Determination of Low Level NDMA in Soils


PURPOSE: This technical note describes the low level detection of N-nitrosodimethylamine (NDMA) by gas chromatography mass spectrometry (GC-MS) and gas chromatography with a nitrogen-phosphorus detection (GC-NPD). Detection limit studies were performed using several soil types to demonstrate the detection of NDMA at less than 1 µg/kg.

INTRODUCTION: NDMA (CAS number: 62-75-9) is a semivolatile organic compound that is highly toxic and a suspected human carcinogen. It has a molecular structure \((\text{CH}_3)_2\text{N} - \text{N}=\text{O}\) with a molecular weight of 78.04 g/mol; it appears as a yellow liquid at ambient temperature with a density of 1.005 g/mL and water solubility of 0.29 g/mL at 20 °C.

NDMA is a by-product or waste product of several industrial processes, including production of liquid rocket fuel 1,1-dimethylhydrazine, inhibition of nitrification in soil, and manufacturing of rubber, polymers, and lubricants. NDMA occurrence is not only limited to regions near industrial facilities; its detection at other sites appears to be associated with chlorine/chloramine disinfection of water and wastewater. NDMA contamination of drinking water is of particular concern due to its high toxicity (California Department of Health Services (CDHS) 2006), and difficulties in detecting it at low concentrations and removing it from drinking water because it does not readily biodegrade, adsorb, or volatilize.

Due to concerns over its potential environmental and health impacts, NDMA has been listed as an emerging contaminant, which necessitates its accurate and reliable detection and quantitation at low levels in complex environmental matrices (U.S. Environmental Protection Agency (USEPA) 2008). USEPA Regions 3, 6, and 9 have established screening levels for NDMA in residential soils at 3.0, 2.3, and 9.5 µg/kg, respectively (USEPA 2004, 2007a, 2007b). However, USEPA published methods using GC-MS, GC-MS/SIM, and GC-NPD typically have approximate MDLs of 100, 10, and 5 µg/kg, respectively. The purpose of this research project is to develop and demonstrate an MDL of 1 µg/kg in soils using standard USEPA SW-846 methods with minimal modifications (USEPA 1996). The U.S. Army Engineer Research and Development Center, Environmental Chemistry Branch (ERDC-ECB) conducted a series of tests to determine the MDLs for NDMA in soils using modifications of EPA GC-MS/SIM and GC-NPD methods. The work was performed in support of the HTRW EMCX, U.S. Army Corps of Engineers, Formerly Used Defense Site (FUDS) program. This technical note provides the procedures and results of the study. For further information on the project design, refer to the scope of work developed by the ERDC and HTRW EMCX (Appendix A).
MATERIALS AND METHODS:

Soils. Four soils were used to determine MDLs for NDMA: hydromatrix (a diatomaceous earth), an ERDC reference soil, a Grenada Loring (GL) reference soil, and an ASTM Fat Clay. Hydromatrix (Catalog # 198003) was purchased from Varian, Inc. (Lake Forest, CA) and used as received. The ERDC and Grenada Loring reference soils were air-dried (<3 percent moisture) and ground with a mortar and pestle to pass a #40 sieve. The ERDC and Grenada Loring reference soils were collected from field sites in Mississippi, and are currently being used as reference soils in ongoing research projects. The ERDC loess soil was collected from the Engineer Research and Development Center, and detailed geochemical characterizations of this soil have been reported elsewhere (Tardy et al. 2003; Larson et al. 2005). The silty loam soil of the Grenada-Loring series (Alfisols order) was collected from the Brown Loam Experimental Station, Learned, MS, after the top 12 cm were removed to eliminate unwanted vegetation. Detailed geochemical properties of the Grenada Loring soil have also been reported previously (Bednar et al. 2008). The American Society for Testing and Materials (ASTM) certified Fat Clay soil (CH-1) is described as a Vicksburg Buckshot Clay (ASTM 1997), and consists of 98.8 percent fines (passes #200 sieve); no other geochemical data was provided by ASTM for the CH-1 fat clay soil. Geochemical properties of the test soils are listed in Table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>ERDC Loess</th>
<th>Grenada Loring</th>
<th>ASTM Fat Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Sand</td>
<td>1.1</td>
<td>3</td>
<td>1.2</td>
</tr>
<tr>
<td>% Fines (clay and silt)</td>
<td>98.9</td>
<td>97</td>
<td>98.8</td>
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<tr>
<td>pH</td>
<td>8.7</td>
<td>6.7</td>
<td>–</td>
</tr>
<tr>
<td>Cation exchange capacity (meq/g)</td>
<td>0.05</td>
<td>0.075</td>
<td>–</td>
</tr>
<tr>
<td>% Organic carbon</td>
<td>0.9</td>
<td>0.7</td>
<td>–</td>
</tr>
</tbody>
</table>

