^{31}P MAS NMR – A Useful Tool for the Evaluation of VX Natural Weathering in Various Urban Matrixes

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Contamination Risk Assessment

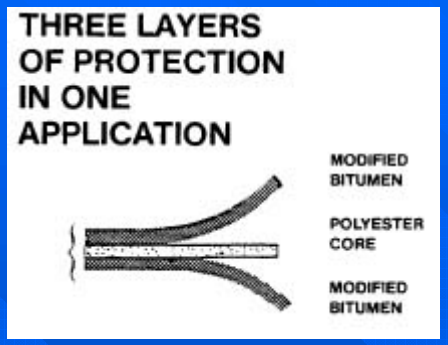
- Recent unconventional terror attacks:
  - 1995 Tokyo subway GB attack
  - 2001 US anthrax envelops
  - Numerous threats by various terror groups worldwide
- Unconventional Terrorism aimed at civilians:
  - Large population
  - Versatile ages and health conditions
  - Physically and mentally sensitive when compared to the military.

Major Goal: Help Defense Planners

- Analysis of the risk emerging from contaminated urban matrixes helps decide:
  - What to instruct population at the initial stage, after contamination
  - What to do with the contamination:
    - » Let it weather naturally
    - » Decontaminate actively (which decon and how much to use)
  - When it is safe to bring population back (full remediation)

Urban Area
(Matrixes Likely to be Contaminated)

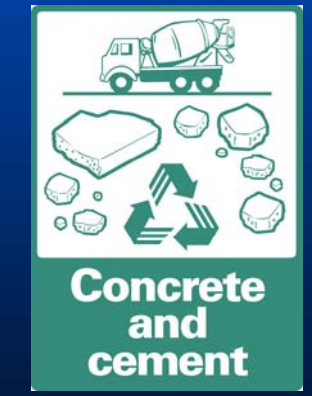
Plants



Roofs

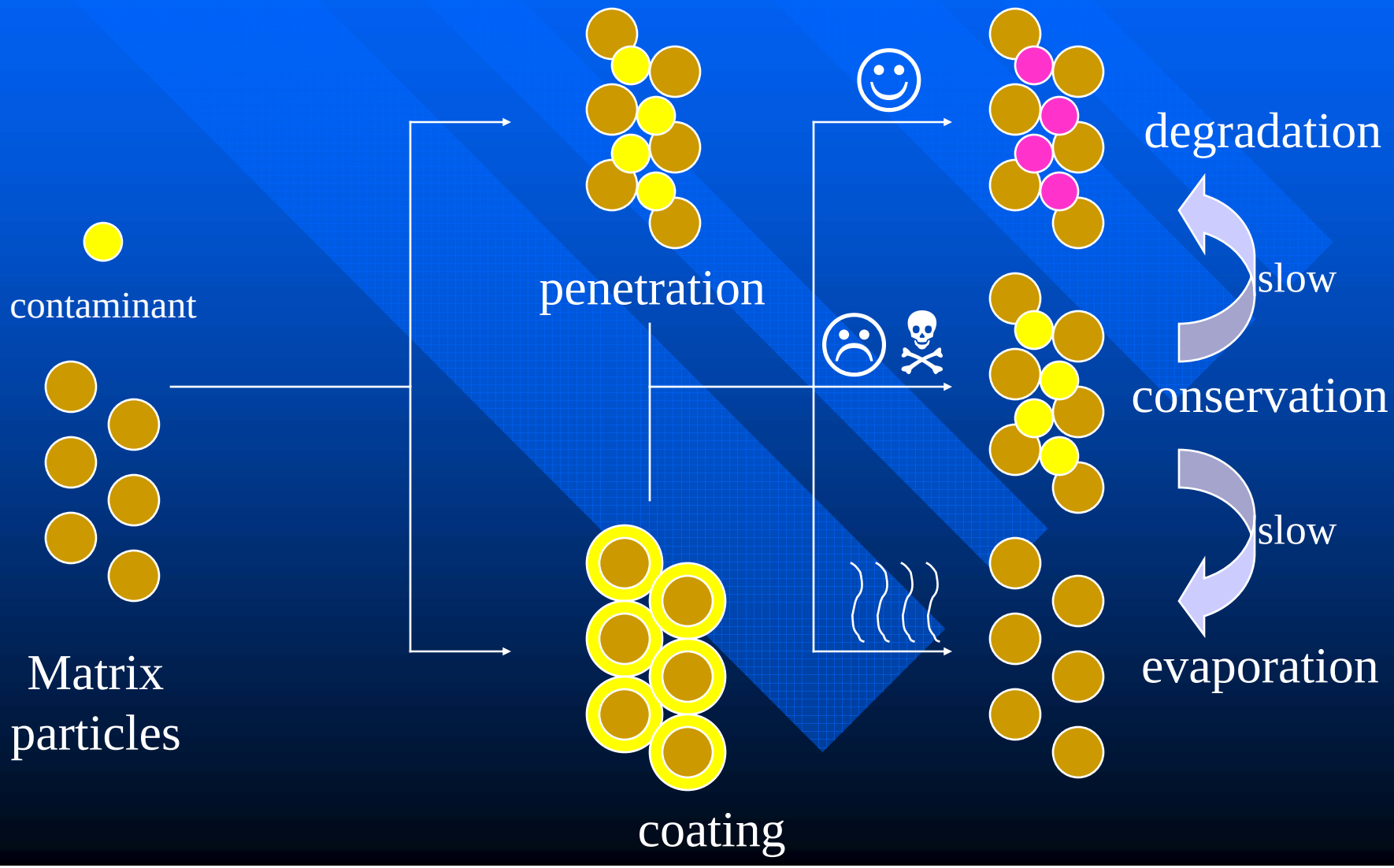
Roads and Runways

Soil / Sand



Buildings and
Pavements

Interactions of Organic Matter and Urban Matrixes



Evaluation of Organic Matter on Matrix Particles

- Extraction
  - Need to find suitable solvent
    - » e.g. heptane and toluene dissolve asphalt and bitumen
  - Sometimes requires additional steps
    - » e.g. add base
  - Destructive
- Solid State NMR
  - ✓In most cases involves no solvent
  - ✓Carried out directly on particles
  - ✓Not destructive; same sample is analyzed many times
  - - Limited resolution

Related Published Works

- Reactions of VX, GB, GD, and HD with Nanosize Al_2O_3. Formation of Aluminophosphonates.

