

## MuniRem Remediation – Lessons Learned

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### ***ABSTRACT***

*Several soil remediation processes were investigated to mitigate the environmental impacts of energetic materials in military ranges and training areas. However, very few efforts were devoted to assess the sample preparation and analytical chemistry of soils undergoing remediation, which is the objective of this work.*

*Laboratory experiments were performed with soils contaminated with 2,4,6-trinitrotoluene (TNT) that were exposed to MuniRem™. To mimic realistic remediation conditions, TNT was ground to particles smaller than 1 mm prior their mixing with soil. After the duration of the treatment, the samples were analyzed following SW-846 U.S. Environmental Protection Agency Method 8330B.*

*Results indicate that, although a significant portion of TNT was readily degraded upon contact with the remediation reagents in the soil, a small part of TNT (15%) was degraded during the extraction, after soil collection. The amount of MuniRem™ required to completely degrade 10 mg TNT dispersed in 50 to 100 g sand varied from 500 mg for jars experiments to 3000 mg for small columns experiments. Moreover, a difference as large as 40% degradation was observed between samples located at the top of the column and those located near the bottom. Finally, a 20% increase in the amount of water added to the column resulted into a 15% increase of degradation.*

*From these findings, it appears crucial to develop more efficient soil sample treatments that will successfully neutralize remediation reagents and prevent additional degradation from happening during the extraction process, therefore leading to a more accurate determination the remediation efficiency.*

## 1.0 INTRODUCTION

It is well known that Energetic Materials (EM) tend to accumulate on the soil surface of military Ranges and Training Areas (RTA) and sometimes leach into nearby surface water and groundwater, potentially causing adverse environmental impacts or health effects and even trigger legal issues if EM concentrations are above environmental or health criteria.

To address this issue, several biological, physical, chemical or thermal soil and water remediation processes were investigated (Kalderis et al., 2011). The success of a specific remediation methodology is dependent on several factors, such as the type of contaminants, their depths, their degradation pathways, their physical and chemical properties, the type of soil, the proximity of sensitive fauna, flora or human receptors, etc. A risk assessment must be performed prior to field trial to evaluate if the remediation could lead to additional potential adverse environmental impacts or health effects. For example, a chemical remediation producing a soluble degradation product, toxic for aquatic species, in the vicinity of a water source, would not constitute a viable option. Remediation strategies must also be cost-effective and be easily applicable even in remote location, which can constitute a challenge in military RTAs. Examples of remediation strategies that gained popularity in recent years due to their relatively low cost, their ease of use and their claimed efficiency, are MuniRem™ and hydrated lime, which rely on chemical reduction with dithionite (Boparai et al., 2008; Nzungu, 2014), or on the basic hydrolysis of EM (Davis et al., 2006; Hansen et al., 2003; Larson et al., 2007, 2008a, 2008b; Martin et al., 2012), respectively.

The efficiency of remediation methods is generally assessed with the SW-846 U.S. Environmental Protection Agency (USEPA) Method 8330B, which prescribes to dry the entire samples at room temperature until constant weight and to remove particles larger than 2 mm by sieving. The dry samples are then pulverized to reduce the homogeneity using a ring puck mill, as mechanical grinders, mortar and pestle are not effective (Walsh et al, 2002). The subsample for extraction is then built by spreading the entire sample onto a clean surface and collecting at least 30 different increments. The extraction is then performed by shaking 10 g of sample into 20 mL of acetonitrile for 18 hours. The extract is then filtered through a 0.45 micron Polytetrafluoroethylene (PTFE) filter and analyzed by High Pressure Liquid Chromatography (HPLC).

However, the effect of the close contact of the remediation reagent and the energetic materials during the whole sample preparation process and analysis has, to the best of our knowledge, seldom been documented. Larson et al. (2012) reported that a significant part of the energetic material degradation occurred during sample preparation and analysis when hydrated lime was not properly neutralized before the extraction, thus leading to overestimated efficiency or, as mentioned by the authors, to the “report of false degradation as legitimate results”. Although the occurrence of degradation in the absence of a mobile phase (i.e., in dry samples) is not probable, the degradation could possibly continue during the drying step (wet samples), the extraction step (acetonitrile) or the analysis step (methanol/water). Additional degradation could also be induced by the homogenization process, which potentially could, for example, produce more heat or more mechanical pressure than in the absence of remediation reagent. This would lead to irreproducible and unrepresentative results, and to an overestimation of the remediation efficiency.