Extraction techniques. All soil samples were extracted with a Dionex Accelerated Solvent Extractor (ASE) 200 following SW-846 Method 3545 with the modification of a higher cell temperature, specifically 120 °C versus 100 °C, and three static cycles versus one cycle. The principle extraction solvent tested for the initial MDL study was 75 percent Methylene chloride/25 percent acetone (v/v), which is a slight modification from the recommended 50:50 ratio in the published method. However, solvent ratios and extraction parameters may be adjusted as needed from the standard method recommendations to improve analyte recoveries. The solvent ratios used for the present work were based on historical experiences with other analytes and soil/sediment matrices. These slight method alterations have been historically observed to increase analyte recoveries and decrease solvent dimerization, which can interfere with instrumental analysis.

Each extraction cell contained 30 g of solid material, spiked to a nominal NDMA concentration of 2.33 µg/kg, and each solid material extraction was replicated up to nine times. After extraction of the spiked soil using the ASE, the extract samples were evaporatively concentrated using a TurboVap II concentrator to a final volume of 1 mL of methylene chloride. The 1-mL final aliquot was spiked with internal standards and analyzed as described below.
Once MDLs were calculated for the initial experiment, an MDL verification study was performed where the spike concentration was lowered to nominally 1.67 µg/kg. This value is less than two times the target MDL (1 µg/kg) and approximately two times the calculated MDL for the hydromatrix samples, as described in the results section below.

**Instrumentation.** The GC-MS used for analysis was an Agilent 6890 gas chromatograph with a 5973 mass selective detector operated by Agilent ChemStation Software. The temperature program was as follows: 40 °C for 1 minute, 10 °C/min ramp to 100 °C, 25 °C/min ramp to 280 °C, hold for 3 minutes, and a final clean out 5 °C/min ramp to 300 °C. An Agilent HP5MS 30 m × 0.25 mm ID × 0.00025 mm capillary column was used to achieve analyte separation. The retention time of NDMA on the GC-MS using this column and temperature program was nominally 2.54 minutes. The GC/MS internal standards, base-neutral surrogates, and instrument and method quality control were followed as specified in the standard method. The instrument SIM ions were as follows: 1,4-dichlorobenzene-d₄, 152 and 150 (internal standard for analyte); NDMA, 74 and 42 (analyte); naphthalene-d₈, 136 and 108 (internal standard for surrogate); nitrobenzene-d₅, 82 and 128 (surrogate). The m/z 74 ion was used as the primary ion for NDMA analysis due to interferences observed on m/z 42 in some matrices. The instrument was calibrated using standards with concentrations of 0.050, 0.10, 0.25, 1.0, 2.0, 4.0, 10, and 20 µg/mL, and an internal standard concentration of 2.0 µg/mL. A second-source calibration verification standard of 2.0 µg/mL was used to verify instrument performance and accuracy of the primary standard. All standards and matrix spike analytes were purchased from Supelco (Bellefonte, PA).

