

FINAL REPORT

Phototransformation, Sorption, Transport, and Fate of Mixtures of NTO, DNAN, and Traditional Explosives as a Function of Climatic Conditions

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Table of Contents

1. Abstract.....	1
2. Executive summary.....	2
2.1. Introduction	2
2.2. Objectives	2
2.3. Technical Approach.....	2
2.4. Results and Discussion	6
2.5. Implications for Future Research and Benefits	14
3. UV irradiation experiments of DNAN, NTO, and NQ solids under dry and moist conditions	14
3.1. Background.....	14
3.2. Materials and Methods	14
3.3. Results and Discussion	17
3.4. Conclusions	20
4. Outdoor dissolution and phototransformation studies across climate gradient	20
4.1. Background.....	20
4.2. Materials and Methods	21
4.3. Results	28
4.4. Conclusions	51
5. Linking outdoor phototransformation across different locations to amount of sunlight and laboratory measured quantum yields.....	52
5.1. Background.....	52
5.2. Quantum yield calculation.....	52
5.3. Comparing results across different locations.....	59
5.4. Comparing phototransformation observed in laboratory and field studies	62
5.5. Conclusions	64
6. Batch adsorption studies using soil components	64
6.1. Background.....	64
6.2. Materials and Methods	65
6.3. Results	67
6.4. Conclusions	73
7. References.....	74
8. Appendix.....	1
A1. Results of LC-TOF-MS analysis of TNT, DNAN, RDX, NTO, and NQ solutions exposed to sunlight	1

A2. Phototransformation data and calculations.	26
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List of Figures

Figure 2.1. Left panel: UV reactor setup (A) with cover holding up to eight UV bulbs (B) and plate holding 5 mL glass beakers and foil-wrapped controls (C). Right panel: Microscope images of DNAN (A), NTO (B), and NQ (C) crystals that formed upon evaporation of 0.5 mL of 1 g L ⁻¹ DNAN (in acetonitrile), NTO (in acetonitrile), and NQ (aqueous) solutions.	3
Figure 3.1. UV reactor setup (A) with cover holding up to eight UV bulbs (B) and plate holding 5 mL glass beakers and foil-wrapped controls (C).	15
Figure 3.2. Microscope images of DNAN (A), NTO (B), and NQ (C) crystals that formed upon evaporation of 0.5 mL of 1 g L ⁻¹ DNAN (in acetonitrile), NTO (in acetonitrile), and NQ (aqueous) solutions.	17
Figure 3.3. Nitrogen mass balances of DNAN (A), NTO (B), and NQ (C) irradiated under dry vs. moist conditions (n=3). 2-MeO-5-NP = 2-methoxy-5-nitrophenol, 2-MeO-5-NA = 2-methoxy-5-nitroaniline, 2-MeO-3-NP = 4-methoxy-3-nitrophenol, 4-MeO-3-NA = 4-methoxy-3-nitroaniline, and CNQ = cyanoguanidine.	18
Figure 3.4. Nitrogen mass balances of DNAN (A), NTO (B), and NQ (C) foil-wrapped controls irradiated under dry vs. moist conditions (n=3).	19
Figure 4.1. Photographs of experimental setup in three locations, Mt. Lemmon, AZ (top) Oracle, AZ (middle), and Tucson, AZ (bottom).	24
Figure 4.2. Precipitation over duration of experiment for three experimental locations.	29
Figure 4.3. Daily average UV radiation over duration of the experiment in all three locations..	30
Figure 4.4. Dissolution of constituents from IMX-101 formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.	32
Figure 4.5. Dissolution of constituents from IMX-104 formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.	33
Figure 4.6. Dissolution of constituents from Comp B formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations. No TNT was recovered in solution.	34
Figure 4.7. Dissolution of RDX from C4 formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.	35
Figure 4.8. Dissolution of TNT from TNT powder at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.	36
Figure 4.9. Relationship between mass recovery in solution and mass loss of the particles from (top to bottom) IMX-101, IMX-104, Comp B, and C4 formulation particles, as well as TNT powder at Mt. Lemmon (left) Oracle, AZ (middle), and Tucson (right), locations.	39
Figure 4.10. Dissolution of RDX and HMX from IMX-104 formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.	40
Figure 4.11. Relationships between concentrations (mg L ⁻¹) of DNAN products, 2-MeO-5-NP (2-methoxy-5-nitrophenol), 2-MeO-3-NP (4-methoxy-3-nitrophenol), 4-MeO-3-NA (4-methoxy-3-nitroaniline), and 2-MeO-5-NA (2-methoxy-5-nitroaniline) measured on July 16, 2019.	44
Figure 4.12. Solutions resulting from TNT dissolution and phototransformation collected on December 7 th , 2018, first sampling time after placing the particle outdoors. Vials are	

grouped by 3 replicates in each location, at Oracle, AZ (left), Mt. Lemmon (middle) and Tucson (right).....	45
Figure 4.13. Time zero (top row) and end of experiment (bottom row) photographs for particles of IMX-101 of different sizes, small (rep a) on the left, medium (rep a) in the middle and large (rep c) on the right. Ruler division equals 1 mm. All except small particles at the end of experiment are shown at the same scale.	45
Figure 4.14. Dissolution of constituents from small (top), medium (middle), and large (bottom) particles of IMX-101 formulation in Oracle, AZ location.....	47
Figure 4.15. Dissolution of constituents from small (top), medium (middle), and large (bottom) particles of IMX-101 formulation in Oracle, AZ location after normalizing to surface area.	48
Figure 4.16. Dissolution of constituents from small (top), medium (middle), and large (bottom) particles of IMX-101 formulation in Oracle, AZ location after normalizing to surface area (zoom into NQ, DNAN).	49
Figure 4.17. Relationship between mass recovery in solution and mass loss of the IMX-101 particles of small (red), medium (green), and large (blue) size, at Oracle, AZ location. .	50
Figure 5.1. Experimental setup for laboratory phototransformation experiments: left - Rayonet (RPR-100) 8-bulb reaction chamber (Southern New England Ultraviolet Company, Branford, CT) and right - SaniRay chamber by Atlantic Ultraviolet Corporation, Hauppauge, NY.....	53
Figure 5.2. UV-VIS spectra of the nitroguanidine (NQ) at three different concentrations.	54
Figure 5.3. UV-VIS spectra of the 2,4-dinitroanisole (DNAN) at three different concentrations.	54
Figure 5.4. UV-VIS spectra of the 3-nitro-1,2,4-triazol-5-one (NTO) at three different concentrations.	55
Figure 5.5. Molar absorptivities (extinction coefficients) calculated for NQ, DNAN, and NTO based on their UV-VIS spectra as a function of the wavelength.	55
Figure 5.6. Calculated bond dissociation energies and corresponding photon wavelengths required to break the bonds for TNT, DNAN, NTO, and NQ. Energies for bonds in the aromatic and heterocycle rings are not shown because they exceed the maximum energy of the photons in the sunlight reaching Earth surface (500 kJ mol^{-1} or 239 nm). Values for NTO, NQ, and DNAN were reported earlier in Dontsova et al. (2019). All calculations were performed by Diego Troya.	61
Figure 5.7. Map of the global solar irradiance (https://www.nrel.gov/gis/assets/images/solar-annual-ghi-2018-usa-scale-01.jpg)	62
Figure 6.1. Collection locations of the studied soils among others previously used to evaluate interactions of IM constituents with soils.	65
Figure 6.2. Treatments for water dispersible clay (WDC) used in this study. OM: organic matter; Fe _o : oxalate extractable iron; Fe _d : dithionite-citrate extractable iron.	66
Figure 6.3. Adsorption of DNAN from IMX-101 (Q) by water dispersible clay (WDC) and WDC treated to remove organic matter (OM), oxalate extractable iron (Fe _o) and dithionite-citrate extractable iron (Fe _d) for Catlin, Florence, and Sassafras soils.	71

Figure 6.4. Adsorption of DNAN from IMX-104 (Q) by water dispersible clay (WDC) and WDC treated to remove organic matter (OM), oxalate extractable iron (Fe_o) and dithionite-citrate extractable iron (Fe_d) for Catlin, Florence, and Sassafra soils. 72

List of Tables

Table 4.1. Structural and mass information of parent target compounds.	21
Table 4.2. Temperature and rainfall conditions in Hanover, NH, where previous dissolution experiments were conducted, and Mt. Lemmon, Oracle, AZ, and Tucson, AZ, locations of the current study.....	22
Table 4.3. Experimental design and energetic particle weights.	23
Table 4.4. Total weight in grams of low order detonation residue particles of IMX-101 of different size exposed to rainfall and sunlight in Oracle, AZ location.	23
Table 4.5. Solution concentrations following first monsoon storm (July 26, 2019) in three studies locations on elevation gradient, from top to bottom, Mt. Lemmon, Oracle AZ, and Tucson, AZ. Sum of DNAN products includes 2-MeO-5-NP (2-methoxy-5-nitrophenol), 2-MeO-5-NP (4-methoxy-3-nitrophenol), 4-MeO-3-NA (4-methoxy-3-nitroaniline), and 2-MeO-5-NA (2-methoxy-5-nitroaniline).	42
Table 4.6. Total recovery (%) of IMX-101 constituents from small, medium, and large particles before and after normalizing dissolution by the total SA of the particles.	46
Table 5.1. Measured irradiance in the reactor chamber for two different experimental setup options, Rayonet (Becher et al., 2019) and SaniRay.	53
Table 5.2. Calculated average molar absorptivities (extinction coefficients), ϵ_{λ} , in $M^{-1} cm^{-1}$ for three insensitive munitions compounds (IMC) across three different concentrations in 280 to 600 nm range. The standard deviations were found from the average of three concentrations (for DNAN: 5, 7.5, and 15 $mg L^{-1}$; for NTO: 7.5, 10, and 15 $mg L^{-1}$; for NQ: 1.575, 3.15, and 6.3 $mg L^{-1}$).	56
Table 6.1. Physical and chemical properties of the studied soils (Mark et al., 2016).	66
Table 6.2. Extraction of water-dispersible clay from studied soils.	67
Table 6.3. Properties of whole Catlin, Florence, and Sassafras soils, untreated, and treated water-dispersible clay (WDC).	68
Table 6.4. Freundlich adsorption parameters, K_f and n for DNAN adsorption from IMX-101 in treated clays.	70
Table 6.5. Freundlich adsorption parameters, K_f and n for DNAN adsorption from IMX-104 in treated clays.	73

List of Acronyms

ACN	acetonitrile
AOE	acid ammonium oxalate extraction
BET	Brunauer–Emmett–Teller
CNQ	cyanoguanidine
DCE	dithionite-citrate extraction
DI	deionized
DNAN	2,4-dinitroanisole
1,3-DNB	1,3-dinitrobenzene
DNP	2,4-dinitrophenol
ϵ_{λ}	molar absorptivity also called extinction coefficient ($M^{-1}cm^{-1}$)
ESI	electrospray ionization
Fe_d	dithionite-citrate extractable iron
Fe_o	acid oxalate extractable iron
Φ	quantum yield
GC-MS	gas chromatography–mass spectrometry
H₂O₂	hydrogen peroxide
HPLC	high performance liquid chromatography
HPLC-TOF-MS	high-performance liquid chromatography time-of-flight
mass spectrometry	
IM	insensitive munitions
IMC	insensitive munitions compound
IC	ion chromatography
I_{λ}	irradiance, or radiant flux per area
k	first order transformation rate constant (k)
$k_{a,\lambda}^0$	“near-surface” specific rate of light absorption
K_d	soil adsorption coefficient
K_f	Freundlich adsorption coefficient
λ	wavelength of incident radiation (nm)
LC-MS	liquid chromatography-mass spectrometry
LOD	limit of detection

2-MeO-5-NA	2-methoxy-5-nitroaniline
4-MeO-3-NA	4-methoxy-3-nitroaniline
2-MeO-5-NP	2-methoxy-5-nitrophenol
2-MeO-5-NP	4-methoxy-3-nitrophenol
<i>n</i>	exponent in Freundlich adsorption equation
NO₃⁻	nitrate
NQ	nitroguanidine
NTO	3-nitro-1,2,4-triazol-5-one
OC	organic carbon
OM	organic matter
Q	sorption to solid phase (mg/kg)
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
WDC	water-dispersible clay
SERDP	Strategic Environmental Research and Development Program
SPE	solid phase extraction
SSA	specific surface area
TFA	trifluoroacetic acid
1,3,5-TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
UV	ultraviolet
UV-VIS	ultraviolet-visible

Keywords

Photolysis; Phototransformation; Insensitive munitions; Energetic compounds; Explosive formulations; Dissolution

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1. Abstract

Introduction and Objectives. Project ER-2727 examines what happens to energetic compounds in the field when they are exposed to sunlight, rainfall, and varying temperatures. Most likely route for insensitive and traditional munitions deposition on military training ranges is as residues of low order detonations. The residues are particles that include several energetic components with different properties.

Technical Approach. Project examined traditional formulations like Composition B and C4, with TNT and RDX, as well as recently developed insensitive munitions formulations, IMX-101, and 104 that include nitroguanidine (NQ), 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO). Their dissolution and phototransformation was measured across three locations with different climatic conditions. The project complemented these studies with controlled lab experiments. These measured transformation rates of energetic compounds as a function of amount and wavelength of incident light, whether compounds were in solution or in solid form, in dry or moist conditions, and if they were adsorbed to mineral surfaces. Project also identified products of phototransformation. In addition, ER-2727 looked at adsorption of released compounds to soil and its reactive components to examine mechanisms and factors influencing adsorption. Transport in soils of energetics mixtures resulting from outdoor dissolution and phototransformation was also studied.

Results. The dissolution of energetic compounds followed individual solubilities of the formulation components. NTO dissolved first followed by NQ, DNAN, TNT, and RDX. In two years, up to 96 % of NTO dissolved from IMX-101 particles and only about 5% of DNAN. Dissolution rates increased with decrease in the particle size and this effect could be quantified using calculated surface area of the particles. Dissolution also increased with the amount of precipitation, but relationship was non-linear. Particles in wetter locations dissolved faster possibly due to more frequent rainfall or greater relative humidity between rains.

DNAN, NTO and NQ were shown to transform when exposed to UV light. DNAN transformed to methoxy-nitrophenols, methoxy-nitroanilines, and dinitrophenol; NTO to urazole, nitrate, nitrite, and ammonium, and NQ to guanidine, cyanoguanidine, nitrate, nitrite, and ammonium. Many of these products are more toxic than the parent compounds. Particle wetting did not influence photo-transformation of DNAN, NTO, and NQ, but energetics transformed slower as solids than in solution. For insensitive munitions, about half of particle mass loss was due to phototransformation, and greater loss due to phototransformation was observed for TNT and RDX than IM constituents. However, quantum yields determined in the lab overestimated field rates because light only reached the thin surface layer of the particle.

Batch adsorption studies with soils and soil constituents indicated the important role that phyllosilicate clays play in DNAN adsorption to soils.

Benefits. The project produced data and developed relationships needed to predict the long-term potential of traditional and insensitive munitions to contaminate soil, groundwater, and surface water.

2. Executive summary

2.1. Introduction

Insensitive munitions (IM) are being used on military training ranges along with traditional explosives. While research has provided knowledge about 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO), the behavior of these IM compounds in mixtures resulting from dissolution and phototransformation of IM and traditional explosives has not been extensively studied. In addition, the effect of climatic conditions on the release of DNAN and NTO from formulations has not been examined but is expected to be significant.

2.2. Objectives

The goal of this project was to obtain the data needed to predict the long-term potential of NTO and DNAN to contaminate soil, groundwater and surface water. This project is a continuation of SERDP project [ER-2220](#) that studied dissolution of insensitive munitions under laboratory conditions and at one outdoor site, as well as NTO and DNAN adsorption and attenuation in a variety of soils. The research from this original effort was extended under this project by examining the influence of climate on dissolution and phototransformation of IM and traditional munitions. Reactive soil components, such as organic matter (OM), phyllosilicate clays, and iron oxides, were examined to determine how they contribute to retention of NTO, DNAN, and other IM formulation constituents and what are mechanisms controlling their adsorption.

2.3. Technical Approach

The objectives of the project were addressed with the following tasks: 1) laboratory phototransformation studies to quantify the photolysis of DNAN, NTO, and NQ, work that will allow scaling transformation rates for different climate conditions; 2) outdoor dissolution and phototransformation studies of IM formulations at several locations within an elevation gradient to evaluate the role of climate (rainfall amount and distribution and temperature) on extent of phototransformation; 3) batch adsorption studies using soil components to determine the role of reactive soil constituents in IM attenuation; 4) development of relationships, which use the experimental results to predict the phototransformation, dissolution, and transport behavior of these compounds under a variety of climatic and soil conditions. These tasks are targeted at quantification of solid IM particle phototransformation and dissolution as a function of climate, and characterization of adsorption, attenuation, and transport of released compounds.

To quantify phototransformation of IM constituents under dry and moist conditions, we prepared solid DNAN, NTO, and NQ crystals in triplicate 5 mL glass beakers via precipitation from solution. We then irradiated these samples in a modified Sani-Ray Germicidal Ultraviolet Fixture that houses eight 254 nm, 300 nm, or 350 nm bulbs, representing UV-C, -B and -A, respectively, for either 18 h or 7 d (Figure 2.1). For beakers with moist conditions, we misted them with about 3-5 mg of deionized water once a day using an atomizer spray bottle. In parallel, we ran dry and moist controls wrapped in aluminum foil in the reactor to prevent UV exposure but account for any temperature effects due to heat produced by the UV bulbs. After exposure to UV light, we dissolved the solids and analyzed them using high performance liquid chromatography (HPLC) and ion chromatography (IC). We measured the ultraviolet irradiance in the UV reactor using an optometer.

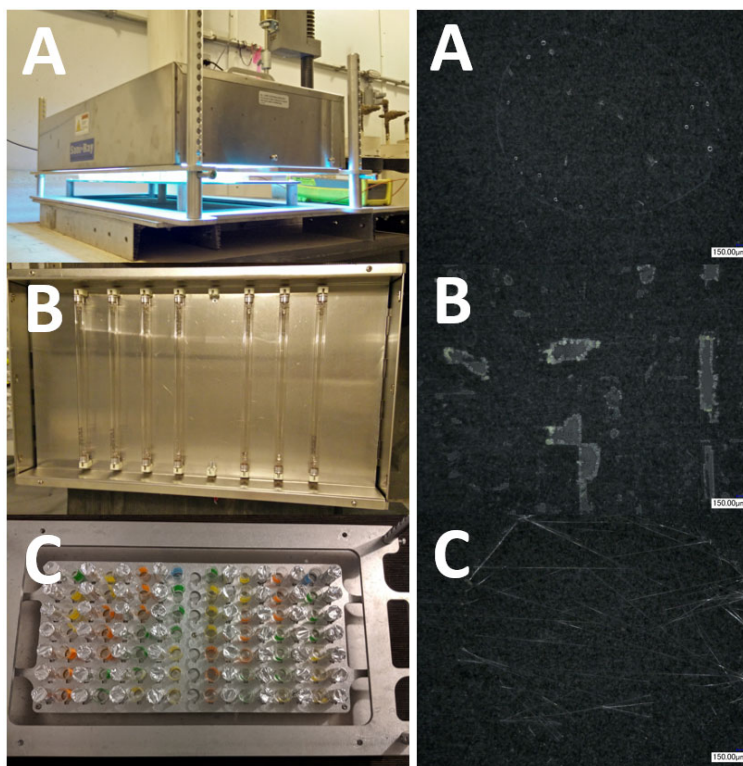


Figure 2.1. Left panel: UV reactor setup (A) with cover holding up to eight UV bulbs (B) and plate holding 5 mL glass beakers and foil-wrapped controls (C). Right panel: Microscope images of DNAN (A), NTO (B), and NQ (C) crystals that formed upon evaporation of 0.5 mL of 1 g L⁻¹ DNAN (in acetonitrile), NTO (in acetonitrile), and NQ (aqueous) solutions.

Table 2.1. Temperature and rainfall conditions in Hanover, NH, where previous dissolution experiments were conducted, and Mt. Lemmon, Oracle, AZ, and Tucson, AZ, locations of the current study.

Location	Average temperature, °F				Annual precipitation	
	January low	January high	July low	July high	inches	mm
Hanover, NH	10	28	59	82	40.11	1019
Mt. Lemmon, AZ	23	49	50	76	29.56	751
Oracle, AZ (Biosphere 2)	35	56	67	92	24.92	633
Tucson, AZ	42	66	76	101	11.92	303

Outdoor dissolution and phototransformation experiments were installed in three locations across the elevation gradient, on top of Mt. Lemmon, Summerhaven, AZ at 9,157 feet above sea level; Biosphere 2, Oracle, AZ at 3,820 feet above sea level; and Tucson, AZ at 2,389 feet above sea level. Climatic conditions are distinctly different between the sites with increase in rainfall and approximately 10 degree decrease in temperature with increase in elevation from site to site (Table 2.1). Comparing with data collected previously in Hanover, NH, and across the three locations in these experiments, allows us to evaluate effect of climate (temperature, rainfall, and sunlight) on energetic particle weathering.

Each site was instrumented to measure solar radiation for the full solar spectrum range and UV light, as well as temperature. IM particles were placed in the Buchner funnels with glass frits (Figure 2.2). Funnels drained into glass bottles housed in the wooden insulated container. Five different materials (IMX-101, IMX-104, TNT powder, Comp B, and C4) were placed at each location, replicated 3 times (a, b, and c). While manufactured IMX-101 and IMX-104, and Comp B residues of low-order detonations were individual particles, due to availability manufactured TNT was a powder and for C4, treatments a and b were mixtures of particles and powder, and C4 treatment c was an individual particle. Comp B and C4 resulted from low-order detonations and were previously exposed to rainfall in outdoor dissolution and phototransformation experiments in New Hampshire (Taylor et al., 2010). In addition, at Biosphere 2 location small, medium, and large particles of IMX-101 resulting from low-order detonations (approximately 0.5 g in each treatment) were also tested.



Figure 2.2. Photograph of experimental setup in Oracle, AZ.

To link outdoor phototransformation across different locations to amount of sunlight they receive we combined measured transformation across different locations and conditions with laboratory measured quantum yields for IMCs. Quantum yields were calculated for NQ, DNAN, and NTO based on phototransformation measurements performed during several laboratory experiments we conducted presented in Chapter 3 of this study and reported earlier (Taylor et al., 2017; Becher et al., 2019; Kadoya et al., unpublished). In order to determine the quantum yields (Φ) of the IMCs, we related experimentally-measured first order transformation rate constants (k) to the “near-surface” specific rate of light absorption ($k_{a,\lambda}^0$) by the molecules of IMCs, using following equation (Rao et al., 2013)

$$\Phi = \frac{k}{\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda}$$

where λ is wavelength of incident radiation (nm).

“Near-surface” specific rate of light absorption is a function of the irradiance (I_{λ}), or radiant flux per area, and molar absorptivity also called extinction coefficient (ϵ_{λ} , $\text{M}^{-1}\text{cm}^{-1}$), or amount of light adsorbed per unit concentration and path length, which we also measured:

$$k_{a,\lambda}^0 = \frac{230 \text{ cm}^3 \text{ L}^{-1}}{6.02 \times 10^{23} \text{ photons mol}^{-1}} \left(\frac{I_\lambda}{\Delta\lambda} \right) \varepsilon_\lambda$$

An optometer and a spectrophotometer were used to measure I_λ and ε_λ values over the UV range for the bulbs centered at 300 and 350 nm. The overall irradiance measured by the optometer was normalized to the spectra provided by the bulb manufacturer, resulting in irradiance values per wavelength. Then, $k_{a,\lambda}^0$ values were determined for each 5 nm interval and summed over the UV range to calculate Φ values. Estimates of k for each of the three outdoor locations were then derived from the experimental Φ values and average $k_{a,\lambda}^0$ values obtained from the SMARTS simulation software.

To determine effect of soil constituents on DNAN adsorption three soils among eleven previously used to evaluate interactions of IM constituents with soils (Dontsova et al., 2014; Mark et al., 2016; Arthur et al., 2017) were used in this study. They differed in texture, pH (which has been shown before to impact adsorption of NTO (Mark et al., 2016), and clay mineralogy. To extract water-dispersible clay ($< 2\mu\text{m}$) soils were exposed to repeated suspension in water and sedimentation. Extracted clay was washed in 1 mol L^{-1} NaCl and treated with 1 mol L^{-1} acetate buffer (pH 5) at 70°C to remove carbonates. It was then subjected to series of treatments described in Figure 2.3. Soils and extracted clays were characterized for external specific surface area (SSA) by nitrogen adsorption (Brunauer–Emmett–Teller, or BET), OC content by combustion, and iron oxides (Soil Survey Staff, 1996).

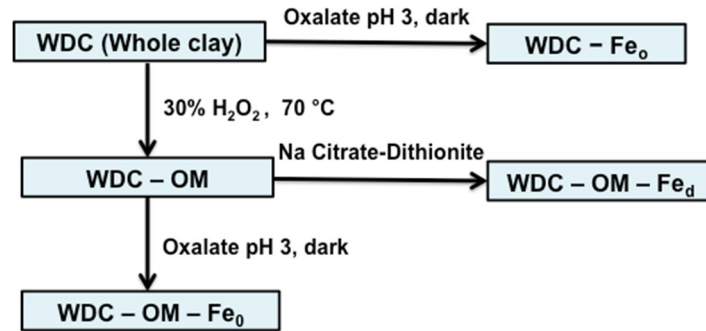


Figure 2.3. Treatments for water dispersible clay (WDC) used in this study. OM: organic matter; Fe₀: oxalate extractable iron; Fe_d: dithionite-citrate extractable iron.

During batch adsorption experiments, IMX-101 and IMX-104 solutions in 0.005 M CaCl_2 were mixed with 0.1 g clay (0.1 g in 4 mL) in glass vials with PTFE-lined screw cap. NaN_3 (0.2%) was added to inhibit microbial activity. Suspensions were agitated on horizontal shaker in the dark at 150 rpm for 24 h to reach equilibrium. IMX-101 and IMX-104 solutions without soil or clay were also included as blank controls and losses were shown to be negligible. All the treatments were carried out in triplicate. After centrifugation, the supernatant was removed and filtered through $0.45 \mu\text{m}$ PVDF membrane before HPLC analysis (Dionex Ultimate 3000 HPLC with a diode array detector, ThermoFisher, MA). Adsorption isotherms were plotted as DNAN sorption to solid phase (Q , mg/kg) versus the aqueous equilibrium concentration (C , mg/L). Linear regression analysis on log transformed solution and clay concentration data was carried out in Microsoft Excel 365 to determine Freundlich adsorption parameters (exponent n and Freundlich adsorption coefficient K_f) for the following equation:

$$\log Q = n \log C + \log K_f$$

2.4. Results and Discussion

2.4.1. UV irradiation experiments of DNAN, NTO, and NQ solids under dry and moist conditions

UV irradiation experiments of DNAN, NTO, and NQ solids under dry and moist conditions indicated that moist and dry particles of DNAN, NTO, and NQ phototransformed at similar rates. DNAN transformed to methoxy-nitrophenols, methoxy-nitroanilines, and dinitrophenol; NTO to urazole, nitrate, and nitrite, and NQ to guanidine, cyanoguanidine, nitrate, and nitrite. Ammonium was not measured but was low in previous experiments in solution (Becher et al., 2019). Rates of phototransformation were lower than measured for same compounds in solution, likely due to limitation on how deep the light can enter the particle. Additional studies are needed to measure light penetration into these compounds in solid form and formulations that contain them.

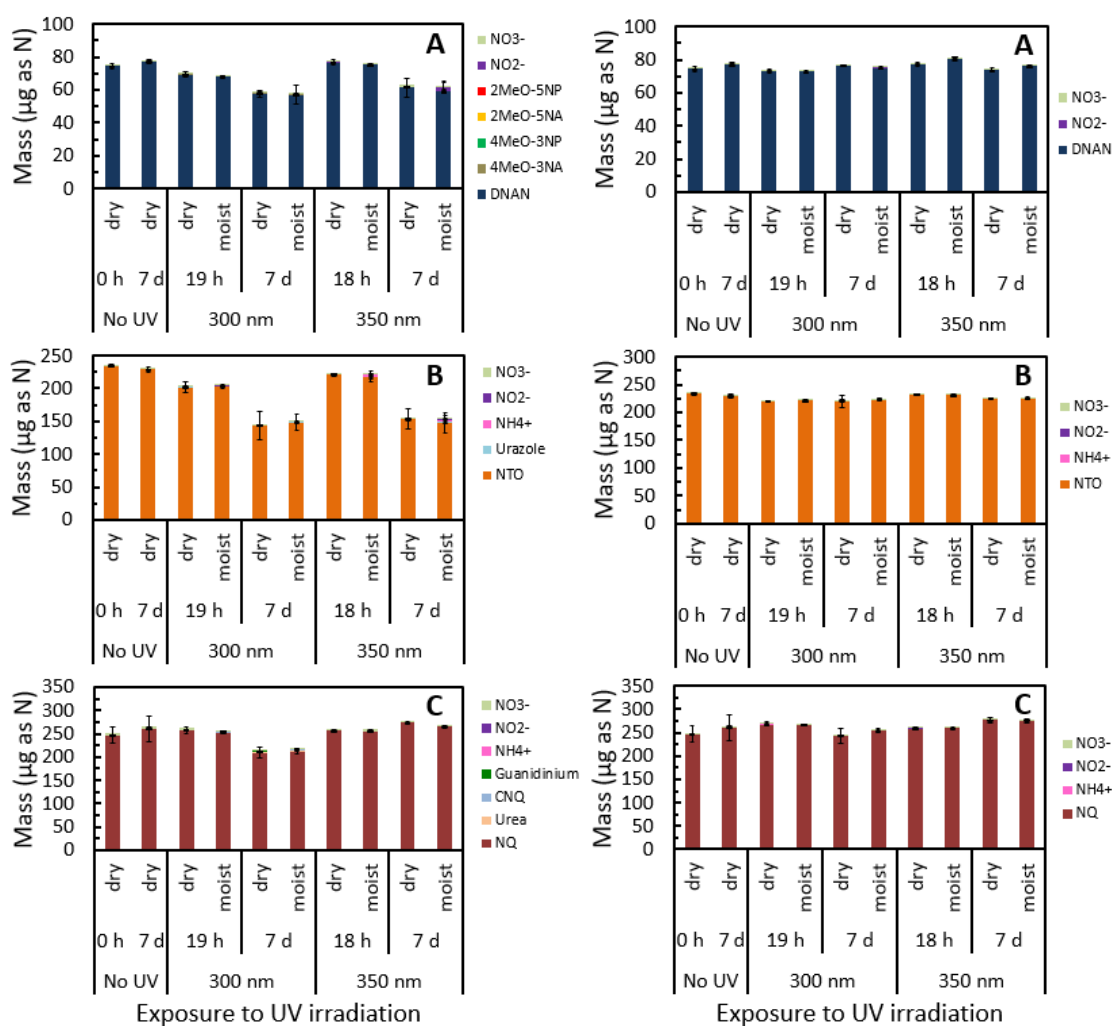


Figure 2.2. Left panel: Nitrogen mass balances of DNAN (A), NTO (B), and NQ (C) irradiated under dry vs. moist conditions (n=3). 2MeO-5NP = 2-methoxy-5-nitrophenol, 2MeO-5NA = 2-methoxy-5-nitroaniline, 4MeO-3NP = 4-methoxy-3-nitrophenol, 4MeO-3NA = 4-methoxy-3-nitroaniline, and CNQ = cyanoguanidine. Right panel: Nitrogen mass balances of DNAN (A), NTO (B), and NQ (C) foil-wrapped controls irradiated under dry vs. moist conditions (n=3).

2.4.2. Outdoor dissolution and phototransformation studies across climate gradient

We have observed the effect of climatic conditions on dissolution of the insensitive and traditional munitions constituents from formulation particles. There was a clear decrease in dissolution, beyond what can be explained by lower total rainfall compared to previous experiment in New Hampshire (Taylor et al., 2015). We also observed differences in dissolution between the locations on elevation gradient in this study. However, the effect of rainfall was non-linear, particularly for IM formulations, IMX-101 and IMX-104 (Figure 2.3). Similar dissolution was observed between two lower elevation locations, even when collected rainfall in lowest elevation was only about half of the one in the middle elevation. This would indicate that perhaps increase in intensity of rainfall does not result in increased dissolution (also supported by lack of increase in dissolution between replicate particles in the same location when they received more rainfall). At the same time, changes in water evaporation due to lower temperature or higher frequency of rainfall may explain increased dissolution at the highest elevation.

About half of the mass loss was not accounted for by parent compound dissolution for IM formulations (Figure 2.4), indicating significant contribution of photo-transformation to the particles fate. No difference in phototransformation of IM constituents was observed between the three locations, but much greater loss of mass for phototransformation was recorded compared to earlier studies in New Hampshire. For traditional munitions particles, Comp B, C4, and TNT powder (Figure 2.4), less than 10% of mass loss was accounted for by dissolution. For these munitions, we observed both difference in mass balance with New Hampshire and between the three locations in Arizona, with greater mass loss at the lowest elevation.

We detected phototransformation products of NTO (urazole), NQ (guanidine, cyanoguanidine, cyanamide, and urea), DNAN (2-MeO-5-NA and 4-MeO-3-NA, nitro-reduction products, as well as 2-MeO-5-NP, 2-MeO-5-NP, and 2,4-dinitrophenol), and TNT (1,3,5-TNB and 1,3-DNB using HPLC) as well as inorganic ions, ammonium, nitrate, and nitrite, that can result from transformation of several constituents. Recovered known products of phototransformation accounted for only a small fraction of mass loss for both insensitive and traditional munitions. There was a trend for greater relative amount of recovered products at the lowest elevation, but it was not strong, and several products showed no correlation with the parent compound concentrations.

When IMX-101 particles of different size were exposed to rainfall and sunlight in Oracle, AZ, decrease in size resulted in increase in dissolution for all energetic constituents (Figure 2.5). However, we successfully accounted for the differences in dissolution by normalizing by surface area using particle mass rather than actual measurements, which are difficult to obtain for irregular-shaped particles. No effect of size on phototransformation, either based on mass balance, or recovery of daughter compounds was observed for particles of different size.

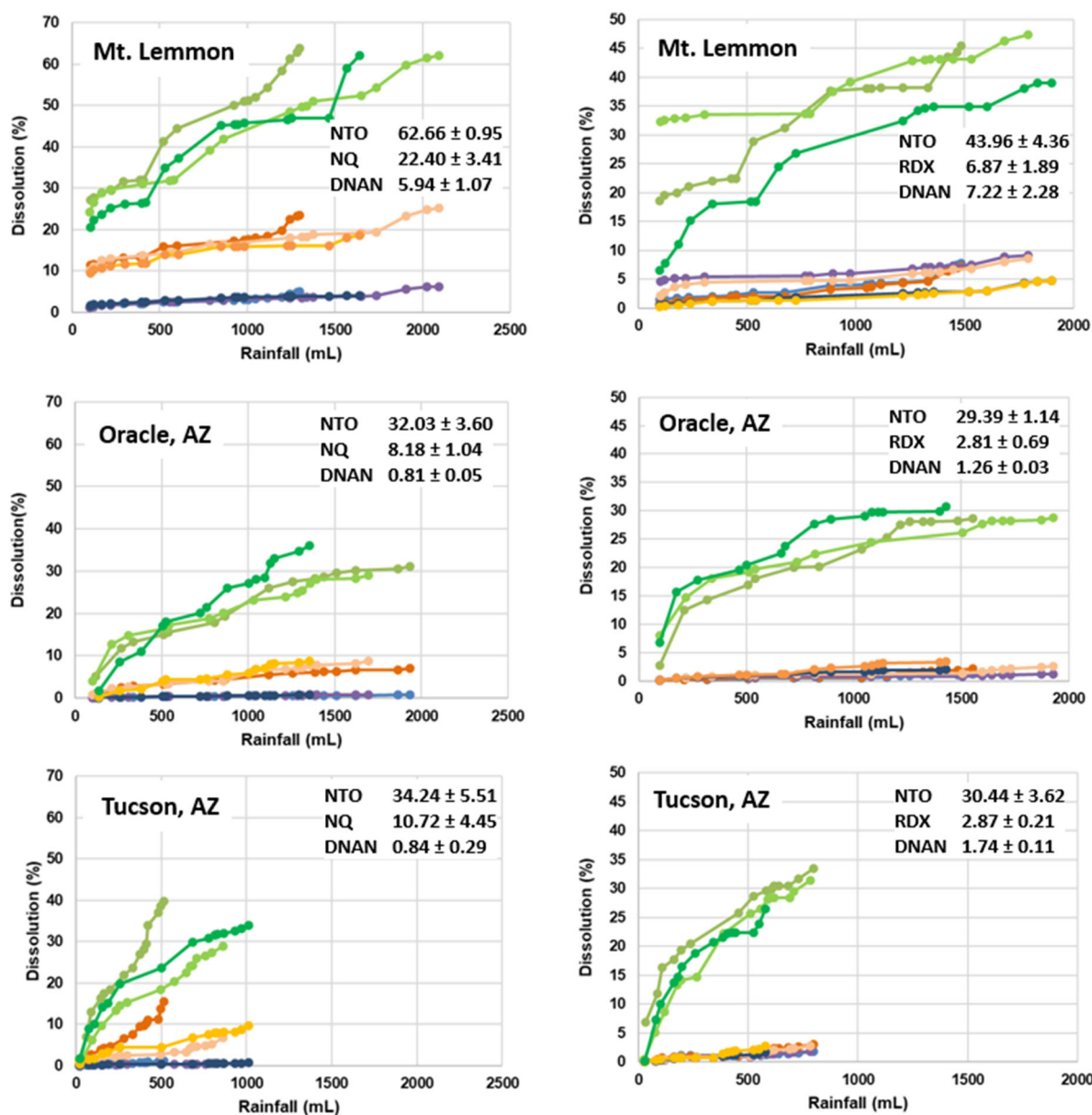


Figure 2.3. Dissolution of constituents from IMX-101 (left, NTO indicated in green, NQ in orange, DNAN in blue) and IMX-104 (right, NTO indicated in green, RDX in orange, DNAN in blue) formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations. Mt. Lemmon received 70.6 inches in 172 events at 0.41 inch/event, < 0.2 inches rains were 6.80 inches total, 9.6%, 87 events; Oracle received 33.03 inches in 104 events at 0.32 inch/event, < 0.2 inches rains were 2.94 inches total, 8.9%, 60 events; Tucson received 19.8 inches in 74 events at 0.27 in/event, < 0.2 in rains were 3.05 inches total, 15.4%, 36 events.