  Wagner *et al.*, *JACS* **2001**, *123*, 1636-1644
- Preliminary Study on the Fate of VX in Concrete.

  Wagner *et al.*, *Langmuir* **2001**, *17*, 4336-4341
- Effect of Drop Size on the Degradation of VX in Concrete.

  Wagner *et al.*, *Langmuir* **2004**, *20*, 7146-7150

- ^{31}P HR-MAS NMR Serves as a Convenient Tool for the Detection of VX Decay on Sand.

  Mizrahi & Columbus, poster presented at Decon 2002 Conference, San-Diego.

Materials

- Mediterranean sea sand
- Negev desert sand (including small rocks)
- Asphalt from local roads (ground by a ball mill)

  mean particle size=21.4 μm, SD=35.9%
- Bitumen-polymer sheets
- New concrete (manually crushed)

  mean particle size=27.6 μm, SD=15.4%

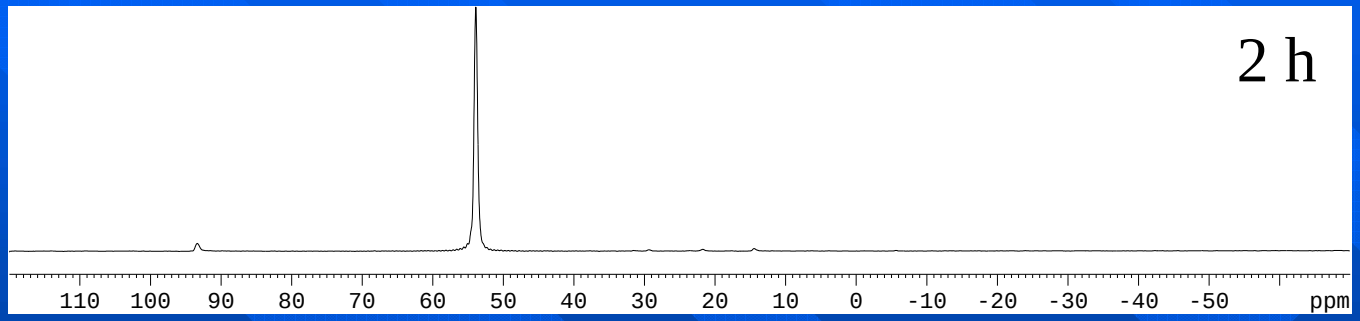
Experimental Method

- 500 MHz NMR (Bruker) equipped with a CP-MAS probe
- 4 mm rotor filled with powder (or a suitable piece of bitumen-polymer sheet), (*ca*. 100 mg)
- Matrix contaminated with ~99% VX (*ca*. 5 mg)
- ^{31}P MAS NMR carried out using direct excitation (no CP) and high-power proton decoupling.

Sand Results or: What on Earth Is Soil?