The GC-NPD used was an Agilent 6890 gas chromatograph with dual nitrogen-phosphorus detectors operated with Agilent Chemstation software. The temperature program was as follows: 40 °C for 2 minutes, 15 °C/min, ramp to 260 °C, hold for 14 minutes. A Restek-5 30 m × 0.53 mm ID × 0.00050 mm capillary column was used as the primary column and a Restek-200 30 m × 0.53mm ID × 0.0015 mm capillary column was used for analyte confirmation. The retention times of NDMA on the Restek-5 and Restek-200 columns, using this temperature program, were 3.56 and 8.73 minutes, respectively. The instrument was calibrated using standards with concentrations of 0.010, 0.025, 0.050, 0.100, 0.500, 1.000, and 2.500 µg/mL. A second-source calibration verification standard of 0.100 µg/mL was used to verify instrument performance and accuracy of the primary standard.

**Results.** The soil samples spiked with a nominal NDMA concentration of 2.33 µg/kg were extracted and analyzed as described above. Table 2 gives the concentration of NDMA detected in each of the replicates for each matrix, the mean concentrations, the mean percent recoveries, the standard deviations, and the calculated MDLs for the analyses by GC-MS/SIM. The MDL was calculated by multiplying the standard deviation by the appropriate Student’s t value, which is determined by the number of sample replicates analyzed (40 CFR Part 136, Appendix B). No experimental values were rejected to create an artificial MDL. Only data for the major ion at m/z 74 is reported, as interferences were observed on the secondary ion at m/z 42 in some of the soils. These interferences are likely due to hydrocarbon moieties co-extracted from the soil matrices, as they were not observed on the hydromatrix samples. Specifically, significant peak tailing, poor analyte response, and incorrect ion ratios were observed for the secondary ion in the soil samples (see chromatograms in Appendix B).
Table 2. Concentrations (µg/kg) of NDMA Determined in Replicate Extractions and Calculated MDLs for GC-MS Analysis.

<table>
<thead>
<tr>
<th>Replicate</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>Mean</th>
<th>%Rec</th>
<th>SD</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydromatrix</td>
<td>1.49</td>
<td>1.68</td>
<td>2.31</td>
<td>1.62</td>
<td>1.60</td>
<td>1.47</td>
<td>1.48</td>
<td>1.90</td>
<td>1.51</td>
<td>72</td>
<td>0.27</td>
<td>0.8</td>
</tr>
<tr>
<td>ERDC</td>
<td>0.76</td>
<td>0.81</td>
<td>1.11</td>
<td>1.03</td>
<td>0.96</td>
<td>0.97</td>
<td>0.97</td>
<td>1.13</td>
<td>na</td>
<td>0.97</td>
<td>41</td>
<td>0.13</td>
</tr>
<tr>
<td>GL</td>
<td>0.85</td>
<td>0.97</td>
<td>0.98</td>
<td>0.84</td>
<td>1.07</td>
<td>1.00</td>
<td>0.89</td>
<td>na</td>
<td>na</td>
<td>0.94</td>
<td>40</td>
<td>0.08</td>
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<tr>
<td>ASTM</td>
<td>0.41</td>
<td>0.89</td>
<td>0.80</td>
<td>0.77</td>
<td>1.08</td>
<td>0.88</td>
<td>0.83</td>
<td>0.78</td>
<td>na</td>
<td>0.78</td>
<td>31</td>
<td>0.19</td>
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</table>

na: Not available due to loss of sample or extraction not performed.

The same sample extracts were also analyzed by GC-NPD. Table 3 gives the concentration of NDMA detected in each of the replicates for each matrix, the mean concentrations, the mean percent recoveries, the standard deviations, and the calculated MDLs for the analyses by GC-NPD. Only the data from the Restek-5 column is reported as some interferences from the soil matrices were observed on the Restek-200 column. The secondary column did not resolve NDMA from an unknown nitrogen- or phosphorus-containing compound in some of the soil matrices, yielding a positive bias, and therefore lack of concentration confirmation. However, with a different column or modified temperature program, confirmation may be achieved; therefore only primary column data are reported.