The main objective of this paper was therefore to verify if additional degradation occurred during sample preparation of soils exposed to remediation reagents, and in the affirmative, to find ways to prevent any unwanted degradation from happening. To achieve this goal, samples of known energetic materials concentrations were prepared by adding 2,4,6-trinitrotoluene (TNT) to general-purpose sand, which was then extracted and analyzed as would be an EM-contaminated soil sample, using SW-846 EPA method 8330b (USEPA, 2006). Soils were spiked with EM particles smaller than 1 mm, which were then dispersed in the soil. This spiking method was deemed more representative of actual RTAs' contaminated soil than spiking clean soils with energetic materials already dissolved in an organic solvent, which may lead to the formation

of a very thin energetic material coating around soil particles with a large surface area (and a greater dissolution rate than 1 mm particles) in soils. Contaminated soils were then exposed to MuniRem™, a dithionite-based remediation reagent advertised by MuniRem Environmental (Duluth, Georgia, USA). Bench scale treatability tests were performed as recommended by the manufacturer.

## **2.0 METHODOLOGY**

### **2.1 Manufacturer's Recommended Bench Scale Treatability Tests**

Five types of MuniRem™ are commercially available. MuniRem-R811E, which also contains lime as one of the major ingredients, is the manufacturer's work horse (sic), the most versatile MuniRem™ product on the market, used for TNT, 1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), lead azide, etc. MuniRem-R541E is used to neutralize and destroy black powder, Composition D, lead styphnate, ANSol, ANFO, etc. MuniRem-R532E is used for propellant destruction. MuniRem-Foam is used to accelerate the destruction of insoluble and poorly soluble explosives such as pentaerythritol tetranitrate (PETN), C4, etc., and may be combined with R811E and R532E for higher efficiency. MuniRem-FE is used to accelerate the destruction of a large mass of bulk explosives.

Prior to field trial, the manufacturer recommends performing bench scale treatability tests using a two-step process that consists of identifying the most effective MuniRem™ product for degrading the energetic materials of concern in a given type of soil, followed by a dose optimization process.

Prior to laboratory testing, information on the concentration of energetic materials in the soil, on the type of soil (clay rich or clay poor), on its water-holding capacity (field capacity) and on its pH must be collected.

#### **2.1.1 Selection of the Best MuniRem™ Formulation**

According to the manufacturer's instructions, the methodology for selecting the best MuniRem™ formulation consists of adding the same mass of well homogenized EM-contaminated soil in appropriate containers, followed by the same mass of MuniRem™ reagent, except for the untreated control sample. After mixing the soil and the MuniRem™, enough water is then added to produce slurry. After 24 hours, the samples are submitted to the laboratory for analysis. The results indicate which type of MuniRem™ is the best formulation for the explosives of concern and the soil type.

#### **2.1.2 Dose Optimization**

According to the manufacturer's instructions, the methodology for dose optimization is similar to that of MuniRem™ selection described in section 2.1.1, with the exception that a different weight of the same MuniRem™ is used instead. More precisely, the selected MuniRem™ formulation is weighed and added to containers already filled with well homogenized EM-contaminated soil. The suggested concentrations vary between 1.25 and 20 times the concentration of energetic materials in the soil. After mixing the soil and the MuniRem™, enough water is then added to saturate the soil and produce slurry. After 72 hours, the samples are submitted to the laboratory for analysis. The results are used to generate a plot of mass of energetic materials removed vs. mass of MuniRem™ reagent.

## **2.2 Laboratory evaluation of MuniRem**

### **2.2.1 Materials**

Acetonitrile (ACN), grade Optima, was obtained from Fisher Chemical. Ethyl acetate (EA), grade Suprasolv for Gas Chromatography/Mass Spectrometry (GC/MS), was purchased from EMD Millipore. Methanol, grade Optima for Liquid Chromatography/Mass Spectrometry (LC/MS), was obtained from Fisher Chemical. Water was demineralized using the NANOpure system from Barnstead. The sand used for the experiments was purchased from Témisca Inc (St-Bruno-de-Guigues, Qc, Canada). MuniRem™ (Formulation MRM-R811E (MRE-SAM-022)) was obtained from MuniRem Environmental (Duluth, GA, USA).

A solution of 3,4-DNT (7.5 mg/mL) was used as an internal standard.

