



Sorption of the Chemical Warfare Agent VX to Clay Minerals and Soils

Kevin M. Morrissey¹, Amanda M. Schenning¹, Kenneth B. Sumpter², and Bruce E. King²

1. Leidos, Inc.; Abingdon, MD 21009 2. U.S. Army, RDECOM, ECBC, R&T Directorate, APG, MD 21010

Abstract

Accurately predicting the fate and transport of the persistent chemical warfare agent O-ethyl-S-[2-(diisopropylamino)ethyl] methylphosphonothioate (VX, Figure 1) in environmental scenarios requires a better mechanistic understanding of the interaction of VX with environmental surfaces. While sorption to soil components, such as clays and organics, is a major factor influencing fate and transport of commercial pesticides in soil environments, little data exists regarding the sorption of VX in these environments. An enhanced mechanistic understanding of how VX interacts with environmental surfaces is critical to the development of effective countermeasures, predictive modeling capabilities, and enhanced detection capability for illicit use scenarios.

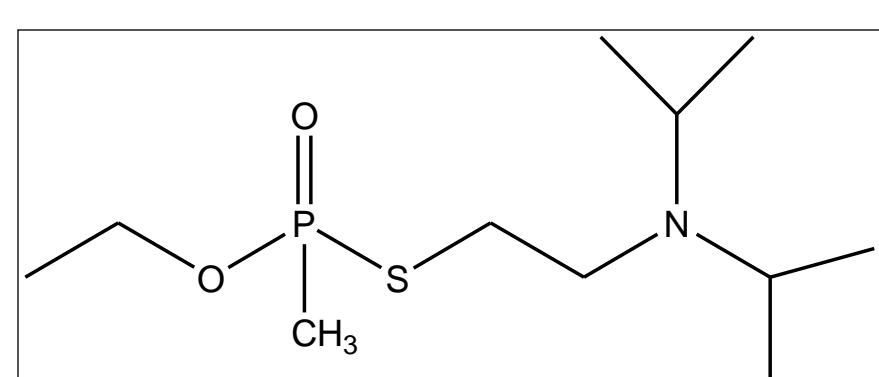


Figure 1. Structure of VX. Reported pKa values of VX range from 8.6 to 9.8, so it exists as an organic cation under most environmental conditions.

Objective

The overall objective of this study is to measure physicochemical parameters, such as partition coefficients (K), of chemical warfare agents. These parameters will then be used to update source terms in various predictive models, such as PEARL and GeoPEARL. The source terms currently used in these models are estimates, and it is hoped by measuring these parameters the accuracy of the models will be improved. A secondary objective of this effort is to achieve a better understanding of how chemical warfare agents interact with environmental matrices.

Experimental

- ✓ A MicroCal VP-ITC ITC was used to directly determine a variety of thermodynamic parameters.
- ✓ Filtered (0.2 μm) and unfiltered samples analyzed by GC/MSD, LC/MS, and CE techniques for VX and multiple degradation products. This allowed degradation in bulk solution to be distinguished from sorption events.
- ✓ Substrates: montmorillonite, kaolinite, and a silty clay loam soil (OC 5.2% and CEC 26.4 meq/100 g).
- ✓ Buffers: pH 4.3, 100 mM sodium acetate buffer, 100 mM total ionic strength with sodium chloride for ITC experiments and sorption isotherms for clay. 10 mM CaCl₂ for isotherm experiments conducted with soil.

Kinetic Profiles

- ✓ Kinetic sorption profiles for VX and select degradation products were conducted at 25 °C and multiple substrate concentrations.
- ✓ Sorption of VX to montmorillonite was very fast, with equilibration occurring by the first sampling point at 15 minutes.
- ✓ Sorption of VX to the silty clay loam soil was slow, with equilibration taking approximately 3 days.
- ✓ VX did not sorb to kaolinite under the conditions used during this study.
- ✓ VX degradation products did not sorb to any of the substrates under the conditions of this study.
- ✓ Recovery of VX decreased with time, consistent with the aging phenomenon reported for commercial pesticides.

