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Detection of explosives and their degradation products in soil environments☆

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Abstract

Polynitro organic explosives [hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6-trinitrotoluene (TNT)] are typical labile environmental pollutants that can biotransform with soil indigenous microorganisms, photodegrade by sunlight and migrate through subsurface soil to cause groundwater contamination. To be able to determine the type and concentration of explosives and their (bio)transformation products in different soil environments, a comprehensive analytical methodology of sample preparation, separation and detection is thus required. The present paper describes the use of supercritical carbon dioxide (SC-CO_2), acetonitrile (MeCN) (US Environmental Protection Agency Method 8330) and solid-phase microextraction (SPME) for the extraction of explosives and their degradation products from various water, soil and plant tissue samples for subsequent analysis by either HPLC–UV, capillary electrophoresis (CE–UV) or GC–MS. Contaminated surface and subsurface soil and groundwater were collected from either a TNT manufacturing facility or an anti-tank firing range. Plant tissue samples were taken from plants grown in anti-tank firing range soil in a greenhouse experiment. All tested soil and groundwater samples from the former TNT manufacturing plant were found to contain TNT and some of its amino reduced and partially denitrated products. Their concentrations as determined by SPME–GC–MS and LC–UV depended on the location of sampling at the site. In the case of plant tissues, SC-CO_2 extraction followed by CE–UV analysis showed only the presence of HMX. The concentrations of HMX ($<$200 mg/kg) as determined by supercritical fluid extraction (SC-CO_2)–CE–UV were comparable to those obtained by MeCN extraction, although the latter technique was found to be more efficient at higher concentrations ($>$300 mg/kg). Modifiers such as MeCN and water enhanced the SC-CO_2 extractability of HMX from plant tissues.

Keywords: Soil; Environmental analysis; Explosives

1. Introduction

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6-trinitrotoluene (TNT) are the most commonly used highly energetic compounds in Armed Forces stockpiles (Fig. 1). Contamination of soil and water by RDX, HMX and TNT is widespread and often caused by various military activities [manufacturing, testing and training, demilitarization, open burning/open detonation (OB/OD)] that are considered important for military operations [1–3]. It has been estimated that during the manufacturing of

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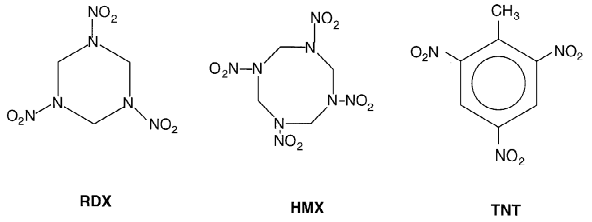

Fig. 1. Chemical structures of hexahydro-1,3,5-trinitrio-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6-trinitrotoluene (TNT).

RDX, up to 12 mg/L may be discharged to the environment in process waste waters [4], whereas a single TNT manufacturing plant can generate over 1.8 megalitres of wastewater per day [5].

Explosives are labile and in the environment can be transformed by sunlight, soil microflora and other indigenous plant species. Also, TNT, RDX and HMX are moderately to weakly soluble in water, 150, 45 and 5 mg/L, respectively [6], and thus can migrate through subsurface soil to cause groundwater contamination. Furthermore, it has been shown that explosives are modestly toxic to aquatic organisms, earthworms, and indigenous soil microorganisms [6–8]. To be able to provide insight into the environmental fate of explosives and the risk associated with their presence, analytical tools capable of measuring these chemicals and their transformation products in various soil environmental media must become available. Presently, chemical and bioanalytical tools, capable of assessing the level of contamination and the hazard of an explosives-contaminated site, are limited. The present study thus describes the use of different extraction techniques, including supercritical fluid extraction with carbon dioxide (SC-CO_2), acetonitrile [US Environmental Protection Agency (EPA) Method 8330] [9] and solid-phase microextraction (SPME), to extract explosives and their degradation products from several environmental samples for subsequent analysis by LC–MS, CE–UV and GC–MS. We used four different environmental samples, including surface and subsurface soils and groundwater obtained from a TNT manufacturing plant and plant tissue samples obtained from plants grown in an anti-tank firing range soil. To validate the SC-CO_2 technique for its extraction efficiency, we repeated the extraction of plant tissues using acetonitrile for subsequent analysis as described by Larson et al. [12] and by EPA Method 8330 [9].