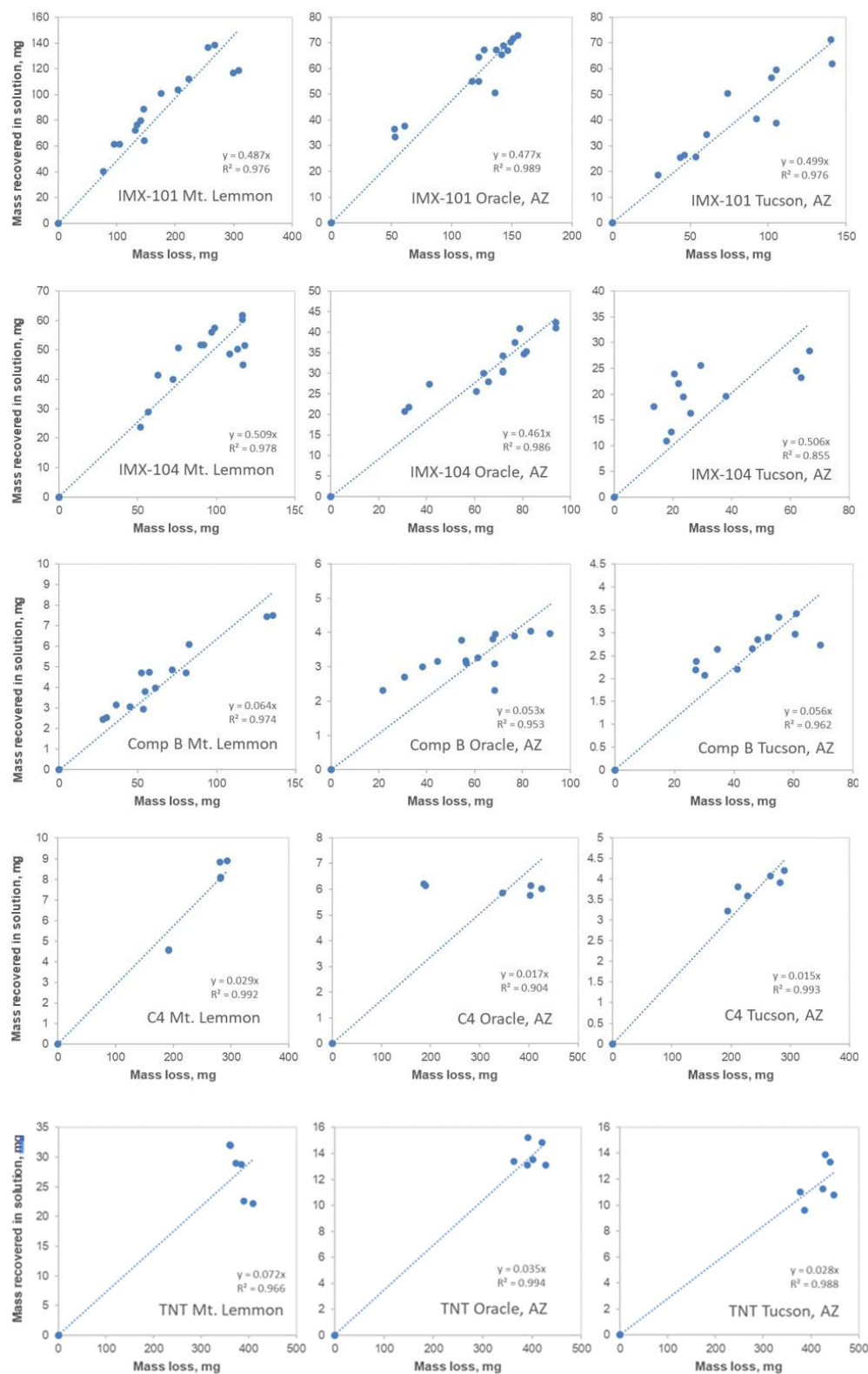


Figure 2.4. Relationship between mass recovery in solution and mass loss of the particles from (top to bottom) IMX-101, IMX-104, Comp B, and C4 formulation particles, as well as TNT powder at Mt. Lemmon (left) Oracle, AZ (middle), and Tucson (right), locations.

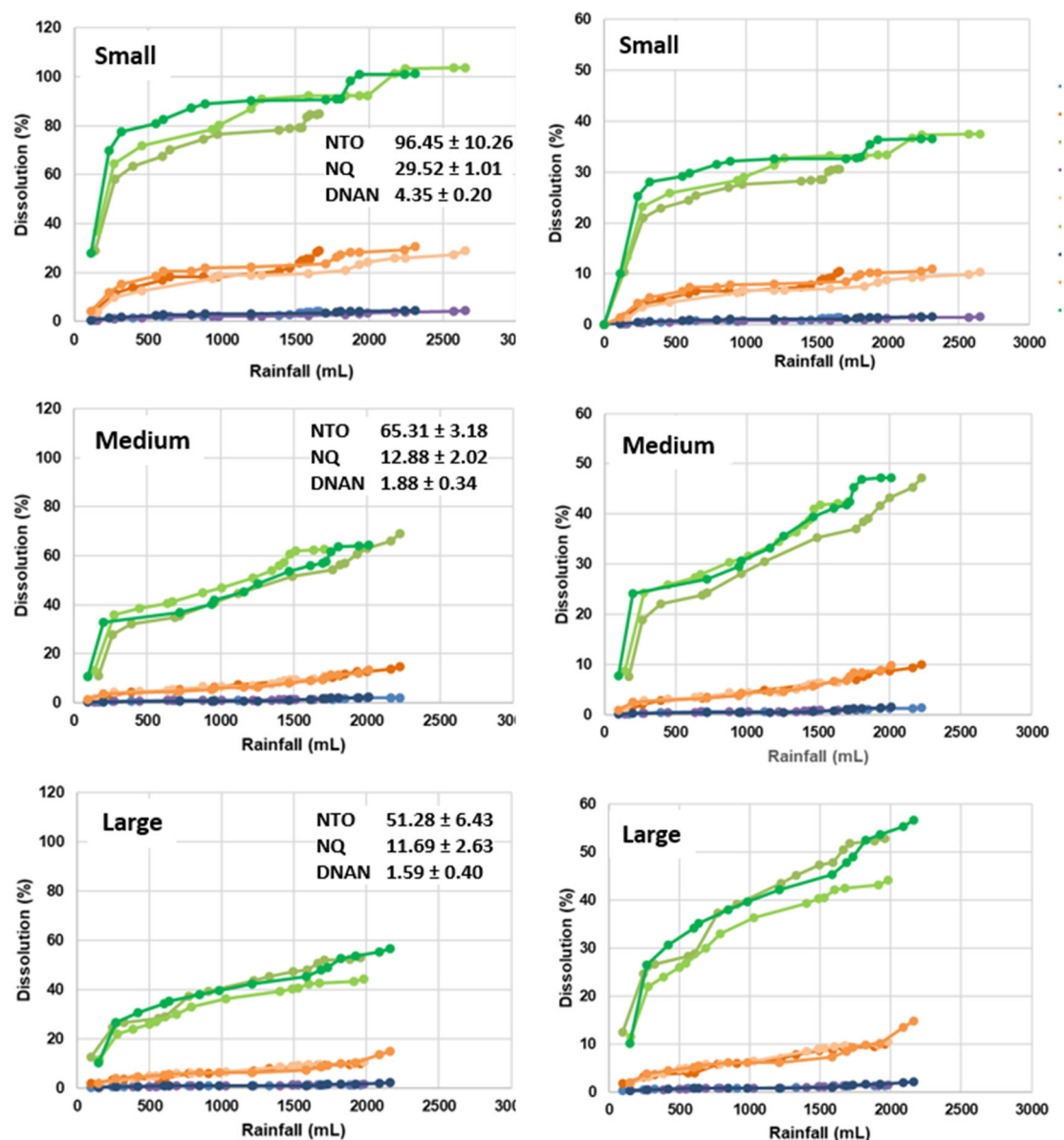


Figure 2.5. Dissolution of constituents from small (top), medium (middle), and large (bottom) particles of IMX-101 formulation in Oracle, AZ location. (left, NTO indicated in green, NQ in orange, DNAN in blue)

2.4.3. Linking outdoor phototransformation across different locations to amount of sunlight and laboratory measured quantum yields

We were able to link measured phototransformation in outdoor and lab experiments to the amount of light received (Tables 2.2 and 2.3). While it is difficult to accurately measure amount of phototransformation in outdoor studies, comparison between three locations on elevation gradient, as well as between current study in Arizona, and similar previous experiments in New Hampshire allow to estimate effect of irradiance on observed phototransformation. We also used quantum yields for each IM compound, averaged from 300 and 350 nm lab experiments, to predict

the amount of phototransformation for individual munitions constituents in the outdoor studies (Table 2.3).

Table 2.2. Parameters used in calculation of half-lives of energetic compounds in outdoor experiments in Arizona: overall "near-surface" specific rate of light absorption, $\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda$, average quantum yields, Φ , 1st order transformation rate constant, k , and average half-life, $t_{1/2}$, dissolved and solid.

IMC	DNAN		NTO		NQ	
Parameter	average	stdev	average	stdev	average	stdev
Mt. Lemmon						
$\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda$ (s ⁻¹)	4.68×10^{-1}	5.10×10^{-2}	3.21×10^{-1}	3.44×10^{-2}	1.88×10^{-1}	3.29×10^{-2}
Dissolved Φ	1.61×10^{-5}	1.42×10^{-6}	4.99×10^{-4}	2.85×10^{-5}	2.19×10^{-3}	2.44×10^{-4}
Solid Φ	2.68×10^{-6}	2.49×10^{-7}	1.55×10^{-5}	1.22×10^{-6}	6.01×10^{-6}	1.29×10^{-6}
Dissolved k (s ⁻¹)	7.53×10^{-6}	1.06×10^{-6}	1.60×10^{-4}	1.94×10^{-5}	4.11×10^{-4}	8.53×10^{-5}
Solid k (s ⁻¹)	1.25×10^{-6}	1.80×10^{-7}	4.97×10^{-6}	6.61×10^{-7}	1.13×10^{-6}	3.13×10^{-7}
Dissolved $t_{1/2}$ (h)	25.57	3.59	1.20	0.15	0.47	0.10
Solid $t_{1/2}$ (h)	153.51	22.00	38.75	5.15	170.60	47.37
Oracle, AZ						
$\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda$ (s ⁻¹)	4.99×10^{-1}	4.75×10^{-2}	3.48×10^{-1}	3.22×10^{-2}	2.05×10^{-1}	3.45×10^{-2}
Dissolved Φ	1.61×10^{-5}	1.42×10^{-6}	4.99×10^{-4}	2.85×10^{-5}	2.19×10^{-3}	2.44×10^{-4}
Solid Φ	2.68×10^{-6}	2.49×10^{-7}	1.55×10^{-5}	1.22×10^{-6}	6.01×10^{-6}	1.29×10^{-6}
Dissolved k (s ⁻¹)	8.04×10^{-6}	1.04×10^{-6}	1.73×10^{-4}	1.89×10^{-5}	4.47×10^{-4}	9.04×10^{-5}
Solid k (s ⁻¹)	1.34×10^{-6}	1.78×10^{-7}	5.39×10^{-6}	6.54×10^{-7}	1.23×10^{-6}	3.36×10^{-7}
Dissolved $t_{1/2}$ (h)	23.96	3.11	1.11	0.12	0.43	0.09
Solid $t_{1/2}$ (h)	143.84	19.15	35.74	4.34	156.68	42.85
Tucson, AZ						
$\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda$ (s ⁻¹)	4.76×10^{-1}	4.37×10^{-2}	3.35×10^{-1}	2.98×10^{-2}	1.98×10^{-1}	3.33×10^{-2}
Dissolved Φ	1.61×10^{-5}	1.42×10^{-6}	4.99×10^{-4}	2.85×10^{-5}	2.19×10^{-3}	2.44×10^{-4}
Solid Φ	2.68×10^{-6}	2.49×10^{-7}	1.55×10^{-5}	1.22×10^{-6}	6.01×10^{-6}	1.29×10^{-6}
Dissolved k (s ⁻¹)	7.67×10^{-6}	9.76×10^{-7}	1.67×10^{-4}	1.77×10^{-5}	4.33×10^{-4}	8.73×10^{-5}
Solid k (s ⁻¹)	1.28×10^{-6}	1.67×10^{-7}	5.20×10^{-6}	6.16×10^{-7}	1.19×10^{-6}	3.25×10^{-7}
Dissolved $t_{1/2}$ (h)	25.12	3.20	1.15	0.12	0.44	0.09
Solid $t_{1/2}$ (h)	150.79	19.70	37.04	4.39	161.79	44.19

Table 2.3. Measured specific first order transformation rate constants (k , s⁻¹) and calculated quantum yields (Φ) for dissolved and solid NQ, DNAN, and NTO at 300 and 350 nm wavelength.

IMC	Wavelength (λ)	First order transformation rate constant (k)		Quantum yield (Φ)		Φ ratio dissolved to solid
		average	stdev	average	stdev	
	nm	s ⁻¹	s ⁻¹			
Dissolved*						
NQ	300	3.63×10^{-4}	2.53×10^{-5}	4.36×10^{-3}	4.87×10^{-4}	
NQ	350	5.91×10^{-7}	5.54×10^{-8}	1.17×10^{-5}	1.90×10^{-6}	
DNAN	300	4.53×10^{-6}	3.11×10^{-7}	1.96×10^{-5}	1.77×10^{-6}	
DNAN	350	1.73×10^{-6}	2.55×10^{-7}	1.26×10^{-5}	2.23×10^{-6}	
NTO	300	2.96×10^{-5}	1.58×10^{-6}	6.93×10^{-4}	5.17×10^{-5}	
NTO	350	2.79×10^{-5}	1.18×10^{-6}	3.04×10^{-4}	2.37×10^{-5}	
Solid**						
NQ	300	2.99×10^{-7}	6.06×10^{-8}	6.01×10^{-6}	1.29×10^{-6}	725.8
NQ	350	-	-	-	-	
DNAN	300	4.02×10^{-7}	3.65×10^{-8}	2.02×10^{-6}	2.01×10^{-7}	9.7
DNAN	350	3.89×10^{-7}	4.88×10^{-8}	3.34×10^{-6}	4.56×10^{-7}	3.8
NTO	300	7.36×10^{-7}	7.12×10^{-8}	2.22×10^{-5}	2.31×10^{-6}	31.2
NTO	350	7.30×10^{-7}	4.95×10^{-8}	8.79×10^{-6}	7.55×10^{-7}	34.6

*Solution samples, Rayonet reactor (Taylor et al., 2017; Becher et al., 2019) and SaniRay reactor (Kadoya et al.) control for indirect photolysis study.

**SaniRay reactor (Kadoya et al.) moist/dry solid particles. Dry and moist samples averaged because there was no difference between the treatments.

2.4.4. Batch adsorption studies using soil components

For all soils highest adsorption was observed for treatments which had OM and iron oxides removed (Figure 2.6) indicating that similarly to what was observed for treated soil clays using pure DNAN, DNAN in energetic formulations, IMX-101 and IMX-104, can be adsorbed by phyllosilicate clays. Adsorption of DNAN from the IMX-101 formulation solutions was not significantly different than observed for pure DNAN for majority of the treatments, but in IMX-104 solutions DNAN adsorption was decreased likely due to competition with RDX and HMX.

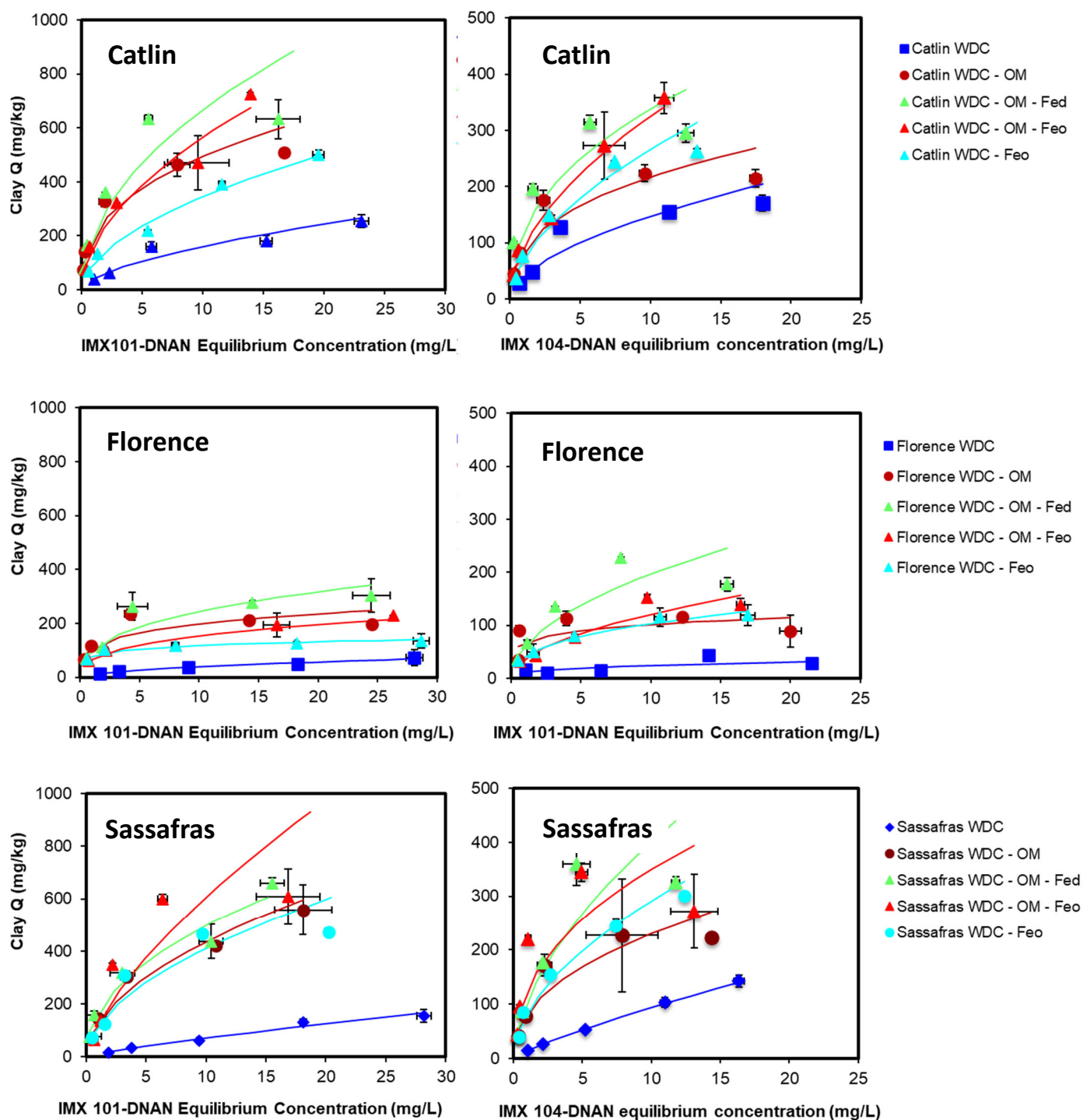


Figure 2.6. Adsorption of DNAN (Q) from IMX-101 (left) and IMX-104 (right) by water dispersible clay (WDC) and WDC treated to remove organic matter (OM), oxalate extractable iron (Fe_o) and dithionite-citrate extractable iron (Fe_d) for Catlin, Florence, and Sassafra soils.

2.5. Implications for Future Research and Benefits

Information obtained from this project improves the ability to accurately predict the release and phototransformation of IM compounds in hot arid regions. It also improves the understanding of the interaction of released compounds with soils, resulting in potential attenuation of these compounds. Being able to predict what proportion of deposited energetic material is lost through photolysis and how much would enter soil and surface waters for different climatic conditions, as well as patterns of release in time, is essential for accurate estimation of the environmental impact of training exercises and combat activities. Since insensitive munitions result in larger percentages of rounds having low order detonations and larger fractions of unconsumed ordinance remaining post-explosion during blow-in-place procedures, predicting the fate of deposited material is even more critical.

3. UV irradiation experiments of DNAN, NTO, and NQ solids under dry and moist conditions

3.1. Background

Insensitive Munitions Compounds (IMCs) 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine (NQ) enter the environment through the incomplete detonation of insensitive munitions (IMs) on training ranges. These compounds absorb light in the ultraviolet (UV) range and have been shown to transform upon exposure to sunlight (Taylor et al., 2017; Moores et al., 2020a). DNAN forms 2-methoxy-5-nitroaniline and 4-methoxy-3-nitroaniline when the *ortho* and *para* nitro groups are reduced to amino groups, respectively (Olivares et al., 2016). DNAN phototransformation products also include 2-methoxy-5-nitrophenol, 4-methoxy-3-nitrophenol, 2,4-dinitrophenol, nitrate, nitrite, and ammonium (Rao et al., 2013; Hawari et al., 2015; Taylor et al., 2017). Similarly, the nitro group of NTO can be reduced under reducing conditions by soil microbes and minerals (Krzmarzick et al., 2015). Phototransformation products of NTO include urazole, nitrate, nitrite, and ammonium (Le Champion et al., 1997; Becher et al., 2019). Products of NQ phototransformation include guanidine, cyanoguanidine, cyanamide, urea, nitrate, nitrite, and ammonium (Burrows et al., 1988; Becher et al., 2019). The resulting phototransformation products are known to be toxic, and in many cases more toxic than the IMCs themselves (Burrows et al., 1988; Moores et al., 2020b). Because solid IMs can dissolve in rainwater, dry on the soil surface, and become moist with dew formation, we wanted to compare the phototransformation of dry DNAN, NTO, and NQ particles with that of particles under moist conditions. We designed experiments based on preliminary results that suggested a difference in phototransformation rates under dry vs. moist conditions.

3.2. Materials and Methods

3.2.1. Chemicals

2,4-Dinitroanisole (DNAN, 97% purity) was obtained from BAE Systems (Falls Church, VA, USA). 3-Nitro-1,2,4-triazol-5-one (NTO) was obtained from Picatinny Arsenal (Wharton, NJ, USA). Nitroguanidine (NQ), 2-methoxy-5-nitroaniline (2-MeO-5-NA, 98% purity), 2,4-dinitrophenol (DNP, 97% purity), cyanoguanidine (CNQ, 99% purity), cyanamide (99% purity), and urazole (97% purity) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Guanidine hydrochloride (99% purity) was purchased from TCI America (Portland, OR, USA). 2-Methoxy-

5-nitrophenol (2-MeO-5-NP, 98% purity) was purchased from Alfa Aesar (Haverhill, MA, USA). 4-Methoxy-3-nitrophenol (2-MeO-5-NP, 95% purity) and 4-methoxy-3-nitroaniline (4-MeO-3-NA, 95% purity) were purchased from Enamine (Monmouth Jct., NJ, USA). 3-Amino-1,2,4-triazol-5-one (ATO) was obtained from Ed Hunt at the University of Arizona. Urea (99% purity) was purchased from Bio-Rad (Hercules, CA, USA). Nitrate, nitrite, and ammonium ion chromatography standards were purchased in solution from Inorganic Ventures (Christiansburg, VA, USA).

3.2.2. *Experimental Setup*

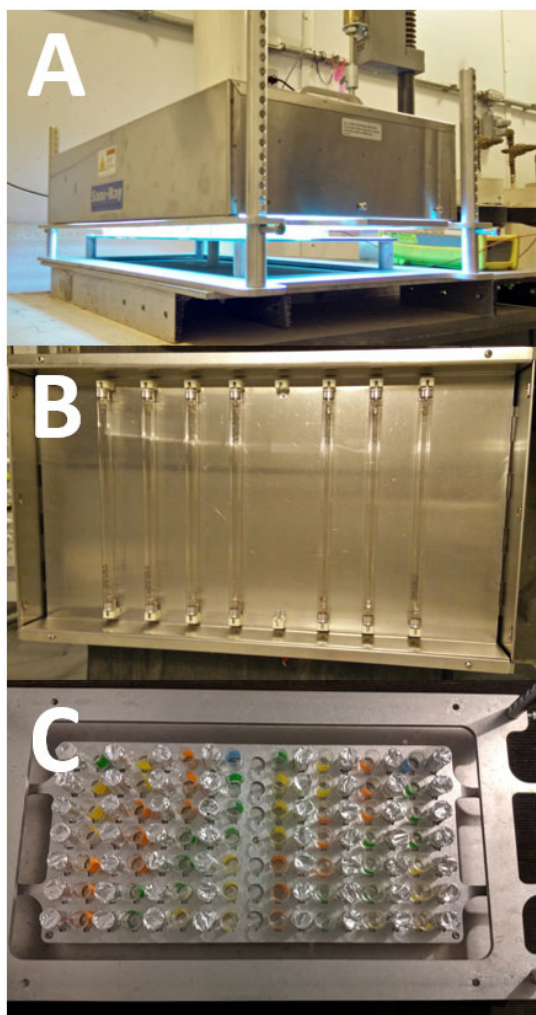


Figure 3.1. UV reactor setup (A) with cover holding up to eight UV bulbs (B) and plate holding 5 mL glass beakers and foil-wrapped controls (C).

We added 0.5 mL of 1 g L⁻¹ DNAN (in acetonitrile), NTO (in acetonitrile), and NQ (aqueous) solutions to 5 mL glass beakers in triplicate, covered them loosely with foil, and let them dry in a fume hood. We optically imaged the resulting crystals with a Keyence VHX digital microscope (Elmwood Park, NJ, USA) fitted with a 20-200x lens. We then irradiated these samples in a modified Sani-Ray Germicidal Ultraviolet Fixture (Atlantic Ultraviolet Corporation,

Hauppauge, NY, USA) that houses eight 300 nm or 350 nm bulbs (Southern New England Ultraviolet Company, Branford, CT, USA), representing UV-B and UV-A, respectively, for either 18 h or 7 d (Figure 3.1). The bulbs were placed about 5 cm above the sample surface. We conducted the experiment in a cold room set at 0 °C to minimize thermal effects, and the average temperature inside the reactor was 17°C. For beakers with moist conditions, we misted them with about 3-5 mg of deionized water (based on an average of ten trials) once a day using an atomizer spray bottle at a height of 12 in. In parallel, we ran dry and moist controls wrapped in aluminum foil in the reactor to prevent UV exposure but account for any temperature effects due to heat produced by the UV bulbs. After exposure to UV light, we dissolved DNAN solids with 3 mL acetonitrile and NTO and NQ solids with 3 mL deionized water and analyzed them using high performance liquid chromatography (HPLC) and ion chromatography (IC).

3.2.3. *Analytical Methods*

3.2.3.1. High Performance Liquid Chromatography (HPLC)

HPLC samples for DNAN analysis were prepared by diluting samples with deionized water resulting in a matrix of 3:1 water:acetonitrile. Samples for NTO and NQ analyses were prepared by diluting samples two-fold with deionized water. Samples were analyzed on an Agilent 1260 Infinity HPLC with diode array detection (Santa Clara, CA, USA). All analyzed compounds were compared with prepared standards in terms of retention times and ultraviolet-visible (UV-VIS) spectra.

DNAN was analyzed using a NovaPak C8 column (3.9 mm x 150 mm, 4 µm; Waters Corporation, Milford, MA, USA) at 28 °C. The injection volume was 100 µL and an isocratic method was used with a flow rate of 1.2 mL min⁻¹, a run time of 10 min, and an eluent composition of 15/85 isopropanol/deionized water with 0.1% acetic acid. Compounds were analyzed at the following wavelengths and eluted at the following retention times: 230 nm at 3.2 min for 4-MeO-3-NA, 230 nm at 3.4 min for 2-MeO-5-NP, 265 nm at 3.8 min for 2-MeO-5-NA, 230 nm at 4.4 min for 2-MeO-5-NP, 265 nm at 4.7 min for DNP, and 295 nm at 7.2 min for DNAN.

NTO was analyzed using a Hypercarb Porous Graphitic Carbon column (2.1 mm x 50 mm, 3 µm; Thermo Scientific, Waltham, MA, USA) at 28 °C. The injection volume was 10 µL, and a gradient method was run at a flow rate of 0.4 mL min⁻¹ for 17 min. The mobile phase consisted of 0.5% trifluoroacetic acid (TFA) in water from 0 to 5 min, 15/85 (v/v) acetonitrile/0.1% TFA in water from 5 to 12 min, and 0.5% TFA in water from 12 to 17 min. Compounds were analyzed at the following wavelengths and eluted at the following retention times: 216 nm at 2.8 min for urazole, 216 nm at 5.6 min for ATO, and 315 nm at 9.6 min for NTO.

NQ was analyzed using a ProntoSIL 200-5-C30 column (4.6 mm x 250 mm, 5 µm; Bischoff Chromatography, Leonberg, Germany) at 28 °C. The injection volume was 20 µL, and an isocratic method with 100% deionized water as the eluent was run at a flow rate of 0.8 mL min⁻¹ for 10 min. Compounds were analyzed at 200 nm and eluted at the following retention times: 3.8 min for urea, 3.9 min for cyanamide, 5.3 min for CNQ, and 6.6 min for NQ.

3.2.3.2. Ion Chromatography (IC)

For DNAN samples in acetonitrile, IC samples were prepared by pipetting 1 mL samples into centrifuge tubes, letting it evaporate in a fume hood, and dissolving the solid residue in 11 mL

deionized water. For aqueous NTO and NQ samples, IC samples were prepared by pipetting 1 mL samples into centrifuge tubes and diluting them with 10 mL deionized water. The samples were analyzed in a Thermo Scientific Dionex Integrion HPIC (Waltham, MA, USA). Nitrate and nitrite were analyzed using a Dionex IonPac AS18 column (4 mm x 150 mm, 4 μ m; Thermo Scientific, Waltham, MA, USA) and a guard column at 30 °C. An isocratic eluent of 25 mM KOH was run at a flow rate of 1 mL min⁻¹ for 16 min. Nitrite eluted at 3.2 min and nitrate eluted at 5.2 min. Ammonium and guanidinium were analyzed using a Dionex IonPac CS19 column (4 mm x 250 mm, 4 μ m; Thermo Scientific, Waltham, MA, USA) and a guard column at 30 °C. An isocratic eluent of 7 mM methanesulfonic acid was run at a flow rate of 1 mL min⁻¹ for 15 min. Ammonium eluted at 4.7 min and guanidinium eluted at 7.6 min.

3.2.4. Irradiance Measurements

We measured the ultraviolet irradiance in the UV reactor using an optometer (Gigahertz Optik P-9710, Newburyport, MA, USA). Three detector heads were used corresponding to UV-A (Gigahertz Optik UV-3701; 315-400 nm), UV-B (UV-3702; 280-315 nm), and UV-C (UV-3718; 254 nm). Irradiance measurements were taken from 56 locations in the reactor (at each possible beaker position directly under a bulb), with the top of the detector head at the same height as where the bottom of the beakers would sit, and averaged.

3.3. Results and Discussion

Figure 2 shows the types of crystals that formed after letting IMC solutions dry on microscope slides. DNAN formed cylindrical crystals that associated in clumps about 100 μ m wide. NTO formed yellow crystals about 50 μ m wide. NQ formed long, interspersed needles about 5 μ m wide.



Figure 3.2. Microscope images of DNAN (A), NTO (B), and NQ (C) crystals that formed upon evaporation of 0.5 mL of 1 g L⁻¹ DNAN (in acetonitrile), NTO (in acetonitrile), and NQ (aqueous) solutions.

Analysis of the data shows that there is no significant difference between moist and dry conditions on the phototransformation rates of DNAN, NTO, or NQ at 254 nm, 300 nm, and 350 nm (Figure 2.3). These nitrogen mass balances show that at least 77%, 62%, and 100% of the initial nitrogen in the DNAN, NTO, and NQ experiments, respectively, were recovered. On average, less than 1% of the initial DNAN, NTO, or NQ was converted to known products detected in HPLC and IC, including minerals NO₂⁻, NO₃⁻, and NH₄⁺. Relatively small unidentified peaks were detected in HPLC chromatograms of irradiated DNAN and NTO, which could be additional products for which we did not have standards. Dark controls indicated no thermal effects of UV exposure on phototransformation rates (Figure 3.4). The time points tested were chosen based on a previous study (Becher et al. 2019), but the IMC transformation rates were significantly slower,

likely because only the surfaces of the solid IMC crystals were exposed to UV light in this study, whereas in Becher et al. (2019), aqueous, well-mixed IMC solutions were irradiated uniformly. This may explain why NQ did not seem to phototransform at the timescales tested and why there was less DNAN and NTO phototransformation than expected.

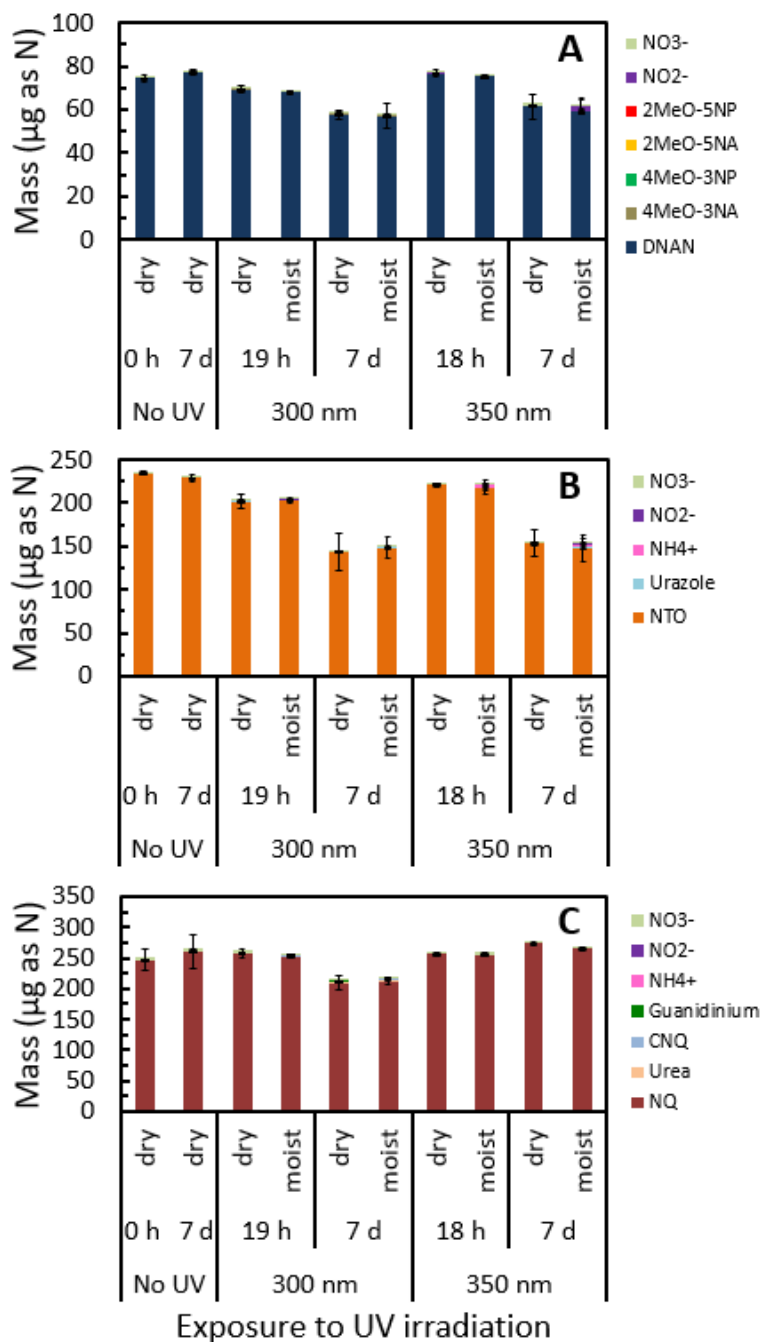


Figure 3.3. Nitrogen mass balances of DNAN (A), NTO (B), and NQ (C) irradiated under dry vs. moist conditions (n=3). 2-MeO-5-NP = 2-methoxy-5-nitrophenol, 2-MeO-5-NA = 2-methoxy-5-nitroaniline, 2-MeO-3-NP = 4-methoxy-3-nitrophenol, 4-MeO-3-NA = 4-methoxy-3-nitroaniline, and CNQ = cyanoguanidine.

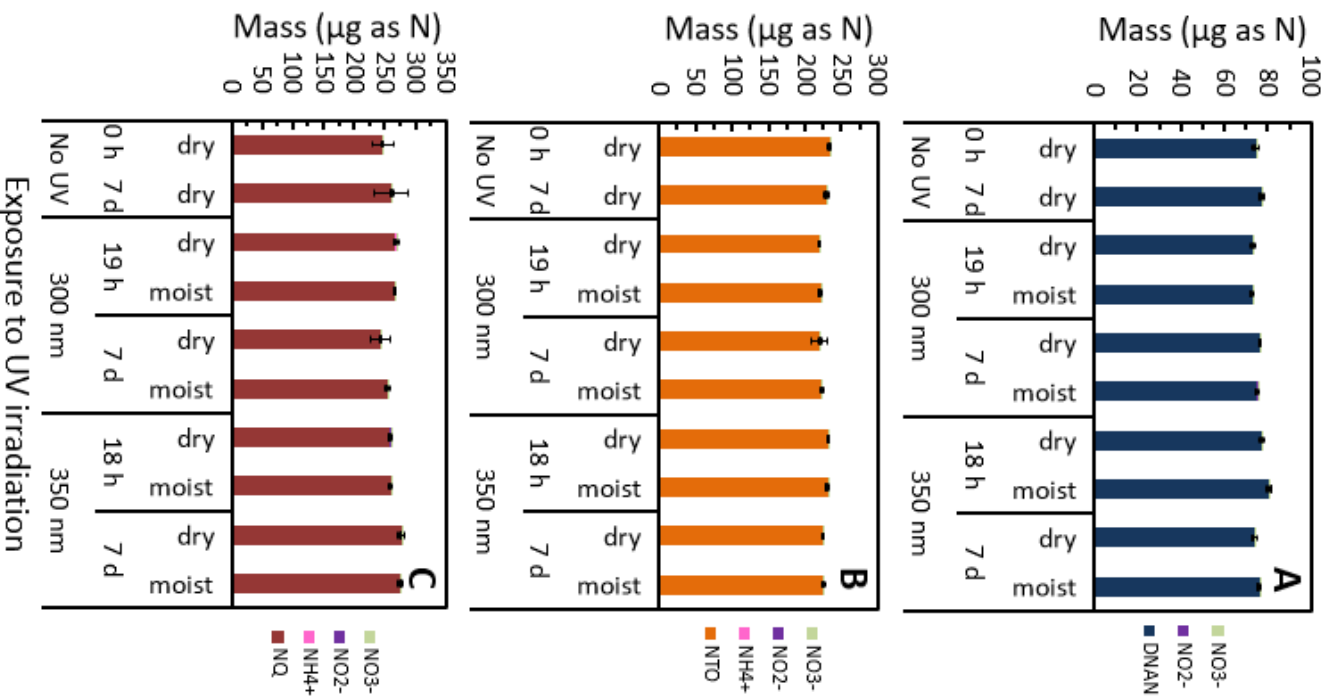


Figure 3.4. Nitrogen mass balances of DNAN (A), NTO (B), and NQ (C) foil-wrapped controls irradiated under dry vs. moist conditions (n=3).

We hypothesized that moist conditions could enhance IMC transformation compared with dry conditions in the context of soils due to the enhanced microbial activity afforded by the aqueous environment (Graebing and Chib, 2004). However, in our simplified study of the phototransformation of moist and dry IMCs on a glass surface, moist conditions did not enhance transformation rates. It is possible that the small amount of water added once a day evaporated due to the heat of the UV bulbs, resulting in similar experimental conditions to those of the dry solids.

However, this is not unlike environmental conditions, in which dew forms during the night and evaporates in the morning. The results of this study are useful for the prediction and modeling of the environmental fate of IMCs. Given the near identical rates of transformation and product formation when irradiating dry and moist IMC crystals, the presence of moisture should not impact the predicted fate of solid IMCs that have dissolved in rainwater and re-crystallized.

3.4. Conclusions

Our studies indicate that moist and dry particles of DNAN, NTO, and NQ phototransformed at similar rates. However, these rates were lower than measured for same compounds in solution, likely due to limitation on how deep the light can enter the particle. Additional studies are needed to measure light penetration into these compounds in solid form and formulations that contain them.

4. Outdoor dissolution and phototransformation studies across climate gradient

4.1. Background

How they enter the environment influences fate and transport of energetic compounds. As they are deposited on the ground as solid particles in formulations, understanding and quantifying their release from formulations and phototransformation in solid and solution form is essential for prediction of their further fate. Here we examine influence of climatic conditions on dissolution and phototransformation of 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ), 2,4-dinitroanisole (DNAN), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and 2,4,6-trinitrotoluene (TNT) (Table 4.1) from energetic formulations, IMX-101, IMX-104, Comp B and C4. Are dissolution rates, particle residence times, transformation products quantified and detected for high rainfall, low sunlight, cold conditions of Northeastern United States (Taylor et al., 2009; Taylor et al., 2015) also applicable for arid and hot conditions in Arizona? Experiments initiated earlier in Arizona (Dontsova et al., 2018) indicate that even after accounting for amount of rainfall, particles were dissolving much slower under arid conditions than under high-humidity conditions. Using elevation gradient in this study, from Tucson, AZ at the lowest elevation with lowest rainfall and highest temperatures to Mt. Lemmon at the highest elevation with lower (sometimes freezing) temperatures and higher and more frequent rainfall, allows us to expand the range of conditions to which we subject particles of energetic formulations. We also examine the effect of particle size on dissolution and phototransformation of IMX-101 particles. This study provided new insights into the photochemical and dissolution behavior of insensitive and traditional munition formulations in natural environment helping in development of appropriate strategies for management of training ranges.

Table 4.1. Structural and mass information of parent target compounds.

Compound	Structure	Formula	MW
NTO (3-nitro-1,2,4-triazol-5-one)		C2H2N4O3	130.01265
NQ (nitroguanidine)		CH4N4O2	104.0334
DNAN (2,4-dinitroanisole)		C7H6N2O5	198.0276
RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)		C3H6N6O6	222.03485
TNT (2,4,6-trinitrotoluene)		C7H5N3O6	227.01785

4.2. Materials and Methods

4.2.1. Experimental setup for dissolution and phototransformation experiment on the climate gradient

Outdoor dissolution and phototransformation experiments were installed in three locations across the elevation gradient, on top of Mt. Lemmon, Summerhaven, AZ at 9,157 feet above sea level; Biosphere 2, Oracle, AZ at 3,820 feet above sea level; and Tucson, AZ at 2,389 feet above sea level. Climatic conditions are distinctly different between the sites with increase in rainfall and approximately 10 degree decrease in temperature with increase in elevation from site to site (Table 3.2). Comparing with data collected previously in Hanover, NH, and across the

three locations in these experiments, allows us to evaluate effect of climate (temperature, rainfall, and sunlight) on energetic particle weathering.

