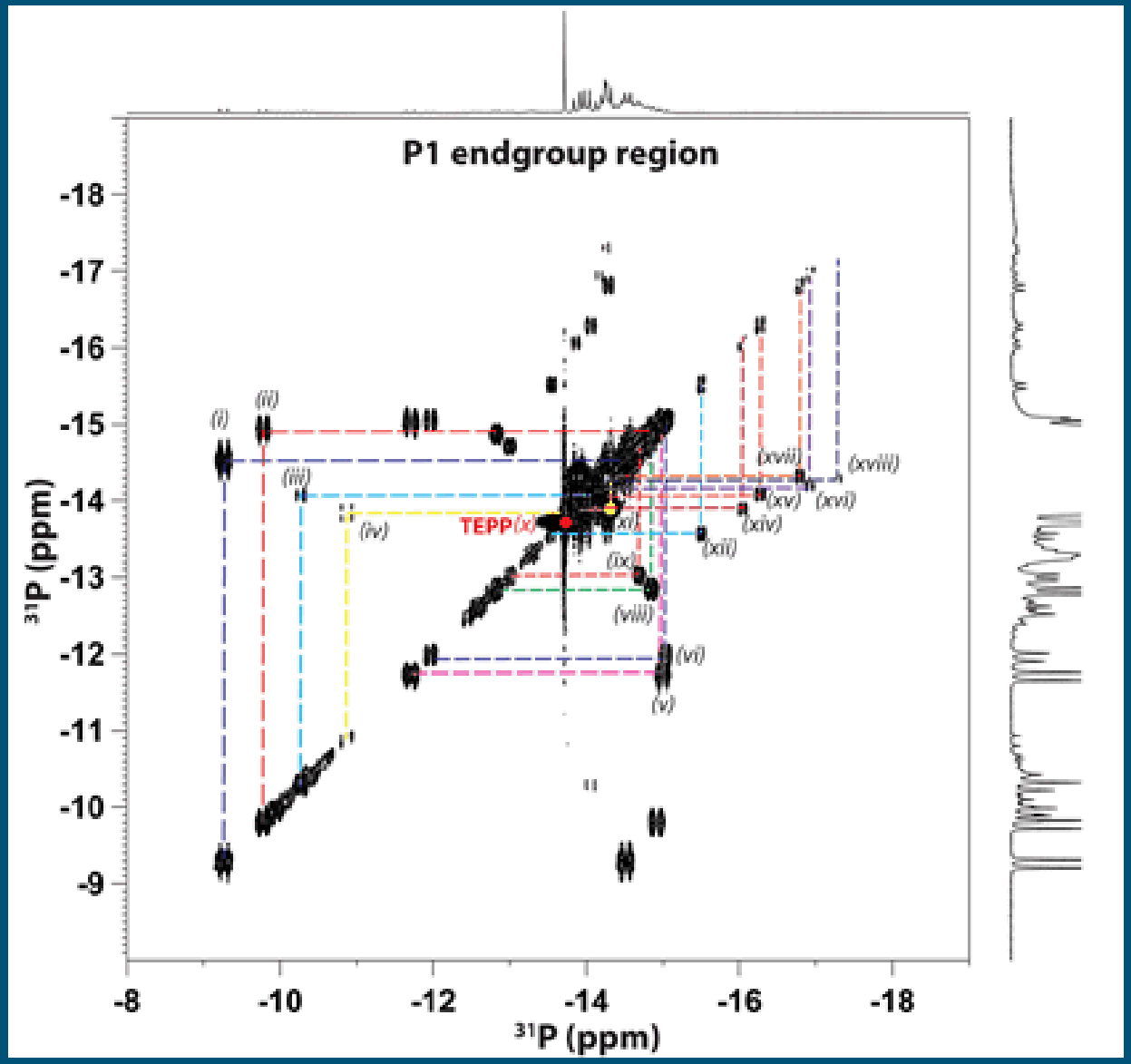
At longer times P-P J coupling results from end group to intra-chain P species.