Table 3. Concentrations (µg/kg) of NDMA Determined in Replicate Extractions and Calculated MDLs for GC-NPD Analysis.

<table>
<thead>
<tr>
<th>Replicate</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>Mean</th>
<th>%Rec</th>
<th>SD</th>
<th>MDL</th>
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<tbody>
<tr>
<td>Hydromatrix</td>
<td>0.56</td>
<td>0.56</td>
<td>0.58</td>
<td>0.76</td>
<td>0.39</td>
<td>0.57</td>
<td>0.51</td>
<td>0.61</td>
<td>0.57</td>
<td>24</td>
<td>0.10</td>
<td>0.3</td>
</tr>
<tr>
<td>ERDC</td>
<td>0.76</td>
<td>0.73</td>
<td>0.77</td>
<td>0.88</td>
<td>0.61</td>
<td>0.61</td>
<td>0.61</td>
<td>na</td>
<td>0.71</td>
<td>30</td>
<td>0.11</td>
<td>0.3</td>
</tr>
<tr>
<td>GL</td>
<td>1.02</td>
<td>1.27</td>
<td>1.05</td>
<td>1.00</td>
<td>1.22</td>
<td>0.90</td>
<td>na</td>
<td>1.09</td>
<td>47</td>
<td>0.13</td>
<td>0.4</td>
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<tr>
<td>ASTM</td>
<td>0.51</td>
<td>0.69</td>
<td>1.17</td>
<td>0.91</td>
<td>1.10</td>
<td>1.04</td>
<td>0.90</td>
<td>0.87</td>
<td>1.25</td>
<td>37</td>
<td>0.20</td>
<td>0.6</td>
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</table>

na: Not available due to loss of sample or extraction not performed.

An MDL verification study was performed on all four matrices by spiking triplicate solid samples with nominally 1.67 µg/kg of NDMA, a value less than two times the target MDL (1 µg/kg), and approximately two times the calculated hydromatrix MDL (0.8 µg/kg) by GC-MS/SIM. The triplicate samples were extracted with 75 percent methylene chloride/25 percent acetone (v/v) and analyzed by both GC-MS/SIM and GC-NPD. The replicate concentrations, mean concentrations, and mean percent recoveries are shown in Table 4.
Table 4. Concentrations (µg/kg) of NDMA determined in the MDL verification study (spike level of 1.67 µg/kg) using 75 percent methylene chloride/25 percent acetone as the extraction solvent mixture.

<table>
<thead>
<tr>
<th>Replicate</th>
<th>Rep1</th>
<th>Rep2</th>
<th>Rep3</th>
<th>Mean</th>
<th>%Rec</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GC-MS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydromatrix</td>
<td>1.40</td>
<td>1.63</td>
<td>1.42</td>
<td>1.5</td>
<td>89</td>
</tr>
<tr>
<td>ERDC</td>
<td>0.51</td>
<td>0.72</td>
<td>0.69</td>
<td>0.64</td>
<td>38</td>
</tr>
<tr>
<td>GL</td>
<td>0.42</td>
<td>0.33</td>
<td>0.24</td>
<td>0.33</td>
<td>20</td>
</tr>
<tr>
<td>ASTM</td>
<td>1.11</td>
<td>0.66</td>
<td>2.05</td>
<td>1.3</td>
<td>76</td>
</tr>
<tr>
<td><strong>GC-NPD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydromatrix</td>
<td>0.73</td>
<td>0.82</td>
<td>0.69</td>
<td>0.75</td>
<td>45</td>
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<tr>
<td>ERDC</td>
<td>0.85</td>
<td>0.71</td>
<td>0.77</td>
<td>0.78</td>
<td>47</td>
</tr>
<tr>
<td>GL</td>
<td>0.73</td>
<td>0.65</td>
<td>0.45</td>
<td>0.61</td>
<td>37</td>
</tr>
<tr>
<td>ASTM</td>
<td>0.51</td>
<td>0.55</td>
<td>0.56</td>
<td>0.54</td>
<td>33</td>
</tr>
</tbody>
</table>

