ENVIRONMENTAL TRANSFORMATION MECHANISMS OF THIODIGLYCOL

K. PATRICK LEE and HERBERT E. ALLEN*
Department of Civil and Environmental Engineering, University of Delaware, Newark, Delaware 19716, USA

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Abstract—The fate of thiodiglycol (TDG) in environmental samples was studied through analysis of batch solid-solution suspensions. We monitored aqueous-phase TDG concentrations and thiodiglycolic acid (TDGA) concentrations by high-performance liquid chromatography with ultraviolet detection. We investigated TDG and TDGA sorption to six soils. Thiodiglycol sorption was insignificant, with a maximum sorption capacity of less than 10 mg/kg. Sorption of TDGA varied, with maximum sorption capacities ranging from 19.9 to 427.4 mg/kg. Photoysis, hydrolysis, and the presence of iron oxide and aluminum oxide had little effect on the fate of TDG and TDGA. However, manganese oxide sorbed TDG and was pH dependent. Biological transformation of TDG to TDGA, with the formation of [(2-hydroxyethyl)thio]acetic acid (TDGMA) as an intermediate, occurred with zero-order rate coefficients ranging from 0 to 6.26 × 10⁻³ mol/L·h⁻¹. Biological toxins hindered this transformation. The major process affecting TDG was biotransformation to form TDGMA and subsequently its biotransformation to TDGA.

Keywords—Thiodiglycol Mustard Environmental fate

INTRODUCTION

The analysis and verification of chemical warfare agents (CWAs) and CWA-related compounds in environmental samples are critical to the success of worldwide chemical weapons disarmament. Reports confirming the use of bis-dichlorodiethyl sulfide (mustard gas [HD]) during the Iran–Iraq War [1–4] substantiate the potential threat of CWAs. Following a CWA exposure incident in 1984 in which several Iraqi soldiers were exposed to sulfur mustard, numerous studies investigated methods of detecting mustard, mustard metabolites, and mustard degradation products from a variety of sample matrices, including biological fluids, clothing, soil, and water [1–14]. The need to verify CWA production and use and to promote peacetime efforts to reduce agent stockpiles has led to the need for improved information on the environmental fate of mustard and its degradation products.

The hydrolysis of HD has been studied extensively. Numerous investigators have reported on the rapid two-step hydrolysis of HD to mustard chlorohydrin (hemimustard) and then to 2,2'-thiodiethanol (thiodiglycol [TDG]) [15–20]. Thiodiglycol is expected to be a major product in environmental samples contaminated by HD; however, little information on the environmental fate of TDG is available in the scientific literature. In a recent interlaboratory comparison coordinated by the Verification Institute for the Chemical Weapons Convention (VICWC), soil samples spiked with TDG (10 mg/kg) were distributed to 19 laboratories worldwide. Only three of the responding laboratories reported any trace of the parent compound [11]. A study of the fate and transformation mechanisms of TDG in soil would help explain the poor results of the VICWC study as well as support the development of accurate HD verification guidelines for environmental media. Responding to the need for more information about the environmental fate of TDG as a potential indicator compound for HD exposures, we investigated several environmental processes that could influence the detection and persistence of TDG.

MATERIALS AND METHODS

Chemicals and soils

We prepared deionized water using a Barnstead NANOpure® (Dubuque, IA, USA) reagent water system fed by a Corning still (Corning, NY, USA). Sodium phosphate monobasic monohydrate, o-phosphoric acid (85%), and acetonitrile (Optima) were obtained from Fisher Scientific (Pittsburgh, PA, USA). Thiodiglycol (2,2'-thiodiethanol, ≥99% pure) was obtained from Aldrich Chemical (Milwaukee, WI, USA). Thiodiglycolic acid (TDGA, 97%) was obtained from Lancaster (Windham, NH, USA). Aluminum oxide (Al₂O₃), iron oxide (Fe₂O₃), and manganese oxide (MnO₂) were obtained from Alpha ÆSAR (Ward Hill, MA, USA). All other chemicals used were reagent grade.