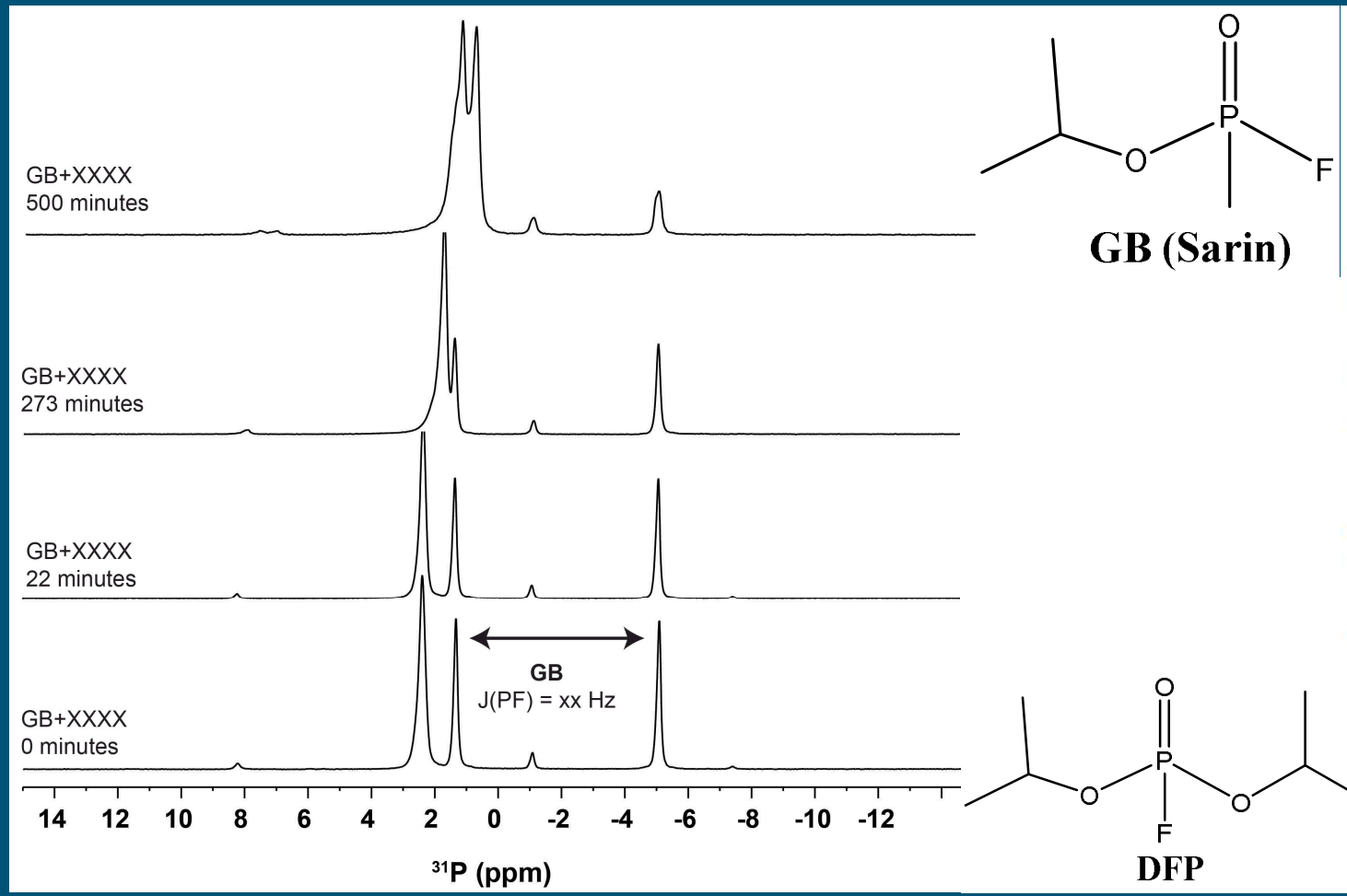
Cascade of Condensation Reactions



Observation of Majority of Dimer Structures