Table 4.2. Temperature and rainfall conditions in Hanover, NH, where previous dissolution experiments were conducted, and Mt. Lemmon, Oracle, AZ, and Tucson, AZ, locations of the current study.

Location	Average temperature, °F				Annual precipitation	
	January low	January high	July low	July high	inches	mm
Hanover, NH	10	28	59	82	40.11	1019
Mt. Lemmon, AZ	23	49	50	76	29.56	751
Oracle, AZ (Biosphere 2)	35	56	67	92	24.92	633
Tucson, AZ	42	66	76	101	11.92	303

Each site was instrumented with the LP02 Hukseflux Pyranometer that monitored solar radiation for the full solar spectrum range (280 to 3000 nm) (Campbell Scientific Inc, Logan, Utah), as well as SU-100-SS Ultraviolet Apogee Sensor (Logan, UT) that measures UV light (250 nm to 400 nm) and 109SS-L65-PT Stainless Steel Temperature Probe (-40 to +70 °C) (Campbell Scientific Inc, Logan, Utah). Instrument readings were recorded using CR1000 Measurement & Control Datalogger by Campbell Scientific Inc. (Logan, Utah).

At each location, IM particles were placed in the Buchner funnels with glass frits (4 cm diameter with 145–175 µm openings) (Figure 3.1). Funnels drained into glass bottles housed in the wooden insulated container. Five different materials (IMX-101, IMX-104, TNT powder, Comp B, and C4) were placed at each location, replicated 3 times (a, b, and c) (Table 3.3). While manufactured IMX-101 and IMX-104, and Comp B residues of low-order detonations were individual particles, due to availability manufactured TNT was a powder and for C4, treatments a and b were mixtures of particles and powder, and C4 treatment c was an individual particle. Comp B and C4 resulted from low-order detonations and were previously exposed to rainfall in outdoor dissolution and phototransformation experiments in New Hampshire (Taylor et al., 2010).

2 ppm and 10 ppm individual solutions of pure DNAN, NTO, NQ, RDX and TNT were prepared in duplicate and placed inside the same containers that contained glass bottles for collecting drainage. Bottles with dark controls were covered in foil to prevent light reaching the solutions. In addition, at Biosphere 2 location small, medium, and large particles of IMX-101 resulting from low-order detonations (approximately 0.5 g in each treatment) were also tested (Table 3.4, Figure 3.2). As a result, on Mt. Lemmon and in Tucson there were 15 funnels with samples plus two controls without particles and at Biosphere 2, 24 funnels (15 + 9) with samples and two controls.

Manufactured IMX-101, IMX-104, and TNT were kindly provided by Dr. Stephen Fallis and Dr. Gregory Ostrom, Naval Air Warfare Center Weapons Division, China Lake. Comp B and C4 residues of low-order detonations, as well as particles of IMX-101 of different size obtained from low order detonations were received from the Cold Regions Research and Engineering Laboratory.

Experiment was started on Mt. Lemmon on October 10th, 2018, in Tucson, AZ on October 30th, 2018 (instruments were set up on November 2nd), and in Oracle, AZ on October 31st. Experiment was completed and samples removed on November 13th, 2020 after a large rainstorm across all three locations. During this rainstorm the setup at Tucson, AZ was destroyed due to strong winds. Because of this solution was not collected at this location for the last date, however, particles of energetics were recovered.

Table 4.3. Experimental design and energetic particle weights.

Mt. Lemmon			Tucson, AZ			Oracle, AZ		
Treatment		particle weight, g			particle weight, g			particle weight, g
IMX-101	a	0.5042	IMX-101	a	0.5003	IMX-101	a	0.7327
	b	0.5677		b	0.4715		b	0.7620
	c	0.3776		c	0.5780		c	0.6758
IMX-104	a	0.2235	IMX-104	a	0.1515	IMX-104	a	0.2207
	b	0.1960		b	0.1390		b	0.1908
	c	0.2260		c	0.1556		c	0.2419
TNT powder	a	0.4525	TNT powder	a	0.4776	TNT powder	a	0.4602
	b	0.4585		b	0.4861		b	0.4510
	c	0.4592		c	0.4588		c	0.4519
Comp B	a	0.5046	Comp B	a	0.3535	Comp B	a	0.5734
	b	0.3952		b	0.3160		b	0.4666
	c	0.4547		c	0.4221		c	0.5625
C4	a	0.3012	C4	a	0.3107	C4	a	0.4804
	b	0.3059		b	0.3125		b	0.4040
	c	0.1969		c	0.2277		c	0.2237

Table 4.4. Total weight in grams of low order detonation residue particles of IMX-101 of different size exposed to rainfall and sunlight in Oracle, AZ location.

Treatment	Small	Medium	Large
Replication A	0.5294	0.5523	0.5582
Replication B	0.5275	0.5628	0.3931
Replication C	0.5001	0.4997	0.3800



Figure 4.1. Photographs of experimental setup in three locations, Mt. Lemmon, AZ (top) Oracle, AZ (middle), and Tucson, AZ (bottom).

4.2.2. Experimental setup for identifying phototransformation products in solutions exposed to sunlight

The outdoor photodegradation experiment for energetic solutions was conducted at Biosphere 2, Oracle, AZ, roof site where solutions were irradiated under natural sunlight between June and July of 2019. The aqueous solutions in 250 mL bottles contained individually spiked nitroaromatic and nitroheterocyclic compounds including DNAN, NTO, RDX, NQ, and TNT. The initial concentration for each parent compound was 50 mg L⁻¹. After more than 50% of photolysis removal of parent compound and change in color (at 3 days, 1 week and 3 weeks of exposure), the aqueous samples were collected and extracted by solid phase extraction as described in section 4.2.3.2.

4.2.3. Quantification of parent compounds and phototransformation products for solid energetics and formulations

4.2.3.1. High Performance Liquid Chromatography (HPLC)

Sample analysis was performed across several labs and several instruments were used for analysis. For majority of the samples, concentrations of the parent compounds (DNAN, NTO, RDX, HMX, NQ, and TNT) and products of their transformation in the samples were analyzed using high performance liquid chromatograph (HPLC) system (Dionex Ultimate 3000, Sunnyvale, USA) with a diode array detector (ThermoFisher, MA). The method for NTO was adapted from Le Campion et al (1999). The mobile phase for NTO analysis consisted of acetonitrile/water (v/v, 75:25) with 0.1% trifluoroacetic acid (TFA). The mobile phase flow rate was 1 mL min⁻¹. NTO were separated and detected using a Hypercarb column (Thermo Scientific, 4.6 × 150 mm, 5 μm) under wavelength of 315 nm and the column temperature was maintained at 32 °C. DNAN, its products 2-methoxy-5-nitroaniline and 4-methoxy-3-nitroaniline, RDX, NQ and TNT were quantified using C18 Acclaim reversed phase column (Thermo Scientific, 4.6 × 250 mm, 5 μm) with mobile phase ratio of methanol/water (v/v, 43:57) (Olivares et al., 2013b). The mobile phase flow rate was 1 mL min⁻¹. DNAN, 2-methoxy-5-nitroaniline, 4-methoxy-3-nitroaniline, and NQ were detected at 300 nm, while RDX and TNT were detected at 254 nm.

To quantify transformation products of TNT, we analyzed samples using Acclaim Explosives E2 (4.6 x 250 mm, 5 μm) column. We used 8330 standard initially to screen for all included compounds, but after only 1,3,5-trinitrobenzene (1,3,5-TNB) and 1,3-dinitrobenzene (1,3-DNB) were detected, we quantified them separately. The conditions were: isocratic with 1 mL min⁻¹ flow for 21 min for 1,3,5-TNB and 1,3-DNB) and 35 min for 8330. The eluent was 43:57 v/v methanol/water. Retention times were approximately 11.4 min for TNB and 13.2 min for DNB.

Samples collected in the last half year of the experiment were analyzed on an Agilent 1260 Infinity HPLC with diode array detection (Santa Clara, CA, USA). All analyzed compounds were compared with prepared standards in terms of retention times and UV-VIS spectra.

Samples containing IMX-104, C4, Comp B, PAX-21, and TNT, RDX, and DNAN controls were analyzed using a NovaPak C8 column (3.9 mm x 150 mm, 4 μm; Waters Corporation, Milford, MA, USA) at 28 °C. The injection volume was 20 μL and an isocratic method was used with a flow rate of 1.2 mL min⁻¹, a run time of 5-18 min (depending on the anticipated compounds), and an eluent composition of 15/85 (v/v) isopropanol/0.1% acetic acid in deionized (DI) water. Compounds were analyzed at the following wavelengths and eluted at the following retention

times: 210 nm (HMX 1.5 min, 1,3,5-trinitrobenzene 2.6 min, RDX 3.0 min, TNT 5.6 min, tetryl 6.3 min, nitroglycerin 8.8 min, 2,6-dinitrotoluene 13.4 min, 2-amino-4,6-dinitrotoluene 14.3 min, 4-amino-2,6-dinitrotoluene 16.0 min), 230 nm (4-methoxy-3-nitroaniline 2.2 min, 4-methoxy-3-nitrophenol 3.5 min, 2-methoxy-5-nitrophenol 4.4 min), 254 nm (1,3-dinitrobenzene 5.1 min, 2,4-dinitrotoluene 11.1 min), 265 nm (2-methoxy-5-nitroaniline 3.8 min, 2,4-dinitrophenol 4.7 min), and 295 nm (DNAN 7.4 min).

Samples containing IMX-101, IMX-104, and NQ controls were analyzed using a ProntoSIL 200-5-C30 column (4.6 mm x 250 mm, 5 μ m; Bischoff Chromatography, Leonberg, Germany). For IMX-101 analysis, two methods (1 and 2) were used. Method 1 was run at 25 °C with an injection volume of 20 μ L and consisted of a gradient method run at a flow rate of 0.5 mL min⁻¹ for 28.5 min. The mobile phase consisted of (A) 0.1% trifluoroacetic acid (TFA) in DI water and (B) methanol with the following intervals and compositions (v/v %): 0-8 min [100% A], 8.5-25 min [35% A/65% B], and 25.5-28.5 min [100% A]. Compounds were analyzed at the following wavelengths and eluted at the following retention times: 216 nm (urazole 7.3 min, cyanoguanidine 8.5 min), 230 nm (4-methoxy-3-nitroaniline 16.7 min, 4-methoxy-3-nitrophenol 18.7 min, 2-methoxy-5-nitrophenol 20.4 min), 265 nm (NQ 10.6 min, 2-methoxy-5-nitroaniline 19.5 min, 2,4-dinitrophenol 22.7 min), 295 nm (DNAN 23.9 min), and 315 nm (NTO 16.2 min).

Method 2 was run at 28 °C with an injection volume of 20 μ L and consisted of a gradient method run at a flow rate of 0.8 mL min⁻¹ for 13.5 min. The mobile phase consisted of (A) DI water, (B) 0.1% TFA in DI water, and (C) methanol with the following intervals and compositions (v/v %): 0-5 min [100% A], 8-10 min [20% B/80% C], and 10.5-13.5 min [100% A]. Compounds were analyzed at the following wavelengths and eluted at the following retention times: 195 nm (urea 3.8 min) and 216 nm (cyanamide 3.9 min). IMX-104 analyses were run at 25 °C with an injection volume of 20 μ L and consisted of a gradient method run at a flow rate of 0.8 mL min⁻¹ for 18.5 min. The mobile phase consisted of (A) 0.1% TFA in DI water and (B) methanol with the following intervals and compositions (v/v %): 0-8 min [100% A], 10-15 min [20% A/80% B], 15.5-18.5 min [100% A]. Compounds were analyzed at the following wavelengths and eluted at the following retention times: 216 nm (urazole 4.6 min), 315 nm (NTO 13.6 min). NQ controls were analyzed at 28 °C with an injection volume of 20 μ L and consisted of an isocratic method of 100% DI water run at a flow rate of 0.8 mL min⁻¹ for 10 min. Compounds were analyzed at the following wavelengths and eluted at the following retention times: 200 nm (urea 3.8 min, cyanamide 3.9 min, cyanoguanidine 5.3 min) and 254 nm (NQ 6.5 min). While control samples were analyzed, the results are not presented here because long-term exposure to outside conditions resulted in sample evaporation and contamination. As treatment solutions unlike controls were removed after each rainfall, they were not subject to the same exposure.

4.2.3.2. Ion Chromatography (IC)

For majority of the samples, concentrations of nitrate (NO₃⁻) and ammonium (NH₄⁺), known NTO, NQ, and DNAN photodegradation products, were determined using Ion Chromatograph system (Thermo Scientific Dionex ICS-5000+) with 35 mM KOH isocratic eluent. For nitrates, we used the capillary IC using an Ion Swift MAX-100 0.25 mm × 250 mm column with a flow rate of 0.012 mL min⁻¹. The ammonium method used an analytical microbore column (2 mm × 250 mm IonPac 12A) with a flow rate of 0.25 mL min⁻¹.

The remainder of the samples was analyzed using the following procedure. IC samples were prepared by pipetting 1 mL samples into centrifuge tubes and diluting them with 10 mL

deionized (DI) water. The samples were analyzed in a Thermo Scientific Dionex Integrion HPIC (Waltham, MA, USA). Ammonium and guanidinium were analyzed using a Dionex IonPac CS19 column (4 mm x 250 mm, 4 μ m; Thermo Scientific, Waltham, MA, USA) and a guard column at 30 °C. An isocratic eluent of 7 mM methane sulfonic acid was run at a flow rate of 1 mL min⁻¹ to separate 25 μ L injections. Ammonium eluted at 4.7 min and guanidinium eluted at 7.6 min. Nitrate and nitrite were analyzed using a Dionex IonPac AS18 column (4 mm x 150 mm, 4 μ m; Thermo Scientific, Waltham, MA, USA) and a guard column at 30 °C. An isocratic eluent of 25 mM KOH was run at a flow rate of 1 mL min⁻¹ to separate 25 μ L injections. Nitrite eluted at 3.0 min and nitrate eluted at 4.6 min. Guanidinium analysis resulted in false positives and is not reported further.

4.2.3.3. Gas Chromatography–Mass Spectrometry (GC-MS)

To identify and quantify the main photolysis products of IMs in selected samples exposed to rainfall and sunlight in Oracle, AZ, samples were extracted and concentrated by solid phase extraction (SPE). 20 mL of rain effluent was passed through preconditioned Oasis HLB cartridges (60mg/3cc, Waters, Massachusetts) at a flow rate of 5 mL min⁻¹. The loaded cartridges were rinsed with 10 mL water to remove sample matrices and then allowed to dry under vacuum (20 in Hg) for 20 min before the transformation products were eluted with 2 mL methanol for further GC/MS analysis. Quantification of DNAN transformation products was carried on Agilent 5975 GC-MSD system coupled to an Agilent 7890A GC (Agilent Technologies, Santa Clara, CA) with selected ion modes (SIM). The oven temperature was 75°C for 2 min, then ramped at 20 °C per minute to 220 °C and held for 10 min. The injection port temperature was 200 °C. Sample was injected with 1 μ L under split-less mode. The recoveries of DNAN transformation products: 2-methoxy-5-nitrophenol (2Meo-5NP), 4-methoxy-3-nitrophenol (4Meo-3NP), 4-methoxy-3-nitroaniline (4-MeO-3-NA), and 2-methoxy-5-nitroaniline (2-MeO-5-NA) were 95.9 $\pm$ 1.8%, 79.0 $\pm$ 1.2%, 92.9 $\pm$ 0.9%, and 102.3% $\pm$ 0.5%, respectively.

4.2.2. Identification of the phototransformation products in solutions exposed to sunlight

To better identify and quantify the main photolysis products of nitroaromatic and nitroheterocyclic compounds in energetic solutions exposed to the sunlight, the aqueous samples were extracted and concentrated by solid phase extraction (SPE). After pre-conditioning SPE cartridge with 3 mL methanol and then 3 mL water, 20-50 mL of aqueous samples were passed through preconditioned Oasis HLB cartridges (60mg/3cc, Waters, Massachusetts) at a flow rate of 5 mL min⁻¹. The loaded cartridges were rinsed with 10 mL water to remove sample matrices and then allowed to dry under vacuum (20 inHg) for 20 min before parent compounds and transformation products were eluted with 2 mL methanol. The eluted samples were filtered through 0.45 μ m PVDF membrane for further HPLC and liquid chromatography-mass spectrometry (LC-MS) analysis. The remaining parent compounds (DNAN, NTO, RDX, NQ and TNT) concentrations in the samples were quantified using HPLC (Dionex Ultimate 3000, Sunnyvale, USA) with a diode array detector (ThermoFisher, MA) as described in section 3.2.3.1.

After solid phase extraction, samples were analyzed using an Agilent 1290 Infinity LC system coupled to Agilent Q-TOF/MS (6550 iFunnel) system. 1 μ L of sample was injected onto an Agilent C18 column at 25 °C and separated using a mobile phase gradient at 0.5 mL/min over 13 min. The mobile phase was a mixture of LC-MS grade water and acetonitrile (ACN) with following gradient program: 0-0.5 min, 10% ACN; 0.5-5.5 min increased ACN from 10% to 80%; 5.5-8.5 min, held at 80% ACN; 8.5-9 min, decreased ACN from 80% to 10%; 9-13 min, held at 10% ACN. Reaction products were detected using electrospray ionization (ESI) mass spectrometry

in negative ion modes. The generated LC-MS raw data were analyzed by Agilent MassHunter Qualitative Analysis Software.

4.3. Results

4.3.1. Environmental conditions across three study locations

Over the two years of experiment, the three sites, Mt. Lemmon, Oracle, AZ, and Tucson, AZ, received different amount of precipitation, some of it as snow on the highest elevation location, Mt. Lemmon. The amount of precipitation measured across three locations decreased from highest to lowest elevation, with M. Lemmon receiving a total of 70.6 inches, Oracle, AZ, 33.0 inches, and Tucson, AZ, 19.8 inches over almost exactly two years of the experiment that started in the fall of 2018 and ended in the fall of 2020. These amounts are consistent with the annual means for the highest and lowest elevations (Table 3.1) but was lower than annual average for the middle location, Oracle, AZ. The amount of rainfall in each event also decreased with decrease in elevation, from 0.41 inches at the highest elevation, to 0.32 inches per event at the middle location and 0.27 inches per rain at the lowest elevation.

Since previous measurements in Hanover, NH and Oracle, AZ, indicated the there was much smaller dissolution measured in Arizona that can be explained by decrease in amount of received rainfall assuming same amount of dissolution per amount of rainfall (Qin et al., 2021), we also calculated the number of small rainfall events that were less than 0.2 inches and the amount of water in these events. These rains were separated because we expect that they can possibly contribute to dissolution of the particles (and also phototransformation, if phototransformation is enhanced by presence of free water, which was not proven true by work described in Chapter 2), but would we entrained on the particle and frit not result in any leachate that we could collect. There was proportional decrease in both number and amount of rainfall in these small events: 6.80 inches on Mt. Lemmon, with 87 small events, and 9.6% of total for the site; 2.94 inches in Oracle, AZ with 60 events, and 8.9% of rainfall; and 3.05 inches in Tucson, AZ, with 36 events, and 15.4 % in small rains. Roughly half of all rains across all three locations were these small events, but they were responsible for only 11.3% of total precipitation. Both number of small rains and amount of water in these rains decreased with number and total amount of water overall for the three locations, but percent water contributed by these rains was higher at the lowest location. In general, rainfall in AZ is characterized by distinct seasonality with summer and winter monsoons and prolonged periods of no rain. However, in 2020, the summer monsoon was extremely small as can be seen on Figure 3.2.

Measured amount of UV light received across the three locations (Figure 3.3) was similar, with no clear trend (average irradiance over two years of 220.1 W m^{-2} on Mt. Lemmon, 240.1 W m^{-2} in Oracle, AZ, and 232.8 W m^{-2} in Tucson, AZ. There were some differences between locations: the maximum average daily values for irradiance were lowest at the lowest elevation. However, Mt. Lemmon location had higher number of rainy and cloudy days, bringing down the average irradiance. There was a clear seasonal change in irradiance across all three locations. We measured but do not report total amount of light received because we have shown earlier that light in the larger wavelength (visible range) would not have sufficient energy to break bonds in molecules that are part of these formulations (Dontsova et al., 2018; Qin et al., 2021).

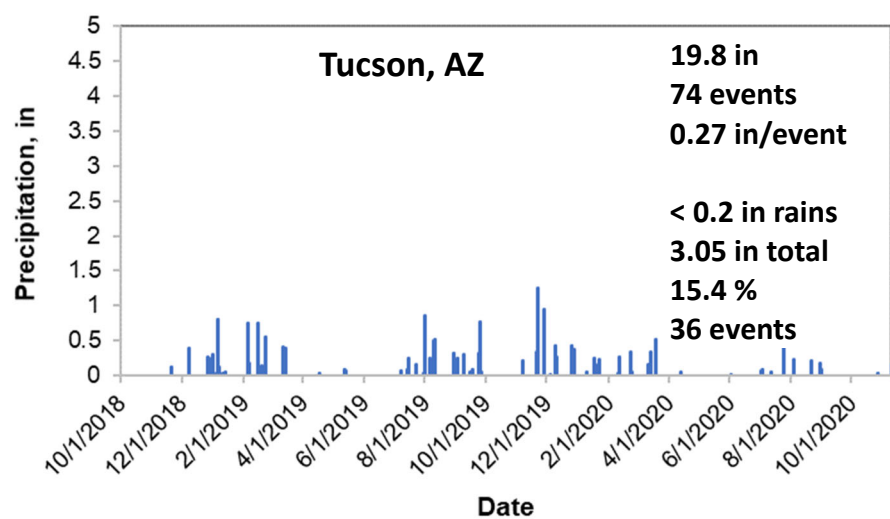
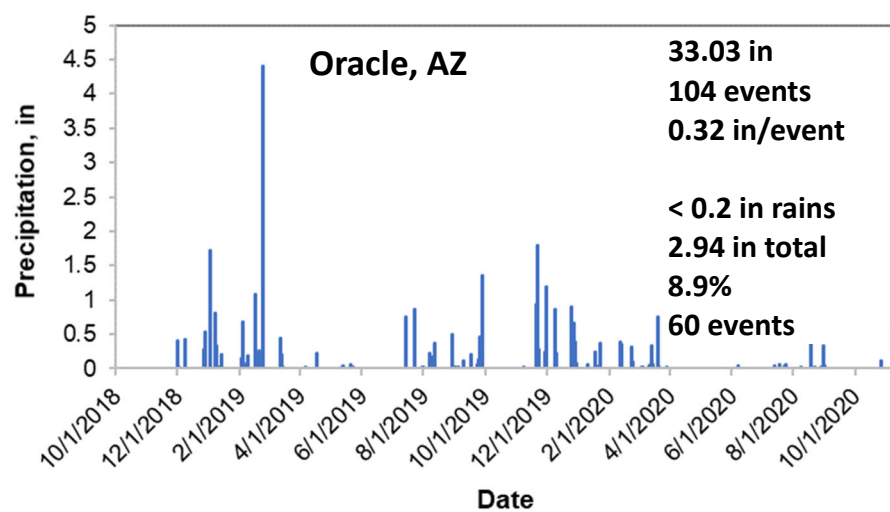
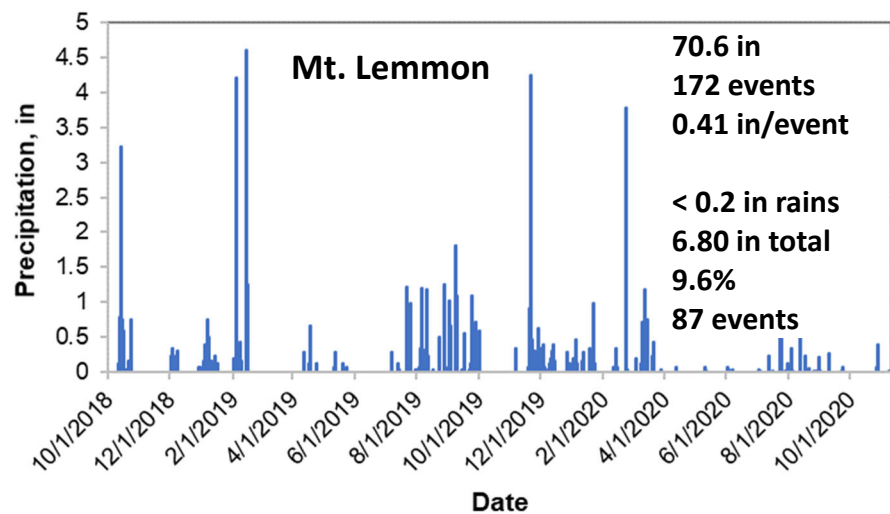


Figure 4.2. Precipitation over duration of experiment for three experimental locations.

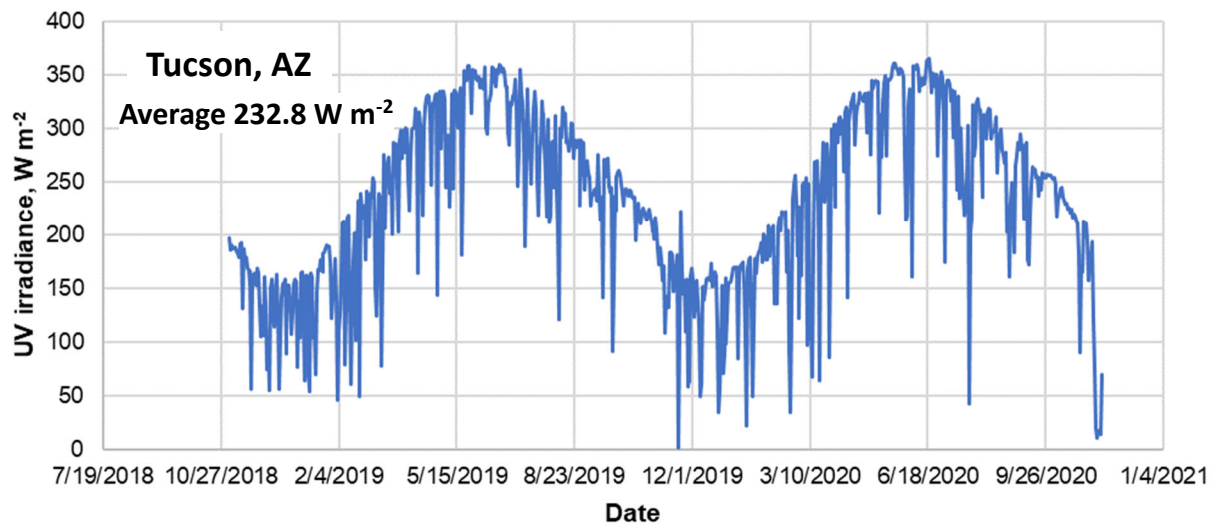
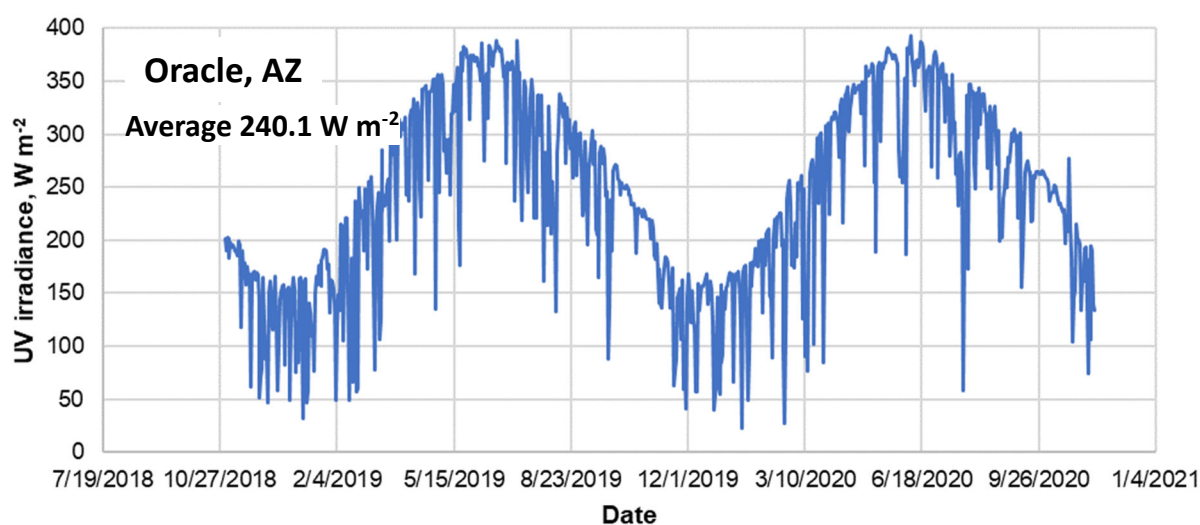
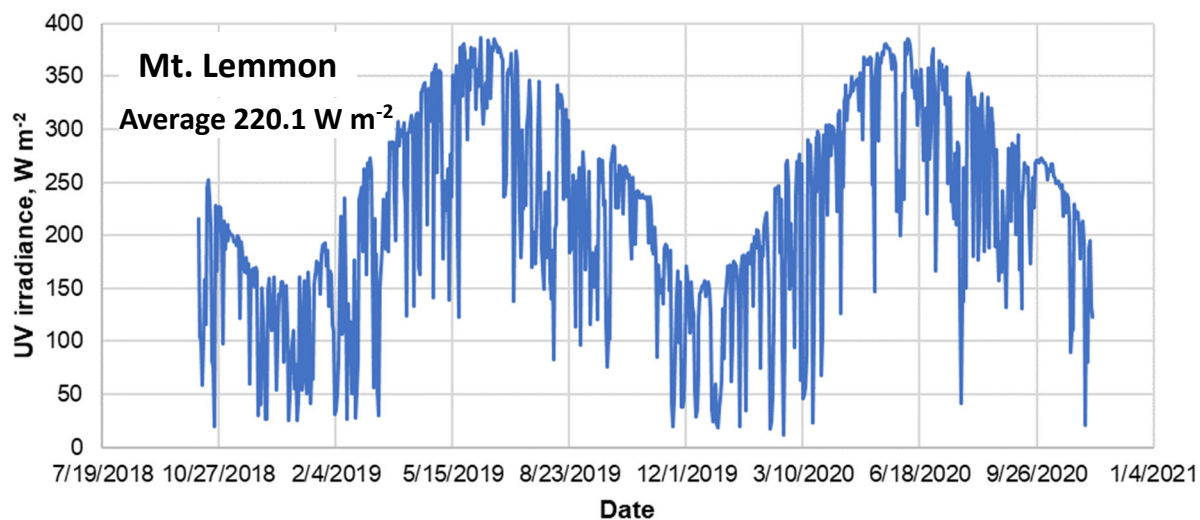


Figure 4.3. Daily average UV radiation over duration of the experiment in all three locations.

4.3.2. Effect of environmental conditions on dissolution and phototransformation of energetic particles across three study locations

4.3.2.1. Dissolution of parent compounds

We observed dissolution of all four formulations and TNT across the three locations on elevation gradient (Figures 4.4-4.8). Similar trends in dissolution were observed: dissolution of IM constituents followed their solubility with NTO dissolving first followed by NQ and DNAN in IMX-101 particles and by DNAN and RDX in IMX-104 particles. Slower dissolution of RDX was supported by formation of a whitish cover on the surface of IMX-104 particles as they weathered and NTO and DNAN were removed. Particles also developed a pitted surface where more soluble components were present originally (see Figure 4.12 for example).

In general, a consistent rate of dissolution for each compound was observed across time, except for NTO in IMX-104 particles which dissolved more quickly in the beginning and then dissolution slowed down. This decrease in dissolution is attributed to removal of NTO on the surface of the particles, while it remains in inner layers of the particle, as only 30-40% of NTO originally present was removed.

After two years of exposure to rainfall 63% of NTO was dissolved on Mt. Lemmon, and 32 and 34% in Oracle and Tucson locations, respectively, or about half, from IMX-101. Similarly, 22.4% of NQ dissolved on Mt Lemmon and 8 and 11% at two lower elevations, a little less than half. DNAN dissolution also showed similar behavior, 6% on Mt Lemmon and only 0.8% on lower elevations, more than seven times lower. In IMX-104, 44% of NTO dissolved on Mt. Lemmon vs. 30% in Oracle and Tucson. Seven vs. 3% of RDX, and 7 vs. 1.26 and 1.74% of DNAN in Oracle and Tucson, respectfully.

For Comp B (Figure 4.6), no TNT was recovered in solution. As these were low-order detonation residues that were previously exposed to rainfall in New Hampshire, we hypothesize that TNT was leached out of the particles earlier. RDX followed similar trend to IM constituents. 2.1% of RDX was recovered on Mt. Lemmon, 1.2% in Oracle, and 1.44% in Tucson. For C4 (Figure 4.7), 2.9, 2.02 and 1.53% of RDX was recovered, closer to what we would predict based on rainfall. TNT was placed as a powder, only form available. We recovered 6.1, 3.1 and 2.8% of TNT on elevation gradient from high to low elevation. As can be seen from figures, amount of rainfall recovered was not always the same for the same location across different treatments.

For IMs, differences in amount of dissolution were not significant different between Oracle and Tucson (except for DNAN in IMX-104), but amount of rainfall was more than twice in Oracle if we use amount of solution collected and 1.7 times greater if we use independently measured values for precipitation. Notably, differences in dissolution as a function of rainfall between the replicate particles ((Figures 4.4-4.8) are not observed if dissolution is plotted as a function of time (not shown). That is similar amount of dissolution happened between the particles, even of recorded amount of rainfall between the particles was different.

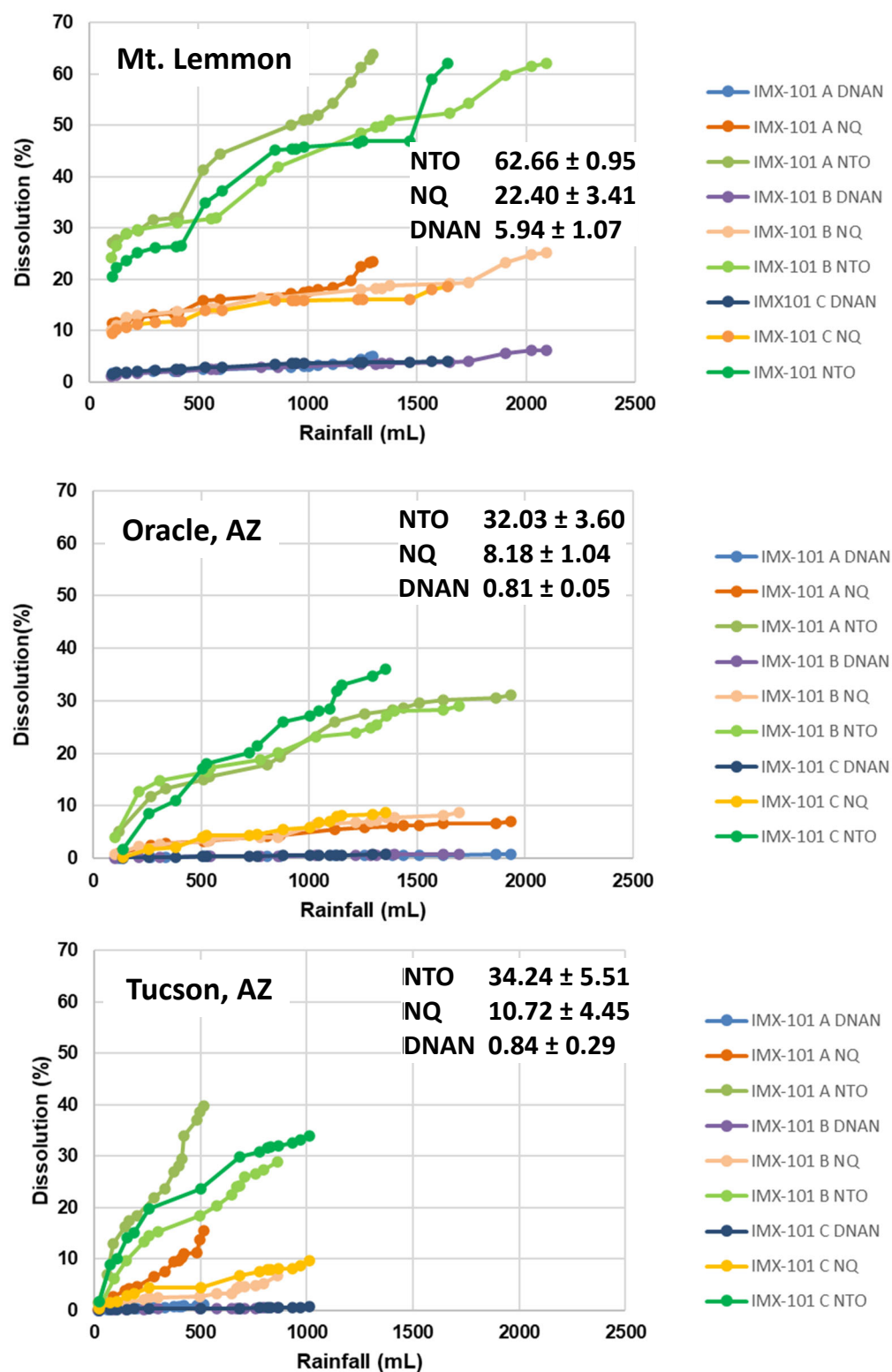


Figure 4.4. Dissolution of constituents from IMX-101 formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.

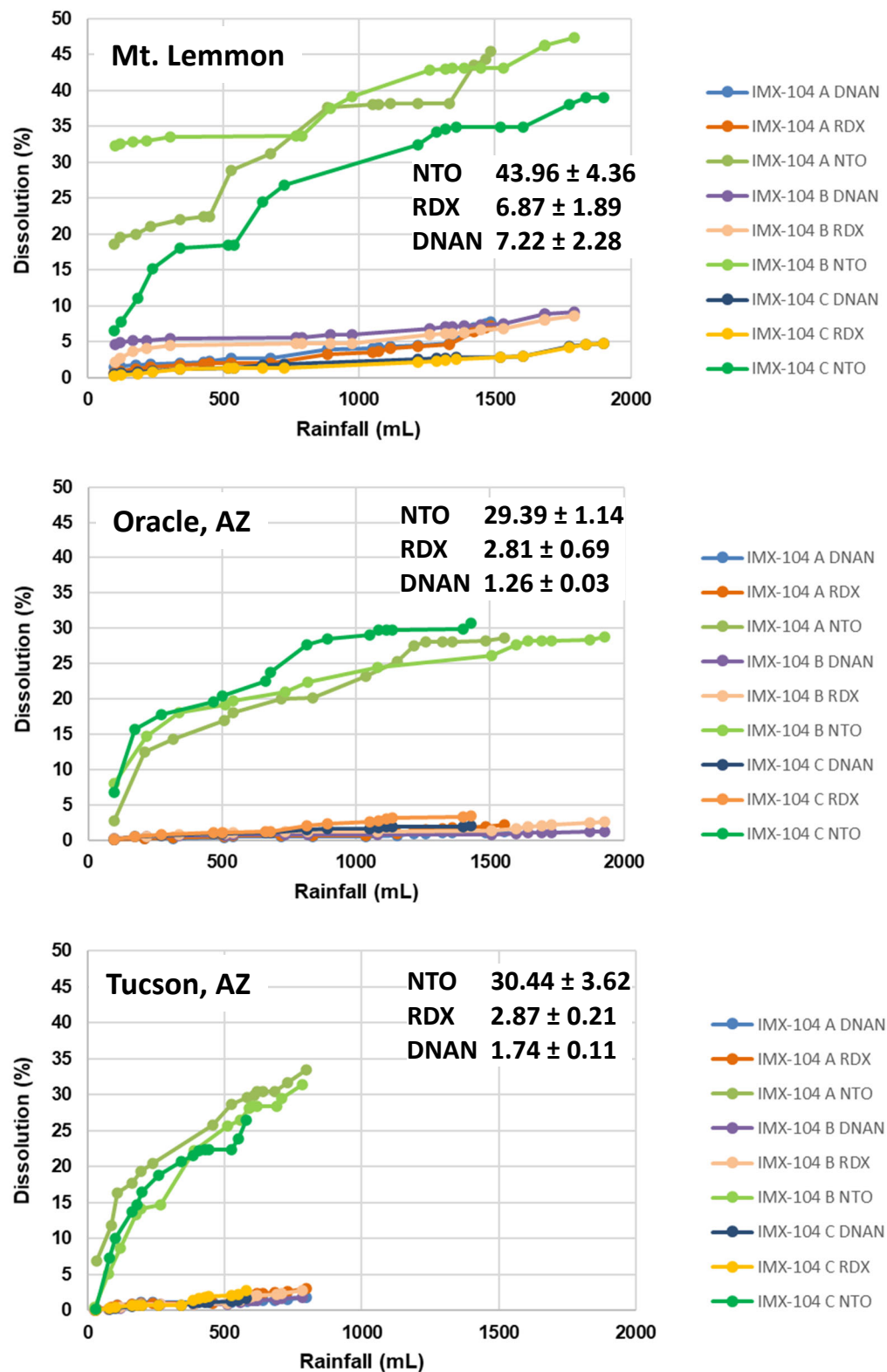


Figure 4.5. Dissolution of constituents from IMX-104 formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.