Time “0” comparison between sea and desert sand

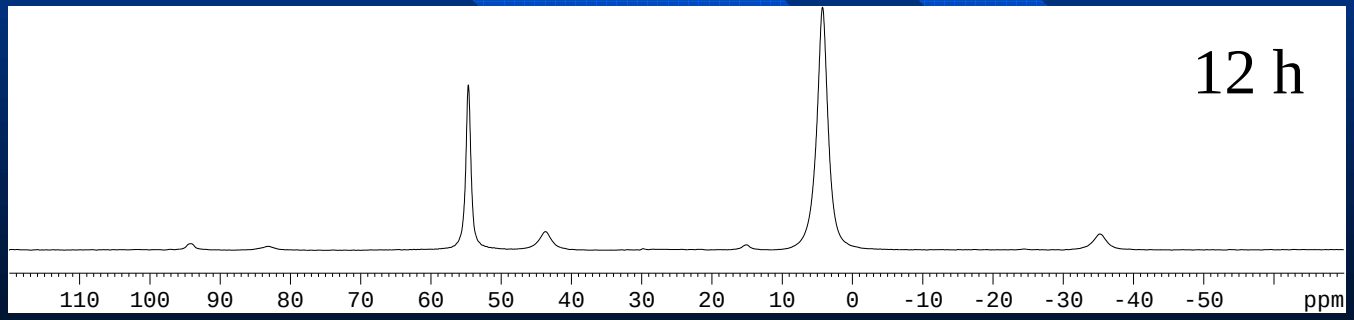
Sea sand



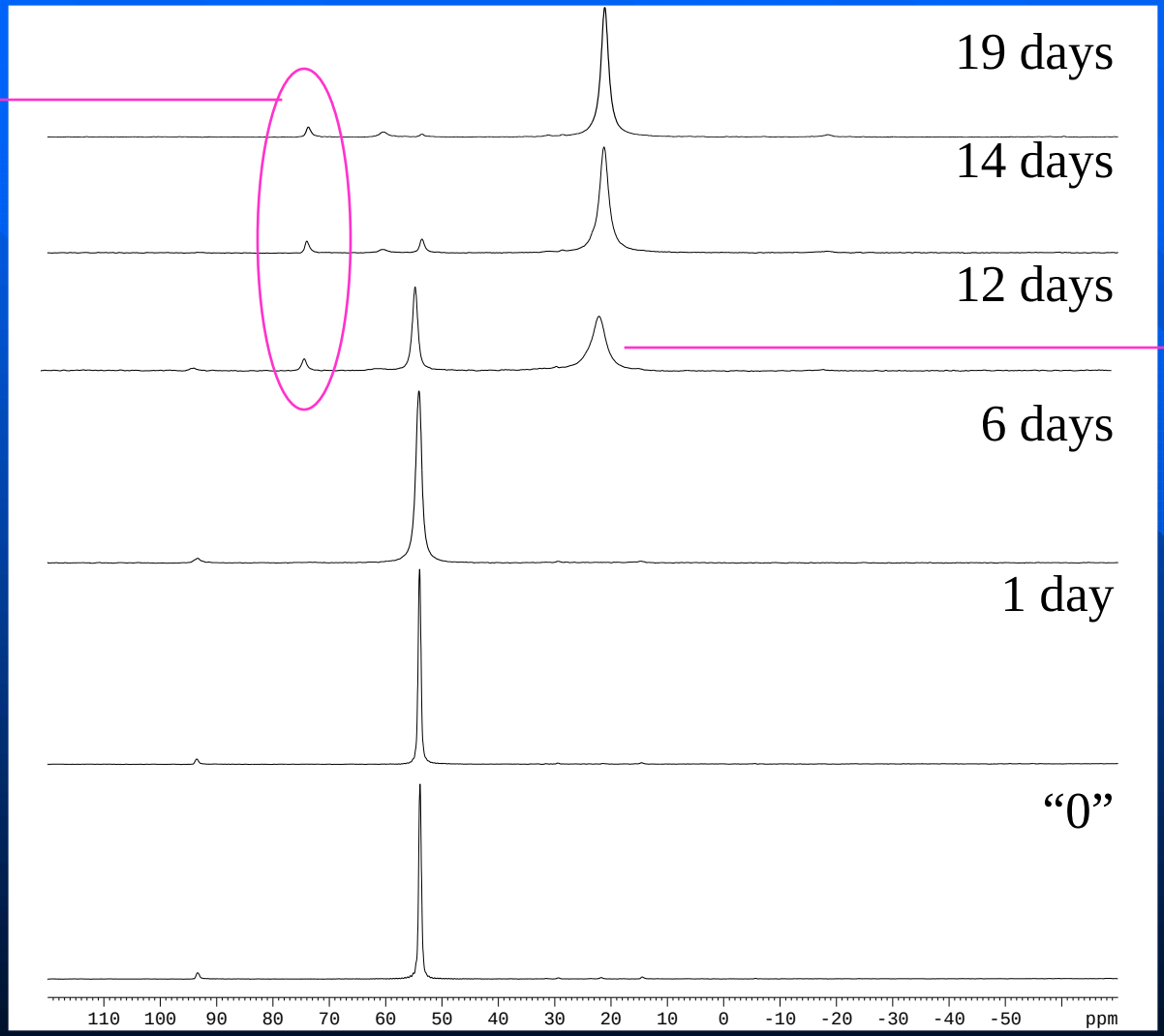
VX

“endogenic” phosphate(s)

Desert sand



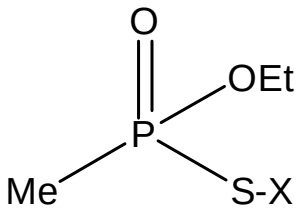
VX Degradation on Sea Sand



3-4%
S^- moiety
~75 ppm

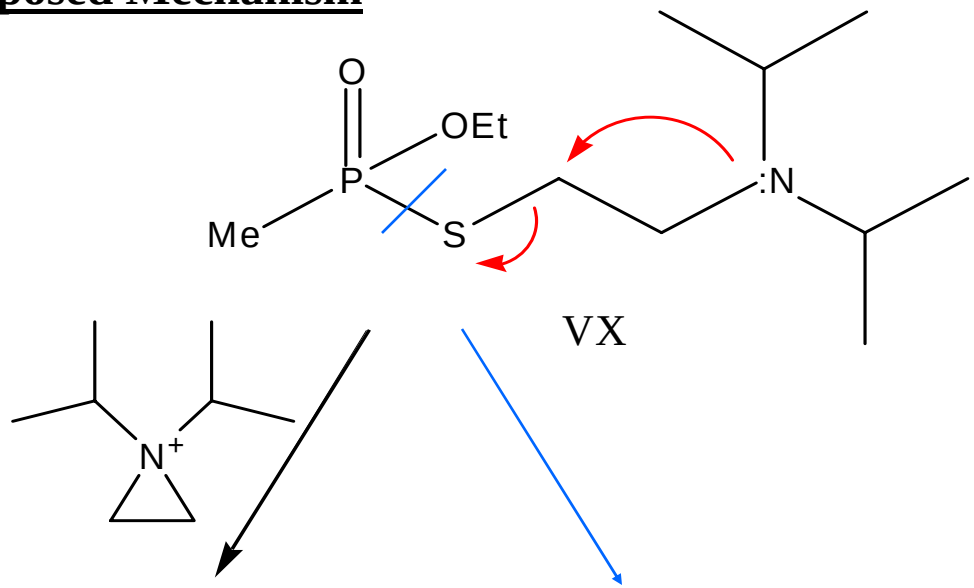
Phosphonate degradation product

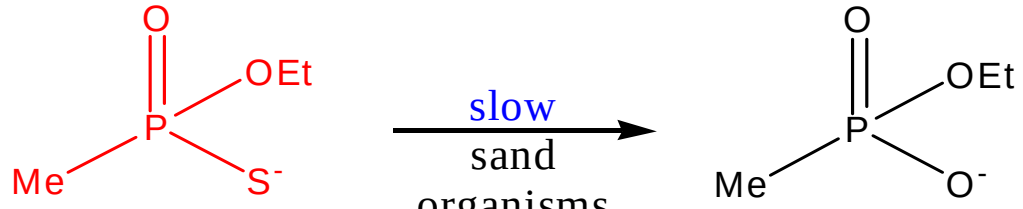
Unusual intermediate During VX Degradation on Sea Sand



x=K salt (solution NMR)	71.51 ppm
x=K salt (spike on sand)	75.51 ppm
x=H	85.75 ppm