2. Experimental

2.1. Reagents and chemicals

The explosives TNT, RDX and HMX were obtained from the Defence Research Establishment Valcartier (DREV, Quebec, Canada). 2-Amino-4,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT) were from Omega (Quebec, Canada), 2,4-diamino-6-nitrotoluene (2,4-DANT) and 2,6-diamino-4-nitrotoluene (2,6-DANT) were from AccuStandard (New Haven, CT, USA). Na_2SO_4 and acetonitrile (MeCN) were from Fisher Scientific (Montreal, Canada). Carbon dioxide was obtained from Air Products (Allentown, PA, USA). Stock solutions (10 mL of 2 mg/mL) of 2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT were prepared in MeCN.

HMX contaminated soil was obtained from an anti-tank firing range site at Wainright, Canada. Contaminated surface and subsurface soil and groundwater were obtained from a former TNT manufacturing plant at Valleyfield, Canada. Soil sampling at different depths (0 to 1.5 m) was carried out using a backhoe and groundwater was collected from a well (9 m) located close to the soil sampling area using a Waterra (Mississauga, Canada). Further details on soil sampling and collection of groundwater were obtained from drilled wells prepared as described by Pennington et al. [10]. Phytoextraction experiments were carried out in a greenhouse by growing plants in a contaminated soil obtained from a firing range as described previously [11].

2.2. Analysis of soil and plant tissue samples

2.2.1. Sonication with MeCN

Plant tissue extracts from plants (shown in Table 3) grown in contaminated soils were prepared and analyzed using the methods outlined by Larson et al. [12]. Briefly, finely cut samples (ca. 4 g) of the tested plants were suspended in 10–20 mL of ice-cold deionized water and homogenized for sub-

sequent lyophilization prior to sonication with MeCN. The sonicated mixture was then centrifuged and the supernatant decanted, mixed with deionized water and filtered using Millex HV 0.45 μm. In the case of soil and subsurface soil, extraction was carried out as described in EPA Method 8330 [9]. Briefly, soil samples were first passed through a 2 mm sieve and homogenized by grinding with a mortar, then thoroughly sonicated with MeCN for 18 h for subsequent analysis by HPLC–UV (254 nm).

2.2.2. SC-CO_2 extraction

Plant tissue samples from either the leaves, stem or roots were freeze-dried and mixed with sodium sulfate or inert sand ($d < 0.5$ mm) to sufficiently fill the extraction cell (5 mL) for the SFE extractor (Dionex SFE 703). After passing through the extraction cell, SC-CO_2 is allowed to pass through a restrictor wherein SC-CO_2 is depressurized gently to ambient pressure to allow CO_2 gas to escape leaving behind the extracted analytes in specially designed collection vials. Analytes were extracted at 300 atm (280 mL/min gas) for 30 min and collected in vials containing 10 mL MeCN. Extraction was repeated using water (5%, v/w) and MeCN (4%, v/w) as co-solvents. The modifier was either added to the sample in the extraction cell (static addition) or mixed with CO_2 prior to extraction (dynamic addition).