Soil characterization (Table 1) was done in our laboratory and at the University of Delaware Soil Testing Laboratory. Soils were characterized for the percentage of sand, silt, clay, and soil pH using the standard procedure of the University of Delaware laboratory [21]. Organic matter content of the soils was determined using the Walkley–Black wet combustion method [21]. Metal oxide content was determined in our laboratory using a perchloric–nitric acid digestion extraction [22] followed by metal analysis on a Perkin Elmer (Norwalk, CT, USA) 5000 atomic absorption spectrophotometer.

We studied four soils obtained from U.S. military installations and two from an interlaboratory collaborative exercise [11]: Dugway Proving Ground (DPG), an alkaline, calcareous, sandy clay loam; Fort McClellan (FMC), an acid sulfate, Piedmont clay loam; Rocky Mountain Arsenal (RMA), a mildly alkaline, calcareous, sandy loam; woodstone sandy loam (WSL), a mildly acidic, sandy loam (characteristic soil of Aberdeen Proving Ground); treaty soil 1 (TS1), a mildly acidic,
Environmental transformation mechanisms of thiodiglycol

We examined various soil/solution ratios (5–40 ml H₂O/polypropylene copolymer (PPCO) centrifuge tube containing 1 g of (0–40 mg/L) to a Nalgene (Rochester, NY, USA) polypropylene vial for analysis. We removed 10 ml of supernatant with a pipette, we added 20 ml of TDG or TDGA solution (0–40 mg/L) to a Nalgene (Rochester, NY, USA) polypropylene vial for analysis.

We found an intermediate degradation compound that was observed in the TDG standards. No degradation was observed in similar standards stored in PPCO tubes. All three compounds (TDG, TDGA, and TDGMA) were present in the solutions that had been stored in the glass vials. Degraded standards were analyzed, and the TDG and TDGA concentrations were determined. We calculated TDGMA concentrations by mass balance. By correlating peak area with the TDGMA concentration calculated by mass balance, we generated a linear calibration curve for TDGMA.

We made all pH measurements with a Fisher Scientific pH meter calibrated at pH 4, 7, and 10.

### Sorption isotherms

We prepared soil–solution samples containing either TDG or TDGA as described above. Triplicate soil suspensions were shaken horizontally in the dark for 24 h. The aqueous phase was analyzed, and the TDG and TDGA concentrations were determined. Solid-phase concentrations were calculated by mass balance. We fit the sorption isotherms to the Langmuir isotherm model, which allowed us to account for both the strength of binding and the saturation of the solid.

\[
\Gamma = \frac{x}{m} = \left(\frac{Q_{\text{max}} k c_{\text{eq}}}{1 + k c_{\text{eq}}^d}\right) c_{\text{eq}}
\]

where \(\Gamma\) is the adsorbed concentration of compound (mg/kg), \(x\) is the amount of compound adsorbed (mg), \(m\) is the mass of soil (kg), \(Q_{\text{max}}\) is the maximum amount of compound that can be adsorbed (mg/kg), \(k\) is the adsorption constant (L/mg), and \(c_{\text{eq}}\) is the equilibrium concentration of compound in the aqueous solution (mg/L).

### Photolysis

We followed method 600 of the U.S. Environmental Protection Agency (EPA) [24] to investigate TDG and TDGA photolysis. We prepared triplicate aqueous samples of TDG and TDGA (20 and 50 mg/L) in borosilicate glass test tubes and exposed them to rooftop sunlight. Identical samples were covered with aluminum foil and placed alongside the experimental samples, which were not covered. The samples were left outdoors continuously for 2 weeks. The late spring weather was mostly sunny with little precipitation. Sample integrity was not jeopardized because of restricted rooftop access and placement security. Samples were taken for analysis after 4, 9, and 14 d of irradiation.