Proposed Mechanism

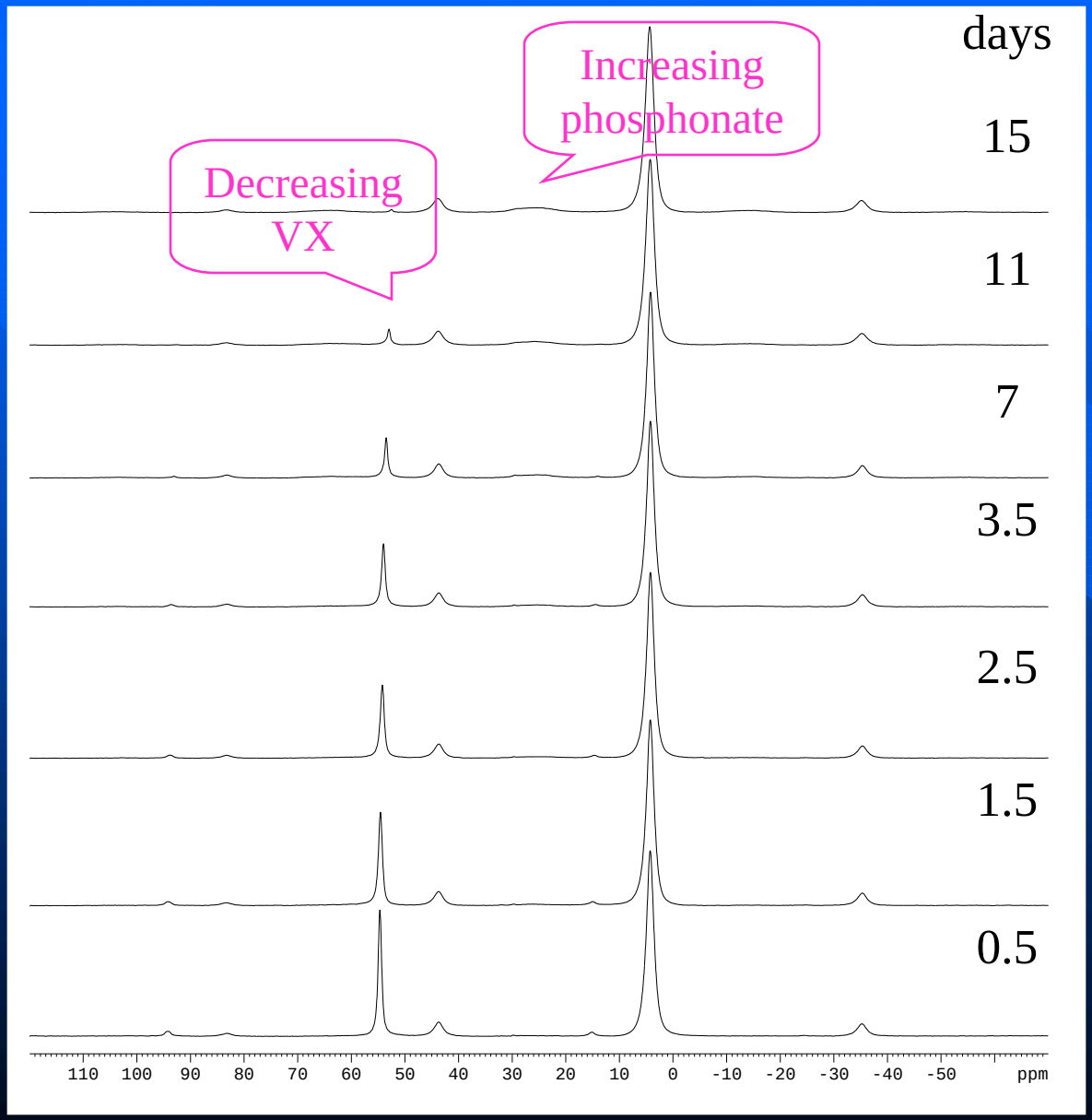




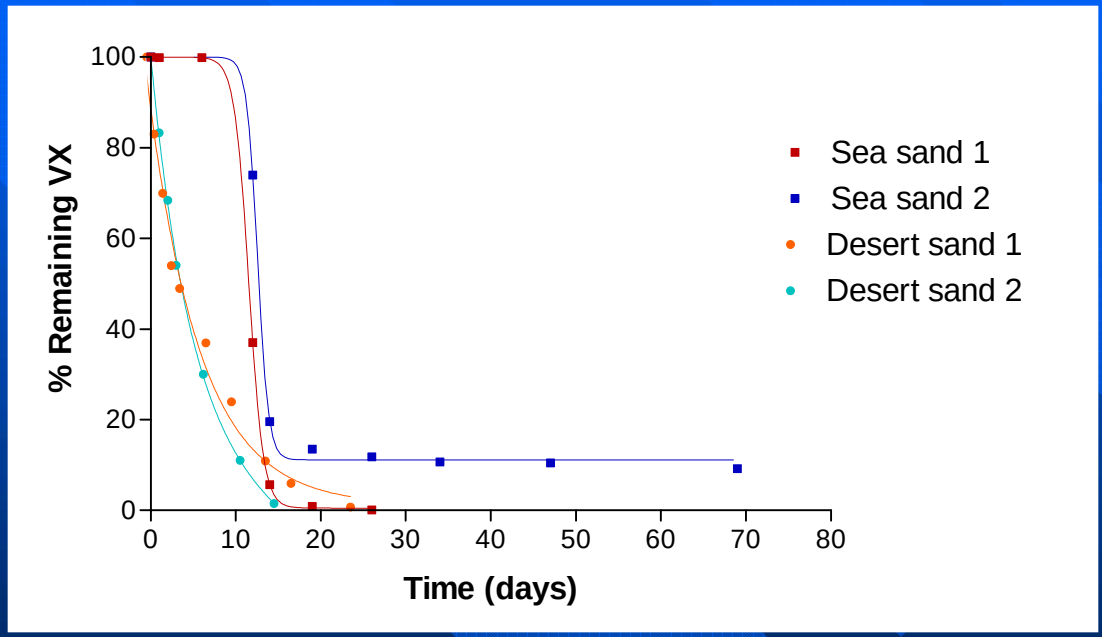
phosphonothiolate
~75 ppm

phosphonate

VX Degradation on Desert sand



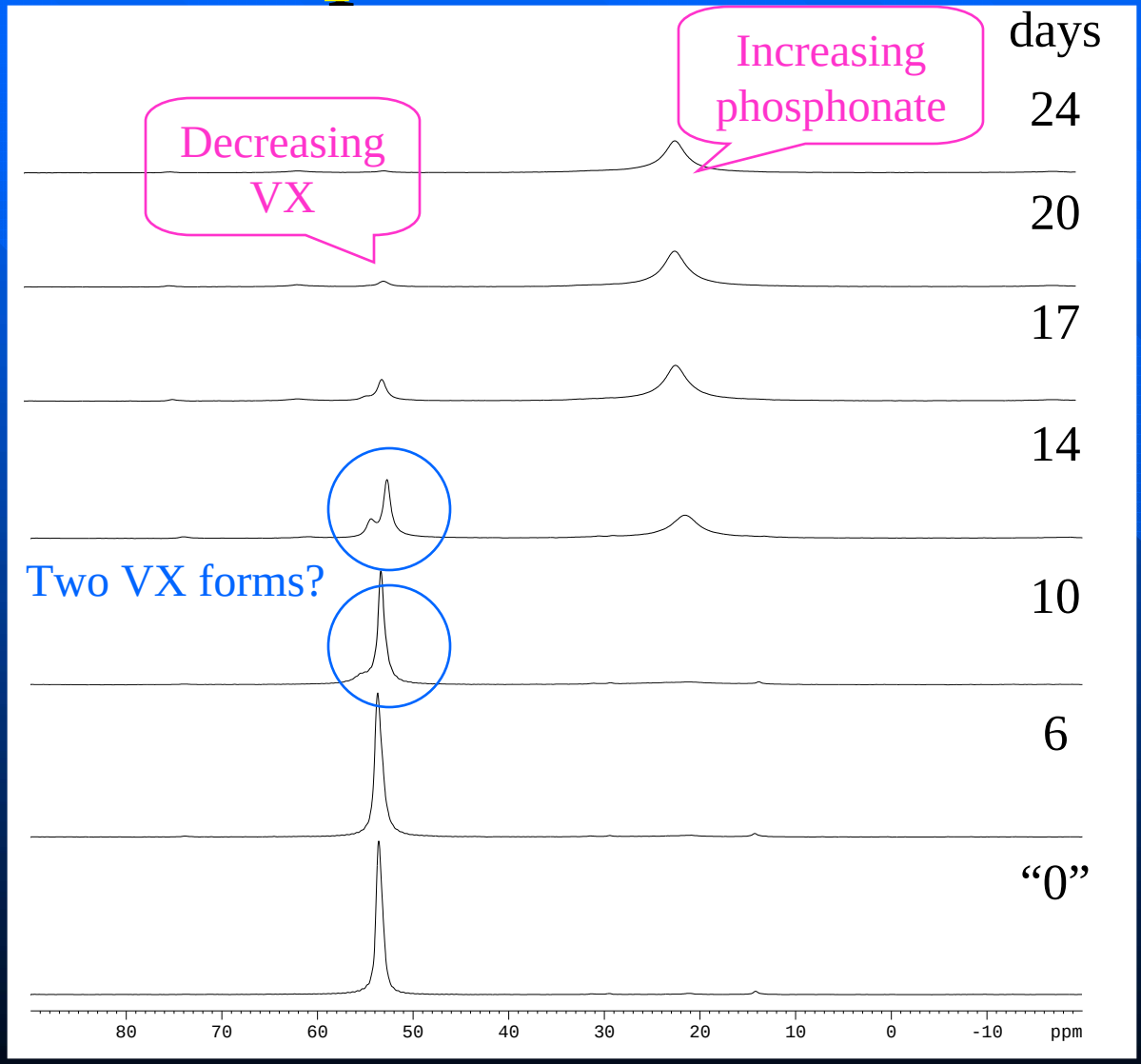
Fate of VX on Sand
A Comparison



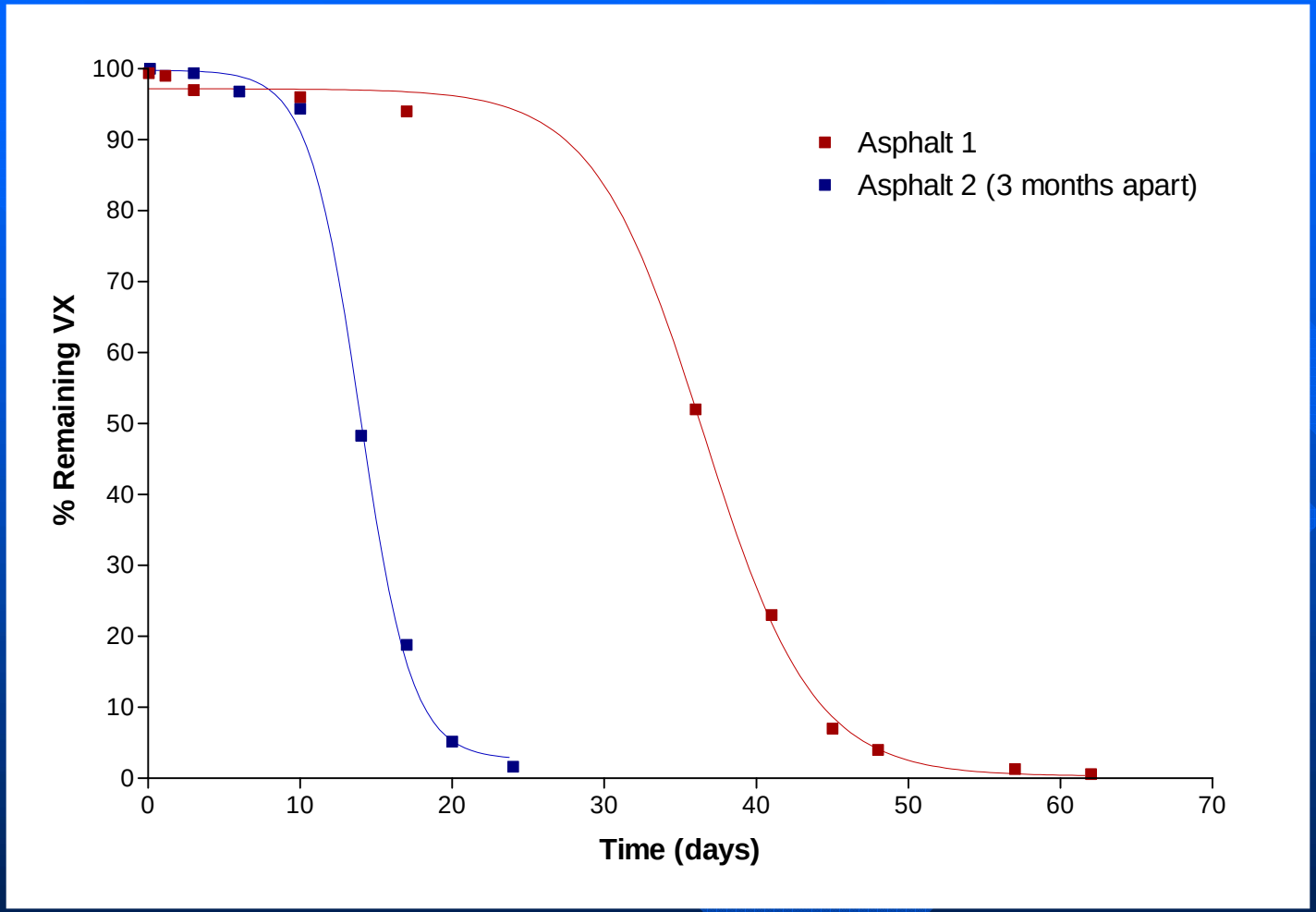
Fate of VX on Sand

- Different behavior of VX on sea and desert sand:
  - VX degradation on desert sand:
    - » Starts immediately and takes 18-24 days.
  - VX degradation on sea sand:
    - » Delayed for ca. 15 days (autocatalytic?)
    - » High inconsistency between sea sand samples
      - Full degradation takes 26-70 days
- Proposed explanation: sea sand contains salts:
  - VX is less absorbed into sea sand;
  - Peaks are sharper;
  - Degradation is delayed and sometimes uncompleted.