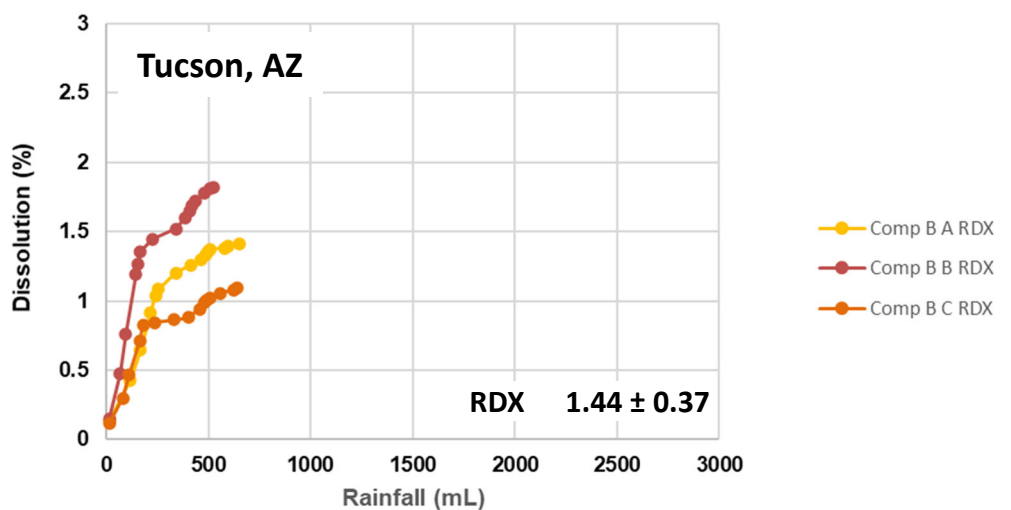
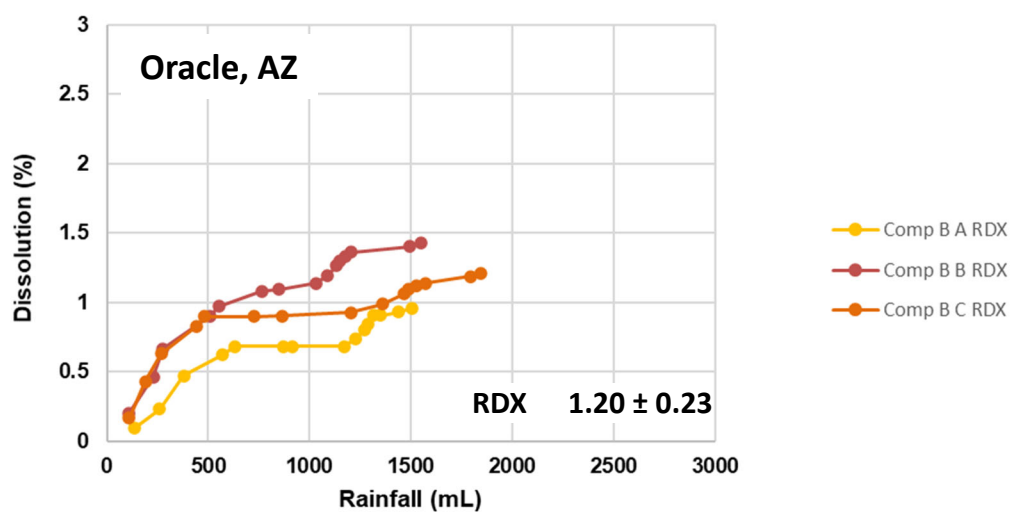
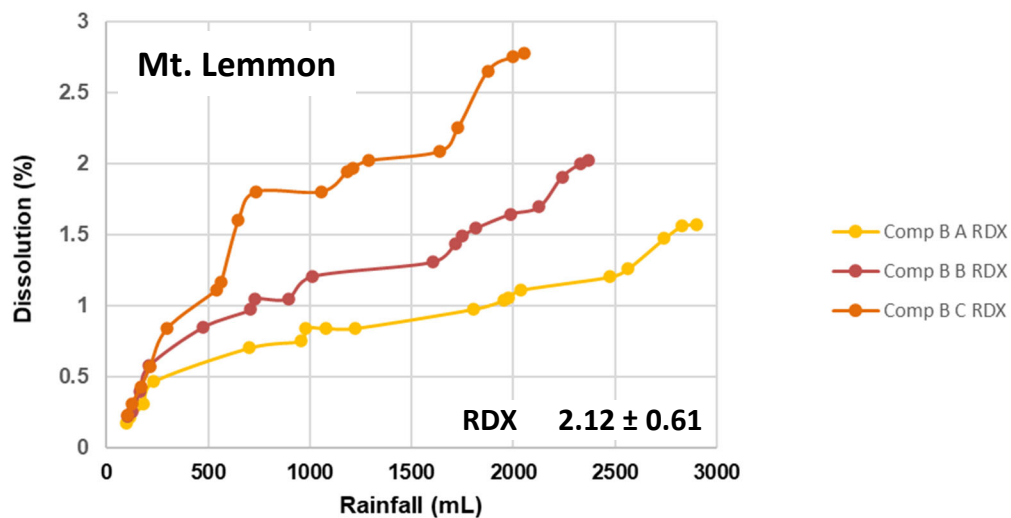


Figure 4.6. Dissolution of constituents from Comp B formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations. No TNT was recovered in solution.

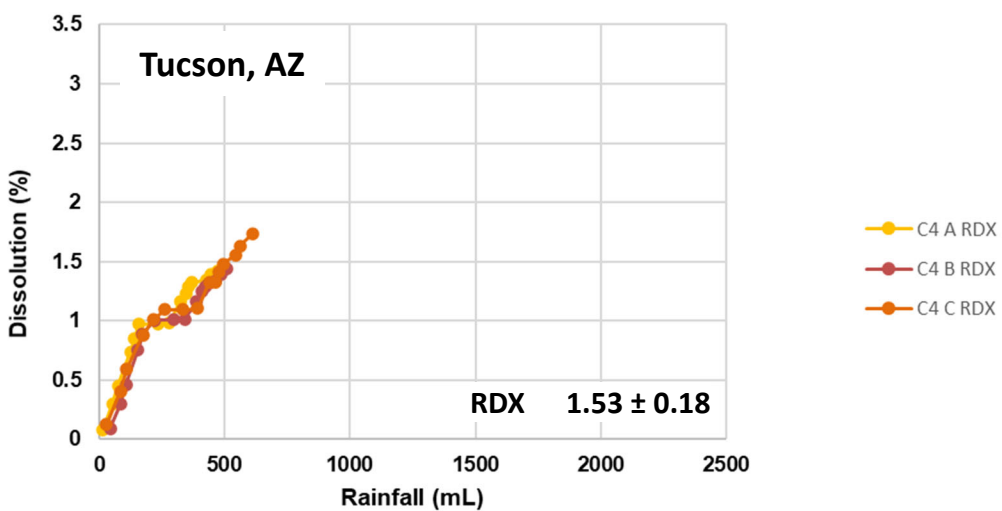
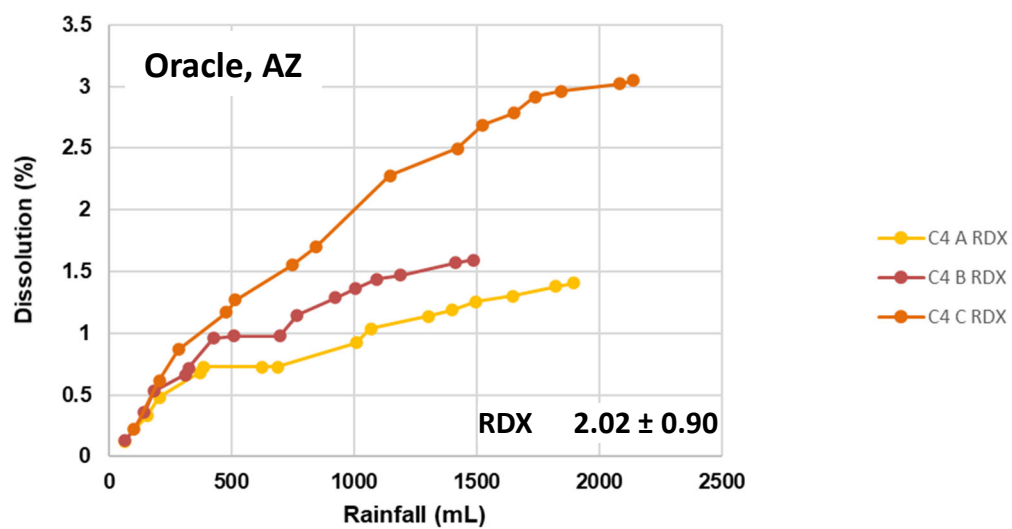
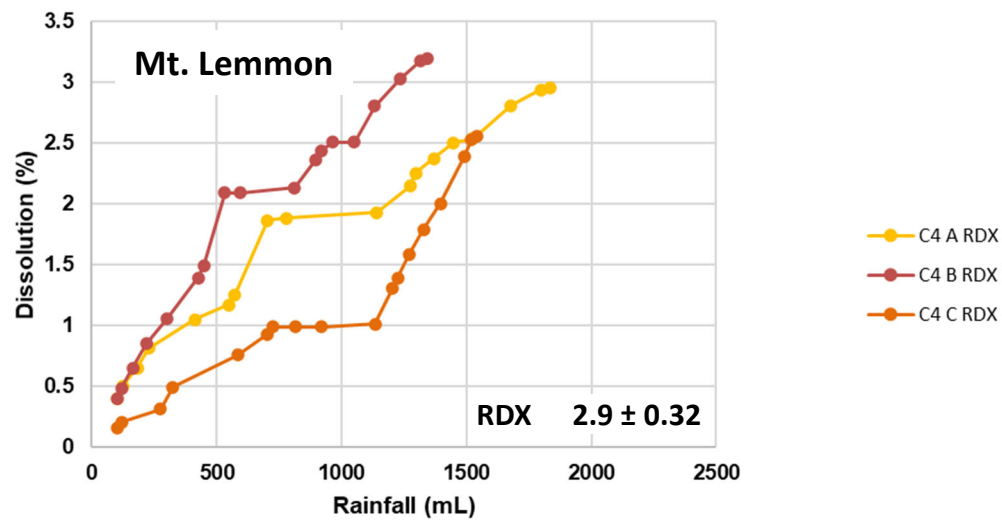


Figure 4.7. Dissolution of RDX from C4 formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.

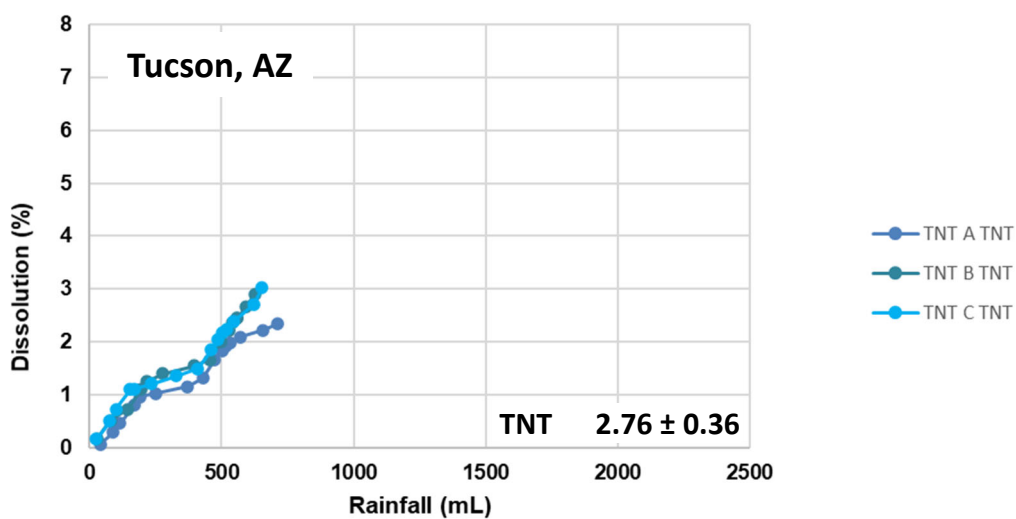
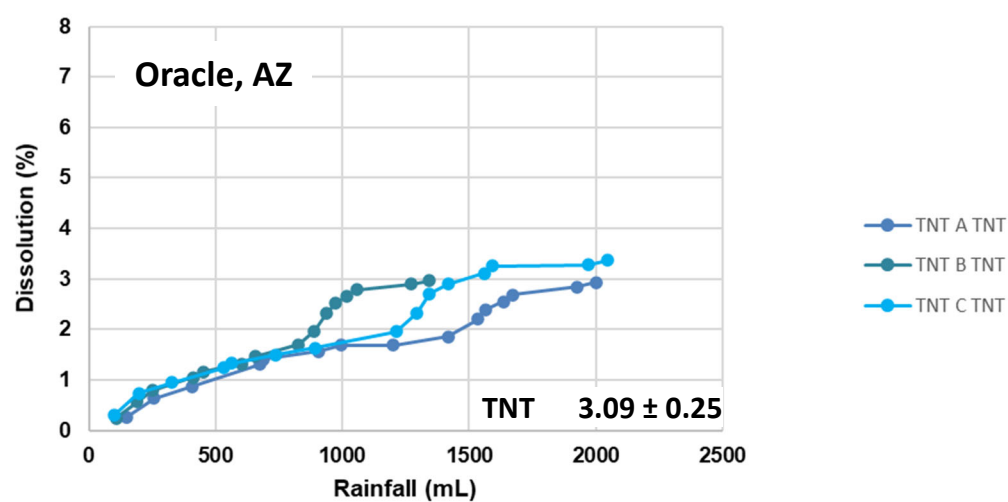
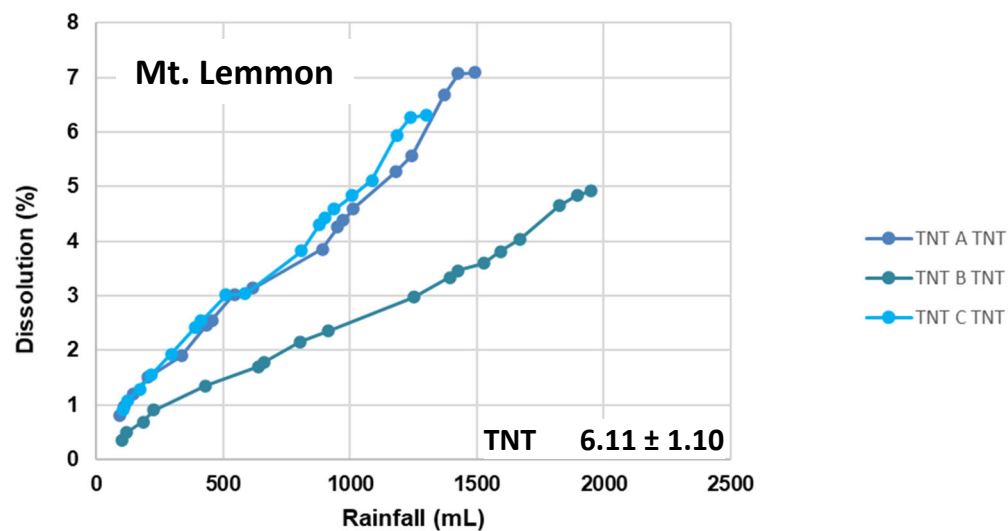


Figure 4.8. Dissolution of TNT from TNT powder at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.

To conclude, while clearly present, the effect of rainfall on dissolution of energetic constituents was not linear. Increase in solubility of energetics with increase in temperature (Boddu et al., 2008; Hawari et al., 2015; Kim et al., 1998a, 1998b; Mudryy et al., 2011; Smith & Cliff, 1999) can possibly explain increased dissolution at lowest elevation at the same rainfall amount. We can also explain it by disagreement between recorded and actual rainfall. Across the three locations, while recorded rainfall decreased gradually from highest to lowest elevation (Figure 3.2), rainfall we collected in the funnels (plotted on x-axes on Figures 4.4-4.8) was similar between Mt. Lemmon and Oracle, AZ locations, and about one half of that amount in Tucson, AZ location. While it is possible that rainfall heterogeneity is responsible for the difference between the locations, it can be also explained by what happened with precipitation after it was deposited. Small amount of rain can be retained on the frits and evaporate before it has a chance to drain into a flask. However, as discussed in section 3.3.1 there was a gradual change between the number and volume of small rainfall events across all locations. There is also a possibility that in the higher elevations due to windier conditions less rainfall is entering the funnel. Some of these differences will happen before rain reaches the particle while others after, making it difficult to predict impact on dissolution based on recorded rainfall due to other factors influencing behavior of the precipitation. Differences in how quickly rain evaporated can also affect both the amount of water entering the flasks, but also how long water persists on the particle surfaces. We hypothesize that dew may also be an important factor in particle dissolution. It will not be recorded as precipitation but will interact with particle surface allowing dissolution, particularly of material within the particle framework allowing diffusion of dissolved constituents to the surface where they will be removed by next rainfall.

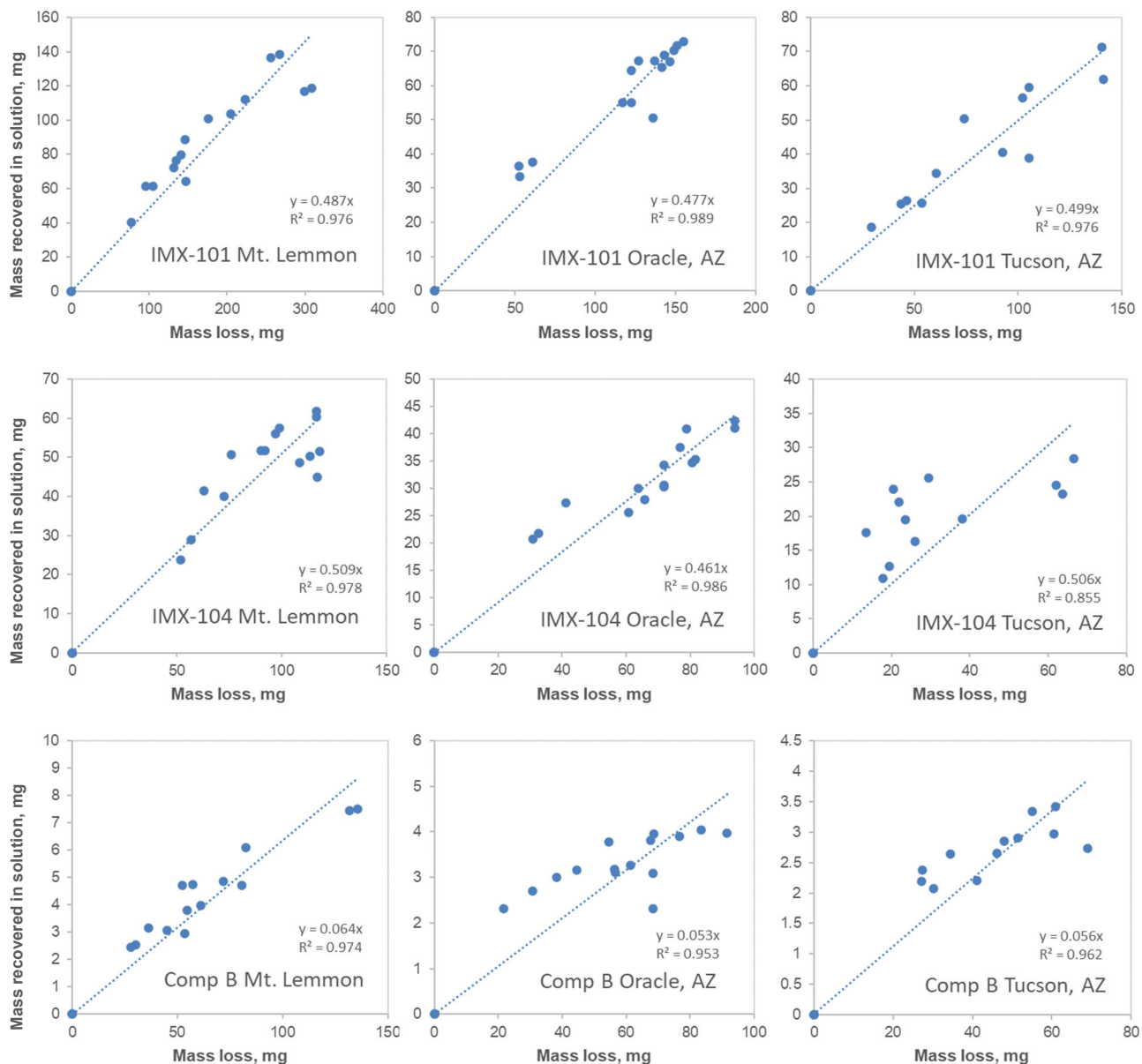
4.3.2.2. Mass balance

Figure 3.9 presents results of the mass balance of the particles during the experiment. We plotted mass loss of the particles based on weighting of the particles performed in the beginning and five times during the experiment, and cumulative recovery of parent compounds in solution. For this analysis, all three replications were combined to give more confidence in obtained regression parameters. For TNT and C4, because material was present as powder and difficult to weigh, we have fewer data points. We can assume that amount that is not recovered as parent compounds has been phototransformed, even if we did not recover missing mass in known products (shown later).

For IMX-101 and IMX-104 particles, there was a significant linear relationship between mass loss and solution recovery, but slope was less than 1, indicating that some material (though we do not know which compounds) was lost to phototransformation. A slope close to 0.5 was observed for both compounds, indicating that 50% of mass was lost and there was no trend with the location. Previous studies in New Hampshire, showed much higher recovery with only 19% missing due to phototransformation for about the same time period (Taylor et al., 2015). This indicated much greater contribution of phototransformation to fate of energetic compounds deposited on the surface in arid conditions.

For traditional munitions formulations, Comp B and C4, and TNT, we measured much lower recovery of the parent compounds. 5-6% was recovered for Comp B, 1.5-2.9% for C4, and 2.8-7.2% for TNT. There was also a trend for greater recovery with increase in dissolution at greater elevation. In previous studies of traditional munitions (Taylor et al., 2010) on average 33% was recovered, including 39% for Comp B, 31% for TNT, and 16% for C4. Similarly to IM constituents, lower recoveries were observed for traditional munitions in Arizona than on New

Hampshire. Relative recovery between the compounds was similar in both locations, with C4 having lowest recovery and Comp B the highest. The fact that Comp B was a particle, while C4 and TNT were present as powder did not seem to significantly impact their loss.



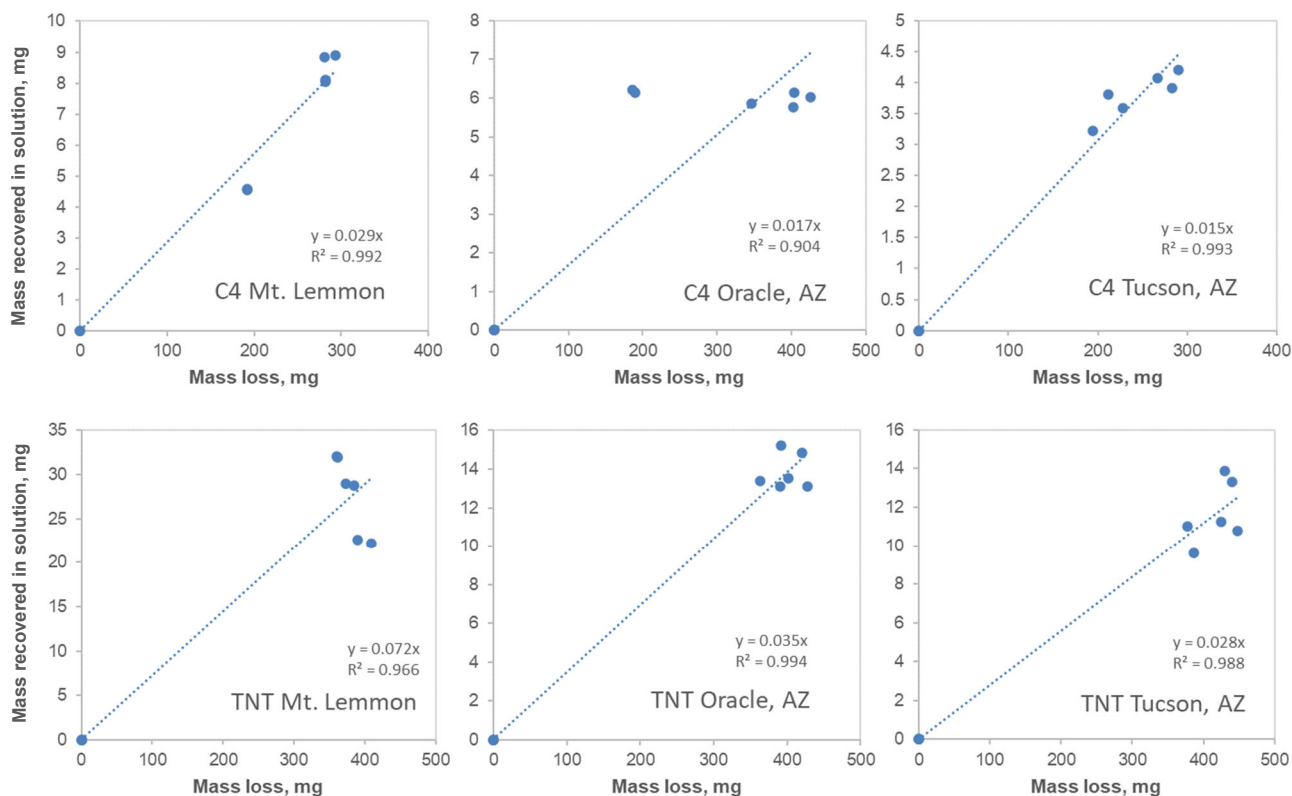


Figure 4.9. Relationship between mass recovery in solution and mass loss of the particles from (top to bottom) IMX-101, IMX-104, Comp B, and C4 formulation particles, as well as TNT powder at Mt. Lemmon (left) Oracle, AZ (middle), and Tucson (right), locations.

In Figures 4.6, 4.7, and 4.9 we are presenting RDX recovery assuming that there is no HMX present in RDX used in preparing formulation. We made this assumption because we did not analyze particles before the experiment and therefore did not have exact amount of HMX present in RDX, however RDX and HMX concentrations in solution resulting from dissolution of the IMX-104 particles indicate that there was about 10% of HMX in RDX (Figure 4.9).

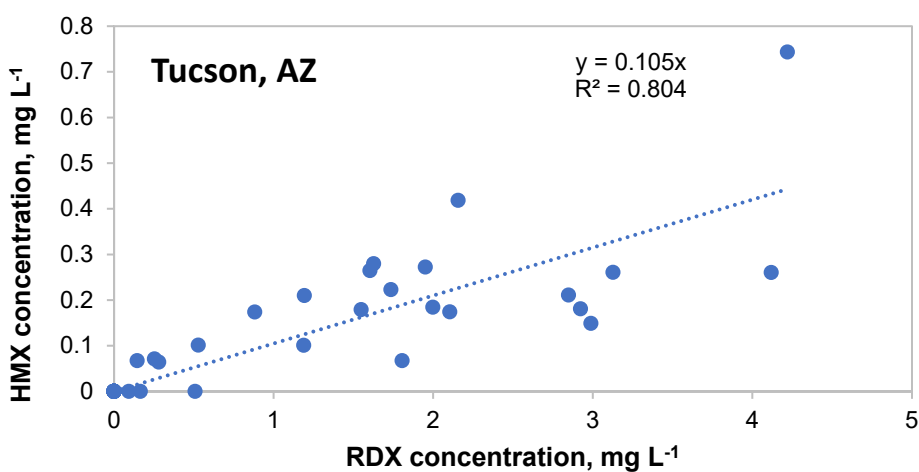
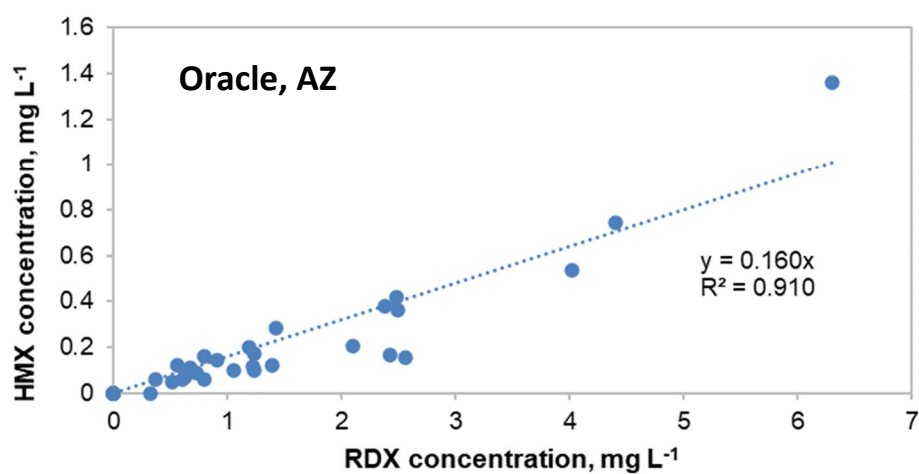
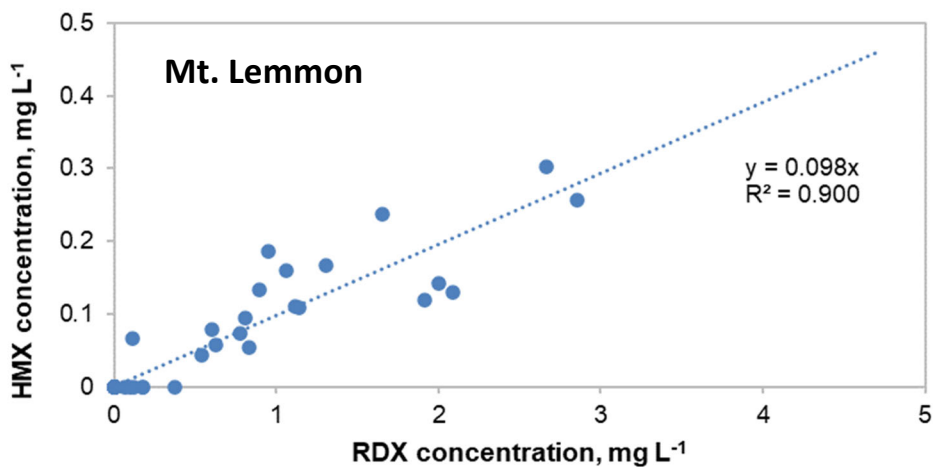


Figure 4.10. Dissolution of RDX and HMX from IMX-104 formulation particles at Mt. Lemmon (top) Oracle, AZ (middle), and Tucson (bottom), locations.

4.3.2.3. Products of transformation

We have detected and quantified following products of transformation for studied compounds. For DNAN, we measured 2-MeO-5-NA and 4-MeO-3-NA, nitro-reduction products, as well as 2-MeO-5-NP, 2-MeO-5-NP, and 2,4-dinitrophenol. Of these, quantifying 2-MeO-5-NP, 2-MeO-5-NP, and DNP required concentrating sample using SPE and therefore these were analyzed only for a subset of samples. For NTO, urazole was the only organic product of phototransformation. For NQ, we measured guanidine, cyanoguanidine, cyanamide, and urea (but as mentioned above (section 3.2.3.2) guanidine results were not consistent and therefore are not reported). Nitrate, nitrite, and ammonium can result from transformation of several different compounds in IMX-101 and IMX-104 formulations. For TNT, we analyzed for a number of products using method 8330b (U. S. Environmental Protection Agency, 2006). However, we only detected 1,3,5-TNB and 1,3-DNB using HPLC.

A subset of samples for the first monsoon rainfall after prolonged dry period, July 26, 2019, was extracted with SPE and analyzed with GC-MS (Table 3.5). For IMX-101, the largest concentrations of DNAN products were observed in the highest elevation, coldest and wettest Mt. Lemmon location, where highest concentrations of DNAN were also observed, but relative to DNAN concentration, fraction of products present was the smallest (16-21%). The highest fraction of products relative to DNAN was found at the lower elevations (up to 127 percent - that is there were more products present than parent compound in solution coming from the particle). There was no direct trend along the elevation gradient, most likely due to the fact that while mid-elevation location was warmer, and DNAN transformation (both bio and photo) increases with temperature, this year, this location received a lot of rain, compatible to the high elevation. Presence of ammonium, nitrate and nitrite cannot be assigned to a single parent compound, but they had higher concentrations in lowest elevation, indicating increased transformation.

While we were able to routinely measure concentrations of anilines, 4-MeO-3-NA and 2-MeO-5-NA, using HPLC, phenols, 2-MeO-5-NP and 2-MeO-5-NP, required SPE and GC-MS analysis. However, having measurements for both groups of compounds for a subset of data (June 26th, 2019) allowed us to develop relationships between the two groups of products for samples where we did measure both to approximately estimate phenols concentrations for all other samples. Figure 3.11 presents relationships between concentrations of 2-MeO-5-NP and 2-MeO-5-NP, 4-MeO-3-NA and 2-MeO-5-NA, and sum of 4-MeO-3-NA and 2-MeO-5-NA and sum of all four compounds. While relationships are not very strong, they are significant and allow estimation of phenol production, even when we do not measure them. We also observe that there is approximately twice as much produced of 2-MeO-5-NA as 4-MeO-3-NA, consistent with reported selectivity for reduction of nitro group in DNAN in ortho-position (Hawari et al., 2015). Formation of 2-MeO-5-NP was preferred over 2-MeO-5-NP. Based on these plots, we can estimate that 1.8 times more phenols was formed than anilines.

Table 4.5. Solution concentrations following first monsoon storm (July 26, 2019) in three studies locations on elevation gradient, from top to bottom, Mt. Lemmon, Oracle AZ, and Tucson, AZ. Sum of DNAN products includes 2-MeO-5-NP (2-methoxy-5-nitrophenol), 2-MeO-5-NP (4-methoxy-3-nitrophenol), 4-MeO-3-NA (4-methoxy-3-nitroaniline), and 2-MeO-5-NA (2-methoxy-5-nitroaniline).

Formulation and location	NTO		NQ		RDX		DNAN		Sum of DNAN products		Fraction of DNAN products relative to DNAN		Ammonium and nitrate	
	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev
	mg L ⁻¹		mg L ⁻¹		mg L ⁻¹		mg L ⁻¹		mg L ⁻¹				mg L ⁻¹	
IMX-101														
Mt. Lemmon	60.99	22.46	29.79	11.55	NA	NA	5.58	1.63	0.874	0.241	0.162	0.056	7.51	1.66
Oracle	12.53	2.18	6.43	1.09	NA	NA	0.72	0.06	0.306	0.085	0.418	0.126	5.87	0.77
Tucson	41.46	28.84	17.91	12.98	NA	NA	1.62	0.46	0.762	0.236	0.580	0.377	13.79	1.18
IMX-104														
Mt. Lemmon	65.90	27.90	NA	NA	1.83	0.45	2.78	0.84	0.547	0.078	0.211	0.083	8.33	1.31
Oracle	11.00	3.01	NA	NA	0.16	0.03	0.23	0.05	0.290	0.025	1.273	0.136	5.43	0.86
Tucson	34.59	36.30	NA	NA	0.30	0.27	1.17	0.93	0.566	0.113	0.618	0.347	12.79	1.98

In the remaining samples analyzed by HPLC, concentrations of measured products in general correlated with the concentrations of dissolved parent compound. While differences were not significant, there was a trend for change in percent of DNAN product, 2-MeO-5-NA with elevation. For IMX-101, DNAN product 2-MeO-5-NA represented 1.3% of DNAN on Mt. Lemmon, while in Oracle it was 1.9%, and 3.4% in Tucson. Another DNAN transformation product, 4-MeO-3-NA represented 0.08% of DNAN on Mt. Lemmon, and 0.3% in Oracle, and Tucson. In IMX-104, 2-MeO-5-NA represented 1.7% of DNAN on Mt. Lemmon, while in Oracle it was 1.2%, and 10.3% in Tucson. 4-MeO-3-NA represented 0.06% of DNAN on Mt. Lemmon, and none in Oracle, and 1.3% in Tucson. For both compounds, Tucson had the highest percent of products relative to parent compounds. Presenting product concentrations relative to parent compound concentrations accounts for differences in sample dilution due to amount of water received, which was significantly lower in Tucson.

Using relationship developed on Figure 3.11 we can multiply obtained values for anilines, 2-MeO-5-NA and 4-MeO-3-NA, by 2.78 to estimate total organic products, including phenols, 2-MeO-5-NP and 2-MeO-5-NP. However, accounting for phenols still gives us much lower value than phototransformation estimated by mass loss of the particle.

In IMX-101 samples, urazole constituted 3.94 ± 0.87 , 1.34 ± 0.32 , and $2.71 \pm 1.50\%$ of NTO for Mt. Lemmon, Oracle, AZ, and Tucson locations, respectively. Differences were significant only between Mt. Lemmon and Oracle locations, and there was no consistent trend with elevation. Some evidence for different time of collection suggests that higher insolation and temperatures in the summer may result in lower urazole concentrations. We analyzed for four products of NQ phototransformation, urea, cyanamide, cyanoguanidine, and guanidine. No cyanoguanidine was detected and due to analytical problems, we did not use values for guanidine. We correlated sum of remaining NQ products, urea and cyanamide, with NQ. Sum of NQ products accounted for 5% of NQ on Mt. Lemmon, mountain, 10% at B2, and 0.6 % in Tucson but relationship is not significant for any of the locations and was driven mostly by cyanamide, which had the highest concentrations.

While in IM formulations we cannot assign inorganic ions to any particular component, we can do so in C4 and TNT. However, for C4, which does not have any other energetics, besides RDX, there was no relationship between concentrations of ammonium, nitrate, and nitrite and RDX for all studied locations.

Visually TNT solutions in Tucson, AZ collected after the first rainfall after placing them outdoors appear to be darker (Figure 4.12) than in other two locations, indicating greater product concentration, however, this can be explained by the lower total volume of rainfall for the Tucson location, 32 mL vs. 118 and 97 mL in Oracle and on Mt. Lemmon. No relationships between concentrations of inorganic ions, ammonium, nitrate, and nitrite and TNT in solution was observed for any location. Average concentrations of 1,3,5-TNB and 1,3-DNB were 0.37 and 0.03 ppm, respectively, on Mt. Lemmon, 0.14 and 0.07 ppm in Oracle, and 0.2 pm and 0.1 ppm in Tucson (representing in Tucson 1.4 and 0.04% of TNT present, NS).