Equilibrium Sorption Isotherms

- ✓ Isotherms conducted at 25 °C using an equilibration time of 1 h for montmorillonite clay (pH 4.3 buffer) and 3 days for silty clay loam soil (10 mM CaCl₂).
- ✓ Utilized a variable substrate to solution (STS) ratio approach, with STS ratios ranging from 1:50 to 1:2500 for the soil and 1:1000 to 1:10,000 for the clay. Samples were slowly stirred (200 RPM) during the equilibration period.
- ✓ Initial VX concentrations were approximately 25 mg/L. **No co-solvent used.**
- ✓ Example isotherms are illustrated in Figure 2.
- ✓ Data evaluated using a Langmuir model.

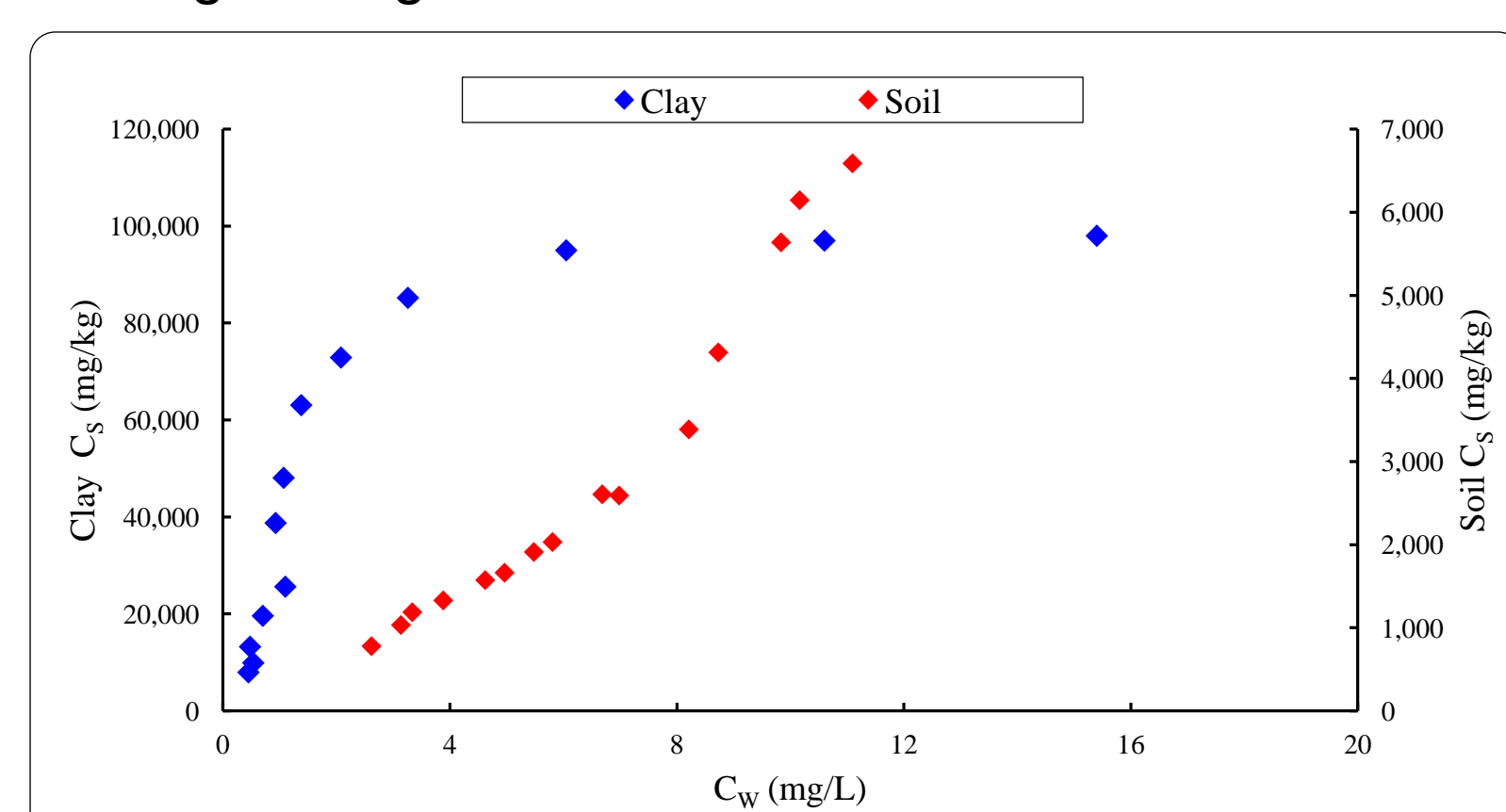


Figure 2. Examples of equilibrium isotherms for VX at 25 °C.

In a 2008 review, malathion was recommended as a surrogate for VX sorption behavior in soil. Reported K_{OC} values for malathion range from 1435 to 2388 L/kg at 25 °C.

Table 1. Summary of Langmuir Isotherm Characteristics. The results are reported as the mean ± SSD.

Model Parameters	Montmorillonite Clay (n=3)	Silty Clay Loam Soil (n=3)
K _d (L/kg)	0.570 ± 0.199	0.0409 ± 0.00514
S _{max} (mg/kg)	119,000 ± 15,000	7,840 ± 1,470
K _{OC} (L/kg)	NA	0.787 ± 0.0989

Data is currently being evaluated using additional models

