

INNOVATIVE METHODS FOR INVESTIGATING THE FATE OF CHEMICAL WARFARE AGENTS IN SOIL

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ABSTRACT

Surface-controlled reactions affecting hydrolysis of organic compounds in the environment can predominate over bulk solution hydrolysis, especially in soil environments. Unpredicted residual levels of chemical warfare agents (CWA) at threat levels in the field necessitated the development of new methods for investigating the fate of CWA delivered onto soil. Design and fabrication of Soil System Units now allows determination of the fate of CWA in soil, as well as investigation of the soil chemical and physical characteristics affecting the persistence of threat from continuing presence of CWA in soil, under conditions that represent those in the field. Initial results show that the Soil System Unit approach is highly effective for investigating the fate of CWA in the soil environment.

1. INTRODUCTION

It has been well established that most chemical warfare agents (CWA) undergo relatively fast hydrolysis in water to form corresponding alkyl methylphosphonates (Clark, 1989). That information has at times been extrapolated to soil systems, under the assumption that similar hydrolysis rates for these compounds occur in soils. However, surface-controlled reactions affecting hydrolysis of organic compounds in the environment can predominate over bulk solution hydrolysis, especially in soil environments (USEPA, 1998; Pignatello, 1989). Unpredicted residual levels of CWA at threat levels in the field resulting from the deposition of CWA onto soil has generated increased concern regarding the predictability of factors known to affect CWA fate in soils. This in turn necessitated the development of new methods for investigating the fate of CWA delivered onto soil, and assessing the influence of soil chemical and physical characteristics on CWA fate and corresponding persistence of a threat hazard from continuing

presence of CWA in soil. A Soil System Unit has been designed and fabricated that allows determination of the fate of CWA in soil, as well as investigation of the soil chemical and physical characteristics affecting the persistence of threat from continuing presence of CWA in soil, using well characterized soils under controlled laboratory conditions that simulate those in the field. Knowledge gained from this approach will help delineate the fate of CWA in soil, the persistence of corresponding threat hazard, and the soil parameters affecting CWA fate. This information can then be used for developing additional guidelines for Warfighter entry into, or contact with, CWA contaminated soils.

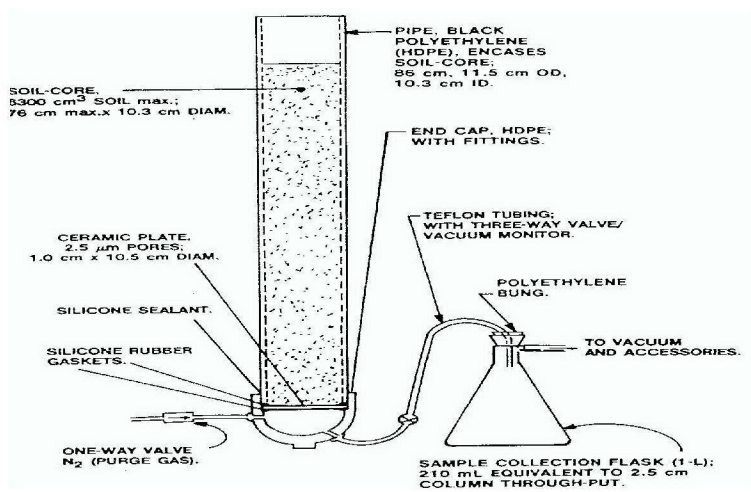
2. TECHNICAL APPROACH

A Soil System Unit (Fig. 1) has been designed to contain centimeters-depth of soil/material being investigated with retaining column appropriately scaled (approx. 10cm diameter and 15cm height). A controlled-pore ceramic plate is installed near the bottom of the Soil System Unit so that a controlled-tension (partial vacuum) may be applied (30-35 kPa), with tension both regulated and monitored. This tension is comparable with that encountered in the field in medium-textured soils as a result of combined soil matric and gravitational forces (Hausenbuiller, 1972; Foth and Turk, 1972). Applying this tension across a controlled-pore ceramic plate allows soil pore-water passage only when tension in the soil is less than 30-35 kPa, yet does not allow the flow of gases unless the gases are dissolved in pore-water. This technique avoids undue passage of gases, internal flooding from the buildup of a hanging column of water in the soil, and artificial changes in soil redox potential in response to steady-state alteration of the soil water content, as can happen when gravitational forces alone are relied upon to promote water flow through soil. The Soil System Units are housed in CWA exposure facilities for the delivery and monitoring of effective concentrations of CWA in soil and the atmospheric concentrations of CWA above the soil surface.