2.2.3. CE–UV analysis of plant tissue extracts

Detection of explosives in SC-CO_2 extracts of plant tissues was performed using either LC–UV or a HP^{3D} CE instrument (Agilent Technologies) coupled with UV detection at 254 nm [11]. The HP^{3D} CE was fitted with a HP G-1600-31232 fused-silica bubble capillary with a total length of 64.5 cm, and an effective length (inlet to detection window) of 56 cm. The voltage was set at 30 kV and the temperature at 25 °C. Samples were injected by applying 50 mbar pressure to the capillary inlet for 5 s. The separation buffer was composed of 2.5 m*M* sodium tetraborate and 12.5 m*M* boric acid (pH 8.5) containing 50 m*M* sodium dodecyl sulfate. Separation time was 8 min with post-conditioning flushes of the capillary after each run in the following sequence: methanol (0.5 min), 0.1 *M* NaOH (0.5 min) and running buffer (3 min) leading to a total analysis time of 12 min.

2.2.4. LC–MS analysis

Degradation products such as the mononitroso derivative of HMX were identified by LC–MS with a Micromass Plattform benchtop single quadrupole mass detector. Analyte ionization was carried out in a negative electrospray ionization [ESI(−)] mode producing mainly the deprotonated molecular mass ion [M − H] as explained by Hawari et al. [13].

2.3. Analysis of groundwater

2.3.1. HPLC–UV

A Waters chromatographic system composed of a Model 600 pump, a Model 717 Plus injector, a Model 996 photodiode-array detector and a temperature control module was used for HPLC–UV analysis. Samples (50 μL) from groundwater were injected directly into a Sulpelcosil C_8 column (25 cm × 4.6 mm, 5 μm). The column temperature was held at 35 °C, the mobile phase composition was water–2-propanol (82:18) and the flow-rate was 1 mL/min. The run time was 40 min. UV detection was carried out using a UV detector at 254 nm. In the case of trace analysis the groundwater sample (500 mL) was first passed through a Sep-Pac Porapac RDX cartridge (Waters) followed by desorption of the collected explosives using MeCN (5 mL) for subsequent analysis by HPLC–UV.

2.3.2. Analysis of surface water for TNT and degradation products using SPME–GC–MS

SPME is a recently discovered technique, which reduces the time required for analysis and enables detection in the μg/L range [14,15]. It is based on the direct adsorption of the analyte from the aqueous phase or the head space of a soil matrix for subsequent desorption into the injector port of a GC for detection. We used fused-silica capillary fibers (1 cm) coated with 85 μm poly(dimethyl)siloxane fitted to an autosampler holder (Supelco, Bellfonte, PA, USA) to adsorb the energetic chemical from contaminated water. Aliquots (2 mL) of water were first filtered (if needed) to remove suspended material prior to SPME analysis. Analytes were extracted (20 min) directly from water onto the fiber and then

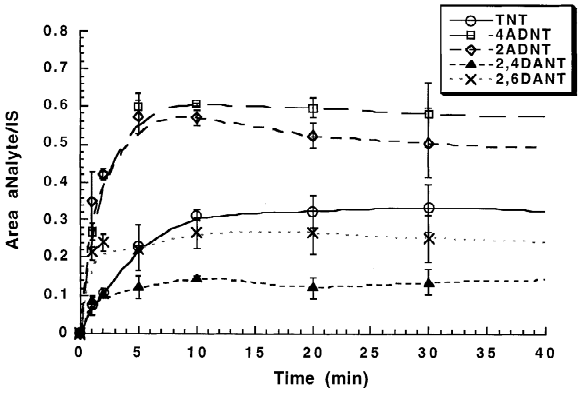

Fig. 2. Representative adsorption isotherms of TNT, 2-ADNT, 4-ADNT, 2,4-DANT and 2,6-DANT using polymethylsiloxane-coated SPME fiber.

thermally desorbed (10 min) inside the GC injector (Varian Saturn II) for detection by MS (SPME–GC–MS). To validate the SPME data we determined the thermodynamic equilibrium for the partitioning of TNT and its amine products (2-ADNT, 4-ADNT, 2,4-DANT and 2,6-DANT) between the aqueous phase and the SPME coating. A 20 min contact time between the analyte(s) and the SPME polymer was found sufficient for equilibrated adsorption of all tested analytes (Fig. 2). Using standard calibration procedures and applying the criteria of a signal-to-noise ratio of 3:1 the detection limits (DLs) for TNT, 2-ADNT, 4-ADNT, 2,4-DANT and 2,6-DANT were found to be 9, 20, 10, 26 and 29 μg/L, respectively. The precision was found to range between 8 and 20% based on 10 SPME–GC–MS determinations of the same standard solution (25 μg/L) for each analyte separately. We obtained a high linear response as indicated by r values of 0.998, 0.997, 0.997, 0.966 and 0.991, respectively, over the concentration range 20 to 800 μg/L.