✓ Experiments examining the sorption of malathion under underway to validate our approach.

Thermodynamics

- ✓ Only the montmorillonite clay has been investigated in any detail. **All data was modeled using cation exchange capacity.**
- ✓ At temperatures above the LCT_{VX} (9.4 °C), ΔH_{obs} for Site One (See Figure) varied from -20.2 to -12.6 kJ/mol, with an average of -15.1±2.26 kJ/mol. The ΔH_{obs} for Site One is consistent with reported ΔH_{obs} values for the exchange of other monovalent cations (K⁺ and NH₄⁺) onto homoionic (Na⁺) montmorillonite.
- ✓ There is a sharp break in ΔH_{obs} for Site One at the LCT_{VX}, with ΔCp values of -0.0533 kJ/mol-K (slope NS) above the LCT_{VX} and 12.9 below the LCT_{VX}.
- ✓ The average K_d for Site One below the LCT_{VX} is 9.04E4±9.9E3 M⁻¹, while it is 2.50E4±5.4E3 M⁻¹ above the LCT_{VX}.
- ✓ Values for ΔG and ΔS indicate the Site One interaction is spontaneous, favored, and enthalpically driven at all temperatures evaluated.
- ✓ At temperatures below the LCT_{VX} a bi-phasic pattern is observed (See Figure 3). The endothermic portion (Site Two) is believed to be a ligand exchange process via the phosphorus.
- ✓ Activation energy of binding for Site One is 39.4 kJ/mol.