### **2.2.2 Selection of the Best MuniRem™ Formulation**

MuniRem™ R-811E was selected based on the manufacturer's recommendations. No laboratory tests were performed to choose the most suitable selection.

### **2.2.3 MuniRem Dose Optimization**

#### *2.2.3.1 According to the Manufacturer's Recommendations*

Sand (50 g), ground TNT (10 mg) and MuniRem™ were precisely weighed into a 120 mL amber jar. After swirling the solid mixture in the jar, the soil was brought to field capacity with the slow addition of 13 mL of demineralized water, followed by the addition of up to 450 mg of MuniRem™. The jar was closed with a PTFE screw cap and left in the dark at room temperature for up to 24 h. Each container was then filled with 60 mL ACN or EA and agitated in a shaker for 30 min. The extract was then filtered with a 0.45-um PTFE Whatman syringeless filter device (autovial) in an amber vial sealed with a PTFE cap/silicone septum (Qorpak, Fisher Scientific). Then, 2.5 mL of this extract was transferred into a 16 x 100 mm borosilicate disposable culture tube (VWR) containing 100 µL of a standard solution of 3,4-DNT. The extract was then evaporated to dryness using a Zymark apparatus, and then filled with 2.0 mL ACN and vortexed. This solution (20 µL) was then added to a LC vial containing 980 µL of a 50/50 methanol/water mixture and analyzed by HPLC. Experiments were performed in duplicate.

#### *2.2.3.2 Small Column Testing*

This test was designed to mimic as closely as possible actual field conditions.

A disposable 50 mL syringe (Becton, Dickinson and Company) equipped with a 0.45 microns 25 mm PTFE filter (PALL Corporation) was placed in a vertical position on a Sep-Pak support, as shown in Figure 1. The syringe was then filled with approximately 100 g (precisely weighed) of sand which was somewhat compacted by slightly hitting the syringe 5 to 10 times. Then, 10 g of precisely weighed TNT was added to the top of the syringe and thoroughly mixed on the top cm with a dessication needle. MuniRem™ (between 40 and 5000 mg) was then precisely weighed, added to the top of the syringe and thoroughly mixed with the same dessication needle that was used to mix TNT. The soil was brought to field capacity by the slow addition of 25 mL of demineralized water, covered with a polyethylene film, and left in the dark at room temperature for up to 72 h. Experiments were performed in duplicate.

After the completion of experiments, the top 5.5 cm of soil was removed from the syringe and placed into a 120 mL amber jar equipped with a PTFE screw cap, while another jar was used for the remaining soil in the syringe. Each container was then filled with 60 mL ethyl acetate and agitated in a shaker for 30 min. The extract was then filtered with a 0.45- $\mu$ m PTFE Whatman syringeless filter device (autovial) in an amber vial sealed with a PTFE cap/silicone septum (Qorpak, Fisher Scientific). Then, 2.5 mL of this extract was transferred into a 16 x 100 mm borosilicate disposable culture tube (VWR) containing 100  $\mu$ L of a standard solution of 3,4-DNT. The extract was then evaporated to dryness using a Zymark apparatus, and then filled with 2.0 mL acetonitrile and vortexed. This solution (20  $\mu$ L) was then added to a LC vial containing 980  $\mu$ L of a 50/50 methanol/water mixture and analyzed by HPLC.



**Figure 1. Small column setup.**

#### **2.2.4 Analyses**

Analyses were conducted using an Agilent Technologies LC series 1100 High Performance Liquid Chromatography (HPLC) equipped with a Supelcosil LC-18 column (25 cm  $\times$  3 mm packed with 5  $\mu$ m particles). The column was maintained at 50.5°C and the flow rate at 0.6 mL/min. A gradient elution method was used in which the initial methanol/water (30:70) was maintained for 2 min, increased to 43/57 for 13 min and finally increased to 100/0 for 12.5 min.

The sample injection volume was 42.0  $\mu$ L. The photodiode array (PDA) detector allowed analyses at four specific wavelengths for optimal light absorption of each analyte, or group of analytes: 214 nm (nitroglycerin); 230 nm (HMX, RDX, 1,3,5-TNB (1,3,5-trinitrobenzene), tetryl, TNT, ADNTs (amino-dinitrotoluenes)); 245 nm (1,3-dinitrobenzene (1,3-DNB), dinitrotoluenes (DNTs) such as 2,4-dinitrotoluene and 2,6-dinitrotoluene); 275 nm (nitrotoluenes (NT) such as 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT), and 3-nitrotoluene 3-NT). A sample changer with refrigerated sample tray keeping samples in the dark at 4.0°C was used. Agilent OpenLab software suite was used to operate the HPLC and acquire data.