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Soil System Unit



General Schematic

Figure 1. Close-up photo of a Soil System Unit, with dissemination device above for delivering chemical warfare agent onto the soil surface. The sampling port on the front of the soil column is located above the soil surface (approx. 2.5cm) for measuring atmospheric CWA concentrations. The end cap contains the controlled-pore ceramic plate, plus ports below the plate to apply the controlled-tension and collect leachate into a sample flask. The General Schematic design (Checkai, 1993) was the basis from which this Soil System Unit was adapted and scaled for investigating the fate of chemical warfare agents in soil.

The device for disseminating CWA onto the soil surface is a syringe-drive system (not shown) linked to a modified spray system nozzle capable of continuously delivering a measured amount of either CWA aerosol or droplets onto the soil surface. Alternatively, individual droplets may be individually delivered using a gas-tight syringe. Artificial precipitation (simulated rainfall) events may be delivered to the soil surface using a synthetic rain generator, or dissemination techniques similar to those for CWA delivery. Soil and atmospheric concentrations of CWA are determined using conventional analytical techniques and methods.

3. EXPERIMENTAL DESIGN

In order to determine whether the Soil System Unit approach is appropriate for investigating the fate of CWA in soils, an initial experiment was

undertaken. A natural soil, Sassafras sandy loam [Fine-loamy, siliceous, mesic Typic Hapludult], was loaded air-dry into the column to a depth of 10cm. The nerve agent Soman (GD; 1,2,2-Trimethylpropyl methylphosphonofluoridate) was then delivered as individual droplets (approx. 3.6μL per droplet) onto the soil surface from a height of 2.5cm using a gas-tight syringe, until a total of 80μL neat GD was applied to the soil. Initial atmospheric concentrations of GD above the soil surface were monitored until they were undetectable. Then a very light simulated rain event, sufficient to just moisten the soil surface, was administered using a synthetic rain generator. A rain event consisted of a total of 1.6mL distilled water being delivered as light mist onto the soil surface. Atmospheric concentrations of GD were monitored following the rain event to determine whether GD was displaced from the soil into the atmosphere, and how long atmospheric GD persisted.

4. EXPERIMENTAL RESULTS

Initial investigation of the fate of the nerve agent GD on natural sandy loam soil showed that displacement of GD from surface-contaminated soil can occur in response to a very light simulated rain event to cause potentially lethal levels in air above the soil (Fig. 2). This result occurred after the level of GD in air had initially diminished to undetectable levels. Furthermore, we found that following a single event of GD deposition onto soil at a nominal battlefield level, GD can be displaced from a surface-

contaminated soil multiple times by light rain events, each resulting in potentially lethal levels in the air above the soils. These multiple reactions occurred over the course of days in response to a series of very light simulated rain events, each sufficient to just moisten the soil surface. The successive displacement reactions were observed after investigators had allowed the GD in the atmosphere above the soil surface to decline between rain events to $<0.05 \text{ mg/m}^3$, the level that is immediately dangerous to life and health (IDLH; Mioduszewski, et. al., 1998) if not in protective gear.