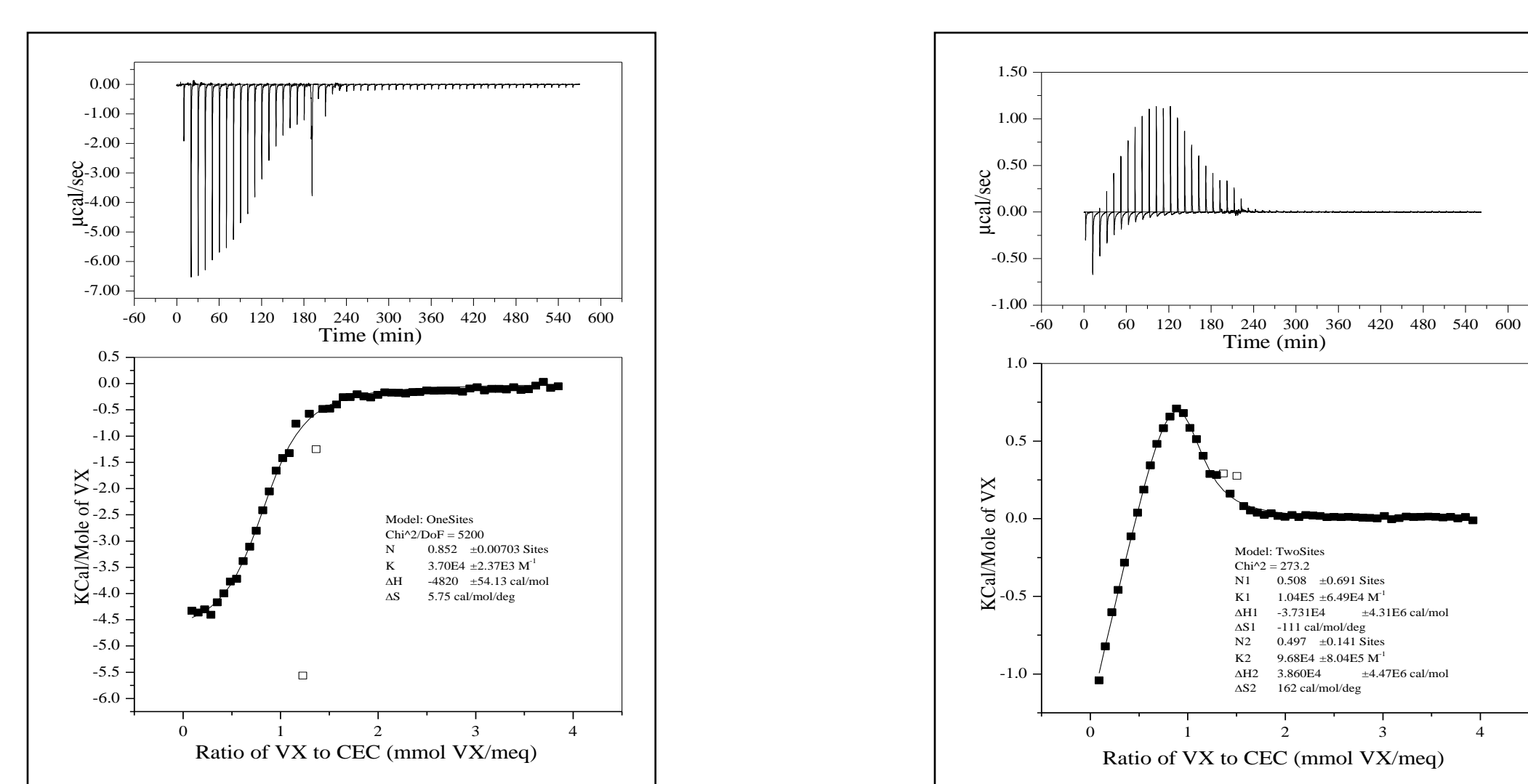


Figure 3. Thermograms of VX titrated into clay suspension at 45 °C (left) and 5 °C (right). Interaction of VX at 45 °C exhibits one binding site while interaction at 5 °C exhibits two binding sites.

Preliminary titrations were also conducted with 2 soils in pH 4.3 buffer at 25 °C. These thermograms are illustrated in Figure 4.