### 3 MUNIREM™ DOSE OPTIMIZATION RESULTS

#### 3.1 Manufacturer's Recommended Method

As reported in Figure 2, that shows the results of each single test that were performed, the quantity of MuniRem™ required to completely degrade ground TNT in a sandy soil was found to vary with the extraction solvent. Indeed, when the samples were extracted in acetonitrile, TNT was completely degraded after the addition of 300 mg of MuniRem™. However, only 85% of TNT was degraded in the presence of 300 mg of MuniRem™ when the extraction was performed in ethyl acetate. The complete degradation of TNT was never reached when ethyl acetate was used as the extraction solvent, indicating that part of the degradation occurred during the extraction step in acetonitrile. Based on the obtained results, it is estimated that approximately 500 mg MuniRem™ would be required to completely degrade TNT.

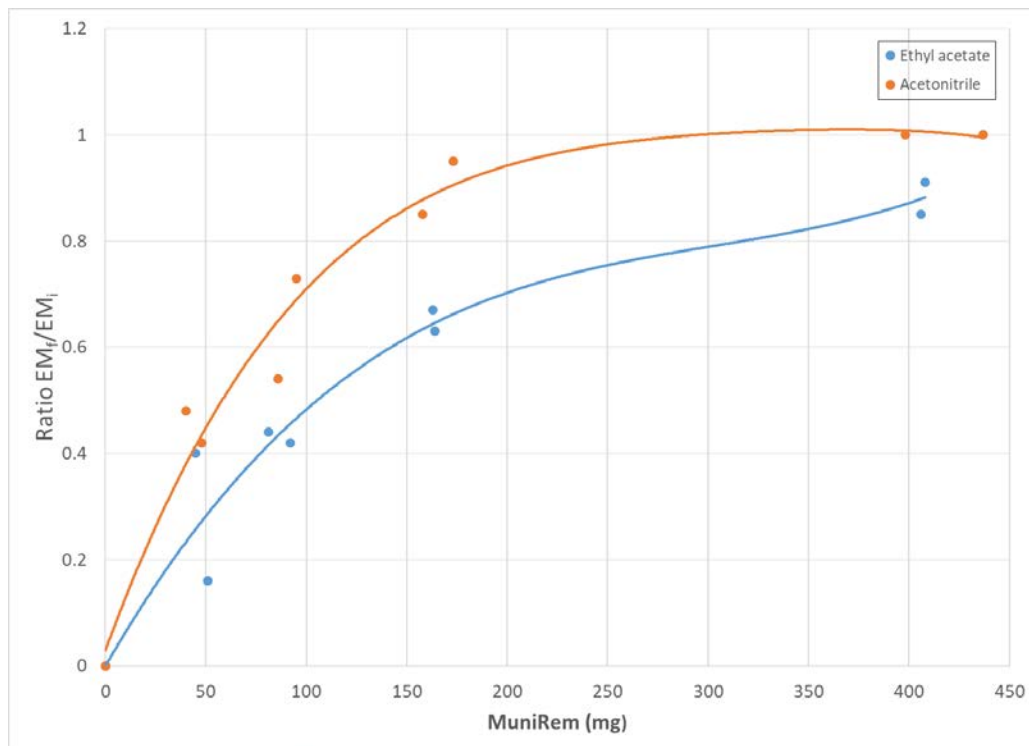


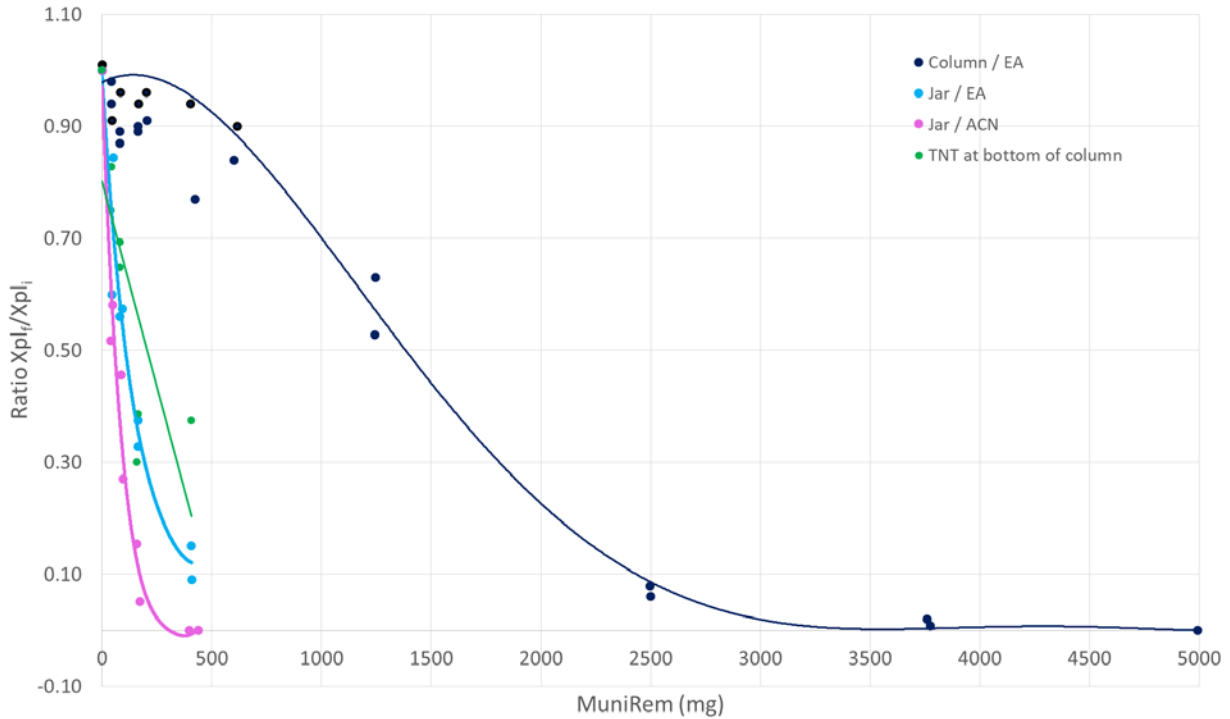
Figure 2. MuniRem™ dose optimization for TNT-contaminated soil after extraction in EA and ACN.