### Hydrolysis

We followed EPA method 600 [24] to investigate TDG and TDGA hydrolysis. We prepared buffers whose final pH values were approx. 4, 7, and 11 in PPCO centrifuge tubes and spiked the solutions with 20 mg/L TDG or TDGA. Sample aliquots were analyzed after 48 and 96 h. Sample solutions were acidified with small volumes of 1 M HNO₃, as necessary to adjust the pH. Samples were prepared in triplicate.

### Effect of metal oxides

We studied TDG sorption onto metal oxides to determine the role of metal oxides in TDG retention by soils. In addition to providing a sorptive site, metal oxides may potentially oxidize TDG. We prepared metal oxide suspensions by placing 0.5 g of Al₂O₃, Fe₂O₃, or MnO₂ into a PPCO centrifuge tube. Twenty milliliters of TDG solution (20 mg/L) was added to the sample vials. Sample pH was adjusted to pH 6 to 9 with 1 M HNO₃. Samples were shaken horizontally for 24 h, then filtered with FP-450 Vericel membranes. Manganese oxide par-

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<table>
<thead>
<tr>
<th>Soila</th>
<th>Sandy b</th>
<th>Silt b</th>
<th>Clay b</th>
<th>Organic matter</th>
<th>MnO₄ c</th>
<th>Fe₂O₃ c</th>
<th>Al₂O₃ c</th>
<th>Surface areaa</th>
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<tbody>
<tr>
<td>DPG</td>
<td>53</td>
<td>14</td>
<td>33</td>
<td>8.5</td>
<td>0.5</td>
<td>0.2</td>
<td>3.20</td>
<td>0.49</td>
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<tr>
<td>FMC</td>
<td>43</td>
<td>21</td>
<td>36</td>
<td>4.7</td>
<td>0.4</td>
<td>0.001</td>
<td>2.22</td>
<td>2.86</td>
</tr>
<tr>
<td>RMA</td>
<td>66</td>
<td>16</td>
<td>18</td>
<td>8.4</td>
<td>0.1</td>
<td>0.009</td>
<td>0.66</td>
<td>3.25</td>
</tr>
<tr>
<td>TSI</td>
<td>88</td>
<td>4</td>
<td>8</td>
<td>6.6</td>
<td>0.4</td>
<td>0.024</td>
<td>3.40</td>
<td>2.56</td>
</tr>
<tr>
<td>TS2</td>
<td>46</td>
<td>28</td>
<td>26</td>
<td>7.9</td>
<td>2.6</td>
<td>0.064</td>
<td>6.10</td>
<td>4.80</td>
</tr>
<tr>
<td>WSL</td>
<td>74</td>
<td>16</td>
<td>10</td>
<td>4.5</td>
<td>1.3</td>
<td>0.031</td>
<td>0.35</td>
<td>2.59</td>
</tr>
</tbody>
</table>

Sources: DPG = Dugway Proving Ground; FMC = Fort McClellan; RMA = Rocky Mountain Arsenal; TS1, TS2 = Verificaton Institute for the Chemical Weapons Convention; and WSL = Woodstone Sandy Loam.

Determinations were performed in triplicate.
particles passed through the filter pores, directly interfering with the analysis (HPLC with ultraviolet [UV] detection). Upon acidification with 1 M HNO₃, these interferences were removed. Metal oxide samples were prepared in triplicate.

**Effect of biological toxins**

We investigated TDG degradation in the presence of biological toxins to determine the role of biological processes in the transformation of TDG to TDGA. The TS1 soil suspensions with TDG (10 mg/L) were prepared as described above. In preliminary experiments, transformation of TDG to TDGA proceeded without delay on the TS1 soil. Soil suspensions containing TDG were prepared with either an anionic or cationic toxin. Sodium azide (NaN₃) or mercuric chloride (HgCl₂) was added to the soil suspensions to yield 50, 100, or 250 mg/L NaN₃ or 30 mg/L HgCl₂. Samples were shaken horizontally for 24 and 48 h, filtered, and analyzed by HPLC–UV. Samples were prepared in triplicate.