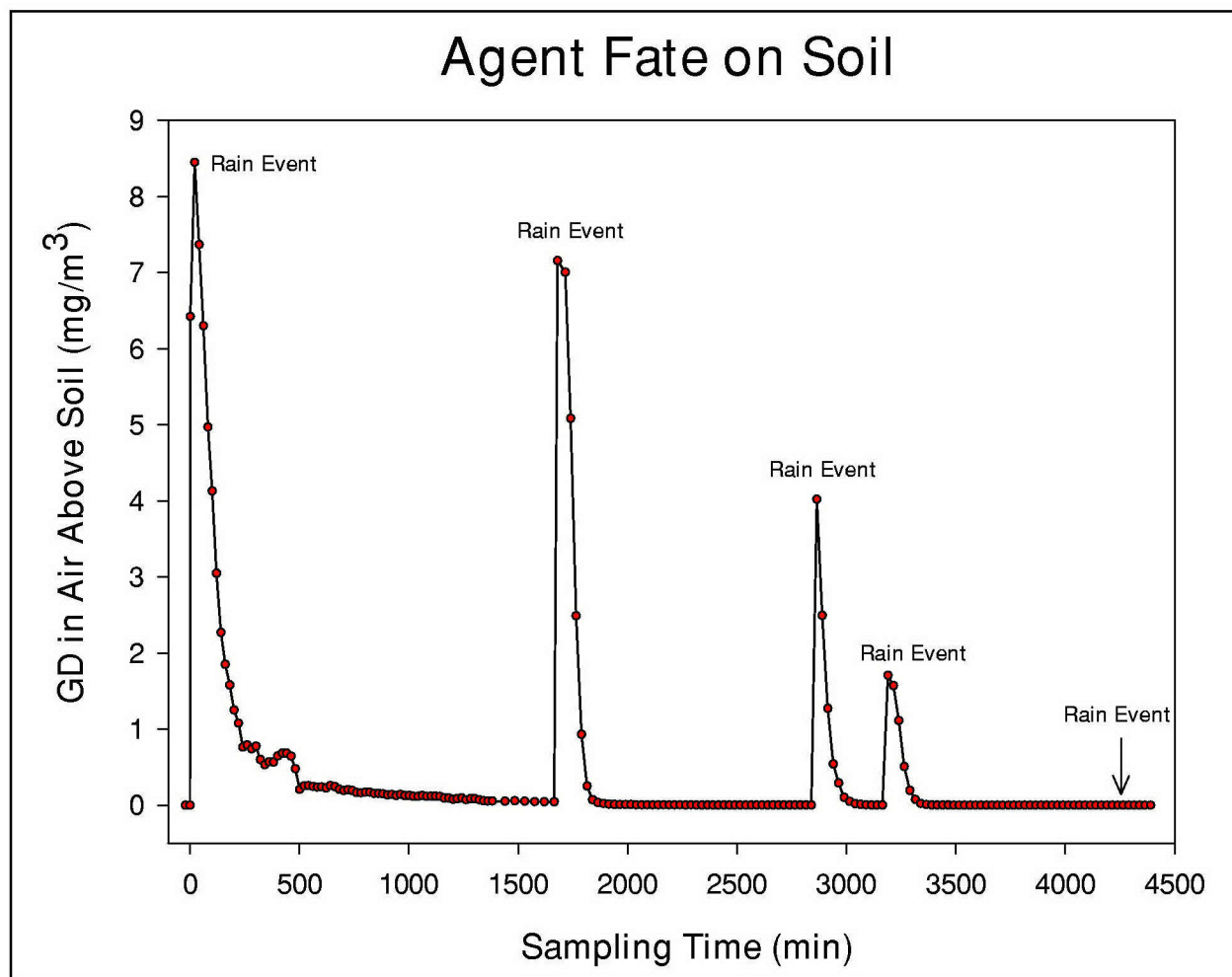


Figure 2. The nerve agent Soman (GD; 1,2,2-Trimethylpropyl methylphosphonofluoridate) was delivered as individual droplets onto soil. Initial atmospheric concentrations of GD above the soil surface were monitored until they were undetectable (Time 0). Very light simulated rain events sufficient to just moisten the soil surface were administered using a synthetic rain generator. Rain events caused displacement of GD from the soil into the atmosphere above the soil. These successive displacement reactions occurred over the course of days in response to a series of very light simulated rain events, and caused the levels of GD in the atmosphere above the soil to increase from undetectable levels to those orders of magnitude greater than the level that is immediately dangerous to life and health (IDLH).

5. DISCUSSION

Results from our initial experiment using the Soil System Unit approach to investigate the fate of GD in a natural soil indicate that this approach is highly effective for investigating the fate of CWA in the soil environment. Using this approach we can investigate the effects of principal soil components on the fate of CWA, as well as determine CWA fate in well characterized natural soils. This information can then be used for developing additional guidelines for Warfighter entry into, or contact with, CWA contaminated soils.

Using the Soil System Unit approach we were able to replicate and investigate the residual levels of CWA previously unpredicted, but found at hazardous levels in the field. Results of our initial experiment showed that persistence of G-agent in soil can be

expected for days following contamination. Furthermore, we established that life threatening atmospheric levels of G-agent may be expected to successively reoccur in response to increasing moisture in soils contaminated with G-agent. This result had not been previously observed. In addition we showed that it takes very little moisture on soil contaminated with G-agent to cause levels exceeding IDLH, even when the atmospheric level of G-agent is initially below detection; the amount of moisture per event that was used in this investigation was less than that which can occur from dew. Of considerable concern is the rate of the G-agent displacement reaction and the levels to which it drives atmospheric concentrations; orders of magnitude greater than IDLH for GD (Fig. 3.). Investigation of CWA fate in soil and environmental factors affecting it will continue.