Degradation of VX on Asphalt Powder

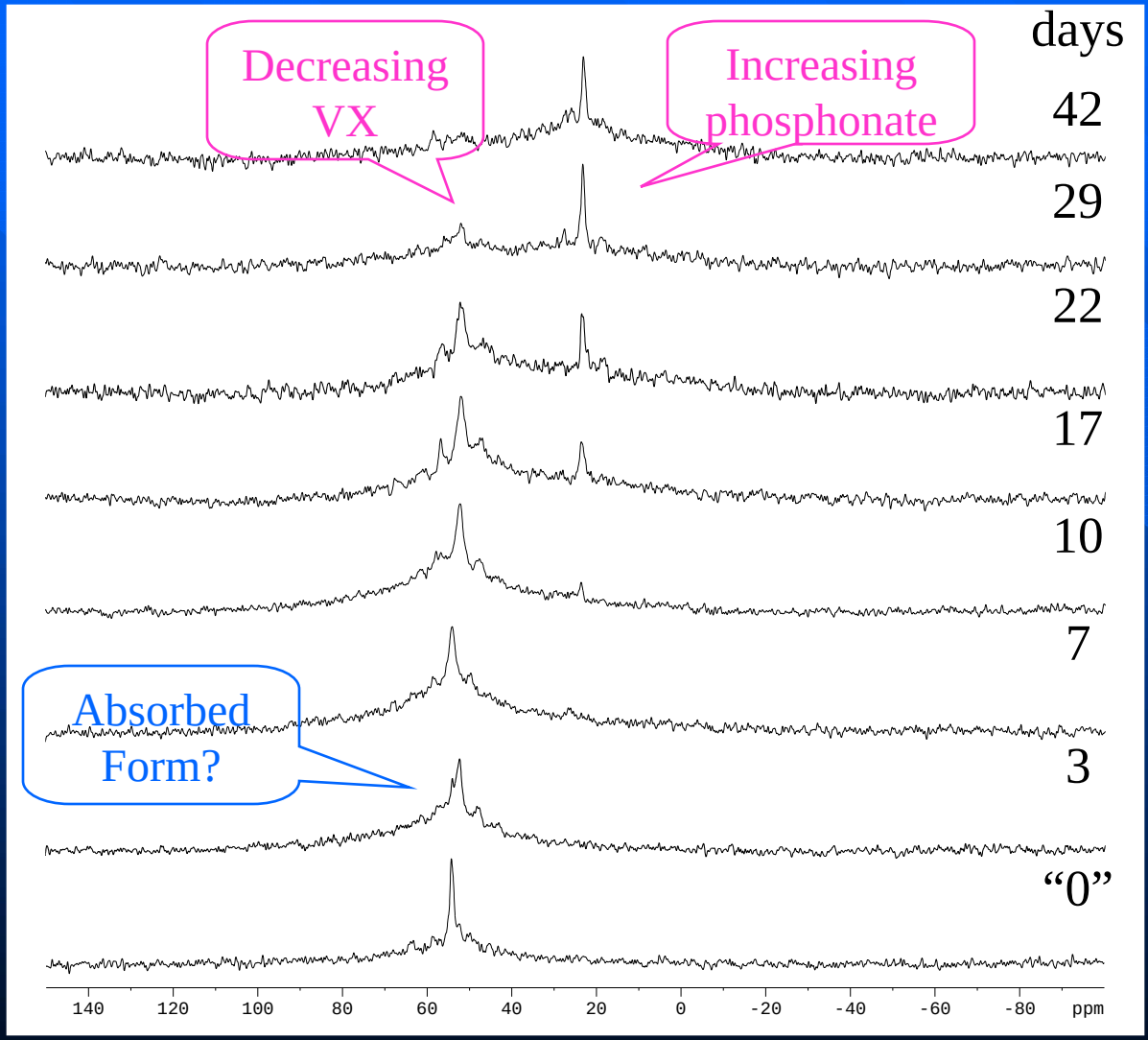


Fate of VX on Asphalt Powder

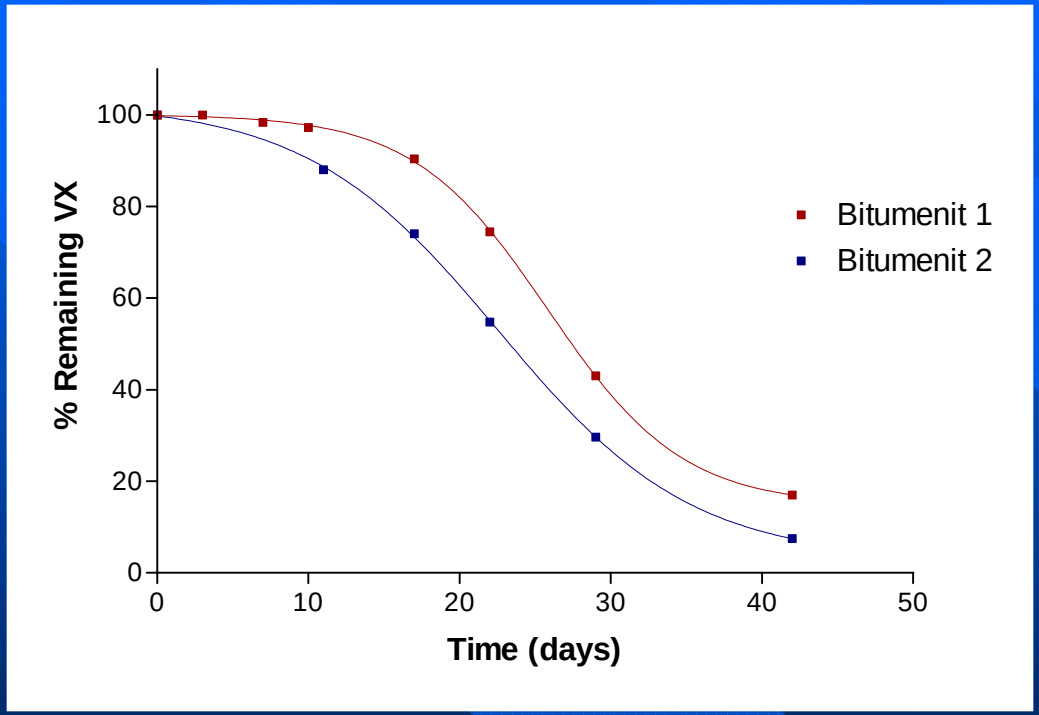


- VX degradation on asphalt powder is delayed for 15-25 days.
- Overall degradation process lasts 25-60 days.
- High inconsistency between samples, due to asphalt nature.