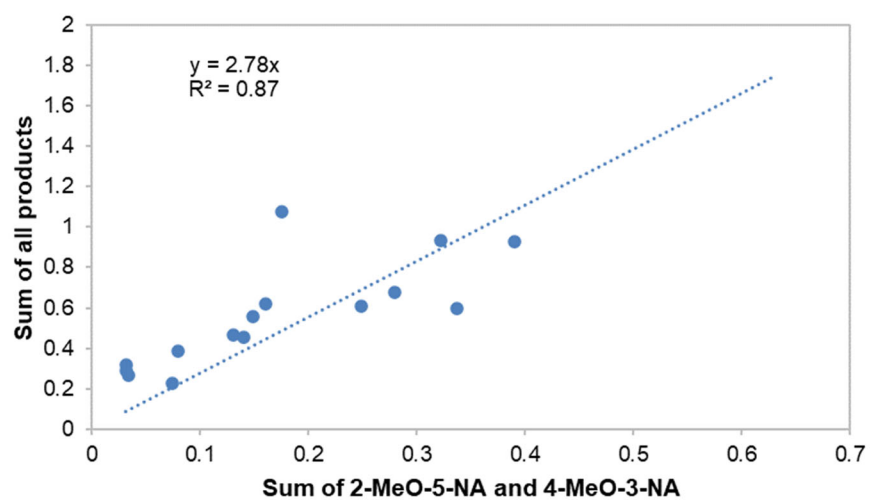
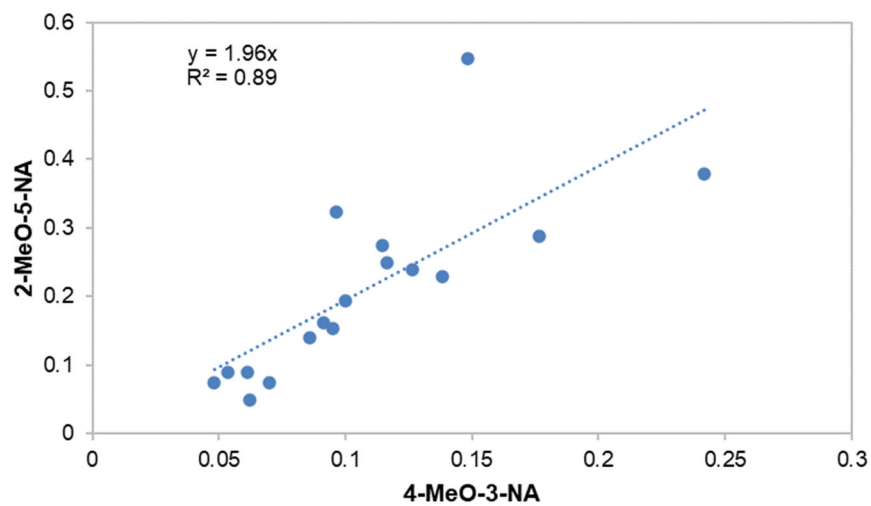
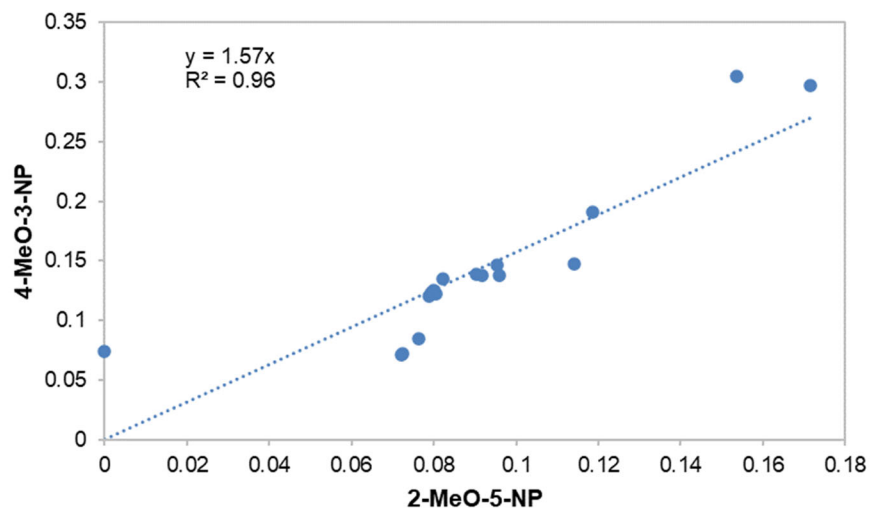


Figure 4.11. Relationships between concentrations (mg L⁻¹) of DNAN products, 2-MeO-5-NP (2-methoxy-5-nitrophenol), 2-MeO-5-NP (4-methoxy-3-nitrophenol), 4-MeO-3-NA (4-methoxy-3-nitroaniline), and 2-MeO-5-NA (2-methoxy-5-nitroaniline) measured on July 16, 2019.

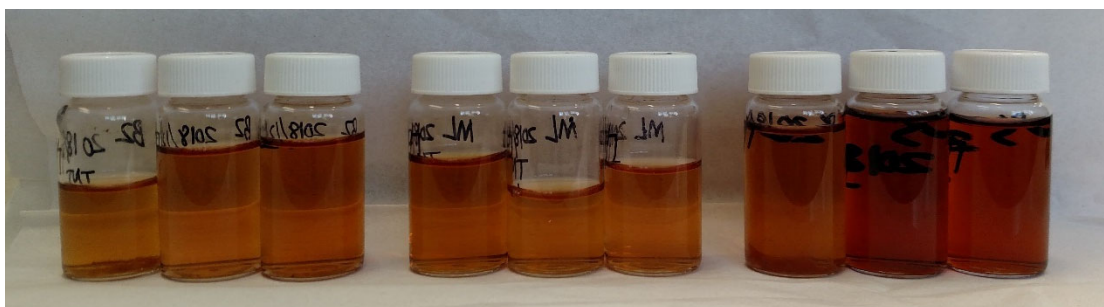


Figure 4.12. Solutions resulting from TNT dissolution and phototransformation collected on December 7th, 2018, first sampling time after placing the particle outdoors. Vials are grouped by 3 replicates in each location, at Oracle, AZ (left), Mt. Lemmon (middle) and Tucson (right).

4.3.3. Size effect on dissolution and phototransformation of IMX-101 particles



Figure 4.13. Time zero (top row) and end of experiment (bottom row) photographs for particles of IMX-101 of different sizes, small (rep a) on the left, medium (rep a) in the middle and large (rep c) on the right. Ruler division equals 1 mm. All except small particles at the end of experiment are shown at the same scale.

Dissolution of particles of IMX-101 of small, medium, and large size (Figure 3.13) but similar total mass exposed to rainfall and sunlight in Oracle, AZ indicated increase in dissolution with decrease in particles size (Figure 3.14). While one particle of large size released 51% of NTO, 12% of NQ, and 1.6% of DNAN it originally contained, two medium size particles released 65% of NTO, 13% of NQ, and 1.9% of DNAN, and 15 small particles released 96% of NTO, 30% of NQ, and 4.4% of DNAN.

To account for the effect of size on particle dissolution, we normalized particle dissolution to the total surface area of the particles. To do this, we divided measured recovery in solution for medium and small particles by a constant (a ratio between average SA of large particle and total actual SA of small or medium particles in each replication). Surface area of the

particles was calculated the following way. Average mass of particle in each replication equaled total mass of the particles in a replication, which we measured, divided by the number of particles. We divided particle mass by bulk density (1.63 g cm^{-3}) to calculate the volume of each particle. The radius of the particle was calculated from the volume, and then SA for each particle calculated using obtained radius using equations for volume and SA of a sphere. Total SA for all the particles in the treatment was calculated by multiplying by the number of the particles in a replication. We obtained correction factors between 1.36 and 1.48 for medium particles relative to large, and 2.67 to 2.77 for small particles.

Resulting values for dissolution (Figures 3.15 and 3.16, Table 3.6) indicate that this correction brings dissolution rates closer. It overcompensates somewhat for NTO (but still brings rates within error of the measurement for large and medium particles) but gives in very good agreement between rates for different particle sizes for NQ and DNAN. Determining dissolution rate for IM constituents based on known rates for a single particle size and known particle weight would simplify significantly prediction of particle dissolution, considering that low order detonations generate a distribution of particle sizes (Taylor et al., 2015; Bigl et al., 2020) and measuring dissolution rates for all of them is not practical. Mass of the particle is a convenient reference, as it is easy to obtain, and measurement is much more accurate than any possible measurement of size for an irregular particle.

Table 4.6. Total recovery (%) of IMX-101 constituents from small, medium, and large particles before and after normalizing dissolution by the total SA of the particles.

Particle size	DNAN		NQ		NTO		Correction factor
	Average	Stdev	Average	Stdev	Average	Stdev	
Measured							
Small	4.35	0.20	29.52	1.01	96.45	10.26	2.77
Medium	1.88	0.34	12.88	2.02	65.31	3.18	1.43
Large	1.59	0.40	11.69	2.63	51.28	6.43	1
Normalized							
Small	1.57	0.07	10.66	0.36	34.85	3.71	
Medium	1.32	0.28	9.01	1.59	45.62	2.78	
Large	1.59	0.40	11.69	2.63	51.28	6.43	

While recovery of energetic constituents in solution as well as loss of mass (Figure 3.17) were affected by particle size, relationship between the two parameters was the same. This indicates that there is no effect of particle size on phototransformation within the range of sizes we examined. No effect of particle size on recovery of phototransformation products was observed, as well.

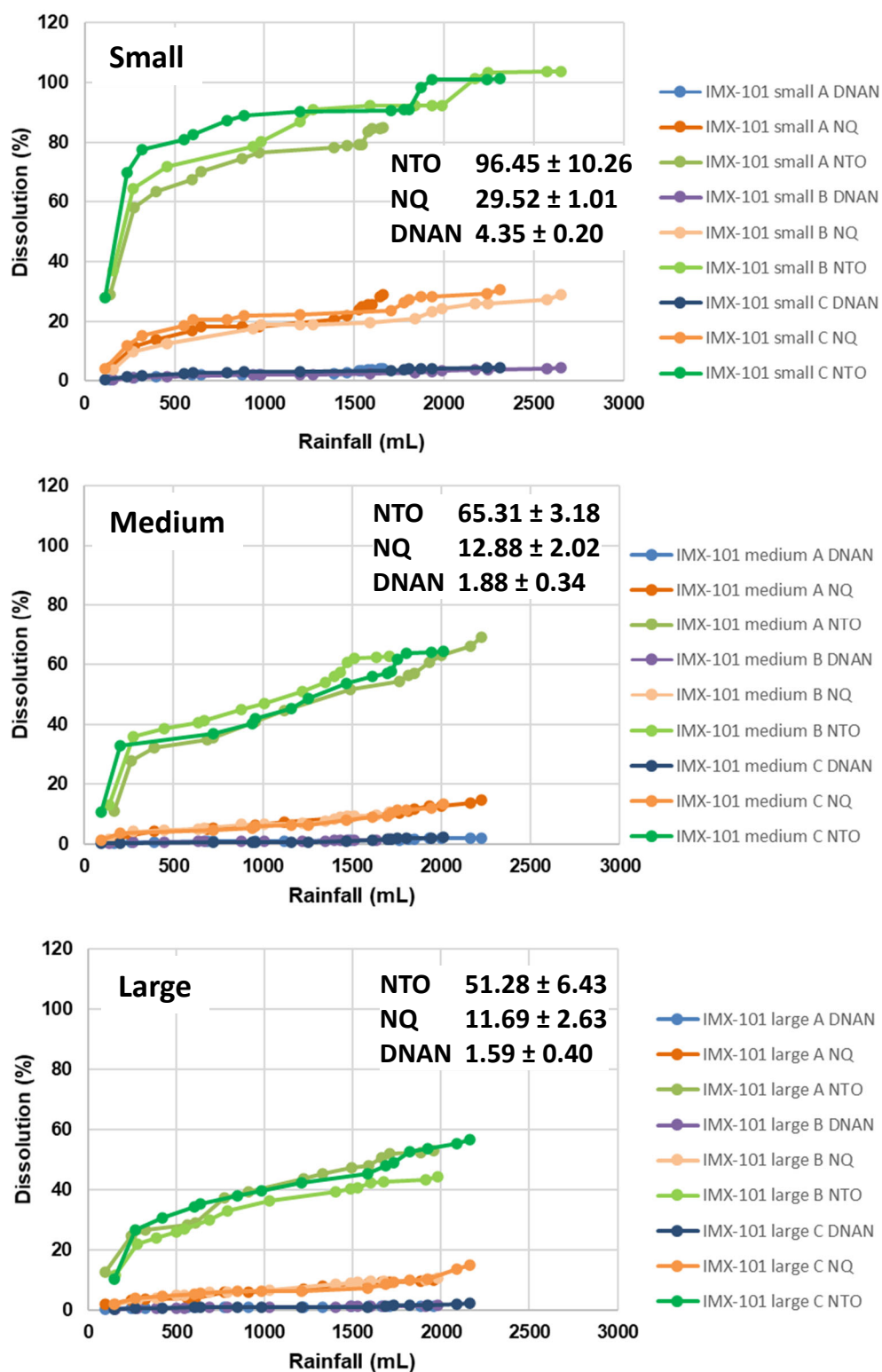


Figure 4.14. Dissolution of constituents from small (top), medium (middle), and large (bottom) particles of IMX-101 formulation in Oracle, AZ location.

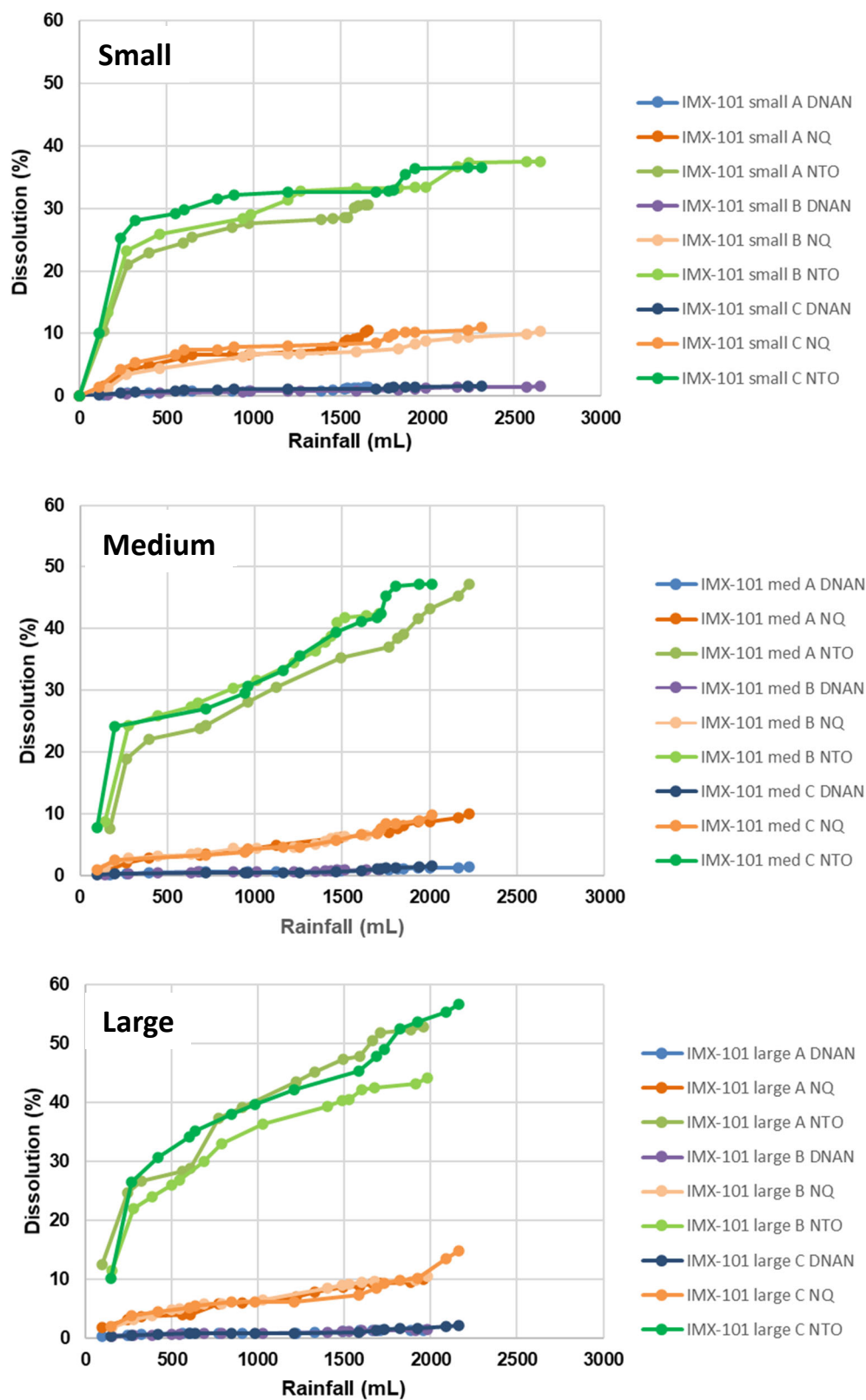


Figure 4.15. Dissolution of constituents from small (top), medium (middle), and large (bottom) particles of IMX-101 formulation in Oracle, AZ location after normalizing to surface area.

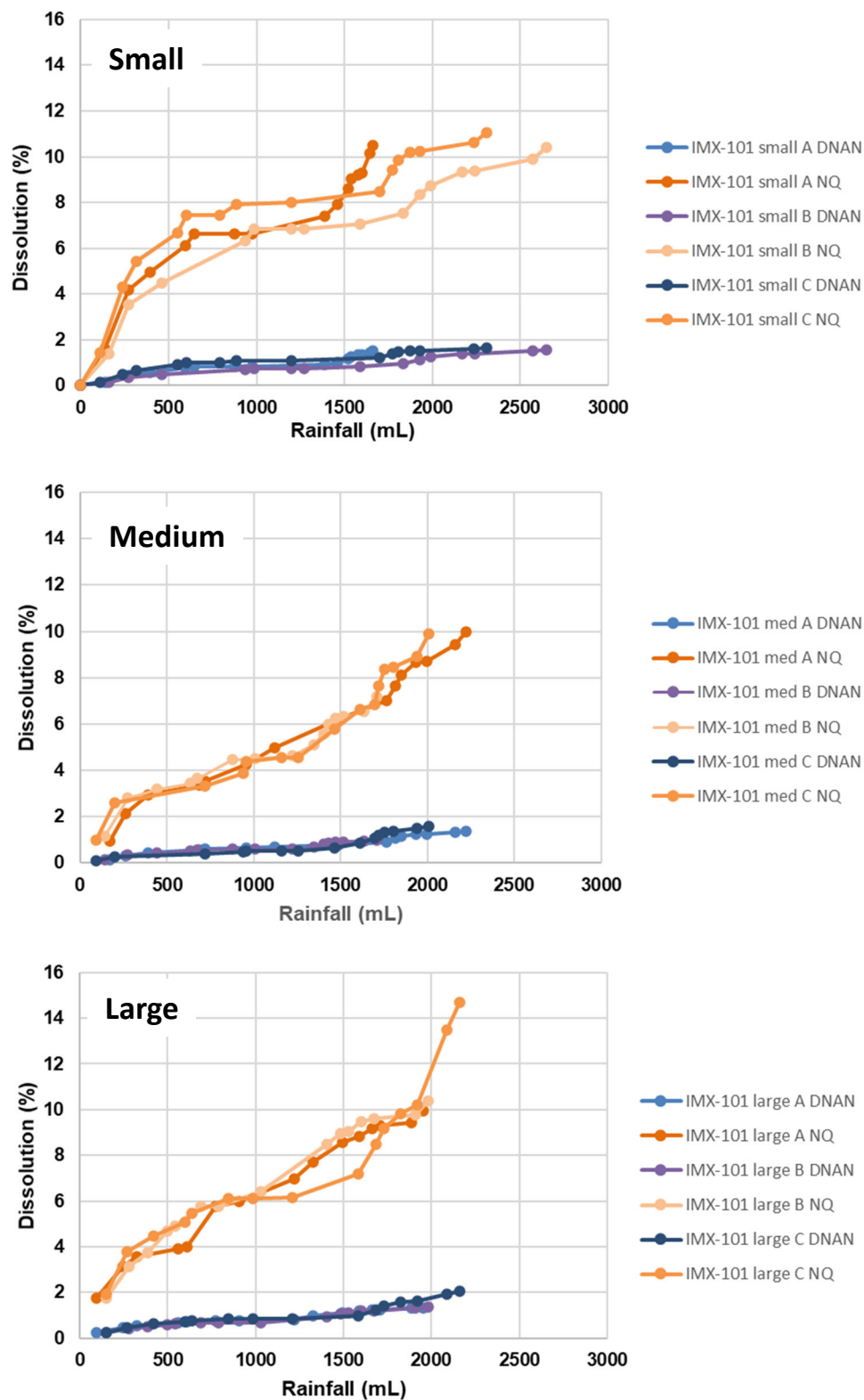


Figure 4.16. Dissolution of constituents from small (top), medium (middle), and large (bottom) particles of IMX-101 formulation in Oracle, AZ location after normalizing to surface area (zoom into NQ, DNAN).

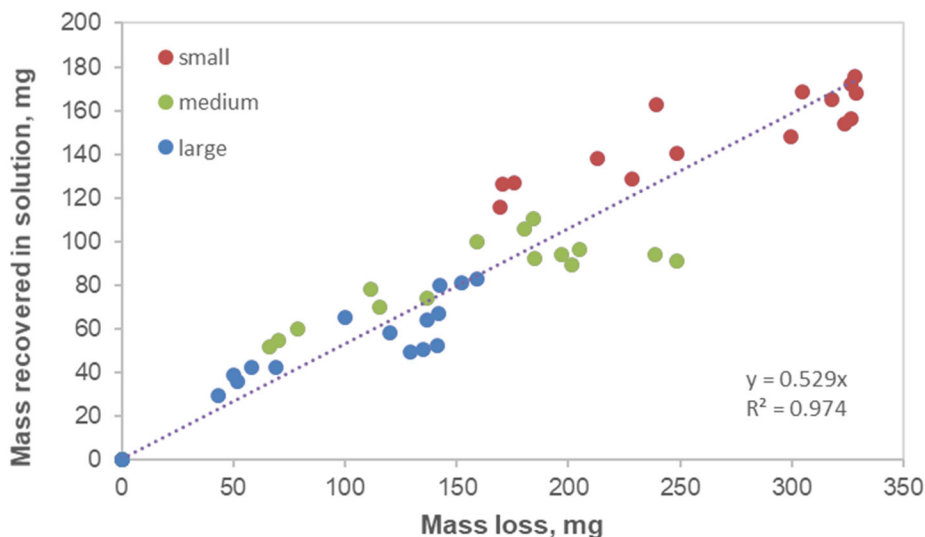


Figure 4.17. Relationship between mass recovery in solution and mass loss of the IMX-101 particles of small (red), medium (green), and large (blue) size, at Oracle, AZ location.

4.3.4. Identification of phototransformation products in solutions exposed to sunlight

To identify phototransformation products of TNT, DNAN, RDX, NTO, and NQ in solutions exposed to sunlight, we left solutions of these compounds on the roof at Biosphere 2 (Oracle, AZ), same place where solid particles were placed. After 3 days, 1 week and 3 weeks of exposure solutions were analyzed by HPLC. In all samples less than 50% of parent compound was remaining indicating phototransformation. Then solutions were SPE-extracted and analyzed by HPLC-TOF-MS to identify transformation products.

No products of RDX, NTO, or NQ were detected in analyzed solutions. All solutions had to be extracted through SPE to protect the instrument and due to low affinity of hydrophilic NTO and NQ for the SPE material they did not retain on the cartridge. However, both NTO and NQ were detected by the instrument when injected directly without SPE (Appendix, pp. A23 and A24). Hydrophilic character can also explain lack of detection of their daughter compounds, however, small size of the products of NTO and NQ transformation can also explain why they were not detected by the high-performance liquid chromatography time-of-flight mass spectrometry (HPLC-TOF-MS).

We were able to detect several products of TNT (Appendix, pp. A1 to A15) and DNAN (Appendix, pp. A16 to A22) transformation. TNT solutions changed color very quickly and following compounds were detected: 3,5-dinitrophenol, isomers 4,6-dinitroanthranil or 4,6-dinitroisoanthril, 1,3,5-trinitrobenzene, 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitrobenzyl alcohol, 2-carboxy-3,3',5,5'-tetranitro-NNO-azoxy benzene, 2,2'-dicarboxy-3,3',5,5'-tetranitroazobenzene, 1,3-dinitrobenzene, 3,5-dinitroaniline, 2,4-dinitrobenzoic acid, and 2-amino-4,6 dinitrobenzoic acid. Structural formulas for all compounds are given in the Appendix.

With time, there was some change in which products remained: 2,4,6-trinitrobenzaldehyde was only present in Day 3 samples, but not at two following sampling times. 2,2'-dicarboxy-3,3',5,5'-tetranitroazobenzene was also only present in Day 3 samples. All other compounds

persisted through the 3-week experiment. Listed compounds are consistent with published reports for TNT phototransformation (for example, Spanggord et al., 1980; Mabey et al., 1983; Spanggord et al., 1983; Prak and O’Sullivan, 2012).

For DNAN, Day 3 there was extremely low 2-MeO-5-NA and 4-MeO-3-NA signal. These are known to be products of microbial transformation of DNAN and are often found in outdoor samples (Taylor et al., 2017; Qin et al., 2021). 2-Methoxy-5-nitrophenol and 2,4-dinitrophenol, were also detected. 2-Methoxy-5-nitrophenol and 2,4-dinitrophenol persisted through Week 1 sampling. These are consistent with compounds reported in the literature for outdoor (Taylor et al., 2017; Qin et al., 2021) and lab studies (Rao et al., 2013; Taylor et al., 2017; Halasz et al., 2018) and also with ones detected in solutions resulting from dissolution and phototransformation of IMX-101 and IMX-104 particles containing DNAN in the current project (section 3.3.2.3.) Among DNAN products 2,4-dinitrophenol is known to be more toxic than DNAN, while other ones are less toxic (Qin et al., 2021).

4.4. Conclusions

We have observed the effect of climatic conditions on dissolution of the insensitive and traditional munitions constituents from formulation particles. There was a clear decrease in dissolution, beyond what can be explained by lower total rainfall compared to previous experiment in New Hampshire. We also observed differences in dissolution between the locations on elevation gradient in this study. However, the effect of rainfall was non-linear, particularly for IM formulations, IMX-101 and IMX-104. Similar dissolution was observed between two lower elevation locations, even when collected rainfall in lowest elevation was only about half of the one in the middle elevation. This would indicate that perhaps increase in intensity of rainfall does not result in increased dissolution (also supported by lack of increase in dissolution between replicate particles in the same location when they received more rainfall). At the same time, change in water evaporation due to lower temperature or higher frequency of rainfall may explain increased dissolution at the highest elevation.

About half of the mass loss was not accounted for by parent compound dissolution for IM formulations, indicating significant contribution of photo-transformation to the particles fate. No difference in phototransformation of IM constituents was observed between the three locations, but much greater loss of mass for phototransformation was recorded compared to earlier studies in New Hampshire.

For traditional munitions particles, Comp B, C4, and TNT powder, less than 10% of mass loss was accounted for by dissolution. For these munitions, we observed both difference in mass balance with New Hampshire and between the three locations in Arizona, with greater mass loss at the lowest elevation.

We detected phototransformation products of NTO, NQ, DNAN, as well as inorganic ions, ammonium, nitrate, and nitrite, that can result from transformation of several constituents. Recovered known products of phototransformation accounted for only a small fraction of mass loss for both insensitive and traditional munitions. There was a trend for greater relative amount of recovered products at the lowest elevation, but it was not strong, and several products showed no correlation with the parent compound concentrations.

When IMX-101 particles of different size were exposed to rainfall and sunlight in Oracle, AZ, decrease in size resulted in increase in dissolution for all energetic constituents. However, we

successfully accounted for the differences in dissolution by normalizing by surface area using particle mass rather than actual measurements, which are difficult to obtain for irregular-shaped particles. No effect of size on phototransformation, either based on mass balance, or recovery of daughter compounds was observed for particles of different size.

5. Linking outdoor phototransformation across different locations to amount of sunlight and laboratory measured quantum yields

5.1. Background

We have conducted outdoor phototransformation experiments on several locations in Arizona and earlier in New Hampshire and performed a number of laboratory studies under more controlled conditions using lamps with a narrower wavelength range. Here we are combining measured transformation across different locations and conditions with known information about amount of light that samples were exposed to, to develop relationships between light exposure and phototransformation of insensitive and traditional munitions.

5.2. Quantum yield calculation

We are presenting below calculated quantum yields for insensitive munitions compounds (IMC), nitroguanidine (NQ), 2,4-dinitroanisole (DNAN), and 3-nitro-1,2,4-triazol-5-one (NTO) determined based on phototransformation measurements presented in Chapter 3 of this study and performed during several laboratory experiments we conducted earlier (Taylor et al., 2017; Becher et al., 2019; Kadoya et al., unpublished). Data from four different sets of laboratory experiments were used to perform these calculations: two studies that examined formation of products of phototransformation for DNAN (Taylor et al., 2017) and NTO and NQ (Becher et al., 2019); as well as two unpublished studies by Kadoya et al. that examined effect of dissolved OM on phototransformation of IMCs (we used only control samples without OM for these estimates), and study that examined phototransformation of IMC in solid phase (This report, Chapter 3).

In order to determine the quantum yields (Φ), we related measured first order transformation rate constants (k) to the “near-surface” specific rate of light absorption ($k_{a,\lambda}^0$) by the molecules of insensitive munitions (IM) compounds, using following equation (Rao et al., 2013)

$$\Phi = \frac{k}{\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda}$$

where λ is wavelength of incident radiation (nm).

“Near-surface” specific rate of light absorption is a function of the irradiance (I_{λ}), or radiant flux per area, and molar absorptivity also called extinction coefficient (ε_{λ} , $M^{-1}cm^{-1}$), or amount of light absorbed per unit concentration and path length:

$$k_{a,\lambda}^0 = \frac{2300 \text{ cm}^3 L^{-1}}{6.02 \times 10^{23} \text{ photons mol}^{-1}} \left(\frac{I_{\lambda}}{\Delta\lambda} \right) \varepsilon_{\lambda}$$

Irradiance can be measured either chemically or physically. In our experiments, we employed P-9710-1 multi-functional light meter by Gigahertz-Optik (Amesbury, MA) with UV-C (254 nm), UV-B (280-315 nm), and UV-A (315-400 nm) detector heads. Here we present values for UV-B (280-315 nm), UV-A (315-400 nm) because very little light in the UV-C (250-280 nm)

range reaches Earth surface. For our experiments we employed two different apparatuses that utilized same lightbulbs (254, 300, and 350 nm) but had different setup (Figure 5.1). Because of this, we have two different sets of values for irradiance (Table 5.1).

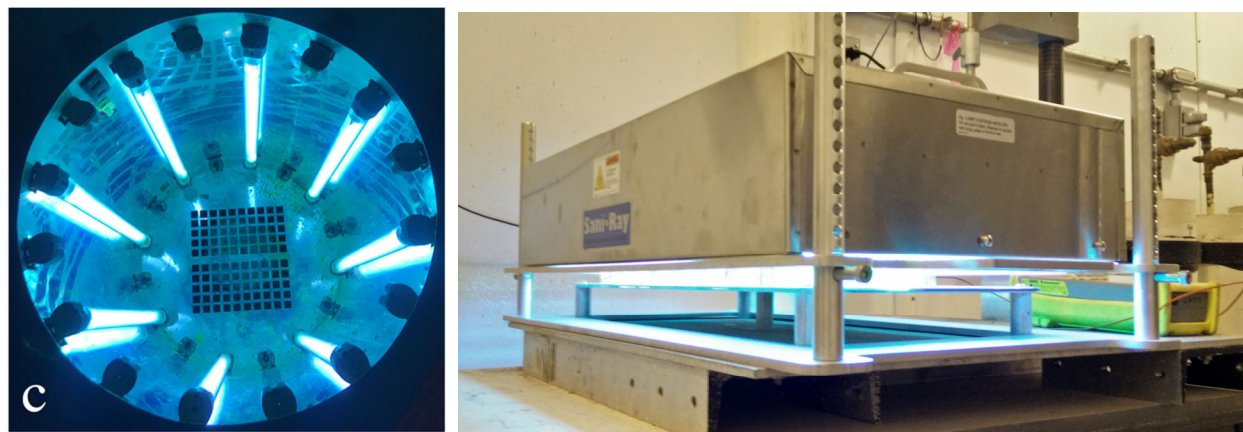


Figure 5.1. Experimental setup for laboratory phototransformation experiments: left - Rayonet (RPR-100) 8-bulb reaction chamber (Southern New England Ultraviolet Company, Branford, CT) and right - SaniRay chamber by Atlantic Ultraviolet Corporation, Hauppauge, NY.

Table 5.1. Measured irradiance in the reactor chamber for two different experimental setup options, Rayonet (Becher et al., 2019) and SaniRay.

P-9710 Detector Head	Irradiance (W m^{-2})*			
	Rayonet		SaniRay	
	Reactor w/ 300 nm Bulbs	Reactor w/ 350 nm Bulbs	Reactor w/ 300 nm Bulbs	Reactor w/ 350 nm Bulbs
UV-B (280-315 nm)	44 ± 2	0.15 ± 0.02	26 ± 4	0.19 ± 0.06
UV-A (315-400 nm)	26 ± 3	76 ± 11	16 ± 3	46 ± 11

*Units given here are W m^{-2} , but they were converted to $\text{photons cm}^{-2} \text{s}^{-1}$ for the calculations of “near-surface” specific rate of light absorption.

UV-VIS light absorption by the IM compounds, NQ, DNAN, and NTO was measured at three different concentrations for each compound over 200 to 800 nm wavelength range (Figures 5.2, 5.3, and 5.4). Using these spectra and known solution concentrations, we calculated molar absorptivities for all three compounds at each wavelength (Figure 5.5, Table 5.2).

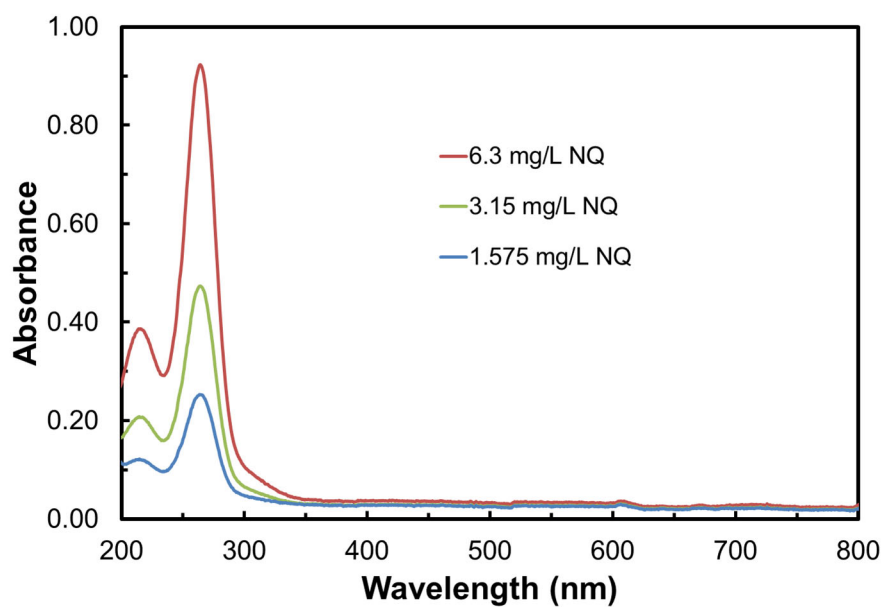


Figure 5.2. UV-VIS spectra of the nitroguanidine (NQ) at three different concentrations.

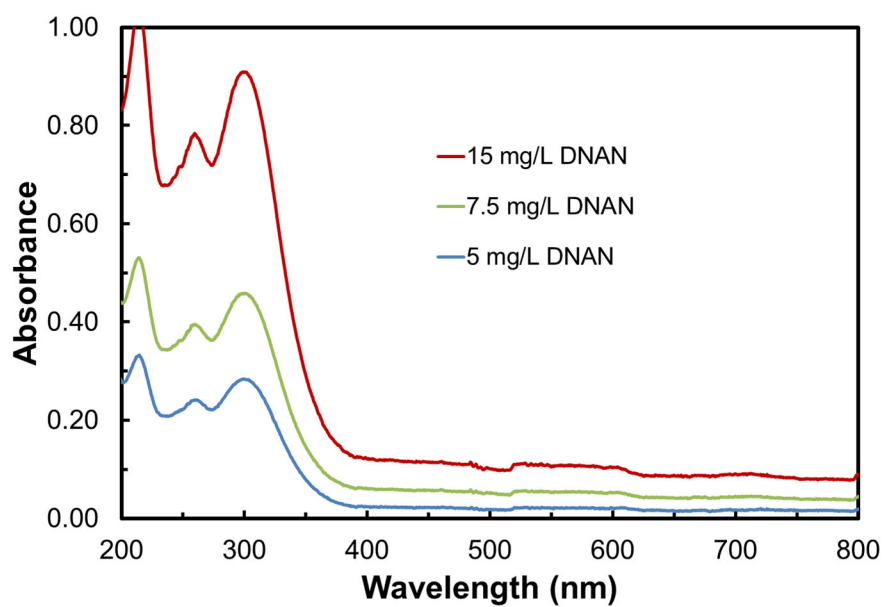


Figure 5.3. UV-VIS spectra of the 2,4-dinitroanisole (DNAN) at three different concentrations.

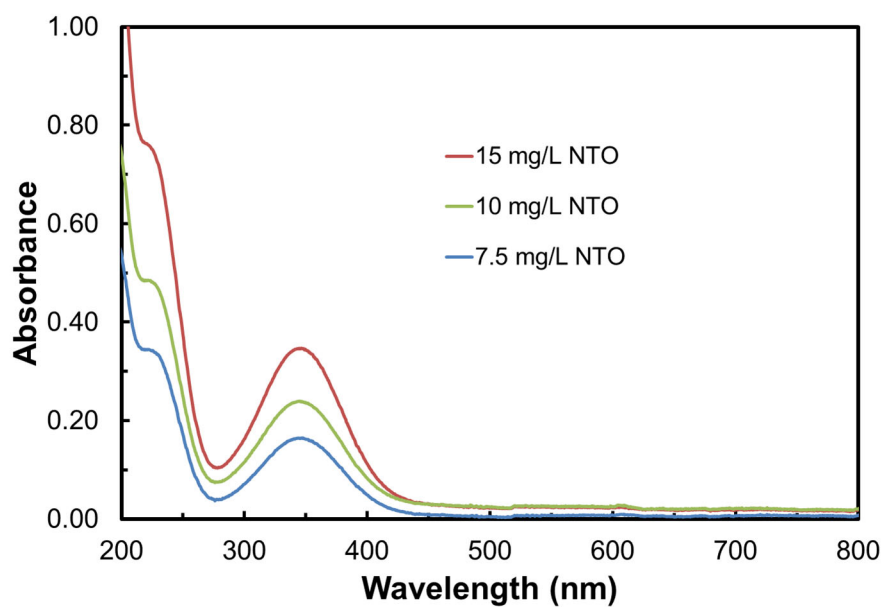


Figure 5.4. UV-VIS spectra of the 3-nitro-1,2,4-triazol-5-one (NTO) at three different concentrations.

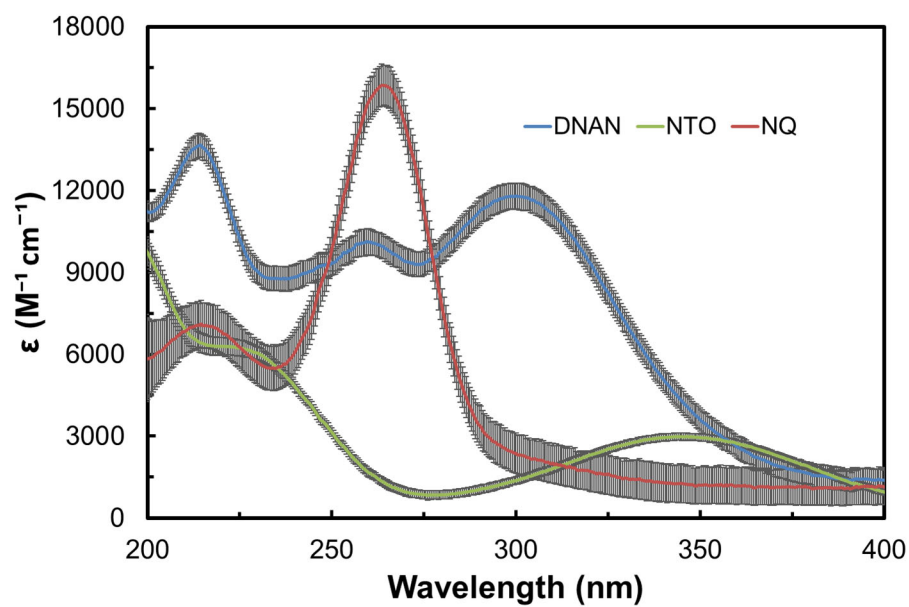


Figure 5.5. Molar absorptivities (extinction coefficients) calculated for NQ, DNAN, and NTO based on their UV-VIS spectra as a function of the wavelength.

Table 5.2. Calculated average molar absorptivities (extinction coefficients), ϵ_{λ} , in $M^{-1} \text{ cm}^{-1}$ for three insensitive munitions compounds (IMC) across three different concentrations in 280 to 600 nm range. The standard deviations were found from the average of three concentrations (for DNAN: 5, 7.5, and 15 mg L^{-1} ; for NTO: 7.5, 10, and 15 mg L^{-1} ; for NQ: 1.575, 3.15, and 6.3 mg L^{-1}).