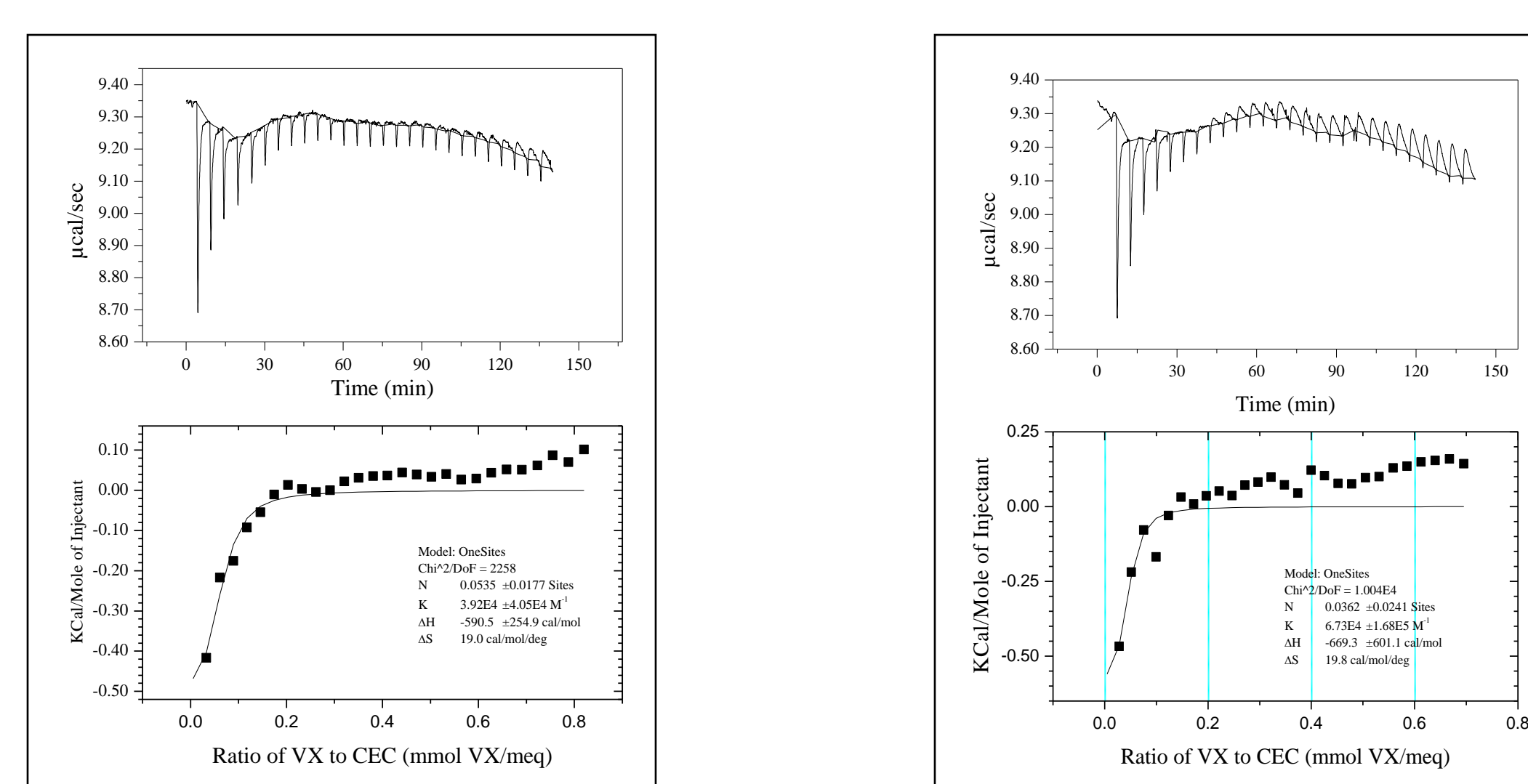


Figure 4. Thermograms of VX titrated into silty clay loam soil suspension (left) and clay loam soil suspension (right). Titrations conducted in pH 4.3 buffer at 25 °C.

Desorption Profiles

- ✓ Initial attempts to construct desorption isotherms were not successful. Using a strong desorption solvent (2-propanol), <0.1% of the VX sorbed from dilute solution was recovered from the silty clay loam soil.
- ✓ Using a prototype "tube in tube" dynamic extractor, the desorption behavior of VX from silicone rubber (control matrix) and silty clay loam soil were evaluated.
- ✓ The sample matrices were spiked with 2 μL of neat VX and the samples allowed to age for 24 h before starting the extraction. Extraction was conducted at 25 °C using 2-propanol. Time point samples were removed and fresh solvent added to maintain sink conditions.
- ✓ Cumulative release curves are illustrated below. Note it takes approximately 2000 min to approach the maximum release of VX. Reported soil extraction methods have extraction times ranging from 1.5 to 20 min.
- ✓ The linear portion of the curve is taken as the steady state release rate of VX from the sample. A non-linear Langmuir model was used to estimate maximum release of VX using a composite data set from both replicates.