**Transformation kinetics**

The transformation of TDG to TDGMA and TDGA was studied to better characterize the fate of TDG in environmental samples. Batch studies were used to investigate the kinetics of TDG degradation. Thiodiglycol soil suspensions for each of the six soils were prepared as described above. Thiodiglycol samples were initially prepared at three concentrations ranging from 5 to 40 mg/L. Samples were shaken horizontally for the desired duration (1, 2, 3, 6, 12, and 24 h) on the first day, then every 12 to 24 h for the next 2 weeks. After filtration, the aqueous phase was analyzed. Batch samples were prepared for each planned sampling duration and were not reused for longer durations. Samples were prepared in duplicate.

**RESULTS AND DISCUSSION**

Very little environmental information pertaining to the environmental fate of TDG [1±20] was obtained from an exhaustive literature search. Knowledge of TDG behavior in environmental media is essential to CWA exposure verification. To obtain environmental fate information on TDG, we investigated several environmental processes using aqueous solutions and/or soil suspensions containing TDG. We conducted this study to supply missing information of the environmental fate of TDG as well as to identify areas where new research may enhance CWA exposure verification techniques.

**Sorption isotherms**

We determined the sorption of TDG and TDGA onto six soils characteristic of U.S. military installations and the VICWC interlaboratory comparison. We initially investigated TDG sorption. Soil suspensions containing 1 to 50 mg/L TDG in the aqueous phase were allowed to equilibrate for 24 h, then filtered. The aqueous phase was then analyzed for TDG. The sample results indicate that the partitioning of TDG to the solids phase is not sufficient to be detected by the analytical method. After the 24-h equilibrium period, the amount of TDG recovered in the aqueous phase was 99 to 100% of the original mass for five of the six soils. With aqueous concentrations nearing the 100% recovery mark, the analytical method was not capable of resolving the difference between the amount of TDG spiked in the original solution and the amount of TDG recovered in the equilibrated solution. With our analytical detection limit of 0.50 mg/L, lower initial concentrations were not feasible for investigation. When it was possible to estimate values of $Q_{\text{max}}$, the estimates for TDG were less than 10 mg/kg. In the sixth soil, TS1, TDG partially degraded during the 24-h equilibrium period. Following identification of the degradation product in the TS1 soil as TDGA, the sorption of TDGA to the six soils was investigated.

We observed TDGA sorption for each of the six soils and generated sorption isotherms for the data using the Langmuirian model (Fig. 1). The experimental range of 1 to 40 mg/L TDGA is far below the water solubility of TDGA. It is assumed that any sorption observed would be a direct result of solid–chemical interaction (electrical or chemical) in a monolayer or multilayer configuration, not a direct result of precipitation. In addition, we limited the experiments to 24 h to minimize the effect of dispersive forces accounted for in more complex sorption models. Based on these limitations, the Langmuir model adequately describes the sorption phenomenon. Langmuirian sorption isotherm parameters (Table 2) for TDGA sorption onto the six soils were generated using the nonlinear regression algorithm built into the graphics package Kaleidagraph®. The high correlation coefficients strengthen the selection of Langmuirian sorption behavior. The value of $Q_{\text{max}}$ for
We investigated hydrolysis of 20- and 50-mg/L solutions of thiodiglycol (TDG) and thiodiglycolic acid (TDGA) in deionized water to determine their fate at the surface or in the subsurface. The hydrolytic studies showed that hydrolysis has no effect on the fate of TDG or TDGA in environmental media.