The enhanced degradation of TNT during extraction with acetonitrile might potentially be explained by the higher solubility of dithionite and lime, which are the major components of formulation R811-E, in the miscible mixture of acetonitrile and water than in ACN or EA alone. Similar results were reported by Larson et al. (2012), who indicated that a significant part of the energetic material degradation occurred during sample preparation and analysis when hydrated lime was not properly neutralized before drying the samples and extracting with ACN. In their case, additional degradation probably also occurred during the drying step.



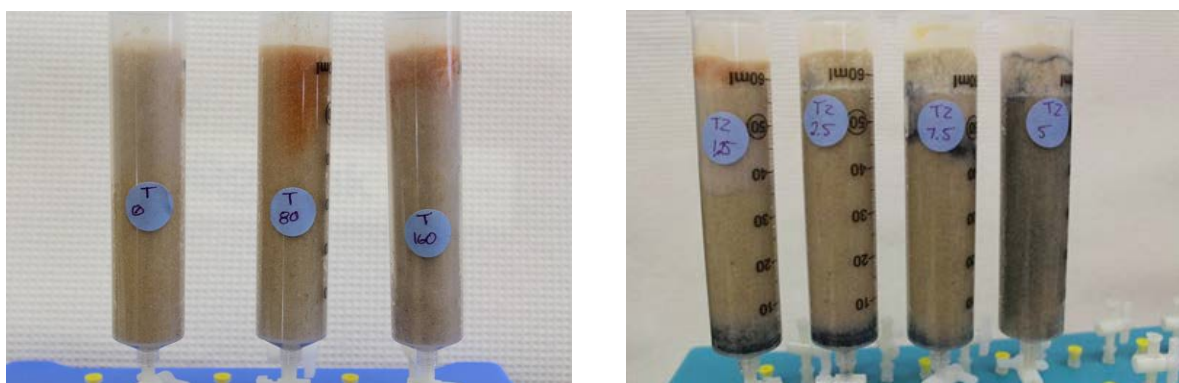
### 3.2 Column Tests

As reported in Figure 3, that shows the results of each single test that were performed, the quantity of MuniRem™ required to completely degrade ground TNT in a sandy soil using the small column setup was 3000 mg. This represents nearly 10 times the required quantity to degrade TNT in jars.