in ^{31}P COSY

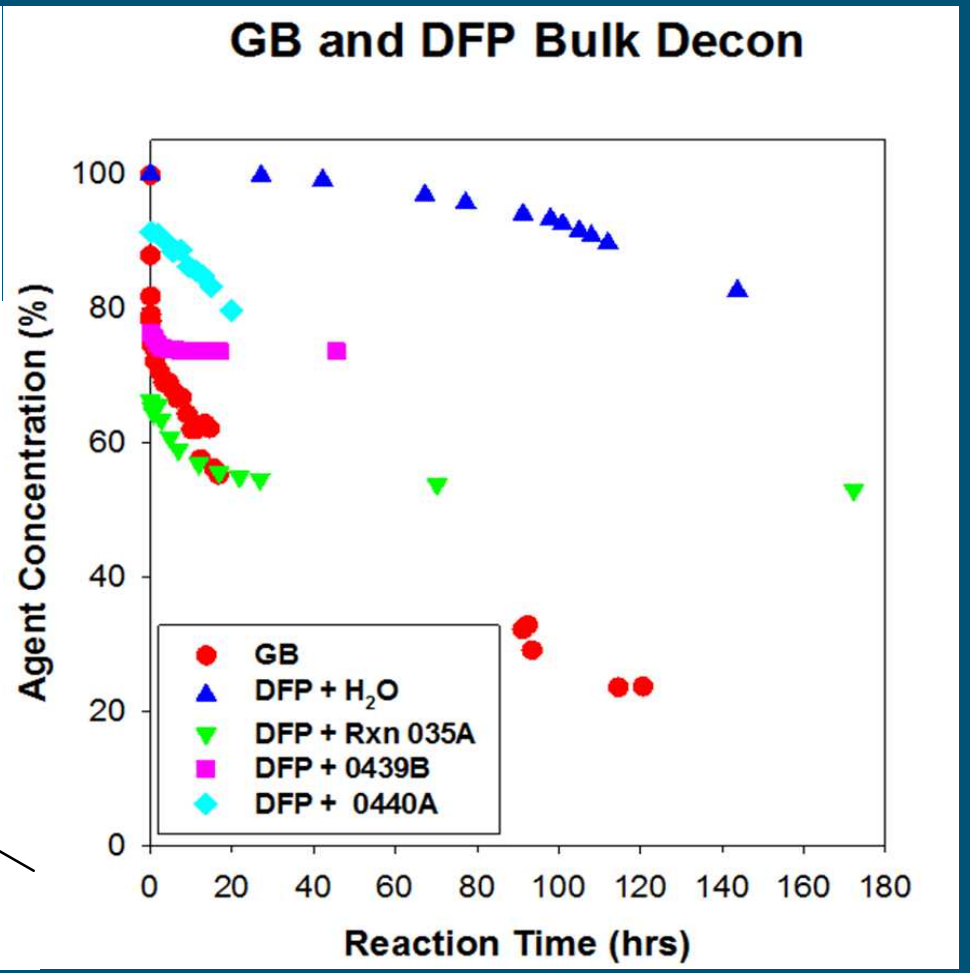


Bulk Decontamination: Agents and Simulants



GB (Sarin)