Degradation of VX on Bitumen-Polymer Sheet



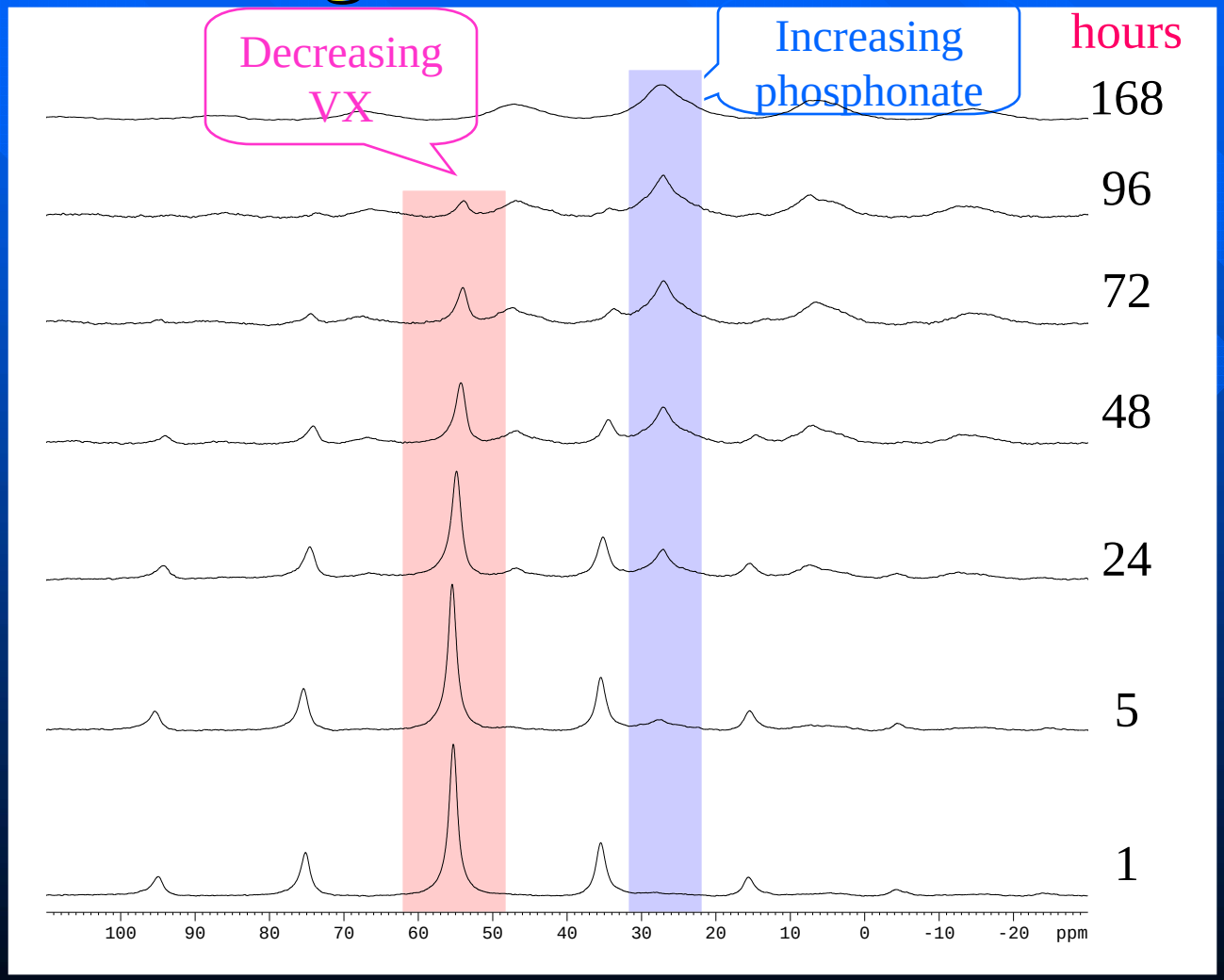
Fate of VX on Bitumen-Polymer Sheet



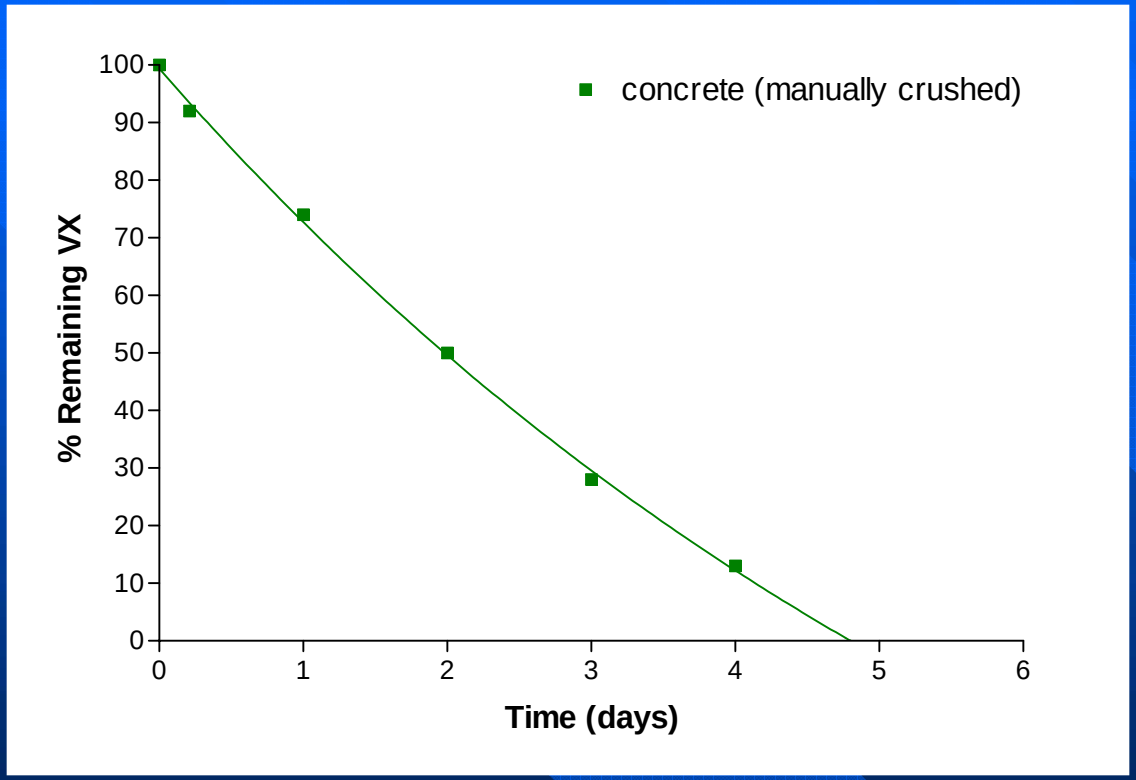
- About 10 days delay in VX degradation process.
- Small VX amounts still evident after 42 days.