3. Results and discussion

3.1. Analysis of water and soil samples from a former TNT manufacturing plant

3.1.1. SPME vs. EPA Method 8330

Fig. 3A shows a typical SPME–GC–MS chromatogram of extracted analytes from a contaminated water sample taken from a ditch nearby a former TNT manufacturing plant. For comparison, we analyzed the same sample by HPLC, as shown in Fig. 3B. The detected products included TNT and several of its partially denitrated and reduced amino products such as 2-NT, 3-NT, 4-NT, 2,6-DNT, 2,5-DNT, 2,3-DNT, 2,4-DNT, 3,5-DNT, 3,4-DNT, 4-ADNT and 2-ADNT (Table 1). The SPME–GC–MS concentrations of TNT and its products are summarized in Table 1. For comparison, we included in Table 1 the concentrations of TNT and its products as determined by LC–UV. In general, a correlation factor as high as 90 to 100% was obtained between LC–UV and SPME–GC–MS. Using standard calibration procedures and a S/N ration of 3 we found that the DL by SPME was slightly lower. For example, the DLs for TNT, 2-ADNT and 4-ADNT were 9, 20 and 10 μg/L, respectively, for SPME and 20, 50 and 50 μg/L, respectively, for HPLC.

Surface and subsurface soil and groundwater samples collected from a different location at the former TNT manufacturing plant were also analyzed. Soils were collected at different depths (0 to 1.5 m) and groundwater was pumped out of a monitoring well 9 m deep that was originally excavated to monitor the fate (transport and transformation) of TNT at the site. As Table 2 indicates we found TNT and two of its monoamino derivatives, 2-ADNT and 4-ADNT, in all tested samples (surface and subsurface soils and groundwater). We detected elevated concentrations of TNT, 2-ADNT and 4-ADNT in samples close to the surface, and concentrations rapidly decreased with depth. For example, the concentrations of TNT, 2-ADNT and 4-ADNT in surface soil were 20 256, 42 and 40 mg/kg, which reduced to 26, 1.46 and 1.78 mg/kg and 0.7, 0.6 and 1.06 mg/kg at 1.5 m depth beneath the soil surface and in groundwater, respectively. The detection of TNT and its amine products in subsurface soil and groundwater clearly indicates the potential migration of these chemicals through subsurface soil to reach the water table. Soil–water partition coefficients (K_d) are important physicochemical parameters, which can provide quantitative evidence of the mobility and migration of chemicals from soil through subsurface soil to cause groundwater contamination. For example, TNT is relatively less soluble in water (150 mg/L) with a soil–water partition coefficient (K_d) of