The analyte recoveries using 75 percent methylene chloride/25 percent acetone (v/v) ranged from 20 to 89 percent when analyzed by GC-MS and from 33 to 47 percent when analyzed by GC-NPD. While recoveries are generally lower than desired (<70 percent observed versus >70 percent for a mid-level LCS spike by Method 8270), they are acceptable considering the surrogate and internal standard recoveries were within acceptable method limits (35–100 percent surrogate recovery and 50–200 percent internal standard response) and the higher relative uncertainties at low concentrations close to the MDLs. Additionally, analyte recoveries are within the Laboratory Control Sample acceptable range (20–115 percent) of the U.S. Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories (DoD 2006). Part of the analyte loss may be attributed to the excessive evaporative concentration needed to achieve the required 1 µg/kg detection limit. Concentration activities also tend to concentrate interferences, which were observed on the GC-NPD secondary column. Co-extracted interferences may be cleaned up by EPA Methods 3610 or 3620, although further work is required to verify analyte recovery and cleanup effectiveness.

The MDL study was repeated using 75 percent hexane/25 percent acetone (v/v) to determine the effect of various solvent mixtures on NDMA extraction efficiency. NDMA analyzed by GC-MS/SIM was not recovered from the solid matrices using 75 percent hexane/25 percent acetone (v/v) as the extraction solvent. This solvent mixture yielded no analyte recovery, although the surrogate and internal standards were within acceptable limits. The lack of analyte recovery is likely caused either by hexane/acetone being a poor extraction solvent or the analyte being lost during the evaporative concentration step because of the relatively lower vapor pressure of hexane compared with methylene chloride. In either case, the lack of analyte recovery supports the use of the methylene chloride/acetone extraction solvent mixture.

Concerns over potential interferences from propionic acid, on analyte ions at m/z 74 and 45, were not observed using a standard of 200 µg/mL propionic acid spiked with 0.10 µg/mL NDMA. The percent recoveries observed for ions 74 and 42 were 80 and 110 percent, respectively. The retention time of propionic acid is 3.22 minutes versus 2.54 minutes for NDMA, indicating that chromatographic separation is sufficient to eliminate this potential interference at ratios of 1:2000.
Additionally, propionic acid did not interfere with NDMA determination by GC-NPD at the same ratio, due to chromatographic separation and specificity of the detector.

APPLICABILITY: The techniques described above were modified from standard EPA SW-846 methods, and are therefore relevant to the same types of samples and matrices as the standard matrices. Care must be exercised, however, with these techniques, as the lower detection limits may result in previously unidentified interferences that are not observed at higher method detection limits.

The work described was accomplished with minimal deviation from the established methods to facilitate direct transfer to knowledgeable laboratories performing similar analyses. Both instruments tested were capable of providing MDLs for NDMA in soil matrices below 1 µg/kg. Although analyte recoveries appeared low on several matrices by both instrumentation techniques, most recoveries are within the Laboratory Control Sample (LCS) acceptable range (20-115 percent) of the DoD QSM. The LCS is nominally spiked at approximately mid-level of the instrument calibration range; the MDL study reported here was performed at the low end of the instrument calibration range, which would have higher relative uncertainties and indicates acceptable recovery of the analyte in these tests.

Determination of NDMA by GC-MS/SIM suffered from few interferences except for the secondary ion in soil matrices at m/z 42, likely due to hydrocarbon interferences. In general, the GC-NPD has slightly more sensitivity than GC-MS, which may allow for lower detection limits; however, it is also prone to interferences in certain soil matrices from as-of-yet unknown nitrogen or phosphorus containing compounds. The conditions tested for GC-NPD allowed a lower MDL to be calculated for the primary and secondary columns in the hydromatrix samples, though the MDLs could not be confirmed due to interferences on the secondary column in all soil matrices.