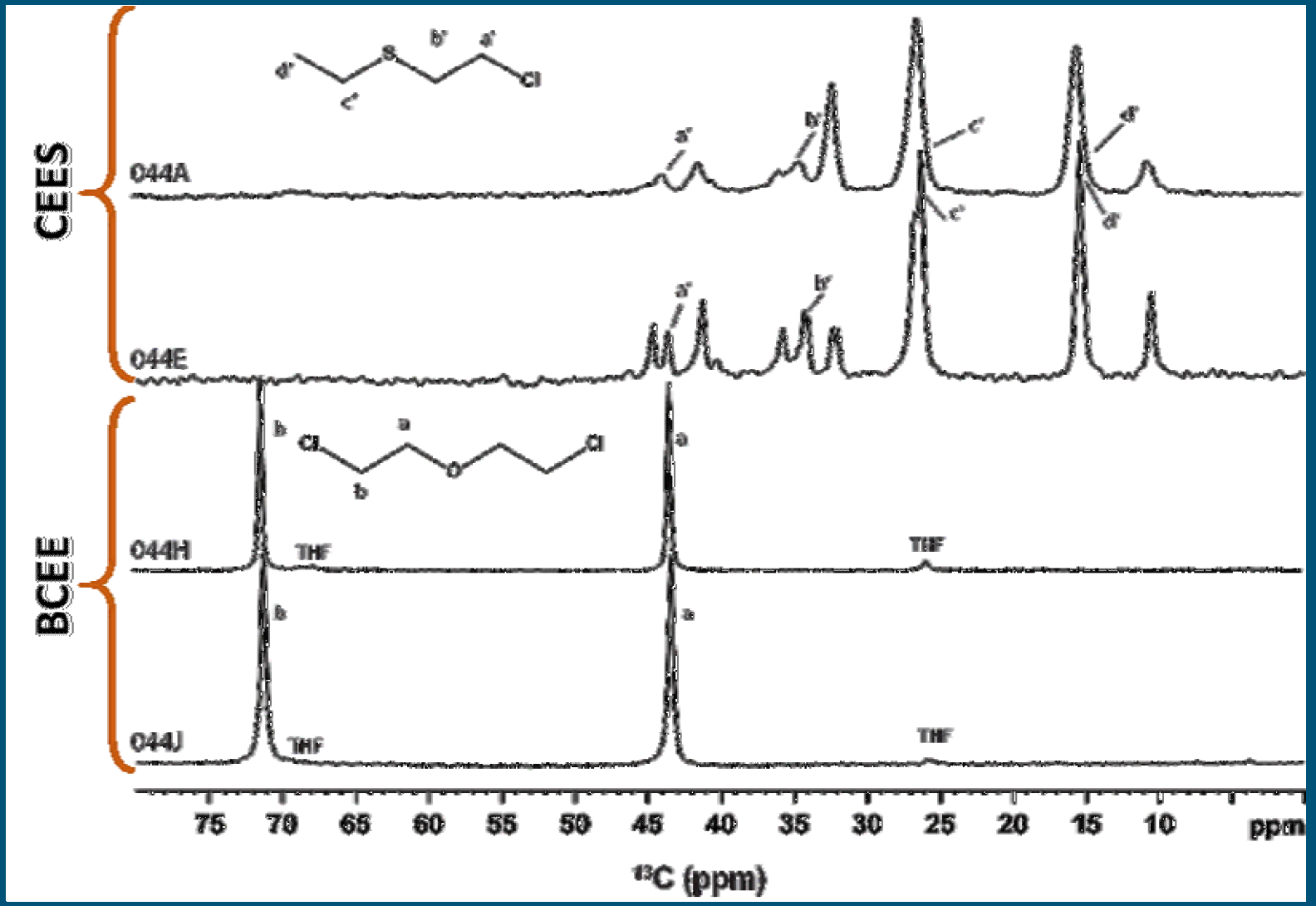
DFP



**GB reactions performed at Edgewood

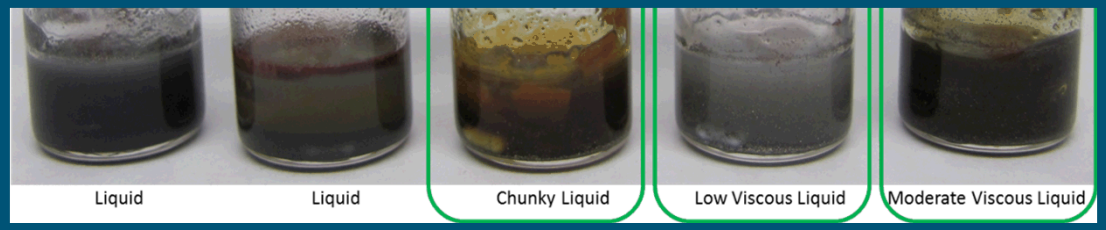
Other Nuclei – ^{13}C NMR Decontamination of HD Simulants

- Reaction chemistry varies with simulant used.
- No large data base comparing reactivities for CWAs and simulants.
- Can provide guidance for selection of simulants in HD directed efforts.