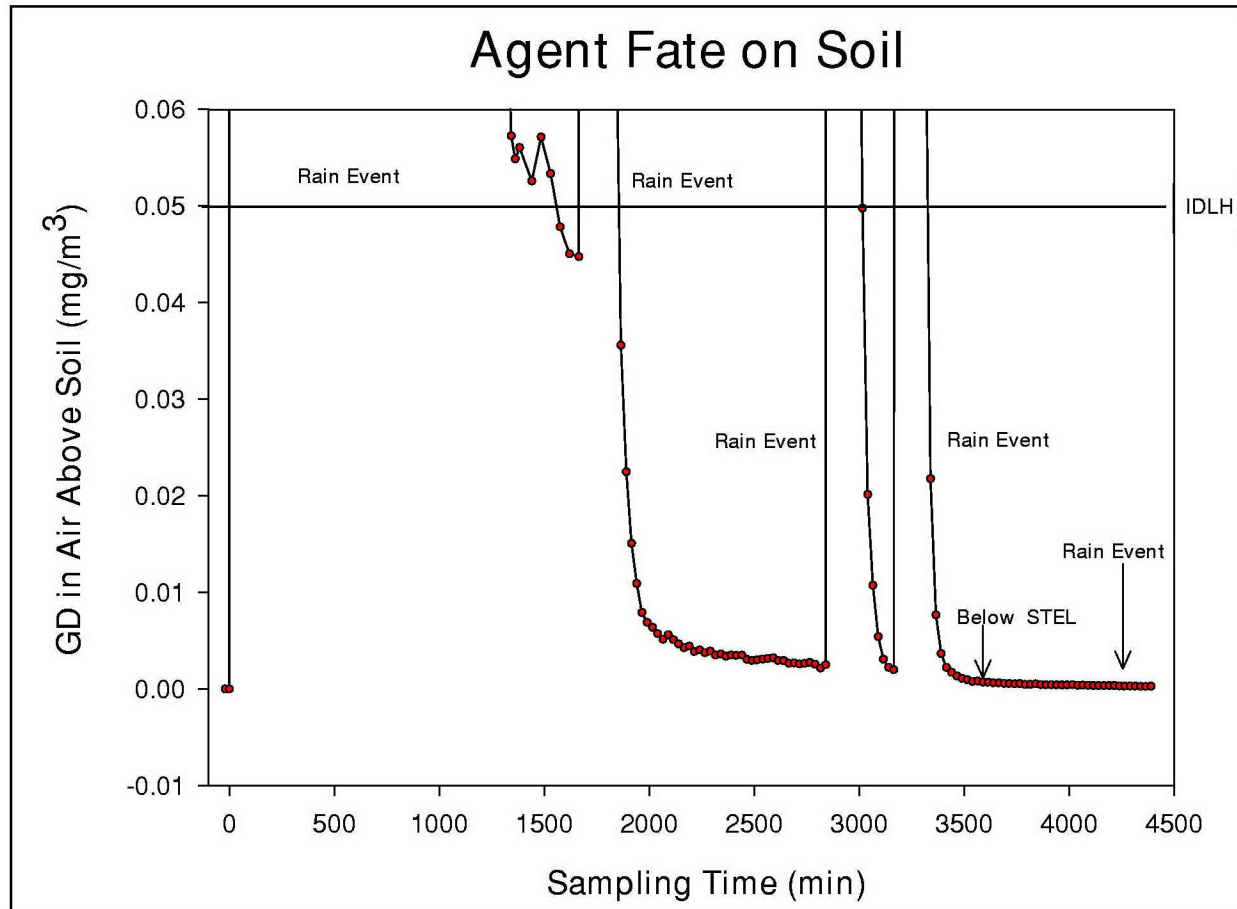


Figure 3. Enlargement of the baseline region of Figure 2: Notice the relationship between atmospheric concentrations of GD in response to simulated light rain events, and the level of GD that is immediately dangerous to life and health (IDLH; $<0.05 \text{ mg/m}^3$) if not in protective gear. This is the first data that shows that atmospheric levels of G-agent that are potentially lethal to an unprotected Warfighter can reoccur in response to rainfall on contaminated soil, and displacement of G-agent into the atmosphere continued for days.

6. CONCLUSIONS

Design and fabrication of these innovative Soil System Units allows determination of the fate of CWA in soil, investigation of the soil chemical and physical characteristics affecting the persistence of threat hazard due to continuing presence of CWA in soil, and use of well-characterized soils under controlled laboratory conditions that simulate those in the field. The Soil System Unit approach is highly effective for investigating the fate of CWA in the soil environment.

Using the Soil System Unit approach to investigate the effects of principal soil components on the fate of CWA, as well as determine CWA fate in well characterized natural soils, allows delineation of soil and environmental parameters affecting CWA fate. This information can then be used for developing additional guidelines for Warfighter entry into, or contact with, CWA contaminated soils. Investigation of CWA fate in soil and environmental factors affecting it will continue.

Persistence of G-agent in soil may be expected for days following contamination. Potentially life threatening atmospheric levels of G-agent can successively reoccur in response to increases in moisture in soils contaminated with G-agent. The amount of moisture required to cause such an event is less than that which can occur from dew.

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