SUMMARY: Methods are described for the determination of NDMA in soils by GC-MS and GC-NPD at 1 µg/kg or less. The techniques described are modifications of standard EPA procedures, including sample evapoconcentration and low concentration instrument calibration, to achieve the low detection limit. Sample interferences from matrix constituents are observed, necessitating that analysts experienced in similar analyses perform the described techniques. However, with appropriate precautions, NDMA can be detected in soil at levels below 1 µg/kg.

ADDITIONAL INFORMATION: This technical note was prepared by Dr. Anthony J. Bednar, research chemist, Environmental Laboratory (EL), U.S. Army Engineer Research and Development Center (ERDC) (Anthony.J.Bednar@usace.army.mil), Richard Karn, SpecPro, Inc., Drs. Chung-Rei Mao, David Splichal, Douglas Taggart, and Kevin Coats, of the U.S. Army Corps of Engineers Environmental and Munitions Center of Expertise (USACE EMCX). The study was conducted in support of FUDS activities. This technical note should be cited as follows:

REFERENCES


NOTE: The contents of this technical note are not to be used for advertising, publication or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such products.
Appendix A
Scope of Work

HTRW CX
Project Management Plan
FY2007 Formerly Used Defense Sites (FUDS)
Extraction Efficiency and Analytical Determination of N-Nitrosodimethylamine in Soils
01-02-07

Introduction: This activity is being performed under the management and control of the Hazardous, Toxic, and Radioactive Waste Center of Expertise (HTRW CX) as a HQUSACE approved activity in the FY2007 FUDS Management and Support Fund Allocation. The work will be conducted at the Engineer Research and Development Center, Environmental Laboratory, Environmental Chemistry Branch. The goal of the project is to determine an optimal extraction and analytical protocol for the determination of NDMA in soil matrices with Method Detection Limits of less than 1 µg/Kg.

Title. Extraction Efficiency and Analytical Determination of N-Nitrosodimethylamine (NDMA) in Soils.

Scope: NDMA has been shown to be a significant carcinogen at extremely low concentrations. Research to date has been performed exclusively in water matrices (treated wastewater effluents, drinking water, and contaminated groundwater) with limited data for contaminated soils. As a future Munitions Constituent (MC) of concern for the Military Munitions Response Program (MMRP), reliable extraction and analysis procedures for detection of NDMA using standard preparation equipment and analytical instrumentation found in environmental laboratories needs to be developed. Various extraction solvents will be used to determine the maximum extraction of NDMA from soils. Instrument parameters will be optimized to determine the minimal amount of NDMA detectable on a standard Gas Chromatograph/Mass Spectrometer (GC/MS) using Selective Ion Monitoring (SIM) mode and on a standard GC using a selective Nitrogen-Phosphorus Detector (NPD). Potential interferences from other contaminants found in field samples will be thoroughly investigated for corrective actions. The ultimate goal is to develop a reliable method protocol with a detection limit of less than 1 µg/kg in common real-world soil matrices.

PDT: Douglas Taggart, Anthony Bednar, Richard Kam, Kevin Coats, and Chung-Rei Mao

Method of Accomplishment: The method development for NDMA will be conducted at the Environmental Chemistry Branch facility in Vicksburg, MS, by Federal and Contractor Employees. The personnel performing the method development have over 30 years combined experience in development of extraction and analytical procedures for organic contaminants. Based on prior experience, it is hypothesized that a modification of EPA SW-846 method 3545A using Pressurized Fluid Extraction for extraction of NDMA from soils will be the preferred method. Analysis using GC/MS with SIM detection will be compared with analysis using GC with a selective NPD detector and dual column confirmation. Known interferences from compounds such as propanoic acid on
Mass Selective Detector will be overcome through a combination of chromatographic optimization and use of multiple ion measurements, as well as comparison with the GC-NPD method.