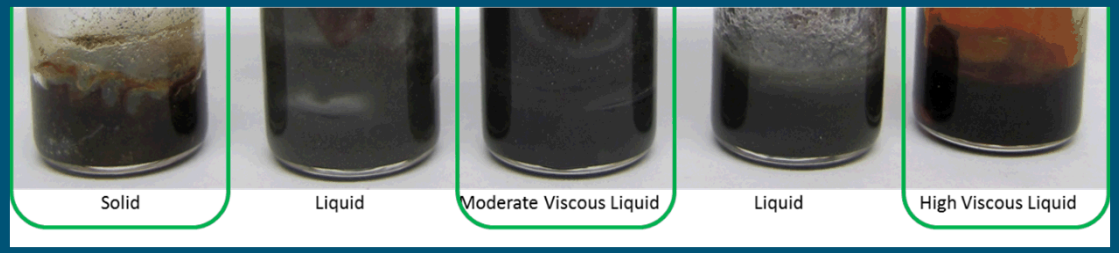


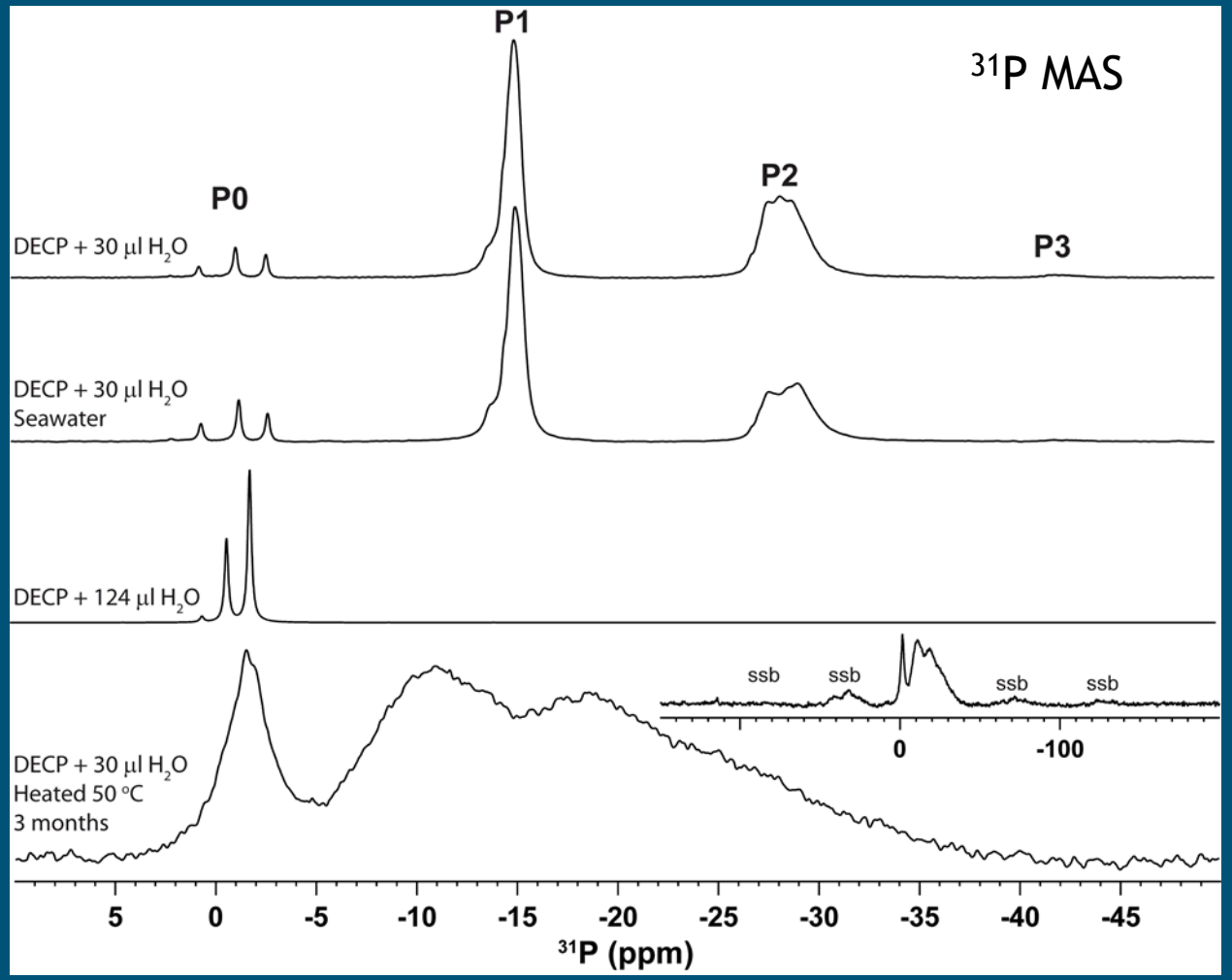
MAS NMR of Solid Precipitate for Many Reactions