✓ Silicone: SS Release Rate = 3640 ng/min
Maximum Release :: 2140 μg, or 90.7 % of applied

✓ Soil: SS Release Rate = 48.0 ng/min
Maximum Release :: 28.3 μg, or 1.7 % of applied

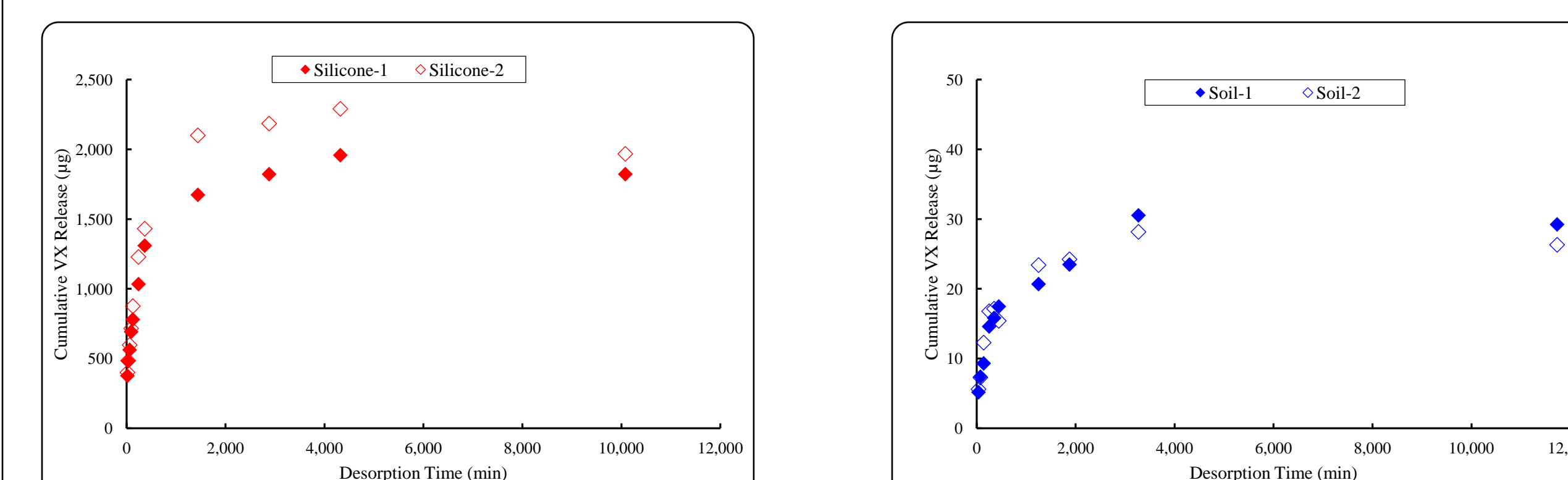


Figure 5. Example cumulative release curves for VX from silicone rubber (left) and silty clay loam soil (right).

Conclusions and On-Going Efforts

- ITC was found to be a useful technique for elucidating sorption mechanisms.
- The sorption of VX to montmorillonite was determined to occur rapidly, and be dominated by a physisorption-type process consistent with an ion exchange mechanism.
- The VX sorption process at temperatures below the LCT_{VX} is complex and needs further investigation.
- Validation of the variable STS ratio approach, coupled with slow stirring, is currently in progress using the silty clay loam soil and malathion.
- Efforts to further optimize the "tube in tube" dynamic extractor are in progress and show promise as an approach to desorbing chemical warfare agents from soils and other complex sample matrices.
- Detailed results of the work conducted with the clays is available in an ECBC technical report.

Morrissey, K.M.; Schenning, A.M.; Cheicante, R.L.; and Sumpter, K.B. *Sorption of VX to Clay Minerals and Soils: Thermodynamic and Kinetic Studies*; ECBC-TR-1016; U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, December 2012; UNCLASSIFIED Report.

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