**Table 2. Langmuirian parameters for thiodiglycol sorption onto soils**

<table>
<thead>
<tr>
<th>Soil</th>
<th>Q_{max} (mg/kg)</th>
<th>Error</th>
<th>k (L/mg)</th>
<th>Error</th>
<th>r²</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPG</td>
<td>19.9</td>
<td>4.2</td>
<td>0.33</td>
<td>0.15</td>
<td>0.9881</td>
<td>2.25</td>
</tr>
<tr>
<td>FMC</td>
<td>427.4</td>
<td>37.5</td>
<td>0.22</td>
<td>0.05</td>
<td>0.9906</td>
<td>1,832</td>
</tr>
<tr>
<td>RMA</td>
<td>22.7</td>
<td>3.1</td>
<td>0.15</td>
<td>0.03</td>
<td>0.9943</td>
<td>1.12</td>
</tr>
<tr>
<td>TS1</td>
<td>36.6</td>
<td>13.9</td>
<td>0.12</td>
<td>0.08</td>
<td>0.9724</td>
<td>16.14</td>
</tr>
<tr>
<td>TS2</td>
<td>25.6</td>
<td>0.9</td>
<td>13.70</td>
<td>12.0</td>
<td>0.9930</td>
<td>7.85</td>
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<tr>
<td>WSL</td>
<td>31.9</td>
<td>1.6</td>
<td>0.71</td>
<td>0.14</td>
<td>0.9953</td>
<td>5.09</td>
</tr>
</tbody>
</table>

*See Table 1 for descriptions of soils.

Table 2 presents the results of the photolysis study. A statistical evaluation of the triplicate studies indicates that the sample mean concentration for both TDG and TDGA samples and controls were within the 95% confidence limit of a fresh standard of equal concentration, indicating no degradation of TDG or TDGA at pH 4, 7, and 11. Hydrolysis of TDG and TDGA at pH 4, 7, and 11 yielded nearly 100% recoveries of the initial 20- and 50-mg/L concentrations of the parent compounds after 48 and 96 h (Table 4). Both TDG and TDGA were observed at the end of the trial period without significant levels of deviation (95% confidence). The nearly 100% recoveries and the absence of any detectable hydrolytic byproducts indicates that hydrolysis has no effect on the fate of TDG or TDGA in environmental media.

**Effect of metal oxides**

Metal oxides are constituents of soils that can both oxidize compounds and produce a sorptive site for compound retention. We investigated the effect of metal oxides to determine the importance of metal oxides in the fate of TDG in soils. The studies produced mixed results. No TDG sorption or degradation was observed with either Fe₂O₃ or Al₂O₃. Aqueous TDG concentrations were nearly 100% at solution pH values from 6.0 to 9.0. Lower pH values resulted in significant solubilization of the metal oxides. Analysis of the HPLC–UV chromatograms of metal oxide samples produced no additional chemical peaks, indicating no degradation of TDG to TDGA.

We observed significant decreases in TDG concentration in solutions containing MnO₂. The small particle size of MnO₂ produced a black supernatant after centrifugation and filtering through 0.45-μm membranes, interfering with HPLC–UV analysis. Before samples were filtered, the pH was measured and the solutions acidified with small volumes of 1 M HNO₃. The resulting clear liquid filtrate was analyzed by HPLC–UV. A correlation between pH and the aqueous-phase TDG concentration was observed and is shown in Figure 2.

Sorption of TDG may be significant in low-pH soils containing high concentrations of MnO₂. The decrease of TDG in the aqueous phase could be attributed to either sorption or degradation. No extraneous peaks occurred in the sample chromatograms; therefore, no degradation of TDG to TDGA was observed. Because no degradation products were detected, coupled with the pH dependency, sorption is believed to be the process involved with the loss of TDG from the aqueous phase. The tested soils contained 0.01 to 2.18 mg MnO₂, and each vial contained 500 mg of MnO₂. The large difference in MnO₂ quantity between the pure MnO₂ study and soil study exaggerates the sorption of TDG to metal oxides and is intended to provide a mechanistic approach to understanding the complex behavior of soil sorption. The sorption results on pure soil samples are presented in Table 3.

**Table 3. Photolysis of thiodiglycol (TDG) and thiodiglycolic acid (TDGA)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. (mg/L)</th>
<th>Final a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Dark control</td>
</tr>
<tr>
<td>TDG</td>
<td>50</td>
<td>49.8</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19.4</td>
</tr>
<tr>
<td>TDGA</td>
<td>50</td>
<td>49.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19.8</td>
</tr>
</tbody>
</table>

*Mean of three samples after 14 d of exposure.
metal oxides are consistent with the lack of TDG sorption onto soil.