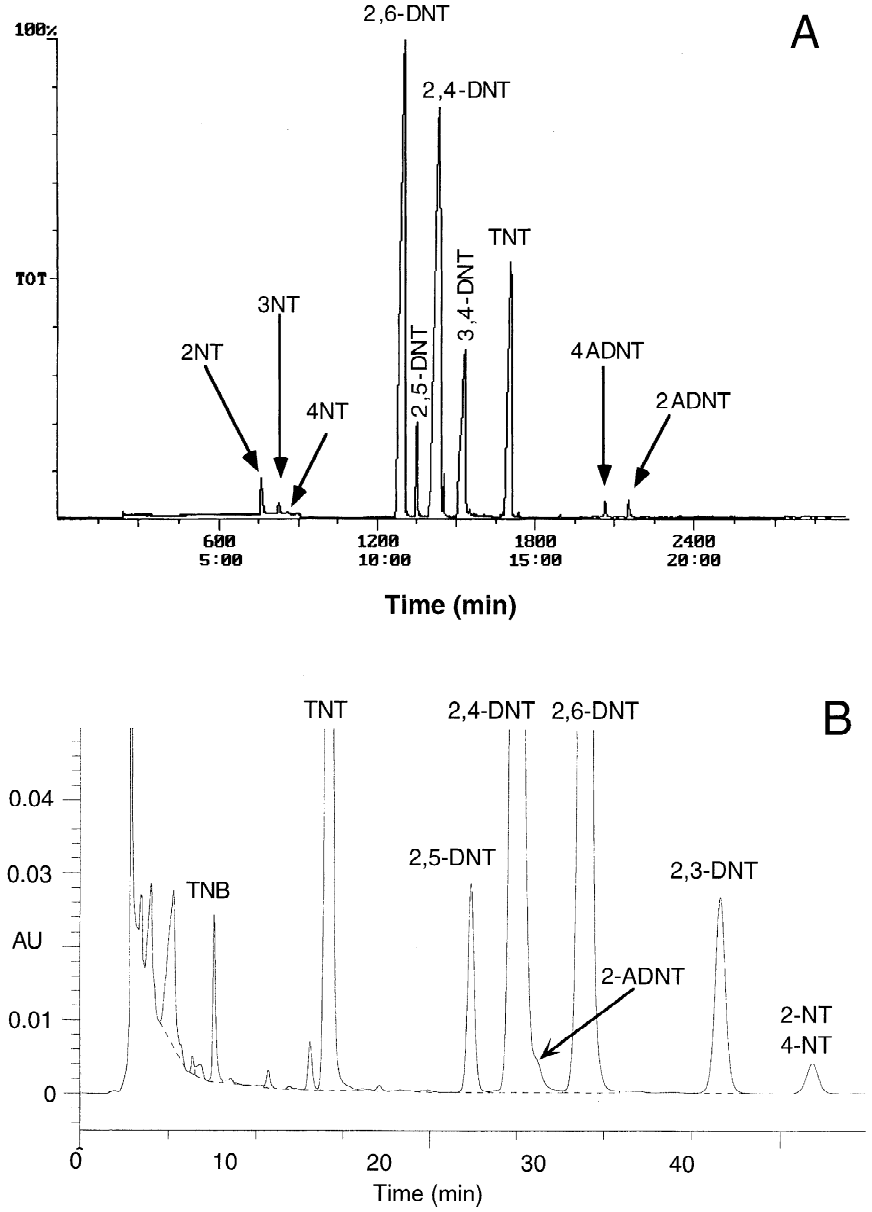

Fig. 3. Analysis of TNT and its derivatives in the aqueous phase of a soil sample obtained from a former TNT manufacturing plant. (A) Typical SPME–GC–MS chromatogram; (B) typical HPLC–UV chromatogram.

6.38 L/kg [16]. Substitution of the $-NO_2$ group with $-NH_2$ is found to increase K_d drastically. For example, the K_d value for 4-ADNT is reported to be 7.91, whereas the further substitution of a second $-NO_2$ group to produce 2,4-diaminonitrotoluene (2,4-DANT) increased the K_d value to 11.96 L/kg [16]. A higher K_d signifies a greater capacity for soil adsorption. In the case of amino derivatives, higher adsorption is caused by strong interactions between the $-NH_2$ groups and soil humic material, therefore making their mobility through subsurface soil much slower compared to TNT.