λ (nm)	DNAN		NTO		NQ	
	average	stdev	average	stdev	average	stdev
280	9817.1	474.5	859.0	154.6	7664.3	728.2
285	10521.1	472.5	922.7	145.7	4975.0	726.4
290	11219.4	501.0	1041.5	160.2	3405.7	734.2
295	11635.1	503.4	1193.4	151.2	2693.7	730.5
300	11797.1	463.8	1374.9	142.4	2369.9	742.4
305	11628.0	466.9	1592.2	138.7	2175.6	732.1
310	11138.0	469.6	1811.2	135.1	2010.4	733.8
315	10355.2	475.9	2056.0	154.7	1852.3	707.6
320	9365.8	463.6	2304.4	143.6	1715.8	734.3
325	8269.9	433.0	2533.3	134.4	1617.8	752.1
330	7102.3	417.7	2714.9	137.9	1466.9	709.5
335	6047.8	417.0	2867.4	124.2	1371.1	701.6
340	5083.6	411.6	2946.4	127.0	1293.4	695.8
345	4289.7	434.6	2978.7	141.2	1276.9	713.8
350	3604.2	417.2	2944.3	128.5	1207.0	672.6
355	3066.6	415.0	2869.7	134.4	1191.6	673.6
360	2602.1	403.8	2730.7	131.5	1181.1	688.5
365	2234.9	404.9	2553.5	125.2	1108.4	633.7
370	1943.9	420.7	2328.1	117.5	1108.4	643.2
375	1771.7	412.2	2090.9	127.7	1140.4	661.2
380	1620.3	408.0	1848.9	124.5	1099.6	646.6
385	1503.1	406.2	1597.7	122.1	1114.5	636.0
390	1390.9	401.8	1345.7	113.8	1101.3	606.7
395	1429.6	383.6	1150.6	112.8	1156.3	652.5
400	1380.7	382.5	955.7	116.2	1140.9	648.8
405	1365.3	396.6	792.4	113.9	1162.4	672.0
410	1344.2	402.3	654.1	120.1	1149.2	657.0
415	1358.3	373.3	550.3	120.1	1160.2	666.9
420	1358.7	387.5	468.1	119.0	1178.4	672.7
425	1331.4	384.4	401.5	127.0	1135.4	641.1
430	1319.1	366.9	354.2	120.8	1132.1	634.1
435	1331.4	367.3	319.5	117.3	1149.2	641.3

440	1329.7	365.7	291.2	121.2	1151.9	646.0
445	1301.9	376.0	269.4	116.7	1120.0	635.7
450	1312.1	367.6	255.5	125.3	1113.4	646.0
455	1299.7	360.3	251.2	116.1	1124.9	651.3
460	1332.3	378.6	255.5	121.4	1154.7	655.4
465	1287.8	360.4	235.8	110.2	1107.3	640.6
470	1256.1	367.3	222.8	118.8	1092.5	622.2
475	1246.5	386.3	212.7	115.8	1063.8	623.7
480	1250.4	358.8	220.2	118.4	1075.4	627.3
485	1298.4	352.6	229.8	120.7	1117.8	637.3
490	1173.8	364.9	197.1	122.3	1033.0	576.4
495	1119.7	372.8	181.8	119.3	990.6	567.3
500	1142.1	368.5	190.0	117.7	1036.8	605.5
505	1128.0	352.6	189.6	113.2	1028.6	586.4
510	1098.1	357.3	171.0	114.4	974.1	540.9
515	1098.1	336.8	170.7	115.3	938.8	528.1
520	1272.9	330.5	228.0	112.7	1110.1	645.2
525	1278.6	352.4	222.7	112.8	1101.3	625.9
530	1266.3	331.9	227.7	106.9	1095.8	641.9
535	1256.1	329.6	226.3	109.3	1076.5	611.0
540	1243.4	356.3	209.0	118.8	1066.6	608.7
545	1243.8	339.7	220.1	108.0	1077.6	639.9
550	1210.4	338.3	211.6	104.7	1019.2	563.3
555	1234.6	334.8	213.9	103.6	1058.9	615.6
560	1229.7	344.7	212.4	109.0	1067.7	623.1
565	1239.0	349.1	216.5	109.2	1056.7	603.8
570	1229.3	344.0	205.9	106.2	1045.7	603.7
575	1235.0	345.7	218.4	101.9	1067.1	609.8
580	1206.4	344.8	217.2	100.6	1046.2	614.0
585	1204.6	353.8	205.1	103.4	1029.1	595.0
590	1203.7	329.0	213.7	103.0	1063.8	627.8
595	1168.5	336.0	203.0	98.6	1025.8	611.4
600	1196.3	322.7	213.4	99.0	1041.3	613.7

Calculated average molar absorptivities (ϵ_λ) and “near-surface” specific rates of light absorption ($k_{a,\lambda}^0$) for both reactors are presented in Tables 5.2 and A2.1 and A2.2, respectively. The overall irradiance measured by the optometer for both the bulbs centered at 300 nm and 350 nm was normalized to the spectra provided by the bulb manufacturer, resulting in irradiance values per wavelength. Then, $k_{a,\lambda}^0$ values were determined for each 5 nm interval and summed over the UV range to calculate overall “near-surface” specific rates of light absorption

$(\sum_{\lambda}(k_{a,\lambda}^0)\Delta\lambda)$, presented by wavelength for each reactor and lamp in Tables A2.1 and A2.2, and summarized in Table 5.3, First order transformation rate constants (k , s^{-1}) for IMCs were determined from change in concentration over time for all four experiments (Table 5.4). Based on values for k and $\sum_{\lambda}(k_{a,\lambda}^0)\Delta\lambda$, we calculated the quantum yields (Φ) (Table 5.4).

Table 5.3. Overall “near-surface” specific rates of light absorption (s^{-1}) by each IMC, summed over the detector ranges ($\sum_{\lambda}(k_{a,\lambda}^0)\Delta\lambda$), for Rayonet and SaniRay reactors and bulbs centered at 300 and 350 nm.

Reactor IMC/ Bulb	Rayonet		SaniRay	
	300 nm	350 nm	300 nm	350 nm
NQ	$(8.34 \pm 0.73) \times 10^{-2}$	$(6.48 \pm 1.05) \times 10^{-2}$	$(4.97 \pm 0.51) \times 10^{-2}$	$(3.96 \pm 0.68) \times 10^{-2}$
DNAN	$(3.33 \pm 0.07) \times 10^{-1}$	$(1.91 \pm 0.10) \times 10^{-1}$	$(1.99 \pm 0.11) \times 10^{-1}$	$(1.17 \pm 0.09) \times 10^{-1}$
NTO	$(5.56 \pm 0.16) \times 10^{-2}$	$(1.36 \pm 0.06) \times 10^{-1}$	$(3.32 \pm 0.18) \times 10^{-2}$	$(8.31 \pm 0.62) \times 10^{-2}$

Calculated quantum yields for dissolved IMCs (Table 5.4) were largest for NQ followed by NTO and DNAN. Our value for NQ was in reasonable agreement with previously published results from other groups. Several studies reported Φ of 0.01 at 300 nm (Spanggard et al., 1987; Haag et al., 1990; Moores et al., 2020a), while our value was 4.36×10^{-3} . Published values for DNAN at 300 nm vary between 3.2×10^{-3} (Moores et al., 2020a) and 3.7×10^{-4} (Rao et al., 2013), while our measurement was lower at 1.96×10^{-5} . For 350 nm, literature yield was 2.9×10^{-4} (Rao et al., 2013) compared to 1.26×10^{-5} in our study. For both studies, there was lower yield reported for larger wavelength, though the difference was not statistically significant. Moores and co-authors (2020a) reported for NTO quantum yield of 5.9×10^{-5} at 300 nm, similar to our measurements. In general, the yields we measured are in good agreement within our studies and with values reported in the literature, particularly for NQ and NTO.

Solid samples exposed to the light showed much lower quantum yields. Quantum yields have been shown before to differ between compounds in solution and adsorbed on the soil surfaces (Balmer et al., 2000). In addition, we were not able to take into account light attenuation in the solid. Plata and co-authors (2008) accounted for light attenuation in the oil films when examining photo-degradation of the polycyclic aromatic hydrocarbons, similarly as it is done for turbid waters. However, we do not believe the approach they used would be applicable to IMCs. They prepared dilute solutions of oil in a solvent, measured their light absorption, and then extrapolated to the undiluted oil film. The thickness of the oil film was well defined, as well. It is challenging to determine how far light can penetrate into the munitions particles, or even crystals of a single IMC as used in this study.

Table 5.4. Measured specific first order transformation rate constants (k , s⁻¹) and calculated quantum yields (Φ) for dissolved and solid NQ, DNAN, and NTO at 300 and 350 nm wavelength.

IMC	Wavelength (λ)	First order transformation rate constant (k)		Quantum yield (Φ)		Φ ratio dissolved to solid
		average	stdev	average	stdev	
	nm	s ⁻¹	s ⁻¹			
Dissolved*						
NQ	300	3.63×10^{-4}	2.53×10^{-5}	4.36×10^{-3}	4.87×10^{-4}	
NQ	350	5.91×10^{-7}	5.54×10^{-8}	1.17×10^{-5}	1.90×10^{-6}	
DNAN	300	4.53×10^{-6}	3.11×10^{-7}	1.96×10^{-5}	1.77×10^{-6}	
DNAN	350	1.73×10^{-6}	2.55×10^{-7}	1.26×10^{-5}	2.23×10^{-6}	
NTO	300	2.96×10^{-5}	1.58×10^{-6}	6.93×10^{-4}	5.17×10^{-5}	
NTO	350	2.79×10^{-5}	1.18×10^{-6}	3.04×10^{-4}	2.37×10^{-5}	
Solid**						
NQ	300	2.99×10^{-7}	6.06×10^{-8}	6.01×10^{-6}	1.29×10^{-6}	725.77
NQ	350	-	-	-	-	-
DNAN	300	4.02×10^{-7}	3.65×10^{-8}	2.02×10^{-6}	2.01×10^{-7}	9.69
DNAN	350	3.89×10^{-7}	4.88×10^{-8}	3.34×10^{-6}	4.56×10^{-7}	3.77
NTO	300	7.36×10^{-7}	7.12×10^{-8}	2.22×10^{-5}	2.31×10^{-6}	31.23
NTO	350	7.30×10^{-7}	4.95×10^{-8}	8.79×10^{-6}	7.55×10^{-7}	34.57

*Solution samples, Rayonet reactor (Taylor et al., 2017; Becher et al., 2019) and SaniRay reactor (Kadoya et al.) control for indirect photolysis study.

**SaniRay reactor (Kadoya et al., this report, Chapter 3) moist/dry solid particles. Dry and moist samples averaged because there was no difference between the treatments.

5.3. Comparing results across different locations

To quantify effect of sunlight on phototransformation of insensitive and traditional energetic compounds, we measured total UV light at 15 min intervals over two years in Arizona (Section 4.2.1, 4.3.1, Figure 4.3). Measurements were performed next to the glass funnels containing energetic particles. However, we tested experimental setup prior to start of the experiment and determined that funnels did not significantly affect the amount of UV light reaching the samples (Dontsova et al., 2019). We focused on UV light, because photons in visible range do not possess sufficient energy to break bonds in the studied compounds (Figure 5.6).

Samples on Mt. Lemmon were placed at 2791 m elevation above sea level, in Oracle, AZ at 1379 m above sea level, and in Tucson, AZ at 728 m above sea level. This is difference of 651 m between Tucson and Oracle, and 1412 m between Oracle and Mt. Lemmon. There is expected 10% increase in UV light with every 1000 m of elevation due to less interception by the atmosphere

according to World Health Organization ([https://www.who.int/news-room/q-a-detail/radiation-ultraviolet-\(uv\)](https://www.who.int/news-room/q-a-detail/radiation-ultraviolet-(uv))). We measured 9% increase in average UV irradiance between Tucson (220.1 W m⁻²) and Oracle (240.1 W m⁻²) locations, but 3% decrease between Oracle and Mt. Lemmon (232.8 W m⁻²) locations, despite increase in elevation. However, UV irradiance is also influenced by cloud cover. For example Becher et al. (2019) measured 9.8 times lower irradiance in UV-A range and 6.5 times lower irradiance in the UV-B range at noon on a cloudy day than on clear one. We can also clearly see on the Figures 4.2 and 4.3 greater frequency of rainy days on Mt. Lemmon and concurrent decrease in UV irradiance.

As discussed in sections 4.3.2.2. and 4.3.2.3, we generally did not detect consistent differences in phototransformation of IM compounds with change in elevation, either based on loss of particle mass or recovery of daughter products. This is consistent with the lack of differences in measured UV radiation. However, there was a trend for increase in a fraction of DNAN transformation products, as well as nitrates and ammonium from higher to lower elevations following first monsoon rain after prolonged period (four and a half month) of no rainfall. This can be related to differences in irradiance, to the higher temperature at the lower elevation, or to increased dissolution at the highest elevation. If we compare with the previous studies in New Hampshire, half of mass lost by the IM particles was not recovered in Arizona, while only 19% in New Hampshire.

Since we do not have same continuous measurements of UV irradiance in New Hampshire studies, only several spot measurements made for UV-A (315-400 nm) and UV-B (280-315 nm) measured separately (Becher et al., 2019), we used total average monthly solar radiation to compare phototransformation at two locations, instead. We assumed that UV-light represents a constant fraction of total light received for both locations. While relative amount of UV light increases with decrease in latitude ([https://www.who.int/news-room/q-a-detail/radiation-ultraviolet-\(uv\)](https://www.who.int/news-room/q-a-detail/radiation-ultraviolet-(uv))), we ignored this for the purposes of this approximation. The total average monthly solar radiation level in Concord, NH it is 4.58 kWh m⁻² day⁻¹ (<https://www.solarenergylocal.com/states/new-hampshire/>), while in Phoenix, AZ it is 6.57 kWh m⁻² day⁻¹ (<https://www.solarenergylocal.com/states/arizona/>), or 43% higher. The value for Tucson from a different resource (Knapp et al., 1980) is 6.99 kWh m⁻² day⁻¹. In fact, the two states represent the opposite extremes for total solar radiation received by earth surface in the United States (Figure 5.7).

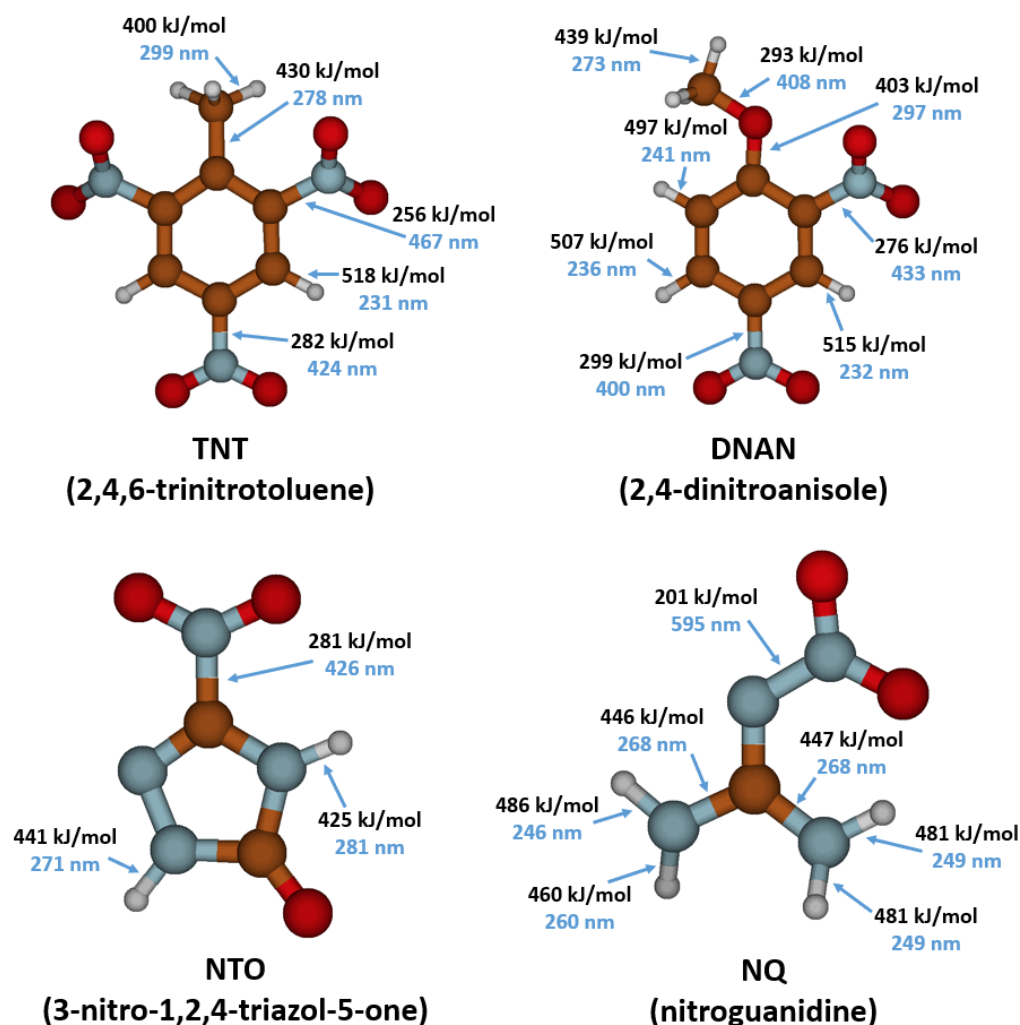


Figure 5.6. Calculated bond dissociation energies and corresponding photon wavelengths required to break the bonds for TNT, DNAN, NTO, and NQ. Energies for bonds in the aromatic and heterocycle rings are not shown because they exceed the maximum energy of the photons in the sunlight reaching Earth surface (500 kJ mol^{-1} or 239 nm). Values for NTO, NQ, and DNAN were reported earlier in Dontsova et al. (2019). All calculations were performed by Diego Troya.

We observed more than doubling of the transformation relative to total mass loss in Arizona compared to New Hampshire for only 43% increase in irradiance. The relationship between transformation rate and photon flux is linear, but we do not have an estimate of the transformation rate in the outdoor study for reasons described above. However, we can use empirical relationship between irradiance and mass loss due to phototransformation we observed, and since studied locations represent extremes of insolation in United States we can interpolate for other locations based on the irradiance.

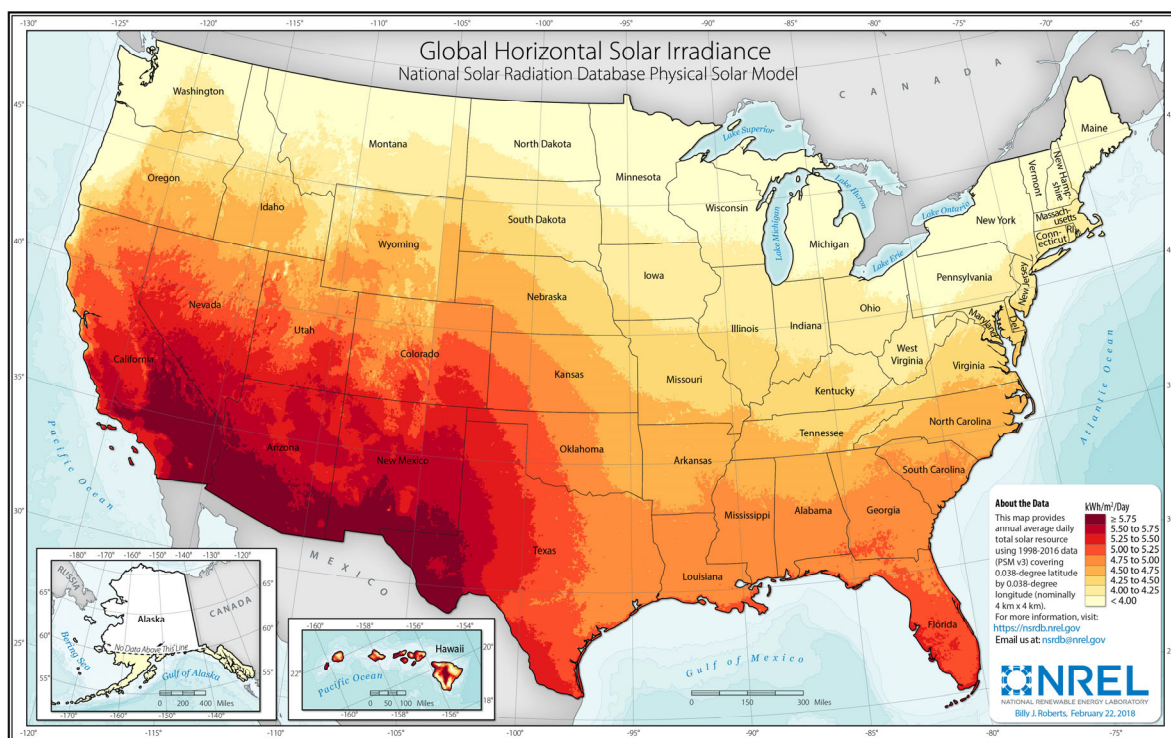


Figure 5.7. Map of the global solar irradiance (<https://www.nrel.gov/gis/assets/images/solar-annual-ghi-2018-usa-scale-01.jpg>)

For the traditional munitions constituents, we see even greater difference in mass loss due to phototransformation between Arizona and New Hampshire. We lost on average for the three elevations 94.5% of Comp B, 98% of C4 and 95.5% of TNT, while on New Hampshire, loss was 61, 84, and 69%, respectively for the same energetics. This is 54% increase for Comp B, 17% for C2, and 38% increase for TNT. We also see differences in transformation across elevations, but since we do not see consistent differences in irradiance, they are harder to interpret, and likely at least partially are driven by differences in dissolution across locations.

5.4. Comparing phototransformation observed in laboratory and field studies

Here we are using quantum yields determined in the controlled phototransformation experiments for individual IM compounds and measured light received by the IM particles to calculate predicted phototransformation rates for NTO, NQ, and DNAN. We compare predicted phototransformation of all IM constituents combined in each formulation to the total phototransformation for each formulation measured in the outdoor experiments based on mass loss.

Applying measured quantum yields to the data we obtained from the outdoor dissolution and photo-degradation experiments presents multiple challenges, because we are exposing to sunlight particles of IM formulations, rather than solutions of pure IMCs. Our experiments indicate that phototransformation can happen both in solution and in solid phase, but with different quantum yields. In addition, in the formulations it is difficult to accurately determine transformation rate, as we do not know the initial concentration of the parent compound exposed to the phototransformation and some daughter compounds resulting from IM phototransformation, such as nitrates, nitrites and ammonium, are common for all compounds in a mixture.

Table 5.5. Parameters used in calculation of half-lives of energetic compounds in outdoor experiments in Arizona: overall "near-surface" specific rate of light absorption, $\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda$, average quantum yields, Φ , 1st order transformation rate constant, k , and average half-life, $t_{1/2}$, dissolved and solid.

IMC	DNAN		NTO		NQ	
Parameter	average	stdev	average	stdev	average	stdev
Mt. Lemmon						
$\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda$ (s ⁻¹)	4.68×10^{-1}	5.10×10^{-2}	3.21×10^{-1}	3.44×10^{-2}	1.88×10^{-1}	3.29×10^{-2}
Dissolved Φ	1.61×10^{-5}	1.42×10^{-6}	4.99×10^{-4}	2.85×10^{-5}	2.19×10^{-3}	2.44×10^{-4}
Solid Φ	2.68×10^{-6}	2.49×10^{-7}	1.55×10^{-5}	1.22×10^{-6}	6.01×10^{-6}	1.29×10^{-6}
Dissolved k (s ⁻¹)	7.53×10^{-6}	1.06×10^{-6}	1.60×10^{-4}	1.94×10^{-5}	4.11×10^{-4}	8.53×10^{-5}
Solid k (s ⁻¹)	1.25×10^{-6}	1.80×10^{-7}	4.97×10^{-6}	6.61×10^{-7}	1.13×10^{-6}	3.13×10^{-7}
Dissolved $t_{1/2}$ (h)	25.57	3.59	1.20	0.15	0.47	0.10
Solid $t_{1/2}$ (h)	153.51	22.00	38.75	5.15	170.60	47.37
Oracle, AZ						
$\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda$ (s ⁻¹)	4.99×10^{-1}	4.75×10^{-2}	3.48×10^{-1}	3.22×10^{-2}	2.05×10^{-1}	3.45×10^{-2}
Dissolved Φ	1.61×10^{-5}	1.42×10^{-6}	4.99×10^{-4}	2.85×10^{-5}	2.19×10^{-3}	2.44×10^{-4}
Solid Φ	2.68×10^{-6}	2.49×10^{-7}	1.55×10^{-5}	1.22×10^{-6}	6.01×10^{-6}	1.29×10^{-6}
Dissolved k (s ⁻¹)	8.04×10^{-6}	1.04×10^{-6}	1.73×10^{-4}	1.89×10^{-5}	4.47×10^{-4}	9.04×10^{-5}
Solid k (s ⁻¹)	1.34×10^{-6}	1.78×10^{-7}	5.39×10^{-6}	6.54×10^{-7}	1.23×10^{-6}	3.36×10^{-7}
Dissolved $t_{1/2}$ (h)	23.96	3.11	1.11	0.12	0.43	0.09
Solid $t_{1/2}$ (h)	143.84	19.15	35.74	4.34	156.68	42.85
Tucson, AZ						
$\sum_{\lambda} k_{a,\lambda}^0 \Delta\lambda$ (s ⁻¹)	4.76×10^{-1}	4.37×10^{-2}	3.35×10^{-1}	2.98×10^{-2}	1.98×10^{-1}	3.33×10^{-2}
Dissolved Φ	1.61×10^{-5}	1.42×10^{-6}	4.99×10^{-4}	2.85×10^{-5}	2.19×10^{-3}	2.44×10^{-4}
Solid Φ	2.68×10^{-6}	2.49×10^{-7}	1.55×10^{-5}	1.22×10^{-6}	6.01×10^{-6}	1.29×10^{-6}
Dissolved k (s ⁻¹)	7.67×10^{-6}	9.76×10^{-7}	1.67×10^{-4}	1.77×10^{-5}	4.33×10^{-4}	8.73×10^{-5}
Solid k (s ⁻¹)	1.28×10^{-6}	1.67×10^{-7}	5.20×10^{-6}	6.16×10^{-7}	1.19×10^{-6}	3.25×10^{-7}
Dissolved $t_{1/2}$ (h)	25.12	3.20	1.15	0.12	0.44	0.09
Solid $t_{1/2}$ (h)	150.79	19.70	37.04	4.39	161.79	44.19

Then we used previously calculated quantum yields for DNAN, NTO, and NQ in solution and in solid form (Table 5.4) and estimated "near-surface" specific rates of light absorption, to calculate transformation rate constants and half-lives of these compounds for each location (Table 5.5). Since laboratory studies were performed using lamps that generated light with maximum at 300 nm (range 280-315 nm) and 350 nm (range 315-400 nm) wavelengths, we determined separate quantum yields for 300 and 350 nm (Table 5.4). However, they were averaged for these calculations, since quantum yield is expected to stay constant across absorption peak (Figure 5.5) (Schwarzenbach et al., 2003). Calculated average molar absorptivities (ϵ_{λ}) (Table 5.2) were

multiplied by irradiance for each 5-nm wavelength interval for each location (Tables A2.3, A2.4, and A2.5 to determine “near-surface” specific rates of light absorption ($\sum_{\lambda}(k_{a,\lambda}^0)\Delta\lambda$). Irradiance by wavelength for the three studied locations was determined by normalizing irradiance by wavelength averaged across the year predicted by the SMARTS: Simple Model of the Atmospheric Radiative Transfer of Sunshine developed by Dr. Christian Gueymard (<https://www.nrel.gov/grid/solar-resource/smarts.html>) by measured irradiance at each site. Obtained values for transformation rate constants for these compounds (Table 5.5) are much higher and half-lives much smaller than expected from observed mass loss of the particles, and this is consistent with the fact that only a very small fraction of the total mass of energetic compound is exposed to the sunlight. Even if we used quantum yield obtained from experiments with the solid particles, we still overestimate observed loss of energetic compounds due to phototransformation.

The challenge is that we do not have a good estimate of penetration depth of UV light into the crystals of individual IM compounds in laboratory experiments and much lower measured quantum yields (section 5.2) indicate that even for thin films deposited from solution, the light was not able to penetrate through the complete layer of IM, particularly for NTO, where 30 times lower quantum yields were measured in solid samples compared with solutions (section 5.2), and the formulations present additional challenge because light may be adsorbed not only by the compound of interest but scavenged by other compounds in the formulation.

5.5. Conclusions

We were able to link measured phototransformation in outdoor and lab experiments with the amount of light received. While it is difficult to accurately measure amount of phototransformation in outdoor studies, comparison between three locations on elevation gradient, as well as between current study in Arizona, and similar previous experiments in New Hampshire allow to estimate effect of irradiance on observed phototransformation. We also used quantum yields for each IM compound to predict amount of phototransformation for individual munitions constituents in outdoor experiments.

6. Batch adsorption studies using soil components

6.1. Background

Under project ER-2727 we have previously conducted batch adsorption studies to determine role of active soil constituents in attenuation of DNAN and NTO using soil clays fractionated to remove reactive soil components, including OM, iron oxides, and amorphous iron (Dontsova et al., 2019). While for NTO there was very low adsorption and no treatment differences were observed, DNAN adsorption was influenced by removal of OM and different forms of iron. DNAN’s behavior was similar to what was observed before for TNT, where adsorption by both phyllosilicate clays and OM play important role with OM being a dominant factor (Dontsova et al., 2009). However for DNAN, layer silicates played greater role in adsorption than for TNT. For RDX, OM was the main factor influencing adsorption, with linear adsorption isotherms indicating partitioning behavior (Dontsova et al., 2009). Nitroguanidine was shown before to have very low adsorption to the soils (Dontsova et al., 2008; Taylor et al., 2012).

In order to determine if DNAN interaction with the active components of the soils (Dontsova et al., 2019) is impacted by presence of other energetic compounds in the formulations, we conducted batch adsorption studies using soil clays fractionated as before to remove reactive

soil components, including OM, iron oxides, and amorphous iron, and two IM formulations, IMX-101, containing NTO, NQ, and DNAN, and IMX-104, containing NTO, DNAN, and RDX .

These experiments employ a subset of eleven whole soils collected across the United States (Mark et al., 2016; Arthur et al., 2017) used to develop relationships between soil properties and adsorption of NTO and DNAN that showed that OC and cation exchange capacity, a function of both OM and clay content as well as clay mineralogy, play important role in DNAN adsorption. Here we focus on effect of mixture on DNAN adsorption by soil clays.

6.2. Materials and Methods

6.2.1 Materials

Three soils among eleven previously used to evaluate interactions of IM constituents with soils (Dontsova et al., 2014; Mark et al., 2016; Arthur et al., 2017) were used in this study. Catlin silt loam was collected at the University of Illinois at Urbana-Champaign university farm, while Sassafras loam and Florence loam were collected at military training ranges in Maryland and Arizona, respectively (Figure 5.1). Their properties previously measured by Mark et al. (2016) are listed in Table 5.1. They differed in texture, pH (which has been shown before to impact adsorption of NTO (Mark et al., 2016), and clay mineralogy. All three soils had mixed mineralogy, but in Catlin and Florence it was dominated by smectite, while Sassafras had more low activity clays. After collection soils were air dried, ground, and passed through 2 mm sieve. We are grateful to Dr. Roman Kuperman, Edgewood Chemical Biological Center and Mike Heitmann, CH2M HILL Englewood, CO for sharing soils used in the experiments. IMX-101 and IMX-104 used in experiments were kindly provided by Naval Weapons Center (China Lake, CA).

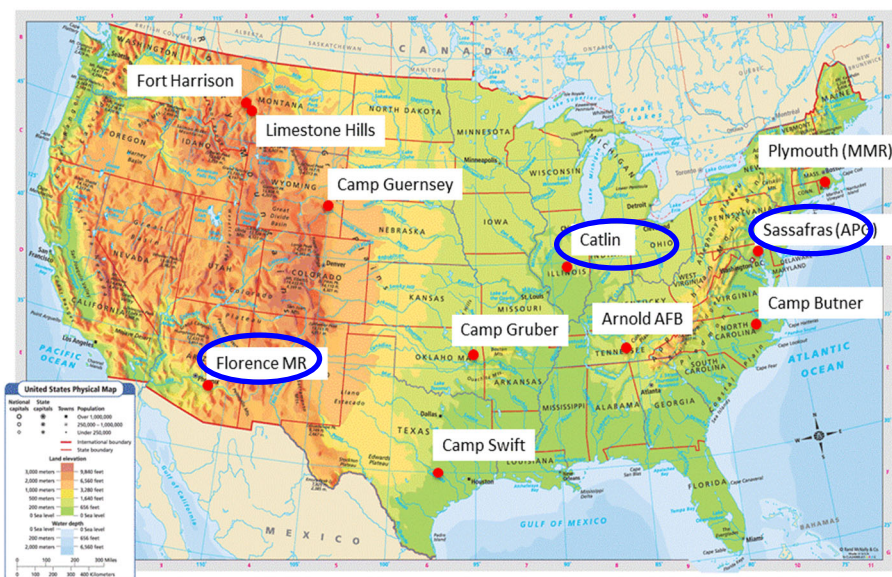


Figure 6.1. Collection locations of the studied soils among others previously used to evaluate interactions of IM constituents with soils.

Table 6.1. Physical and chemical properties of the studied soils (Mark et al., 2016).

Soil	Texture	Clay %	pH	CEC cmol _c kg ⁻¹	Mineralogy
Catlin	silt loam	25.6	7.31	21.4	Smectite, Mica, Kaolinite, Quartz
Florence	loam	26.8	8.0	12.2	Smectite, Mica, Kaolinite, Quartz
Sassafras	loam	16.4	4.4	7.9	Kaolinite, Hydroxyl-interlayered vermiculite, Mica, Chlorite

SSA - specific surface area; OC - organic carbon; CEC - cation exchange capacity

6.2.2. Clay Removal and Treatment

To extract water-dispersible clay ($< 2\mu\text{m}$) soils were exposed to repeated suspension in water and sedimentation. Each soil was mixed with water in 100g to 1L ratio, agitated on shaker at 200 rpm for 24 h, and then clay suspension was removed, flocculated using $0.5 \text{ mol L}^{-1} \text{ CaCl}_2$, and centrifuged. Extracted clay was washed in $1 \text{ mol L}^{-1} \text{ NaCl}$ and treated with 1 mol L^{-1} acetate buffer (pH 5) at 70°C to remove carbonates. Organic matter was removed with 30% hydrogen peroxide (H_2O_2) (Kunze and Dixon, 1986). Sodium citrate-dithionite extraction (DCE) (Kunze and Dixon, 1986) was used to remove free iron-aluminum oxides and hydroxides (Fe_d). Acid ammonium oxalate in the dark (AOE) (Jackson et al., 1986) method was used to remove noncrystalline aluminosilicates and hydrous oxides (Fe_o). All fractionated clay samples were washed with $0.5 \text{ mol L}^{-1} \text{ CaCl}_2$ three times and then washed free of salts with water until no Cl^- was detected by AgNO_3 test. All treated water-dispersible clay samples were freeze dried for storage. Soils and extracted clays were characterized for external specific surface area (SSA) by nitrogen adsorption (Brunauer–Emmett–Teller, or BET), OC content by combustion, and iron oxides (Soil Survey Staff, 1996).

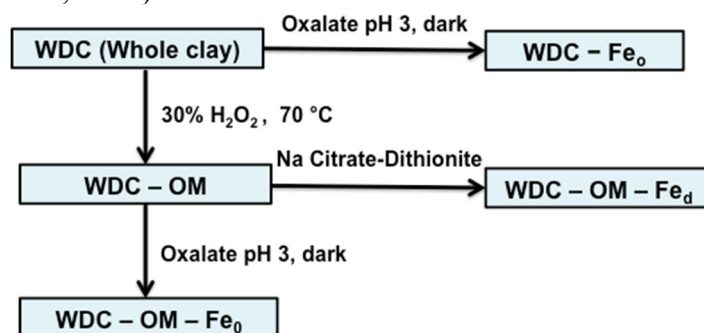


Figure 6.2. Treatments for water dispersible clay (WDC) used in this study. OM: organic matter; Fe_o : oxalate extractable iron; Fe_d : dithionite-citrate extractable iron.

6.2.3. Batch Adsorption

During batch adsorption experiments, IMX-101 and IMX-104 solutions in 0.005 M CaCl_2 were mixed with 0.1 g clay (0.1 g in 4 mL) in glass vials with PTFE-lined screw cap. NaN_3 (0.2%) was added to inhibit microbial activity. Suspensions were agitated on horizontal shaker in the dark at 150 rpm for 24 h to reach equilibrium. IMX-101 and IMX-104 solutions without soil or clay were also included as blank controls and losses were shown to be negligible. All the treatments were carried out in triplicate. After centrifugation, the supernatant was removed and filtered

through 0.45 µm PVDF membrane before HPLC analysis. Adsorption isotherms were plotted as DNAN sorption to solid phase (Q , mg/kg) versus the aqueous equilibrium concentration (C , mg/L). Linear regression analysis on log transformed solution and clay concentration data was carried out in Microsoft Excel 365 to determine Freundlich adsorption parameters (exponent n and Freundlich adsorption coefficient K_f) for the following equation:

$$\log Q = n \log C + \log K_f$$

6.2.4. HPLC analysis

DNAN concentrations in aqueous phase remaining after adsorption were analyzed using high performance liquid chromatography (Dionex Ultimate 3000 HPLC with a diode array detector, ThermoFisher, MA). DNAN was quantified using C18 Acclaim reversed phase column (Thermo Scientific, 4.6 × 250 mm, 5 µm) with mobile phase ratio of methanol/water (v/v, 43:57) (Olivares et al., 2013a). The mobile phase flow rate was 1 mL min⁻¹ and the detection wavelength was 300 nm. The limit of detection (LOD) was 0.015 mg/L.

6.3. Results

6.3.1. Clay Removal and Treatment

In agreement with previous studies that did not have dispersant added (Dontsova et al., 2009), during water dispersible clay removal from the three studied soils it was observed that not all clay originally measured in the soils was extracted (Table 5.2). Catlin, Florence, and Sassafras soils had 26, 27, and 16% total clay (Mark et al., 2016) and WDC of 11, 10, and 6%, respectively, so only 34 to 44% of the clay was extracted with water (Table 5.2). Water-dispersible clay fraction was enriched in OC (1.27 to 1.61 times) and both forms of iron (Fe_o and Fe_d) (1.70 to 4.78 times) compared to whole soils (Table 5.3), in agreement with previous reports (Kjaergaard et al., 2004). The largest difference was observed for Sassafras soil, where Fe_d was almost 5 times higher in WDC than in bulk soil. Specific surface area was also increased in WDC for Catlin and Sassafras soils (3.0 and 5.3 times, respectively), as expected for material that is all composed of particles less than 2 mm in size. However, for Florence soil, BET SSA for WDC was slightly lower than for original soil.

Table 6.2. Extraction of water-dispersible clay from studied soils.

Soil type	Total clay extracted per 1 kg of soil	Percent extracted	Total clay (Mark et al., 2016)
	g	%	%
Catlin	111.42	11.14	25.60
Florence	98.73	9.87	26.80
Sassafras	56.20	5.62	16.40

Table 6.3. Properties of whole Catlin, Florence, and Sassafras soils, untreated, and treated water-dispersible clay (WDC).

Soil/Clay	BET SSA	OC	Fe _d	Fe _o
	m ² g ⁻¹	g kg ⁻¹	g kg ⁻¹	g kg ⁻¹
Catlin soil	4.3	22.0	10.08	2.26
Catlin WDC	13.1	34.8	17.61	4.22
Catlin WDC - OM	41.1	6.3	22.58	6.24
Catlin WDC - OM - Fed	40.2	2.8	4.79	1.05
Catlin WDC - OM - Feo	46.6	5.9	12.61	1.11
Catlin WDC - Feo	13.3	24.4	12.79	1.16
Florence soil	34.2	2.6	6.90	0.15
Florence WDC	27.4	4.1	11.71	0.64
Florence WDC - OM	93.3	1.7	11.27	0.65
Florence WDC - OM - Fed	72.1	1.3	3.08	0.42
Florence WDC - OM - Feo	86.3	3.6	11.73	0.39
Florence WDC - Feo	35.7	5.2	12.16	0.36
Sassafras soil	5.2	17.1	9.37	0.64
Sassafras WDC	27.2	21.8	44.76	1.77
Sassafras WDC - OM	63.7	2.1	50.70	2.16
Sassafras WDC - OM - Fed	77.9	1.7	3.60	0.71
Sassafras WDC - OM - Feo	63.3	2.1	44.93	1.89
Sassafras WDC - Feo	33.5	19.3	47.07	2.24

† OC = organic carbon by combustion after acid pretreatment; SSA = specific surface area by nitrogen adsorption; Fe_d = dithionite-citrate extractable iron, Fe_o = acid oxalate extractable iron.