**Figure 3. MuniRem™ dose optimization for TNT.**

The main reason for this significant discrepancy could be due to the larger solubility of dithionite (and lime) in water as compared to TNT. Indeed, in the small column setup, the addition and mix of MuniRem™ with the top column soil, humid, probably prompted the preferential dissolution of dithionite in water, causing the denser water at the top of the column to drop at its bottom. This hypothesis is supported by the increasing proportion of black spots observed at the bottom of the column, which seems to be directly related to the amount of added MuniRem™, as illustrated in Figure 4. Another result supporting this hypothesis is the much higher TNT degradation obtained with the same setup, but for which ground TNT was deposited on the soil at approximately 18 mm from the bottom of the column, instead of on top of the column (110 mm from the bottom soil). The drop of denser water at the bottom of jars does not produce as significant an effect as in small columns, as the height of the soil in jars was only of 13 to 14 mm compared to 110 mm for the columns.



**Figure 4. Dose optimization for TNT with 0, 80, 160, 1250, 2500, 3750 and 5000 mg MuniRem™.**

Starting from 3750 mg MuniRem™, black spots were also observed at the top of the column, where TNT was located. This corresponds to the MuniRem™ concentration at which a complete degradation of TNT was observed. The black spots could come from the reaction of MuniRem™ with inorganic impurities in the sand, such as iron.

The reaction in small columns was also performed with a larger volume of water (30 vs 25 mL) to check if a slurry-like matrix could help enhance the degradation reaction. This increased the degradation from 6 to 19% for a quantity of 400 mg MuniRem™.

#### **4 DISCUSSION AND CONCLUSION**

Laboratory experiments indicated that, although a significant portion of the EM was readily degraded upon contact with the remediation reagents in the soil, a small part of the EM was degraded during the extraction step of the sample processing, after soil collection. It is suspected that the remaining dithionite within the soil samples, which is soluble in the extraction solvent, further reacted with the solubilized EM once the extraction solvent was added. This led to a slight underestimation (15%) of the amount of EM remaining in the remediated soils and consequently to an overestimation of the remediation efficiency. The results clearly indicate that acetonitrile should not be used as the extraction solvent when dithionite (and lime) are used as remediation reagents, because the solubility of dithionite in a miscible solution of water and acetonitrile is probably still very high. Other organic solvents immiscible with water, such as ethyl acetate, are better suited for the extraction of energetic material contaminated soil samples containing a water-soluble remediation reagent. In addition, the drying step of samples should be skipped, to prevent degradation from happening on wet soils during the drying process.

Another significant finding is related to the fact that the remediation efficiency was dependent on the type of laboratory setup used for the assessment. Indeed, the amount of MuniRem™ required to completely degrade 10 mg of TNT was estimated at 500 mg for jars and 3000 mg for small columns. It is suspected that, in the small column setup, the addition and mix of MuniRem™ with the top column soil, humid, probably prompted the preferential dissolution of dithionite in water, causing the denser water at the top of the column to drop at its bottom. This information was supported by the fact that TNT located in the lower part of the column was way more degraded than TNT located at the top of the column. These findings indicated the potential presence of preferential infiltration pathways in the columns which would draw solubilized dithionite at the bottom of the column. Although the soil in small columns were not as compact as actual soil from RTAs, preferential infiltration pathways are common in sandy soils, of which are made most of the Canadian RTAs soils. The results obtained in this paper probably reflect more closely what happens in an actual EM-contaminated soil than jar experiments. Indeed, soil that has been thoroughly tilled on the first top



30 cm or that has been wetted and well drenched, as recommended by the manufacturer, is probably characterized by the presence of several preferential paths.

From these preliminary findings, it appears crucial to develop more efficient soil sample treatments that will successfully neutralize and/or decompose the remediation reagents and prevent additional degradation from happening during the extraction process, therefore leading to a more accurate determination the remediation efficiency. Additional R&D is also necessary to better understand the sample preparation and analytical chemistry of soils undergoing remediation, as well as what really happens to actual soils undergoing remediation. Future work should include degradation experiments with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), Composition B, octol, 2,4-dinitroanisole (DNAN), nitrotriazolone (NTO), nitroglycerin (NG) and 2,4-dinitrotoluene (2,4-DNT). It is critical to spike with ground EM, rather than solubilized EM, to mimic as closely as possible actual field conditions. Future work should also include other types of terrain and MuniRem™.

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