**Effect of biological toxins**

Preliminary sorption experiments indicated that TS1 soil degraded TDG into two compounds. The compounds were later identified as TDGMA and TDGA. Photolysis, hydrolysis, and metal oxide oxidation were not responsible for the oxidation. Because these experimental processes could not reproduce the transformation, investigations that may have hindered the transformation were performed.

Both an anionic poison, sodium azide, and a cationic poison, mercuric chloride, prevented degradation on the TS1 soil. Control samples containing no poisons degraded TDG, with losses from the 10-mg/L initial concentration up to 17.5% in 25.5 h and nearly 50% after 48 h (Fig. 3). Samples containing NaN₃ exhibited much less TDG loss (2.5±7.5% at 48 h). Samples containing HgCl₂ had 7.5% loss after 48 hours. Samples containing the poisons still exhibited some TDG loss and degradation product build-up; however, the extent of the degradation is significantly less than the controls. Three NaN₃ concentrations and the one HgCl₂ concentration prevented approximately the same amount of TDG degradation.

Two prior studies investigated the biological mineralization of TDG. Beaudry et al. [25] and Sines et al. [26] both elaborate on the ability of *Alcaligenes xylosoxidans* ssp. *xylosoxidans* strain SH42 to mineralize TDG. However, intermediates were not reported in their results. These two studies support the conclusion that TDG is biologically oxidized to TDGA by providing verification that TDG is biologically consumable. In addition, the complete mineralization of TDG could explain the low recoveries of TDG, TDGMA and TDGA after long durations. It is concluded that biological oxidation is responsible for the transformation of TDG to TDGMA and TDGA.

**Transformation kinetics**

Once the transformation mechanism was established, the transformation kinetics were investigated. Concentrations of TDG, TDGMA, and TDGA were monitored for several days. As the experiment proceeded, all six soils showed a decrease in aqueous TDG, an increase followed by a decrease in aqueous TDGMA, and an increase in aqueous TDGA (Fig. 4).

Transformation of TDG began immediately on TS1 soil. Significant levels of TDGMA were detected a few hours after exposure. Before this soil was obtained, TS1 was amended with phosphate and nitrate fertilizers and therefore was expected to be biologically active.

The kinetic data were fit to several kinetic rate laws. The zero-order rate model fit the data best. The observed rate coefficient for TDG degradation was $k = 6.26 \times 10^{-6}$ mol/L·h⁻¹ ($s = 2.6 \times 10^{-7}$). We attempted to determine the rate coefficients for the other two compounds but had too few data points.

A mass balance including aqueous-phase TDG, TDGMA, and TDGA and solid-phase TDGA resulted in total recoveries of 73.7 to 89.2% over the entire test period. The lowest recoveries were observed with the 5-mg/L spiked samples; typical recoveries for the higher concentration runs were nearly 90%. Low recoveries, especially in samples with low initial concentrations, may have resulted from partial mineralization of the TDG and/or TDGA by biological organisms; however, this was not tested for these soils.

Soil kinetics for the WSL soil included a 2-d acclimation period. Aqueous-phase TDG concentrations decreased only slightly in the first 2 d, after which transformation proceeded with a zero-order rate coefficient of $1.01 \times 10^{-6}$ mol/L·h⁻¹ ($s = 4.3 \times 10^{-7}$). Again, insufficient data were generated to determine the rate coefficients for the other two compounds. A mass balance indicates that more than 90% of the spiked mass is recovered as TDGA after 300 h or more. Typical total recoveries (for both the aqueous and solid phases) for all concentrations and durations were 90%.