Table 1
Determination of TNT and its derivatives (mg/kg) in water taken from a ditch nearby a TNT manufacturing plant: SPME–GC–MS vs. EPA Method 8330

Compound	SPME–GC–MS (RSD, %)	HPLC–UV (RSD, %)[a]
2-Nitrotoluene (2-NT)	3.78 (2.26)	2.0 (1.50)
3-Nitrotoluene (3-NT)	1.11 (2.74)	nd
4-Nitrotoluene (4-NT)	0.29 (2.10)	c
2,6-Dinitrotoluene (2.6-DNT)	97.27 (5.40)	100.0 (0.21)
2,5-Dinitrotoluene (2.5-DNT)	8.60 (5.85)	nd
2,3-Dinitrotoluene (2.3-DNT)	[b]	12.6 (0.17)
2,4-Dinitrotoluene (2.4-DNT)	100.49 (4.93)	80.4 (0.03)
3,5-Dinitrotoluene (3,5-DNT)	2.39 (4.87)	nd
3,4-Dinitrotoluene (3,4-DNT)	35.10 (4.56)	[d]
2,4,6-Trinitrotoluene (2,4,6-TNT)	50.16 (3.25)	60.5 (0.09)
4-Amino-2,6-dinitrotoluene (4-ADNT)	0.34 (6.85)	[e]
2-Amino-4,6-dinitrotoluene (2-ADNT)	0.58 (10.1)	[e]

[a] Detected at 254 nm, RSD was calculated based on triplicate analyses. nd, not detected.
[b] 2,3-DNT overlapped with 2,4-DNT.
[c] 2- and 4-NT coeluted.
[d] 3,4-DNT overlapped with 2,6-DNT.
[e] 2- and 4-ADNT coeluted close to 2,4-DNT and 2,6-DNT.

3.2. Determination of explosives in plant tissues

The interest in developing methods for the determination of explosives in plant tissues is related to the fact that phytoremediation is receiving considerable attention as an alternative in-situ remediation technology for the treatment of contaminated soil environments and shallow aquifers [17]. Moreover, phytoremediation represents a very attractive method to be applied in live firing ranges where the presence of unexploded ordances (UXO) prevents the easy use of ex-situ methods.

Table 2
Gradient distribution of TNT and its monoamino products through surface and subsurface soil at a former TNT manufacturing plant. Analyzed using HPLC–UV (254 nm)

Sample	Depth (m)	TNT (mg/kg)	2-ADNT (mg/kg)	4-ADNT (mg/kg)
Surface soil	0.3	20 256	42.0	40.0
Subsurface soil	0.6	50	15.4	14.3
Subsurface soil	0.9	33	3.2	2.3
Subsurface soil	1.2	33	2.2	2.2
Subsurface soil	1.5	26	1.5	1.8
Groundwater	9.0	0.7	0.6	1.1

3.2.1. Sonication versus SC-CO_2

In the present study, SC-CO_2 was employed to extract explosives from various plant tissue samples of plants grown in an anti-tank firing range soil. Besides being solvent free, extraction by SC-CO_2 normally requires less than one-tenth of the time normally required by sonication [18]. Also, carbon dioxide is nontoxic with low viscosity and negligible surface tension. The fluid can thus diffuse through the matrix as a gas and extract the analyte as a liquid at relatively low temperature, thus allowing the recovery of thermally unstable explosives without decomposition.

Table 3 shows the plants used for the phytoextraction of explosives from a contaminated soil. The soil was obtained from a Canadian anti-tank firing range, where a melt-cast explosive composed of 70% TNT, 30% HMX and $<1\%$ RDX was used. A recent characterization study of the site showed the predominant presence of HMX, the concentration of which ranged from 1640 mg/kg near one target to 2.1 mg/kg at a distance of 15 m from the target [19]. As discussed below the other two explosives, RDX and TNT, were apparently removed from their original location by either transformation or transport through subsurface soil.