Method Detection Limits and percent recoveries at the quantitation limits will be determined for the analyte of interest by spiking onto sodium sulfate, a clean silty loam soil from Vicksburg, MS, a loamy Grenada Loring Soil, and a clayey soil with > 50 percent clay.

**Budget:** $46,000.

**Schedule:** Analytical method development with short-term Method Detection Limits will be finished by the end of the 3rd quarter, FY07, the final report will be prepared during the 4th quarter, FY07.

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**Obligation and Expenditure Schedule:** All funds received will be processed through the Environmental Chemistry Branch’s Revolving Fund and will be completely obligated and expended prior to the end of FY07.

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[Signature]
Chung-Rei Mao
Chemist

**CC:**
PDT Members
FUDS Program Manager
HTRW CX Branch Chief of Team Lead
HTRW CX Director
MMCX Director
Appendix B
Chromatograms

NDMA Chromatogram Supplemental Information

1) All GC-MS and GC-NPD chromatograms Y-axes are instrument response and X-axes are time (min).

2) All GC-MS data are reported for the m/z 74 ion, m/z 42 is used for confirmation and interference observations. Many soil matrices have m/z 42 off scale of the m/z 74 ion, and are therefore not shown.

3) Analyte retention time shifts are the result of daily column maintenance, such as injection liner changes and cutting the column to remove contaminated and damaged sections.

a. Hydromatrix, Vicksburg soil, and Grenada Loring soil samples were analyzed by GC-MS on March 14, 15, and 16, 2007; Fat Clay samples were analyzed by GC-MS on March 20 and 21, 2007.

b. Hydromatrix and Vicksburg soil samples were analyzed by GC-NPD on July 7, 2007; Grenada Loring soil and Fat Clay samples were analyzed by GC-NPD on July 24, 2007.

NDMA 2.0 µg/mL CCV standard, GC-MS
Equivalent to 67 µg/kg in a solid sample

[Graph showing chromatogram data]
Hydromatrix Method Blank, GC-MS

NDMA in Hydromatrix 1.67 µg/kg, GC-MS
NDMA in Hydromatrix 2.33 µg/kg, GC-MS

Grenada Loring Soil Method Blank, GC-MS
NDMA in Grenada Loring Soil 1.67 µg/kg, GC-MS

Abundance

Ion 74.00 (73.70 to 74.70): S10.D
Ion 42.00 (41.70 to 42.70): S10.D

NDMA in Grenada Loring Soil 2.33 µg/kg, GC-MS

Abundance

Ion 74.00 (73.70 to 74.70): S04.D
Ion 42.00 (41.70 to 42.70): S04.D
ERDC Soil Method Blank, GC-MS

NDMA in ERDC Soil 1.67 µg/kg, GC-MS
NDMA in ERDC Soil 2.33 µg/kg, GC-MS

ASTM Fat Clay Method Blank, GC-MS
NDMA in ASTM Fat Clay 1.67 µg/kg, GC-MS

NDMA in ASTM Fat Clay 2.33 µg/kg, GC-MS
NDMA 0.1 µg/mL, GC-NPD
Equivalent to 3.3 µg/kg in a solid sample
Hydromatrix Method Blank, GC-NPD

NDMA Hydromatrix Chromatogram, GC-NPD
NDMA in ERDC Soil Chromatogram, GC-NPD

NDMA in ERDC Soil 2.33 µg/kg, GC-NPD
Grenada Loring Soil Blank Chromatogram, GC-NPD

Grenada Loring Soil Method Blank, GC-NPD
NDMA Grenada Loring Soil Chromatogram, GC-NPD

Response

Signal: 048.DINPD1A.CH

Response

Signal: 048.DINPD2B.CH

Response

Signal: 048.DINPD1A.CH

Response

Signal: 048.DINPD2B.CH
ASTM Fat Clay Blank Chromatogram, GC-NPD

ASTM Fat Clay Method Blank, GC-NPD
NDMA in ASTM Fat Clay 2.33 µg/kg, GC-NPD