Transformation of TDG on FMC soil began after a 90-h lag. The kinetic data were again fit to a zero-order model with rate coefficient $k = 9.41 \times 10^{-7}$ mol/L·h⁻¹ ($s = 3.2 \times 10^{-7}$). As time progressed, the recoverable mass in the aqueous phase decreased from 98 to 100% to 3 to 31%. This substantial loss is attributed to the strong sorption of TDGA to the FMC soil. Adjusting for total recovery by accounting for sorption, recoveries ranged from 60 to 86%.

Of the soils tested, DPG and RMA soils were the most unreactive for transformation of TDG, which remained virtually unreacted in these soils for 200 h. Recoveries greater than 95% were obtained in RMA soil 300 h after exposure, most of which remained TDG. The DPG soils produced no indication of degradation 125 h after exposure, with 98 to 100% recoveries.

The transformation of TDG to TDGMA and TDGA is ev-

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**Fig. 2.** Effects of metal oxides on sorption of thiodiglycol (TDG).

**Fig. 3.** Effects of biological toxins on loss of thiodiglycol (TDG).
identically different in each of the soils tested. Each soil had different characteristics, as shown in Table 1. The TS1 soil was the most reactive, degrading TDG immediately upon exposure; however, this soil was amended with fertilizers before our analysis. Soil fertilization is beneficial to microorganisms, and, as a direct result, the biological activity of the soil would be increased. Increased activity would promote quick degradation of TDG to TDGA. The kinetic study on TS1 soil re-affirms this conclusion. In other soils, TDG transformation proceeded after an acclimation period. In both the WSL and FMC soils, it is believed that biological degradation began after organisms in the soils adapted to consume TDG. The organisms share the same ability to adapt to degrade TDG, but at different rates, which were observed as different lag periods. Another potential explanation for the difference is the accessibility of the microbes to consume TDG. Diffusion limitations may slow the acclimation. Horizontal shaking was introduced to minimize the effects of diffuse forces. Aqueous-phase recoveries in FMC soil were low because of the large capacity to sorb TDGA. Transformation on the two highest pH soils, RMA and DPG, did not occur. This lack of activity may be a direct result of the high pH, which may be out of range to sustain microorganism consumption of TDG, or the high clay content, which may hinder solute transport among soil particles. As expected, different soil properties all affected the rate of TDG transformation in soils, hence the rationale for studying multiple soils.

CONCLUSIONS

The transformation of TDG in environmental samples was investigated. Sorption of TDG to soils does not readily occur, indicating that TDG may be an environmentally mobile compound. We found that TDG degrades to TDGA in some soils, with the potential to be completely mineralized. This degradation proceeds through biological oxidation. The presence of metal oxides may play a role in controlling the fate of TDG.

Fig. 4. Kinetics of thiodiglycol (TDG) transformation. (a) Degradation of TDG on TS1 soil. (b) Formation of [(Z-hydroxyethyl)thio]acetic acid (TDGMA) on TS1 soil. (c) Formation of thiodiglycolic acid (TDGA) on TS1 soil. (d) Degradation of TDG on WSL soil. (e) Formation of TDGMA on WSL soil. (f) Formation of TDGA on WSL soil. (g) Degradation of TDG on FMC soil. (h) Formation of TDGMA on FMC soil. (i) Formation of TDGA on FMC soil. Co = initial concentration. See “Materials and Methods” for descriptions of soils.
in soils; however, photolysis and hydrolysis are not likely to have significant effects on TDG fate. Many environmental processes affect the fate of compounds in the environment; however, as shown in this study, not all are always relevant. This study produced some basic information about the environmental fate of TDG and hence the fate of HD. Similar information was previously lacking in the scientific literature. It is now apparent that when a site is tested for mustard contamination, it is important to test not only for HD and TDG but also for TDGMA and TDGA. Currently, these two compounds are not tested for routinely, yet the presence of one or both is more likely in certain environments.

In addition to the work done in this study, to fully assess the environmental fate of TDG, column or flow studies should be performed to simulate environmental mobility. The effect of soils properties, such as organic matter content and cation exchange capacity, on TDG sorption should be assessed. Additional kinetic studies monitoring mineralization of TDG and/or TDGA should also be conducted.

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