Table 3
Concentrations of HMX (mg/kg dry mass) in plant tissue extracts of plants grown on an anti-tank firing range soil detected using CE–UV

Sample	EPA 8330[a] (RSD, %)[b]	Supercritical fluid extraction[c] (RSD, %)[b]
Bush bean: viable shoots	31.6 (5.53)	27.7 (7.14)
Bush bean: viable shoots	77.3 (4.92)	82.8 (5.01)
Bush bean: senescent shoots	217 (1.49)	190 (2.31)
Wheat: senescent shoots	206.8 (4.73)	201.9(1.79)
Wheat: viable roots	62.7 (11.3)	67.9 (1.75)
Alfalfa: viable shoots	250.3 (2.04)	223.8 (5.54)
Canola: senescent shoots	336 (2.02)	199.3 (1.56)
Rye-grass: senescent shoots	387.7 (4.42)	316.9 (4.73)
Rye-grass: viable shoots	415.2 (1.31)	224.1 (1.59)
Wheat: senescent shoots	627.4 (1.96)	454.3 (5.13)

[a] Sonication using MeCN.
[b] RSD, relative standard deviation of triplicate analyses.
[c] MeOH added as a co-solvent.

Table 4
Solvent effect on SC-CO_2 extraction of HMX from dry-grass tissue

Dynamic co-solvent[a]	Static co-solvent[b]	HMX (mg/kg dry mass)
None	None	16
Methanol	None	22.5
Methanol	Methanol	129.8
Methanol	Acetone	22.5
Methanol	Acetonitrile	200.2
Acetonitrile	None	8.9
Acetonitrile	Acetonitrile	150

[a] Added to CO_2 prior to extraction.
[b] Added to the sample before CO_2 extraction.

Table 3 illustrates that only HMX could be detected in all tested plants and accumulated mainly in the blade tissue. We found that sufficiently irrigated wheat and rye-grass cultivars accumulated HMX in their senescent leaf tissue to over 500 mg/kg (plant dry mass basis) from soil with an average HMX concentration of 30 mg/kg (dry weight basis) (Table 3). Only the predominance of HMX (0.10 m*M*) is noted, along with the presence of trace amounts of its reduction product octahydro-1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazine (mn-HMX) as determined by LC–MS. The deprotonated mass ion [M−H] was 16 u less than that of HMX, indicating a difference of one oxygen atom between HMX and its nitroso derivative (mn-HMX). We also observed a 46 u mass ion matching that of a $-NO_2$ group. Interestingly mn-HMX was also found in the soil, indicating that HMX did not biotransform but was extracted by all tested plants.

In addition, Table 3 compares extracted amounts of HMX with SC-CO_2 to those obtained using sonication with MeCN. Both sonication with MeCN and extraction with SC-CO_2 of plant tissues were found to be compatible in their extraction efficiency of HMX, although, at higher concentration ($>$300 mg/kg), sonication was found to be slightly better. Previously, we demonstrated that SC-CO_2 recovery of explosives from soil is compatible with that of EPA Method 8330 [20]. The non-polar character of CO_2 limits its affinity for the extraction of polar molecules, but this difficulty can be overcome by adding a suitable co-solvent either directly to the sample (static solvent addition) or to CO_2 (dynamic addition) prior to extraction [20]. We found that the addition of either MeOH or MeCN as a co-solvent to CO_2 enhanced the extraction efficiency of HMX from rye-grass (Table 4). Also, we found that dynamic addition of the co-solvent to CO_2 was more efficient than static addition in enhancing HMX extractability. The most optimized extraction of HMX was obtained when MeOH was used as both static (4%, v/w) and dynamic co-solvent at the same time (Table 4). For example, the extracted amount of HMX by SC-CO_2 alone was $<$20 mg/kg dry mass, which increased to almost 200 mg/kg dry mass when MeOH was added to both SC-CO_2 (dynamic) and to the sample (static)

4. Conclusions

The present extensive analytical study demonstrates that former explosives manufacturing and training sites can have significant amounts of explosives. The detection of explosives in different natural soil environments, including surface and subsurface soil, groundwater and plant tissues, showed that

contamination by explosives is widespread and can reach the water table and also accumulate in plants.

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