Degradation of VX on Concrete

or: Does Israeli Concrete Obey Dr. Wagner's Observations?



Fate of VX on Israeli Crushed Concrete



- Fast and active degradation, takes less than a week.
- Conforms with previous observations for new concrete.

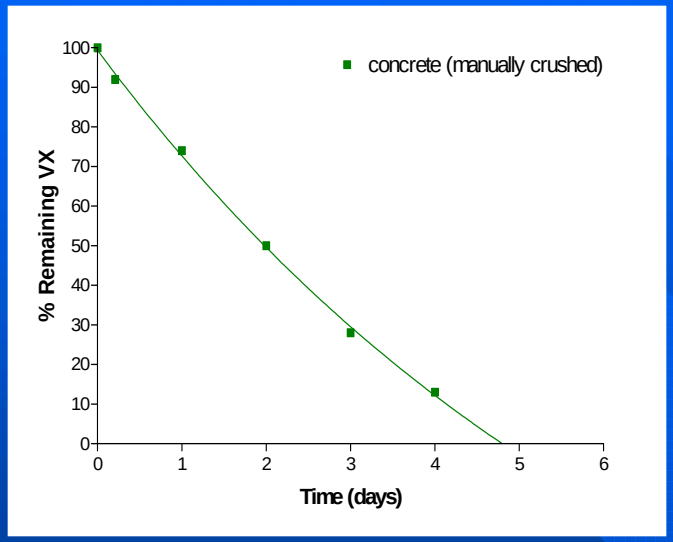
Conclusions - Method

- ^{31}P solid-state NMR has been proven to afford reliable detection of VX on different matrixes.
- Experiments exclude the possibility of desorption.
- Since the method is non-destructive, samples were monitored repeatedly and degradation process easily normalized.
- Method limitation:
  - 2000 scans – down to 50 μg VX per sample
  - Overnight experiment – down to 5-10 μg VX per sample

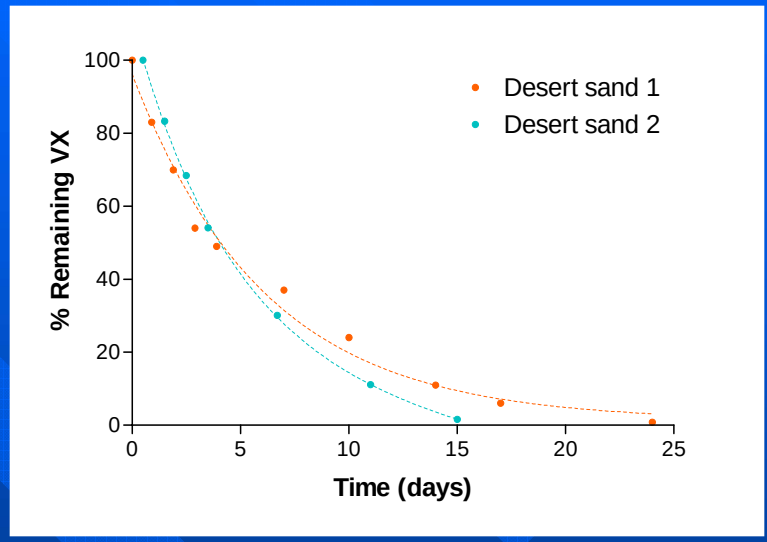
Conclusions - Operational

- One cannot predict the fate of CWAs on any complex matrix, due to:
  - an indefinite number of environmental matrixes
  - highly heterogeneous environmental matrixes
  - CWAs react chemically with most matrixes (beside the physical processes…)
- We propose looking at:
  - the most common matrix likely to face contamination;
  - general trends in behavior of similar matrixes;
  - taking worst-case-scenario as a recommendation for action, for untested matrixes.

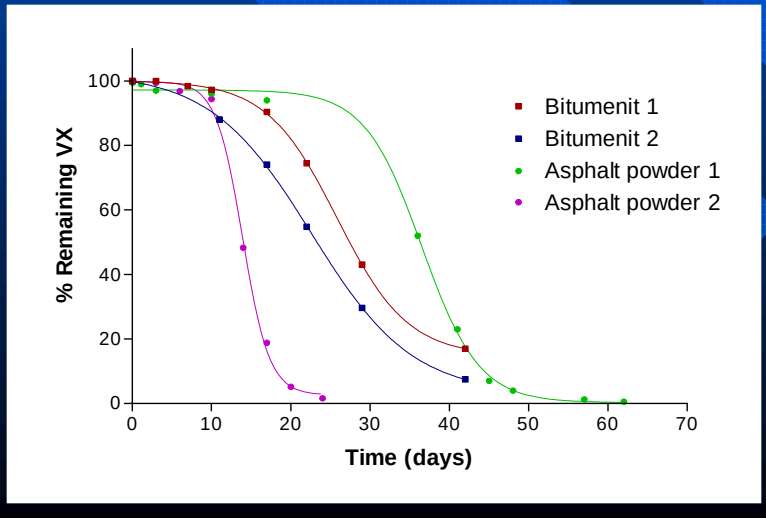
General Trends for VX Fate or Matrix Families



Decontaminating I
Active, Fast almost linear degradation



Decontaminating II
Slower
Follows one- or two-phase exponential decay pattern



Conserving
Slow degradation,
Following a delay

Thank You !!