Chemical treatments (peroxide, AOE, or DCE) did not completely remove iron or OC from WDC (Table 6.3). Extraction efficiency varied greatly among the soils, with peroxide treatments decreasing OC content 1.9 times in Florence and 11.05 in Sassafras relative to untreated WDC. This is likely partially related to total OC content initially in the soil, as small amounts are presumably more tightly held by clay surfaces. In addition, mineralogy of Florence soil is dominated by smectites (Table 6.1) that have high surface area and affinity for OM. Acid oxalate extraction of OC-containing WDC also removed some OC in Catlin (30%) and Sassafras (11%) soils. Dithionite-citrate extraction was more efficient than AOE in removal of iron and resulted in the lowest residual concentrations of Fe_d in all soils and Fe_o in Catlin and Sassafras soils. In soils high in OM, removal of OC increased Fe_d and Fe_o likely because the total fraction of mineral components in WDC increased.

The surface area of WDC was increased after removal of OM about 3 times across all three treatments without OM and three soils (Table 6.3). This agrees with earlier findings for soil clays by Kjaergaard et al. (2004). Increase in SSA was explained by separation of clay particles, which were bound together by OM.

6.3.2. Batch adsorption studies with soil clays

All isotherms were fitted with linearized Freundlich equation (Figures 6.3 and 6.4 and Tables 6.4 and 6.5) and in agreement with previous studies (Arthur et al., 2017; Dontsova et al., 2019) n parameter that describes non-linearity of the curve was significantly different from one. This indicates specific adsorption to active sites and decreasing affinity for DNAN with increase with adsorption rather than partitioning behavior and proportional increase in adsorption with increase in solution concentration.

For all studied soils untreated WDC adsorbed less DNAN from IMX-101 and IMX-104 than all other treatments (Figures 5.3 and 5.4). In experiments with IMX-101, removal of OM significantly increased Freundlich adsorption coefficient, K_f , compared to both untreated clay and WDC-Fe_o which had poorly crystalline iron removed for Catlin soil, and compared with WDC only for Florence and Sassafras soils. This can be partially explained by increase in SSA (Table 6.3) due to separation of clay platelets. However generally, removal of both OM and iron oxides (Fe_d and Fe_o) resulted in largest adsorption even if it did not result in greater SSA than removal of OM alone (Table 5.3). This indicates the importance of phyllosilicate clays in adsorption of DNAN, as removal of OM and iron oxides exposes phyllosilicate clay surfaces. In addition, removal of Fe_o without removal of OM also increased adsorption in all clays without increasing SSA indicating that clay surfaces actively participate in adsorption. Non-linear adsorption (Freundlich $n < 1$) and also supports specific adsorption to clay surfaces rather than partitioning to OM. Increased adsorption with removal of OM is in agreement with several earlier publications (Charles et al., 2008; Zhou, 2008), including one focused on four nitroaromatic compounds including para-nitrocyano benzene, 2,4-dinitrotoluene, 1,4-dinitrobenzene, and 1,3,5-trinitrobenzene (Charles et al., 2008) that showed that adsorption increased after removal of OM and unlike this study explained this by change in available surface area for adsorption due to soil disaggregation alone, but different from what we observed previously for TNT (Dontsova et al., 2009), which decreased adsorption when OM was removed from the clay fraction of the soil, indicating larger role of OM and smaller role of phyllosilicate clays in TNT adsorption compared to DNAN.

For IMX-101, for all three clays majority of the obtained parameters (Table 5.4) were not significantly different than ones observed for each treatment for pure DNAN (Dontsova et al., 2019). The only two exceptions were K_f values for Florence on WDC-OM-Fe_d and for Sassafras for WDC-OM, which were higher for pure DNAN. This is consistent with negligible adsorption of NTO and NQ, the other constituents in this formulation.

However, when comparing adsorption of DNAN from IMX-101 and IMX-104, which also contains NTO and RDX, significant differences were observed. Significantly lower adsorption coefficients were measured for DNAN from IMX-104 in WDC-OM, WDC-OM-Fe_d, and WDC-OM-Fe_o, in Catlin soil; as well as WDC-OM-Fe_o and WDC-Fe_o in Florence soil, and WDC-OM-Fe_d in Sassafras soil. Several other treatments were lower but not at 95% level. The difference between behavior of DNAN in the two formulations can be potentially explained by competition for the sites with other constituents. While in IMX-101 NTO and NQ do not adsorb to soil to an

appreciable extent and DNAN adsorption is not impacted by the formulation, while in IMX-104, which also contains RDX (and HMX) in addition to NTO and DNAN, adsorption is decreased.

Table 6.4. Freundlich adsorption parameters, K_f and n for DNAN adsorption from IMX-101 in treated clays.

Soil/ Treatment	K_f mean	95% CI	n mean	95% CI	R^2
Catlin					
WDC	39.94	23.06 – 69.20	0.60	0.34 - 0.87	0.94**
WDC-OM	199.94	142.24 – 281.01	0.39	0.21 - 0.57	0.94**
WDC-OM-Fe _d	208.38	166.91 – 260.14	0.51	0.37 - 0.64	0.90**
WDC-OM-Fe _o	160.98	131.46 – 197.12	0.54	0.42 - 0.66	0.93**
WDC-Fe _o	98.28	85.31 – 113.22	0.54	0.47 - 0.62	0.97**
Florence					
WDC	11.20	8.97 – 13.98	0.54	0.45 - 0.64	0.99**
WDC-OM	111.01	65.94 – 186.88	0.25	-0.00 - 0.51	0.76
WDC-OM-Fe _d	101.57	77.26 – 133.54	0.38	0.24 - 0.52	0.84**
WDC-OM-Fe _o	68.78	57.30 – 82.56	0.35	0.27 - 0.43	0.92**
WDC-Fe _o	79.64	69.01 – 91.90	0.17	0.10 - 0.23	0.82**
Sassafras					
WDC	10.44	8.11 – 13.44	0.83	0.72 – 0.94	0.97**
WDC-OM	127.61	105.65 – 154.13	0.53	0.43 - 0.64	0.94**
WDC-OM-Fe _d	166.78	136.78 – 203.36	0.47	0.36 - 0.58	0.92**
WDC-OM-Fe _o	124.21	81.28 – 189.01	0.69	0.42 - 0.96	0.81**
WDC-Fe _o	117.91	93.27 – 149.06	0.54	0.41 - 0.67	0.92**

95% CI: 95% confidence interval; *regression $P < 0.05$; ** regression $P < 0.01$.

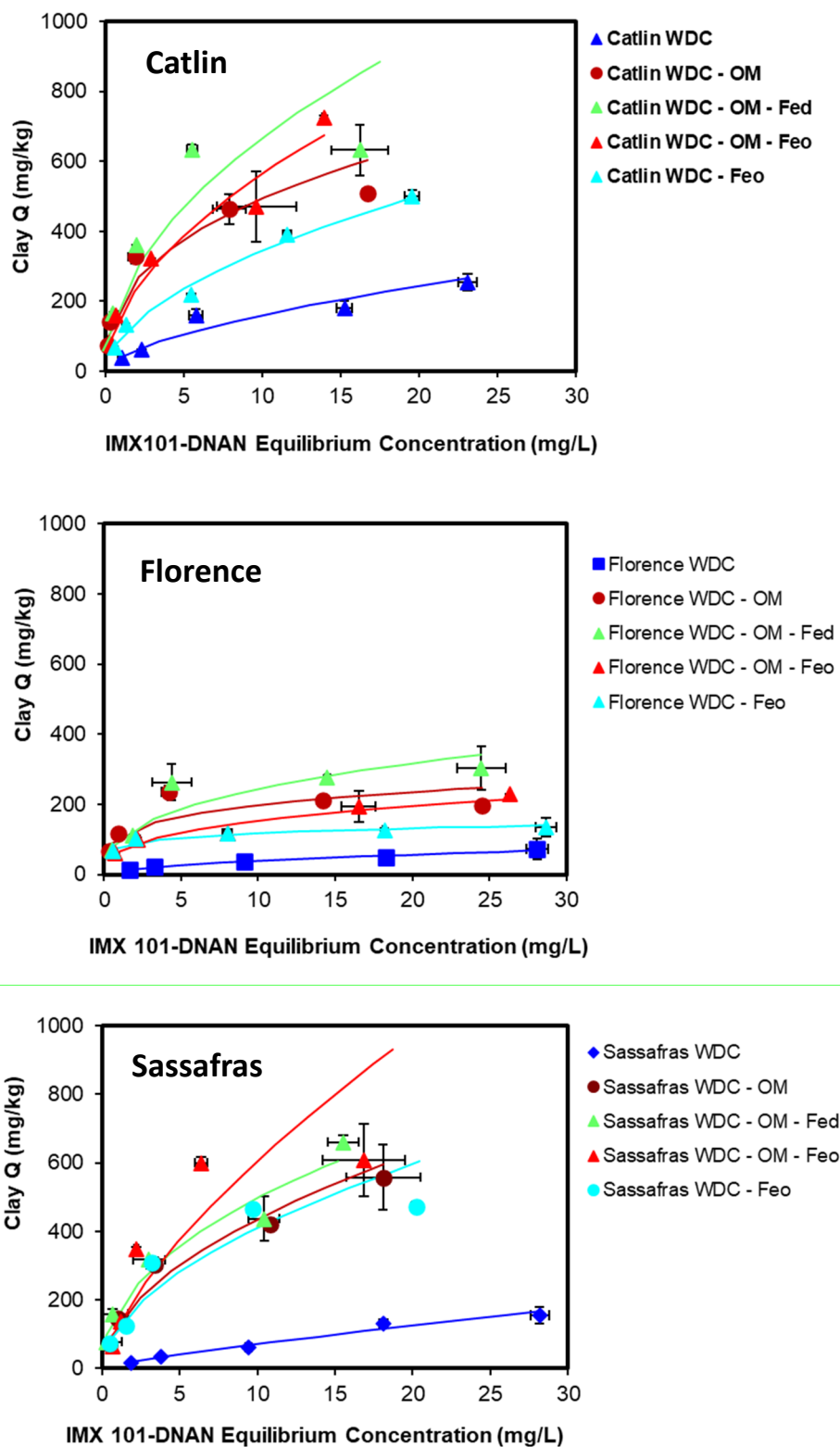


Figure 6.3. Adsorption of DNAN from IMX-101 (Q) by water dispersible clay (WDC) and WDC treated to remove organic matter (OM), oxalate extractable iron (Fe_o) and dithionite-citrate extractable iron (Fe_d) for Catlin, Florence, and Sassafra soils.

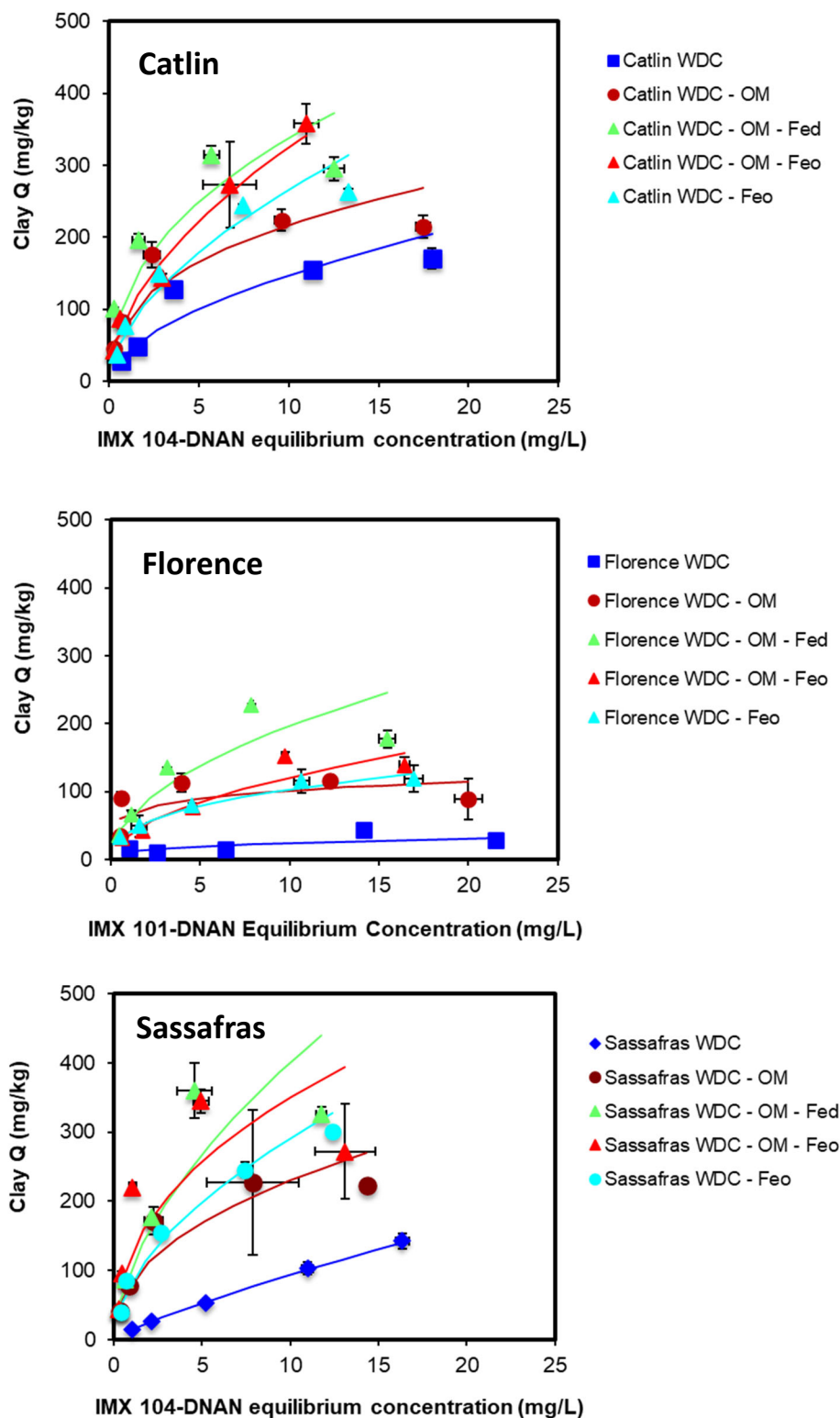


Figure 6.4. Adsorption of DNAN from IMX-104 (Q) by water dispersible clay (WDC) and WDC treated to remove organic matter (OM), oxalate extractable iron (Fe_o) and dithionite-citrate extractable iron (Fe_d) for Catlin, Florence, and Sassafra soils.

Table 6.5. Freundlich adsorption parameters, K_f and n for DNAN adsorption from IMX-104 in treated clays.

Soil/ Treatment	K_f mean	95% CI	n mean	95% CI	R^2
Catlin					
WDC	40.68	22.18 – 74.60	0.56	0.22 - 0.89	0.90*
WDC-OM	89.86	59.02 – 136.83	0.38	0.15 - 0.62	0.90*
WDC-OM-Fe _d	123.46	92.43 – 164.90	0.44	0.26 - 0.62	0.79**
WDC-OM-Fe _o	92.29	78.10 – 109.05	0.55	0.44 - 0.65	0.95**
WDC-Fe _o	71.53	61.27 – 83.50	0.57	0.47 - 0.67	0.96**
Florence					
WDC	11.32	3.58 – 35.80	0.33	-0.24 - 0.89	NS
WDC-OM	67.19	30.51 – 147.97	0.18	-0.24 - 0.59	NS
WDC-OM-Fe _d	61.15	46.88 – 79.76	0.51	0.35 - 0.67	0.87**
WDC-OM-Fe _o	36.78	30.09 – 44.97	0.52	0.40 - 0.63	0.93**
WDC-Fe _o	42.46	34.83 – 51.76	0.38	0.28 - 0.49	0.89**
Sassafras					
WDC	14.10	12.48 – 15.92	0.82	0.76 – 0.89	0.99**
WDC-OM	82.51	61.18 – 111.29	0.45	0.26 - 0.63	0.79**
WDC-OM-Fe _d	105.19	84.40 – 131.10	0.58	0.43 - 0.73	0.91**
WDC-OM-Fe _o	126.67	88.59 – 181.13	0.44	0.20 - 0.67	0.70**
WDC-Fe _o	82.18	69.79 – 96.77	0.55	0.44 - 0.65	0.95**

95% CI: 95% confidence interval; *regression $P < 0.05$; ** regression $P < 0.01$.

6.4. Conclusions

Similarly to what was observed for treated soil clays using pure DNAN, DNAN in energetic formulations, IMX-101 and IMX-104, can be adsorbed by phyllosilicate clays. Adsorption of DNAN from the IMX-101 formulation solutions was not significantly different than that observed for pure DNAN for majority of the treatments, but in IMX-104 solutions DNAN adsorption was decreased likely due to competition with RDX and HMX.

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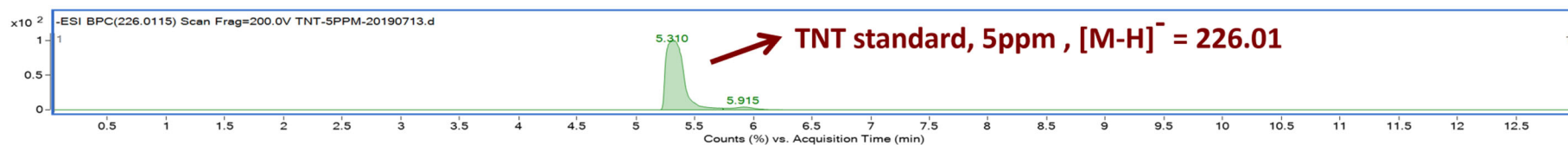
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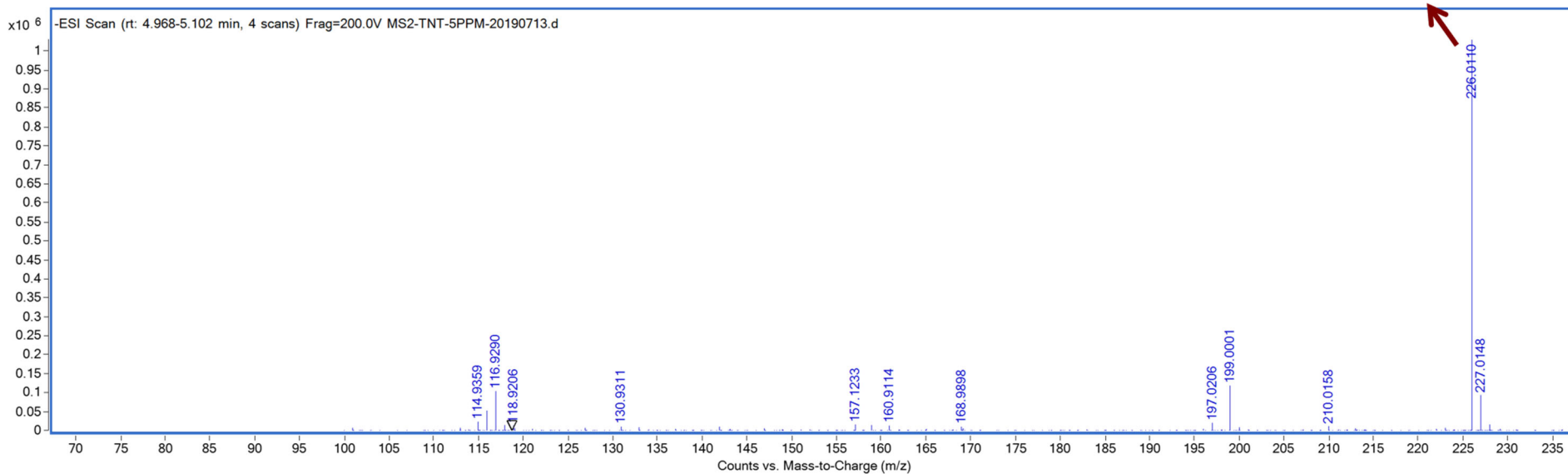
8. Appendix

A1. Results of LC-TOF-MS analysis of TNT, DNAN, RDX, NTO, and NQ solutions exposed to sunlight

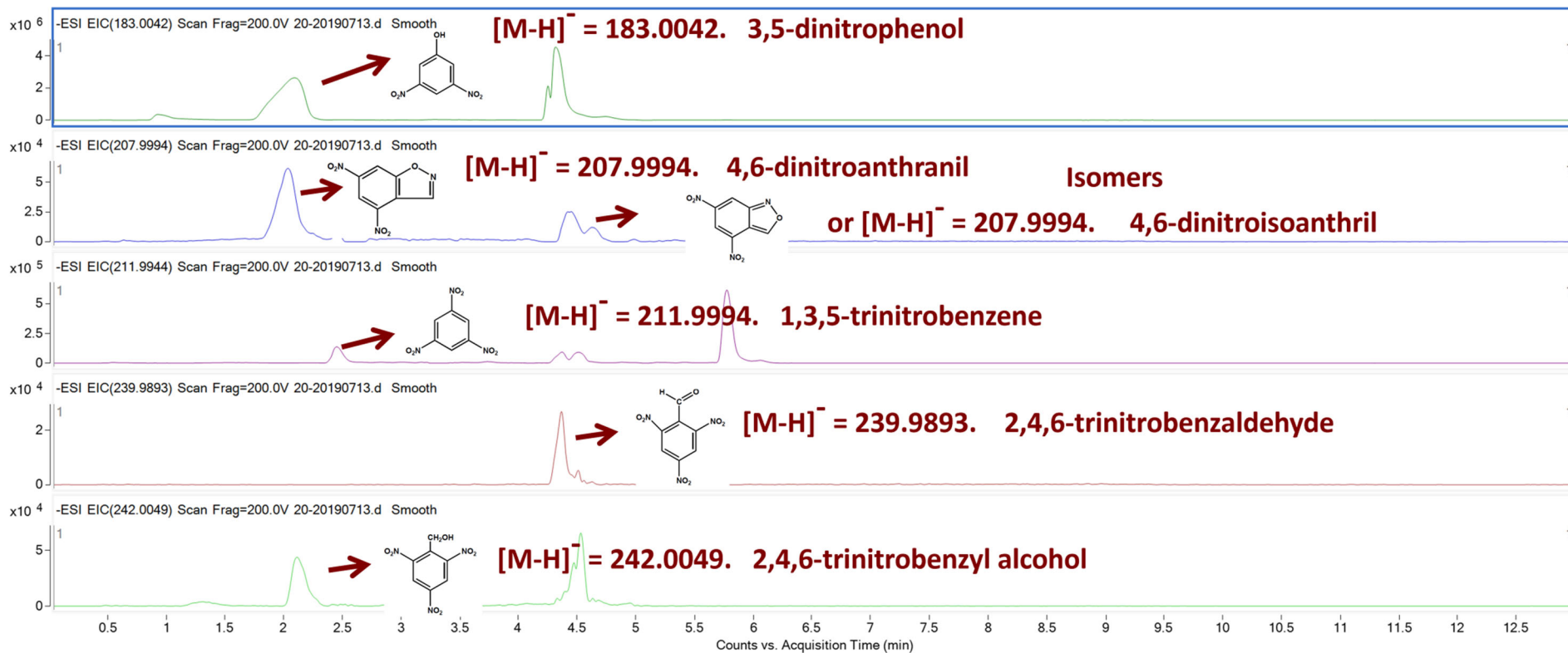
TNT standard



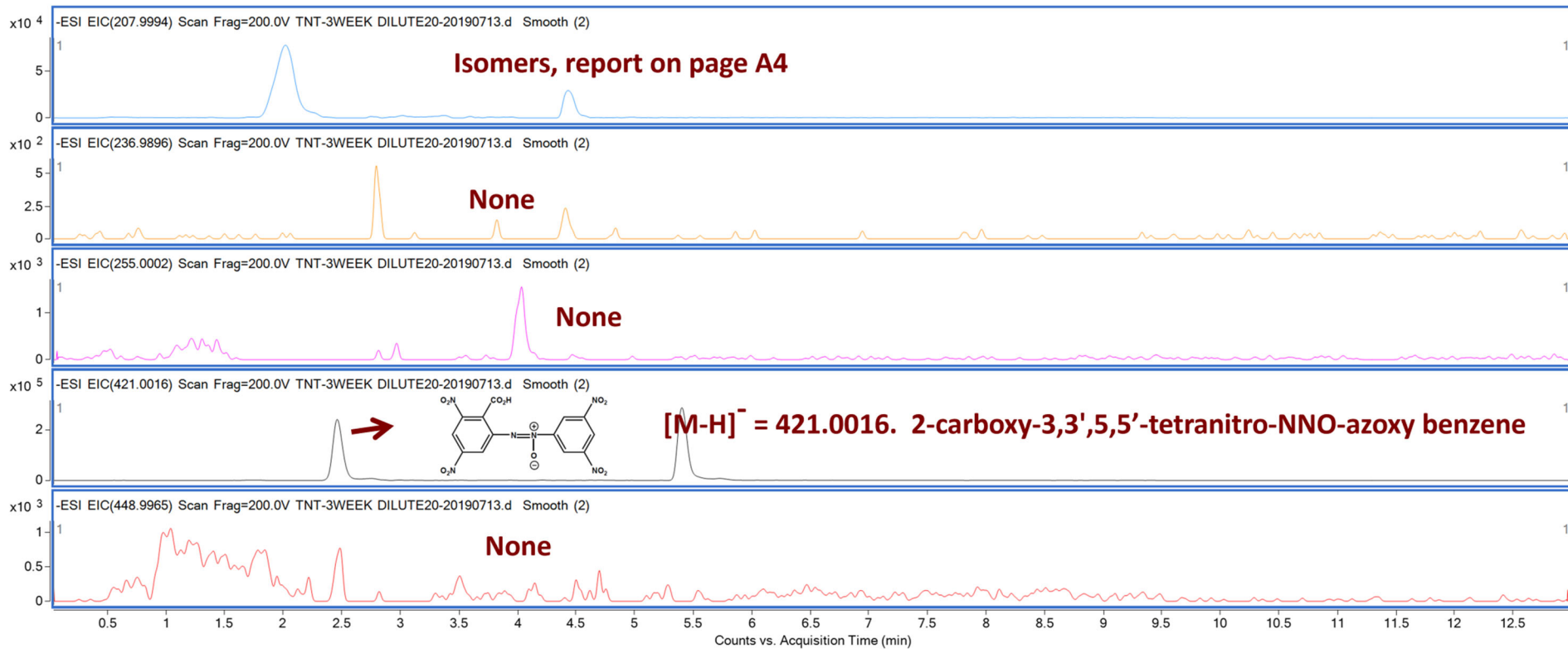
TNT, MS/MS spectrum



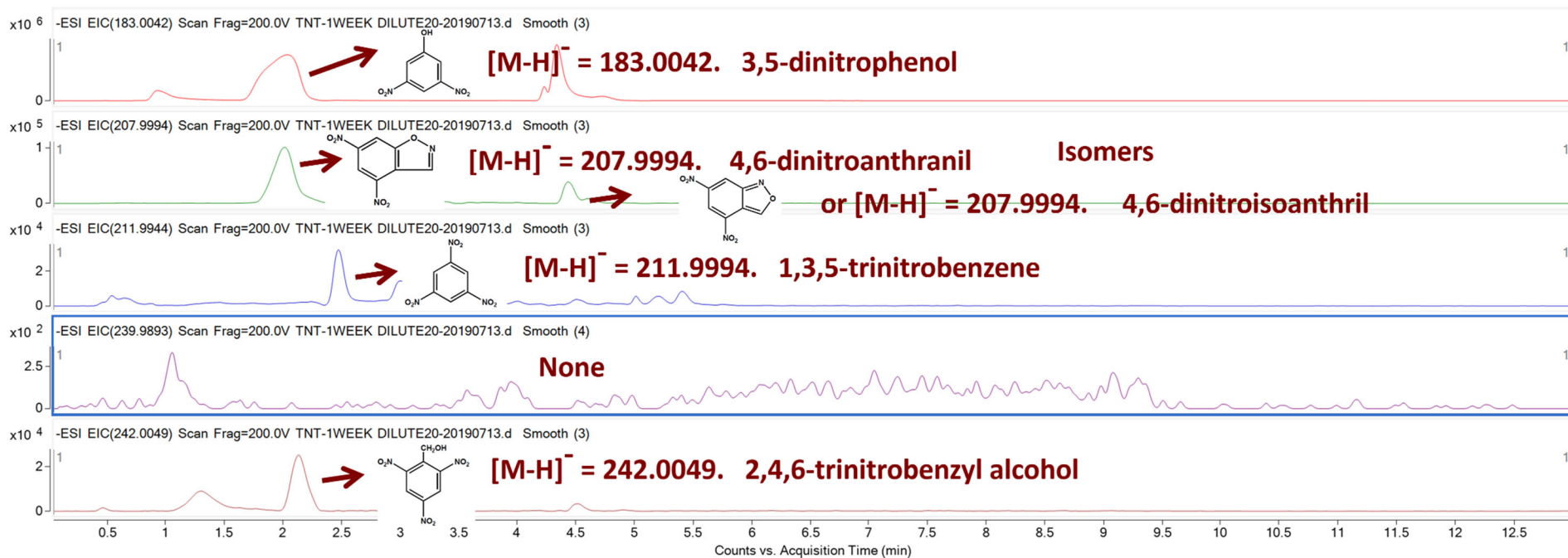
TNT Day 3 sample



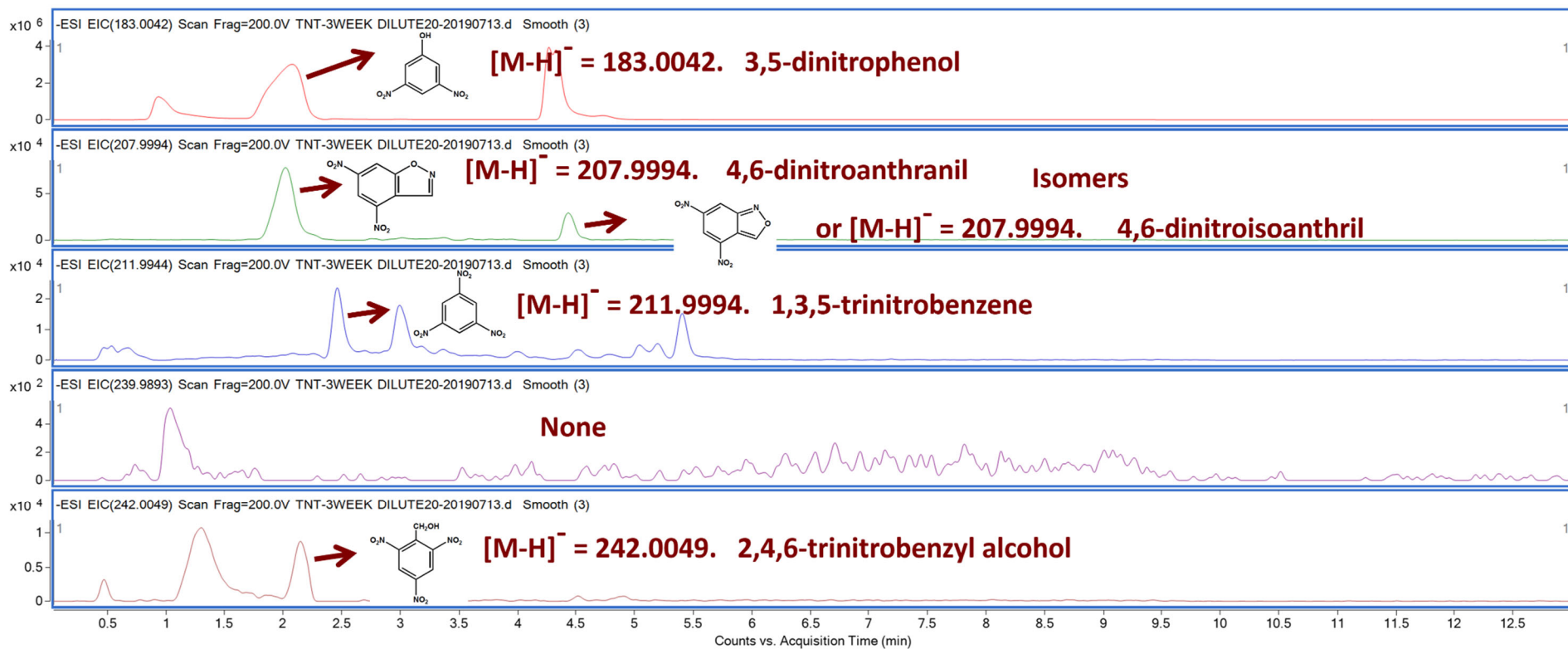
TNT Week 3 sample



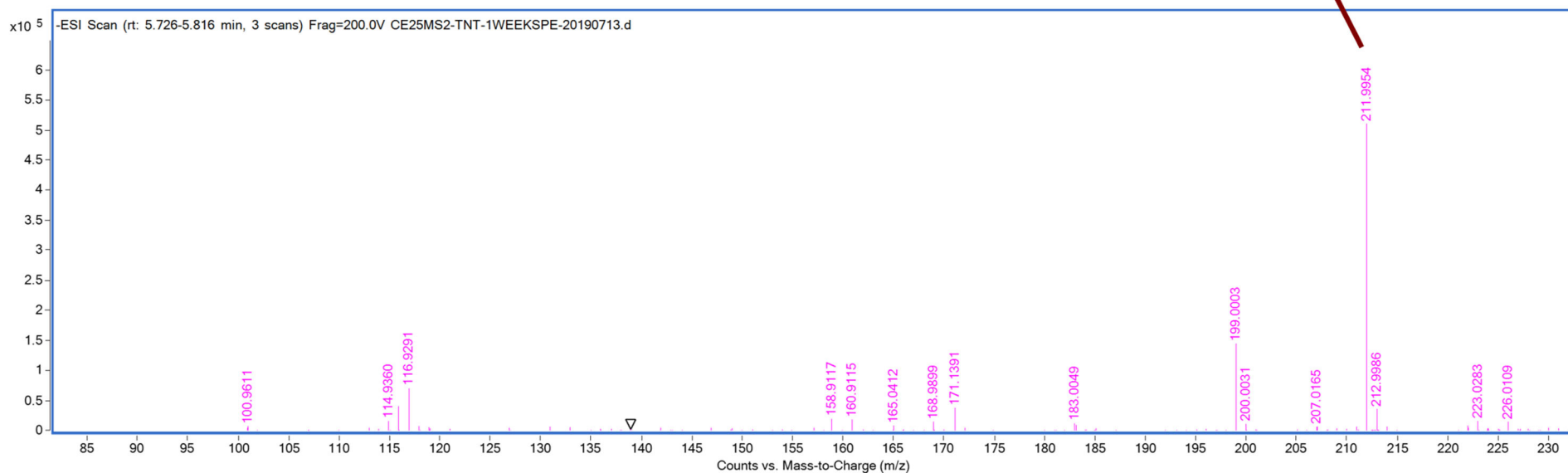
TNT Week 1 sample



TNT Week 3 sample

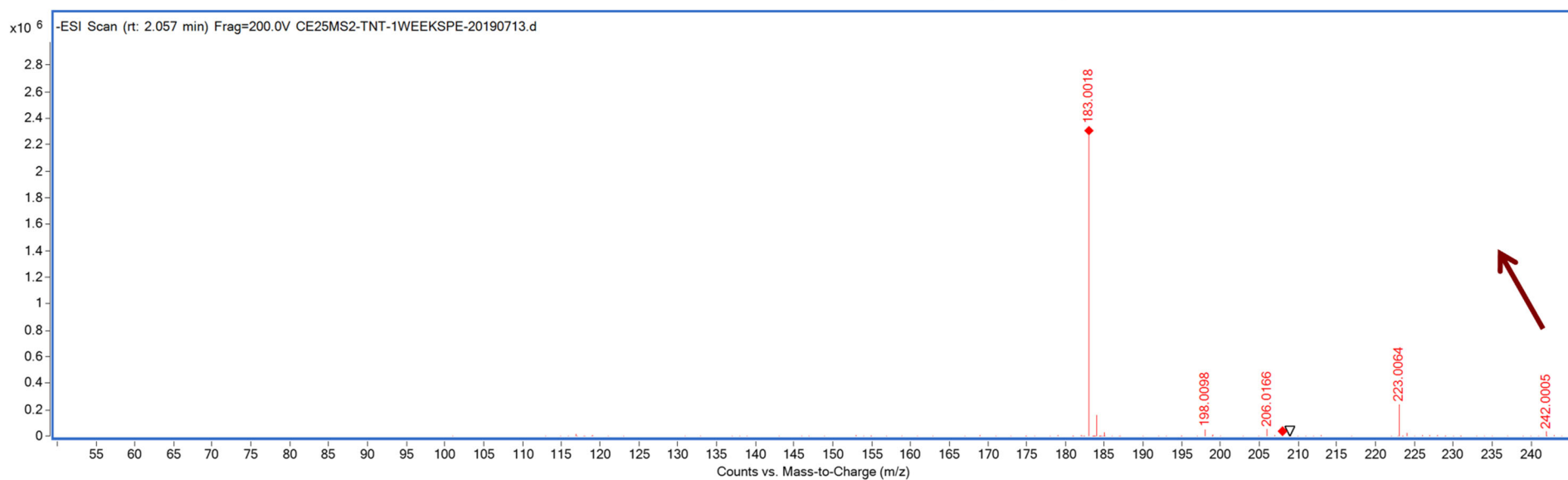


From TNT Week 1 sample
1,3,5-trinitrobenzene, $[M-H]^- = 211.9944$
MS/MS spectrum