BCEE



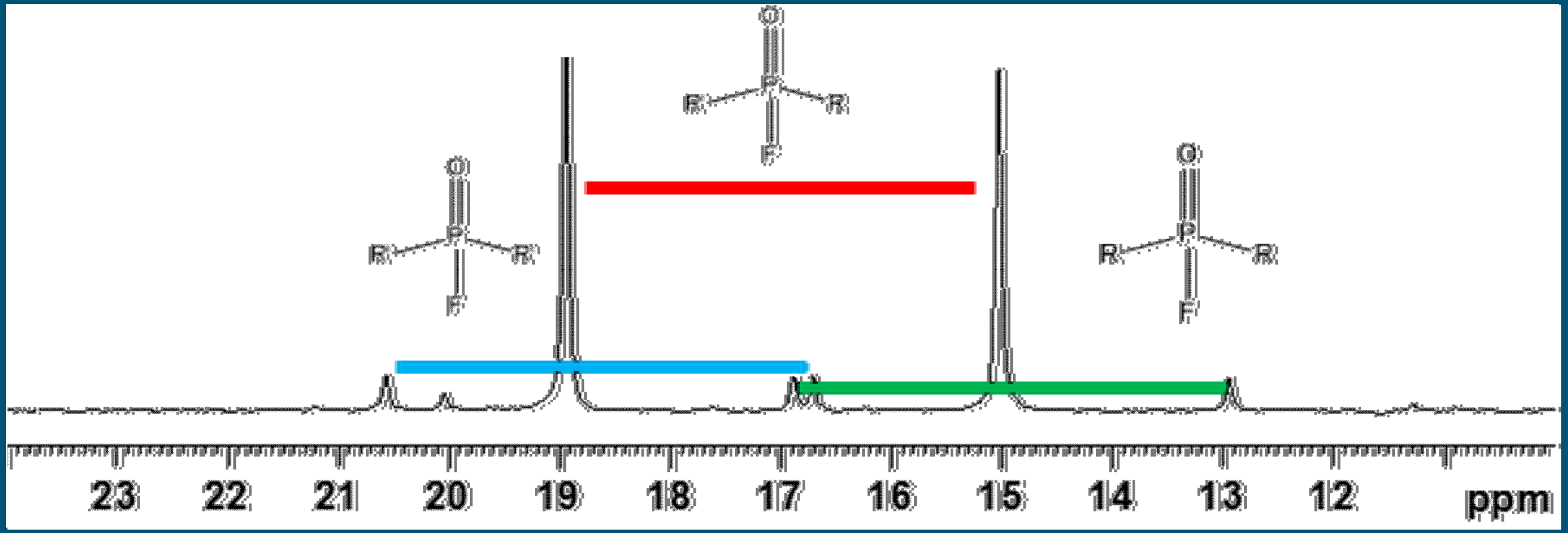
CEES



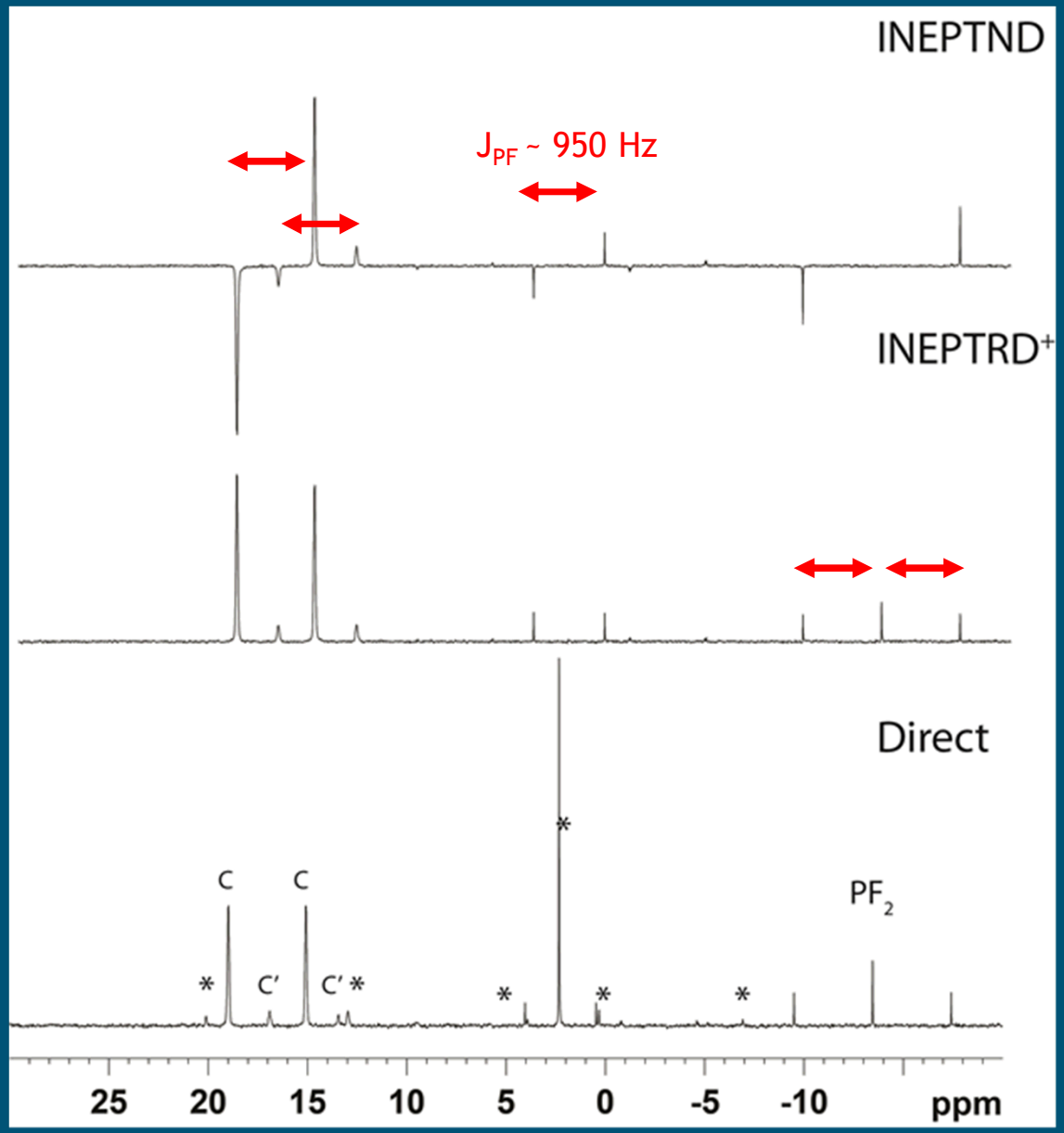


^{31}P NMR Synthetic Signatures - Forensics

- R and R’ different ligands.
- In some instances get combinations during synthesis (Forensics).
- Some decontamination reactions also cause ligand exchange (toxicity?)



^{31}P-^{19}F INEPT NMR of Degradation Species



- For compounds containing P-F bonds the INEPT (Insensitive Nuclei Enhancement by Polarization Transfer) experiment is powerful.
- Immediately can identify compounds containing P-F bonds and those degradation species that do not (*).
- ^{1}H-^{31}P coupling produces small multiplets, some loss of signal intensity.
- Probe limitations… need that ^{1}H-^{19}F-X tunable probe!
- *Observed some significant ^{19}F frequency offset effects with standard 180° pulses… need to explore adiabatic and shaped pulses for broadband excitation.*
- *2D HMQC and HMBC conflicts between large J and gradient pulse lengths.*

Acknowledgements

Dr. Mark K. Kinnan (Sandia), WMD Threats & Aerosol Science Department
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Currently Graduate Student at Ohio State University.

Randi Poirier, Sandia Technical Staff.

UG University New Mexico, Student Intern
Currently Graduate Student at University Colorado Bolder.

Thanks for your attention……