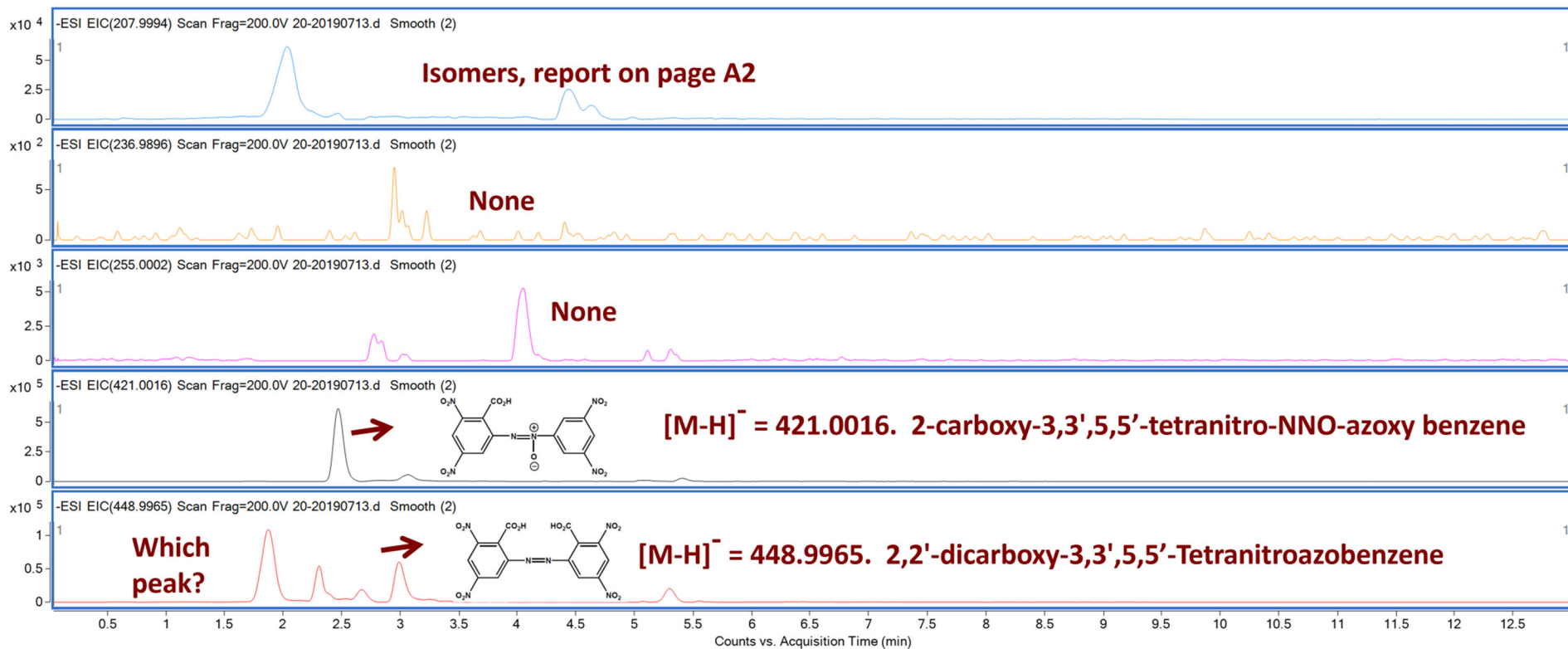


From TNT Week 1 sample

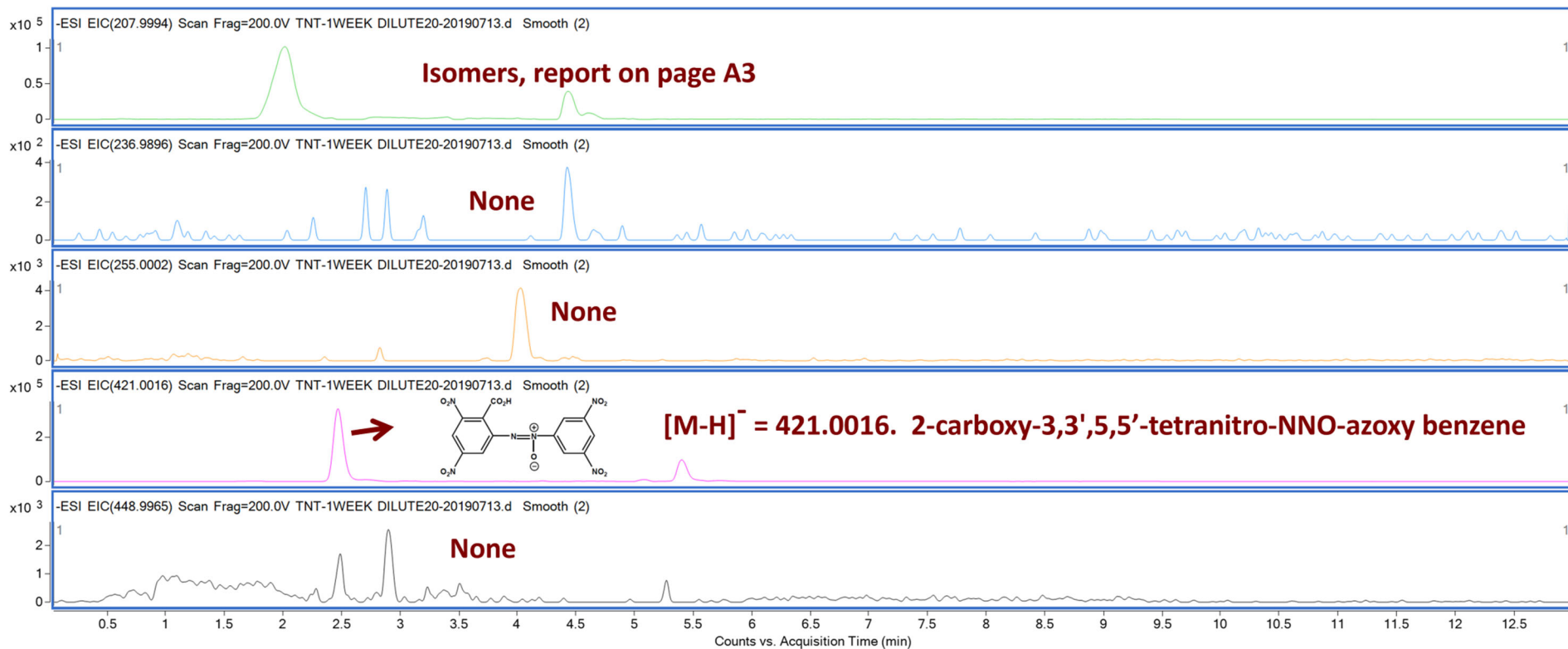
[M-H]⁻ = 242.0049. 2,4,6-trinitrobenzyl alcohol
MS/MS spectrum



TNT Day 3 sample

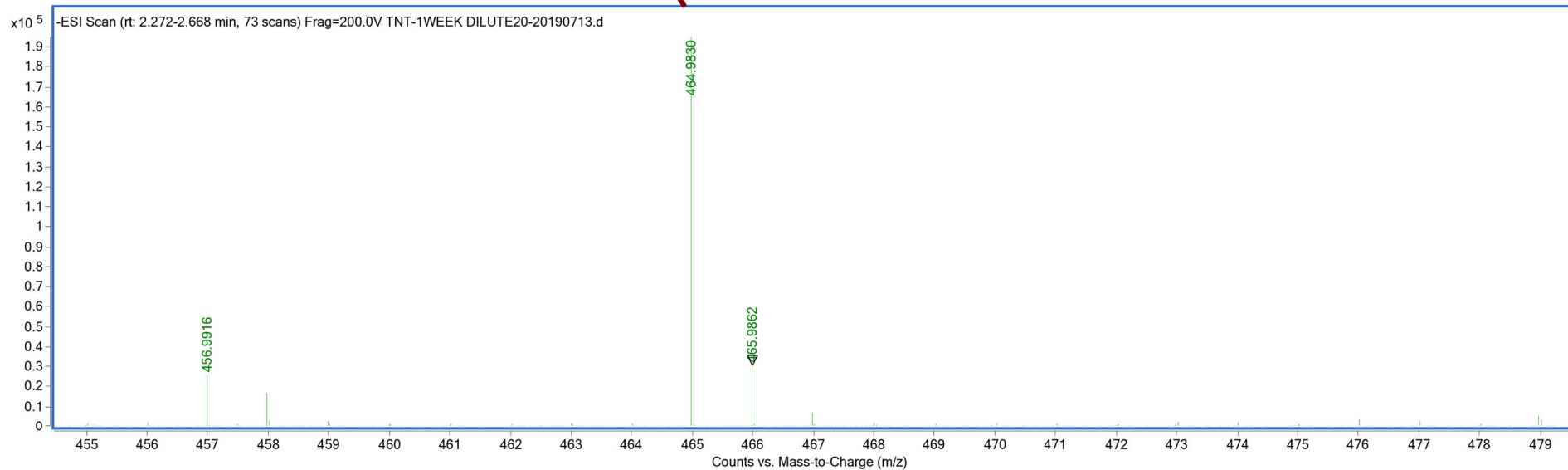


TNT Week 1 sample



From TNT Week 1 sample

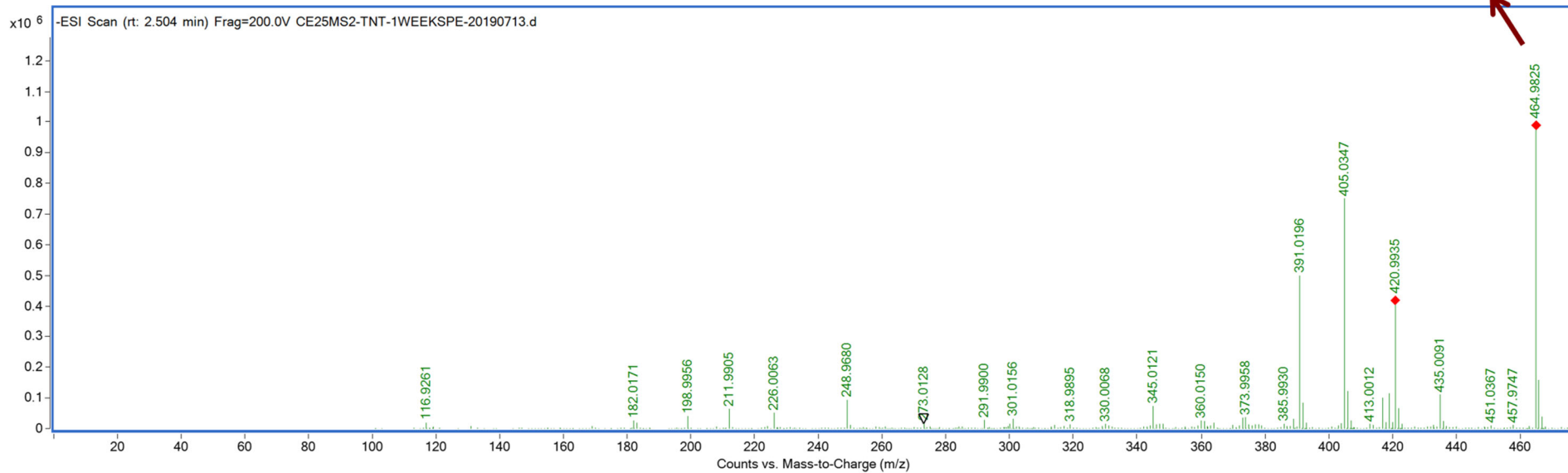
2,2'-dicarboxy-3,3',5,5'-Tetranitroazoxybenzene $[M-H]^- = 464.9915$
MS spectrum



MS/MS spectrum is shown on page A11

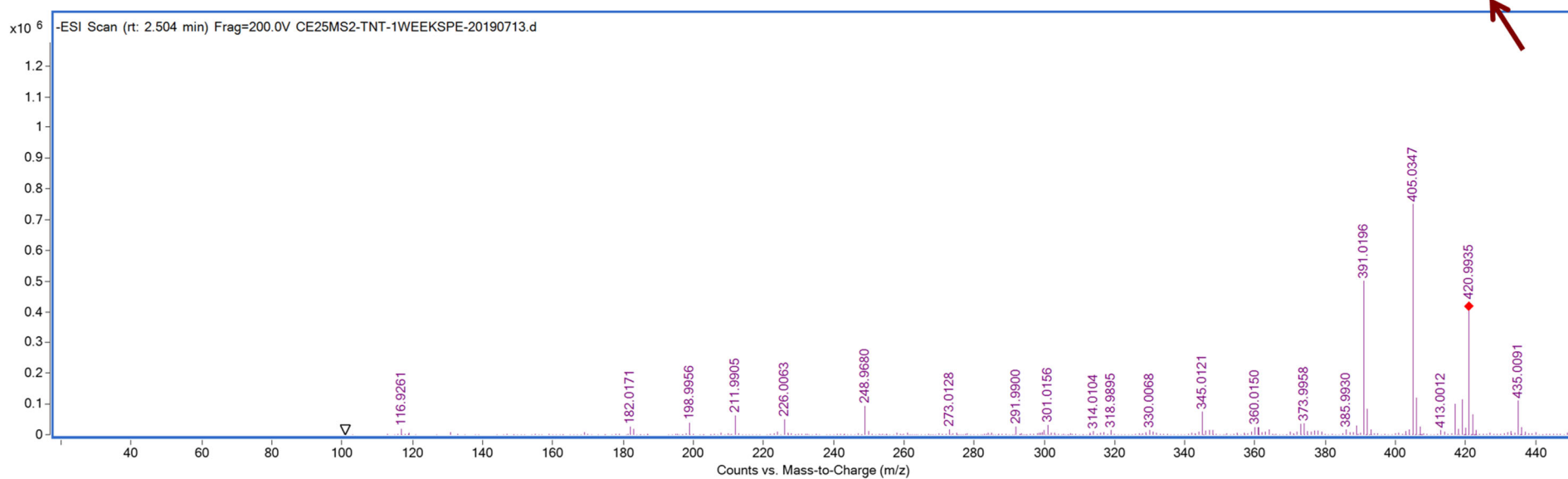
From TNT Week 1 sample

2,2'-dicarboxy-3,3',5,5'-Tetranitroazoxybenzene $[M-H]^- = 464.9915$
MS/MS spectrum

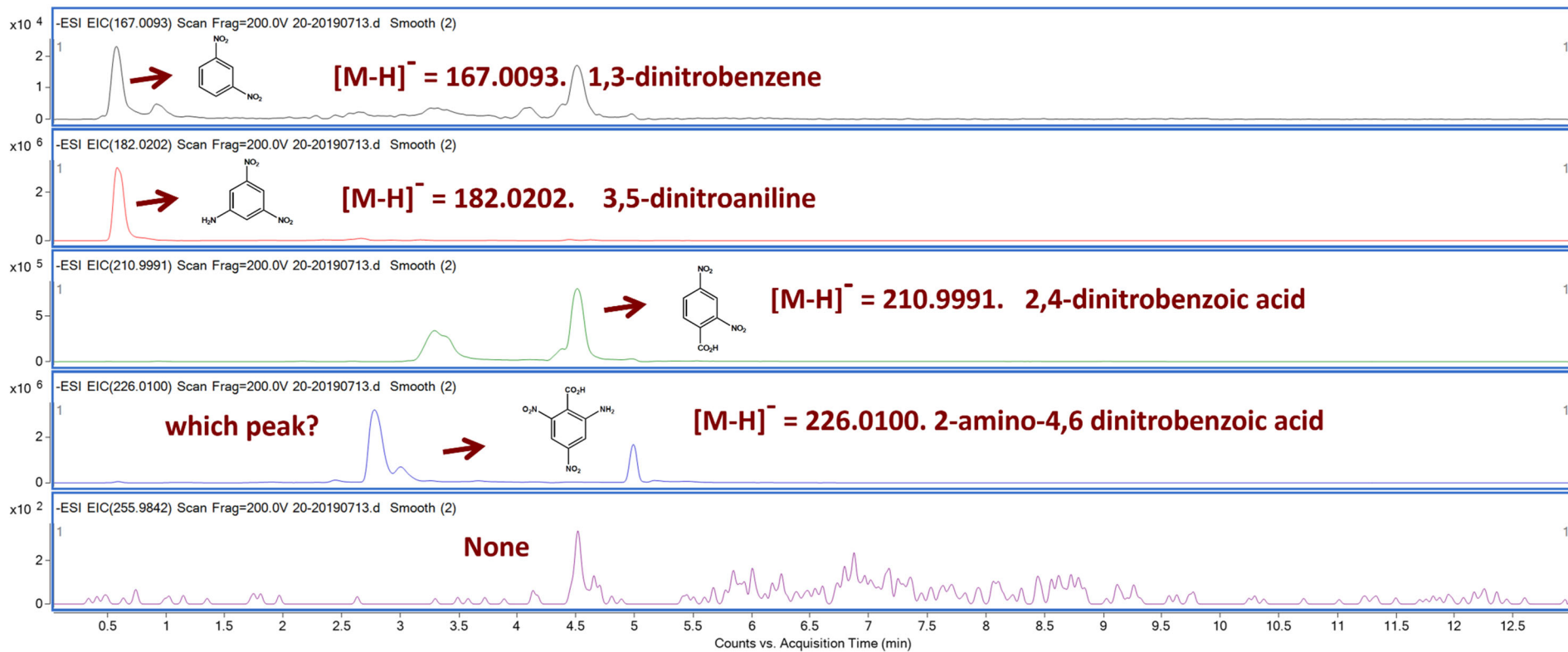


From TNT Week 1 sample

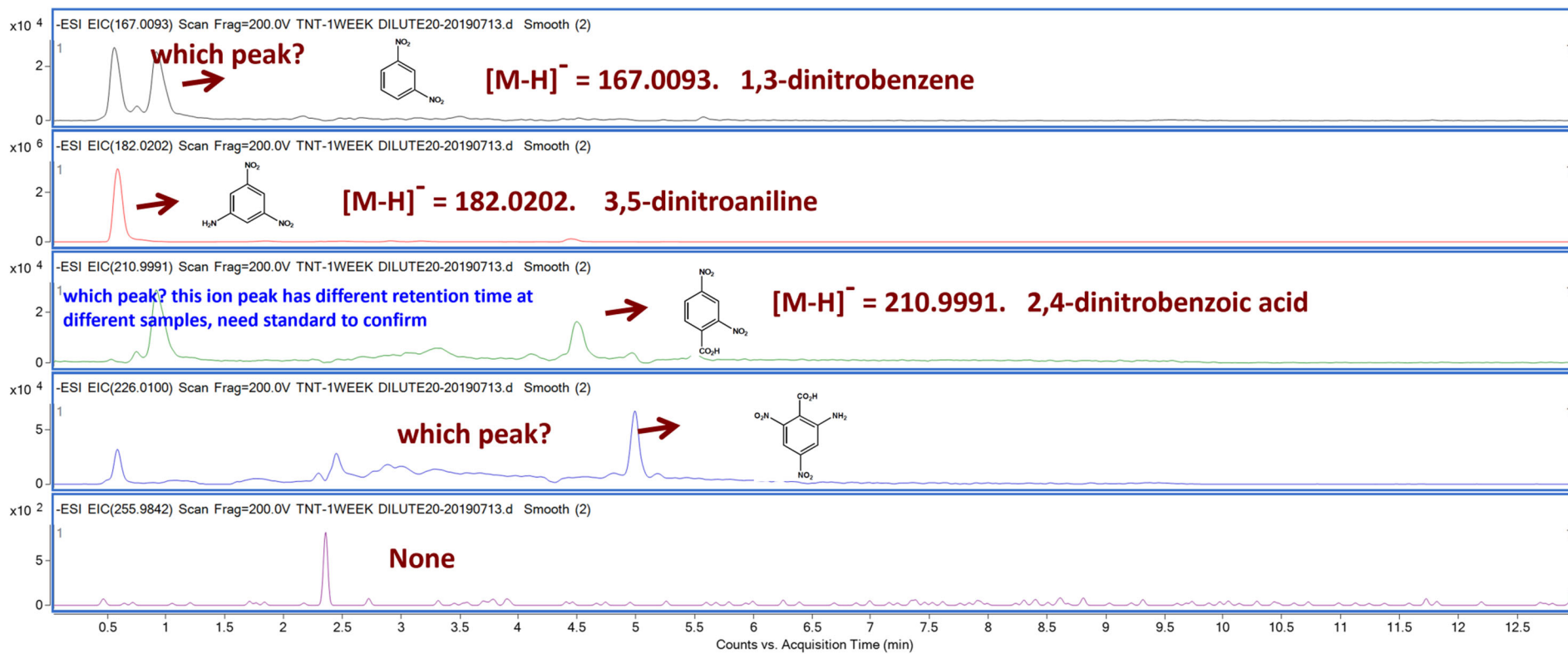
2-carboxy-3,3',5,5'-tetranitro-NNO-azoxy benzene
[M-H]⁻ = 421.0016 MS/MS spectrum



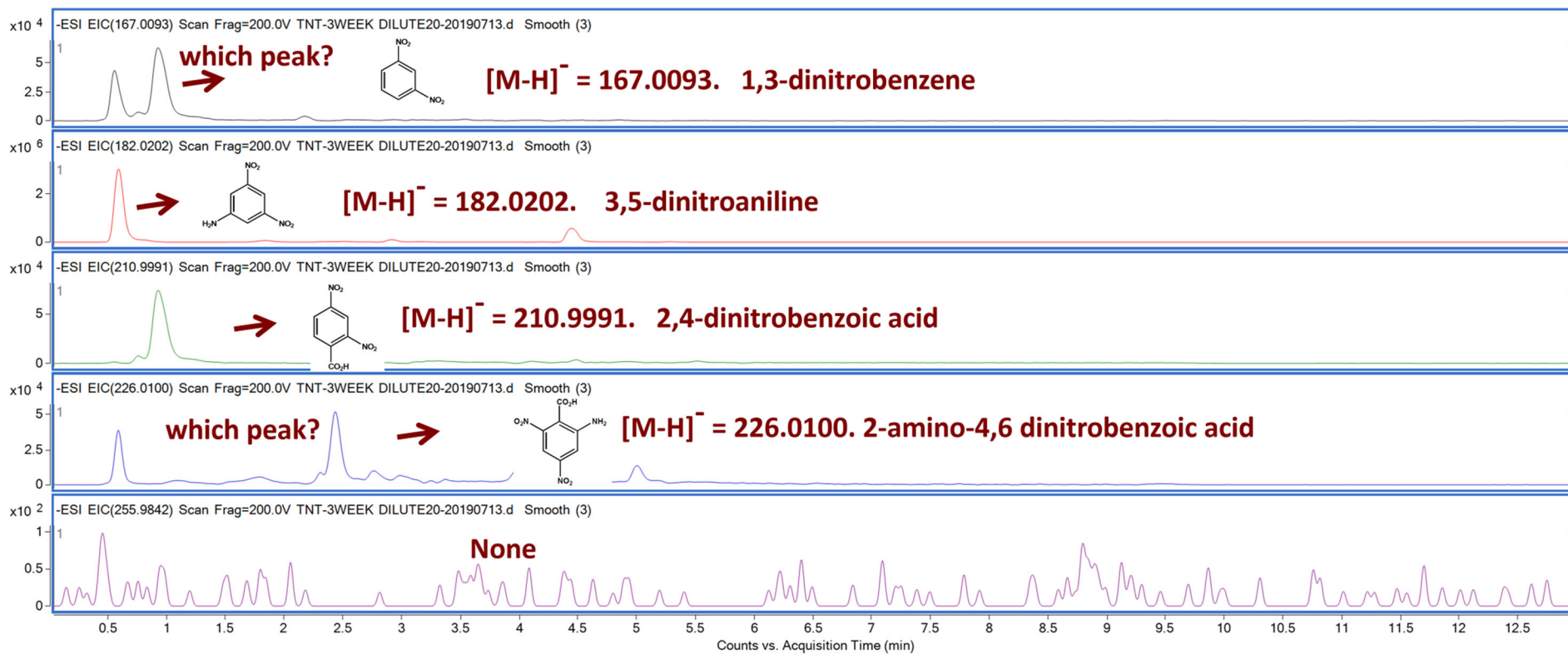
TNT Day 3 sample



TNT Week 1 sample

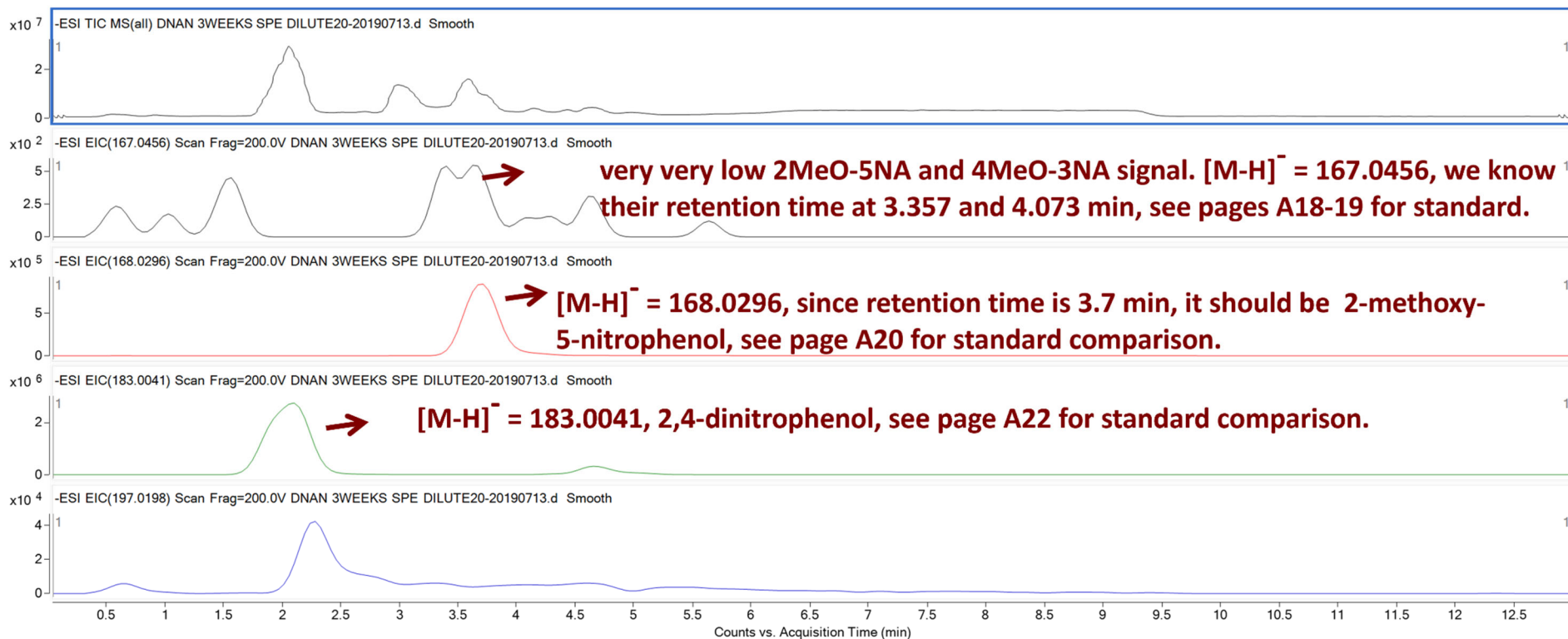


TNT Week 3 sample

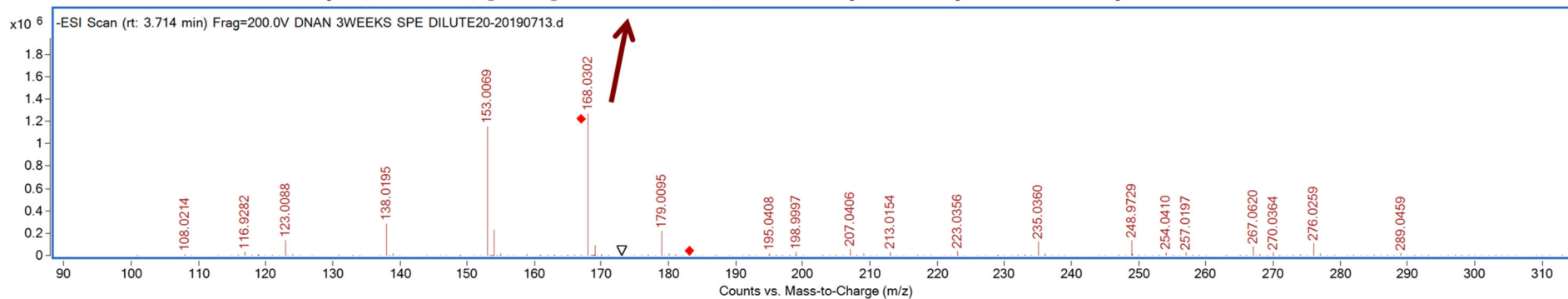


DNAN Week 3 sample

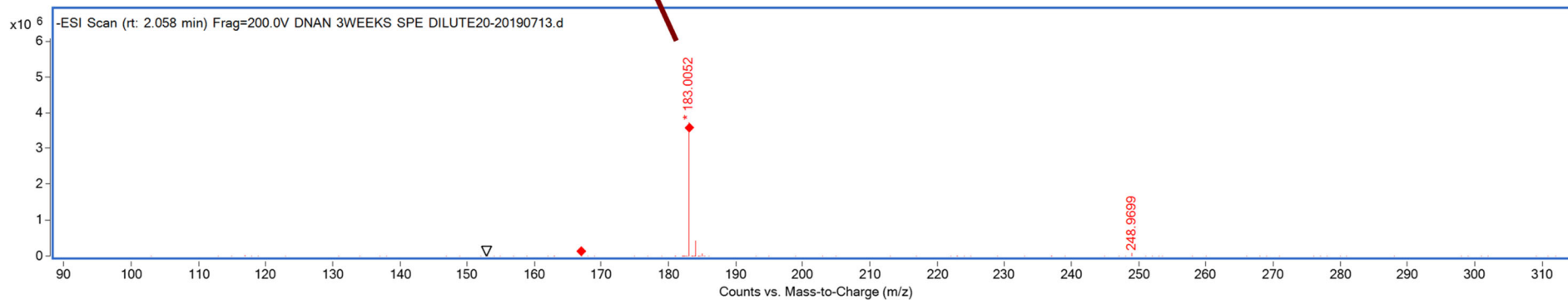
$[M-H]^- = 168.0296, 167.0456, 183.0041, 197.0198$



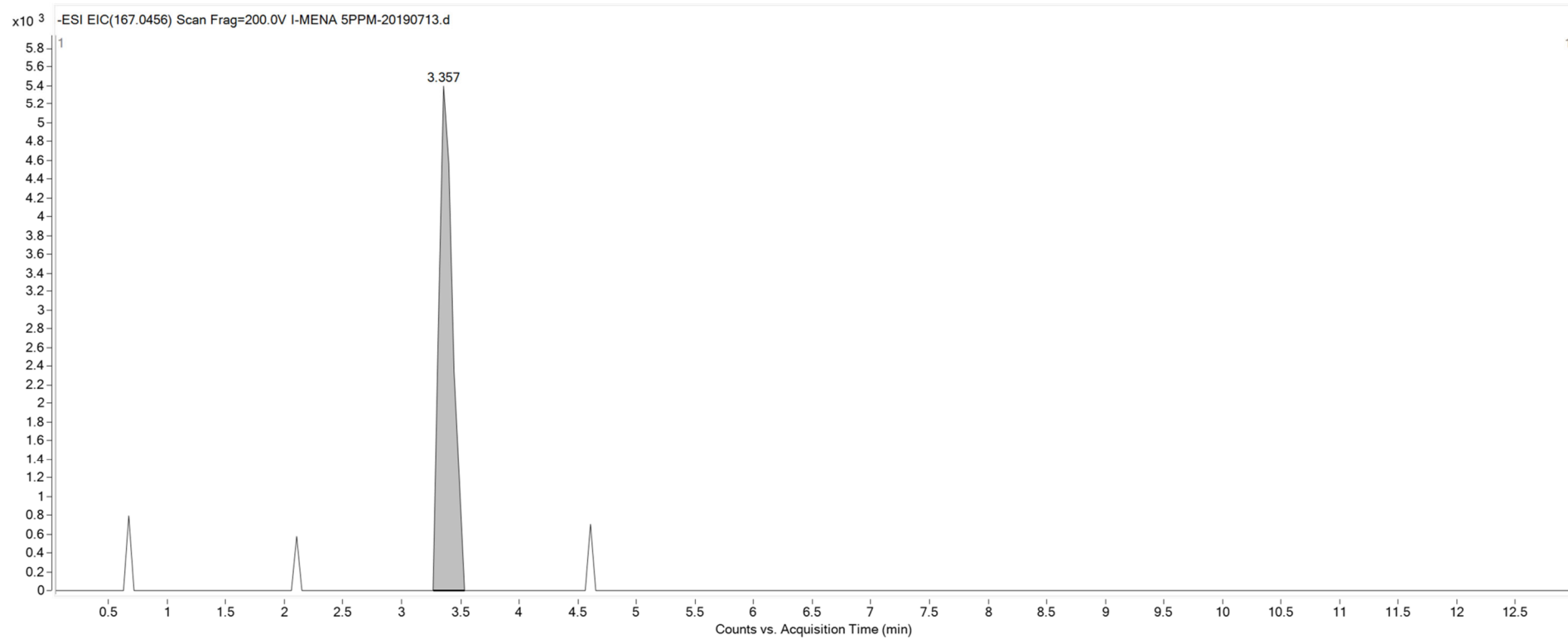
DNAN Week 3 sample, 3.7 min, $[M-H]^- = 168.0296$, 2-methoxy-5-nitrophenol. MS spectrum



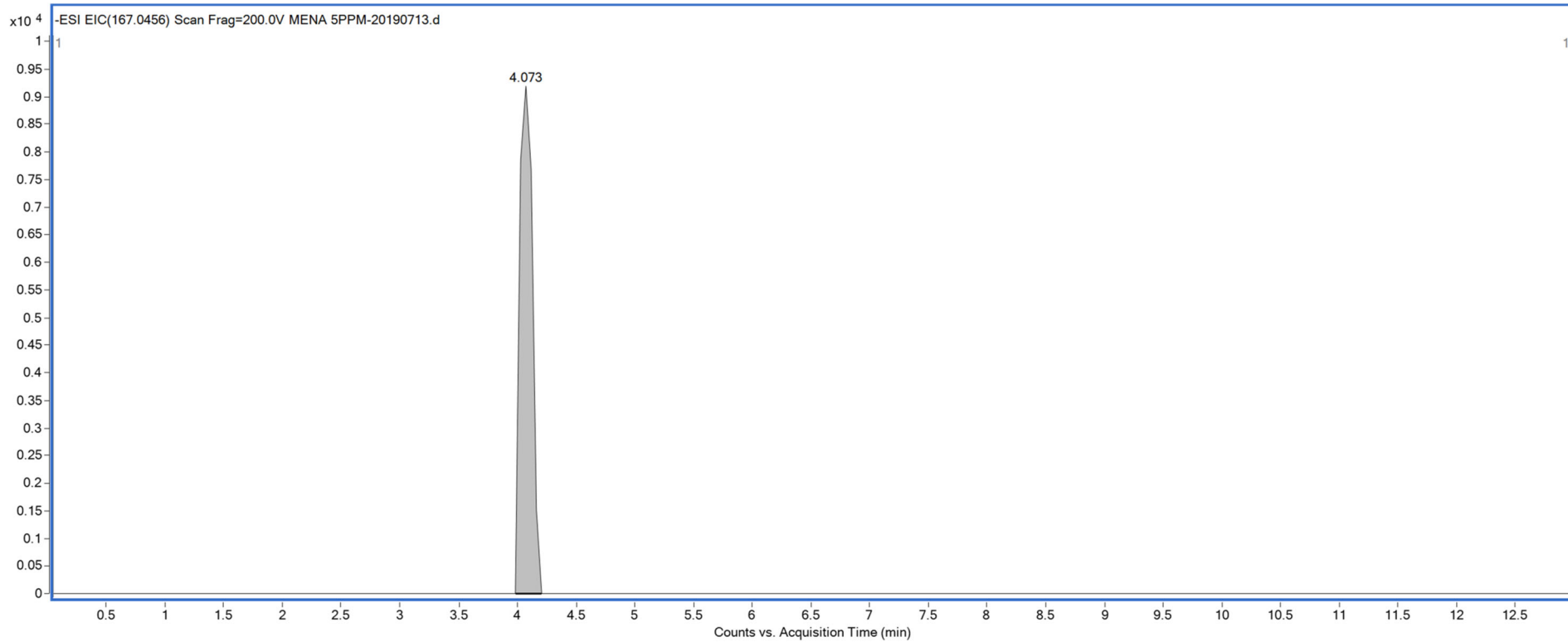
DNAN Week 3 sample, 2.06 min, $[M-H]^- = 183.0041$, 2,4-dinitrophenol. MS spectrum, see page A22 for 2,4-dinitrophenol standard MS spectrum.



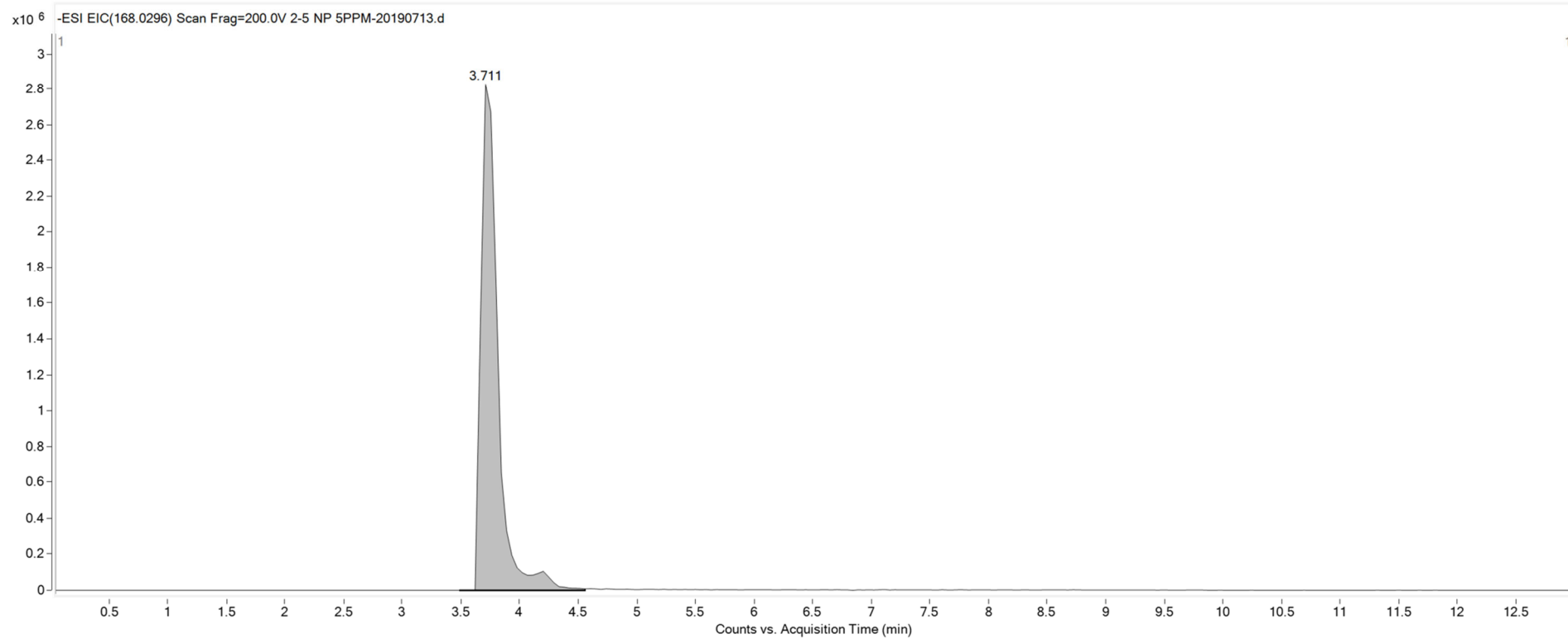
4MeO-3NA standard, 5 ppm, 3.357 min, $[M-H]^- = 167.0456$



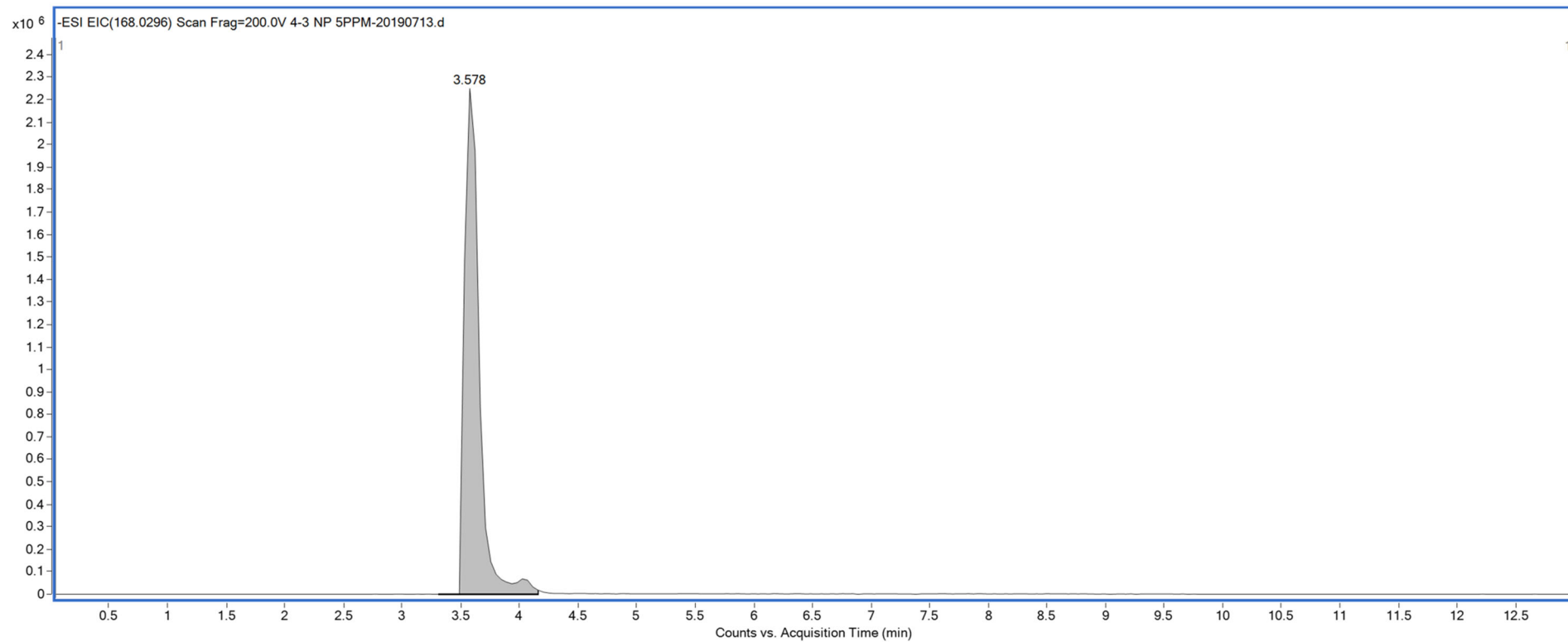
2MeO-5NA standard, 5 ppm, 4.073 min, $[M-H]^- = 167.0456$

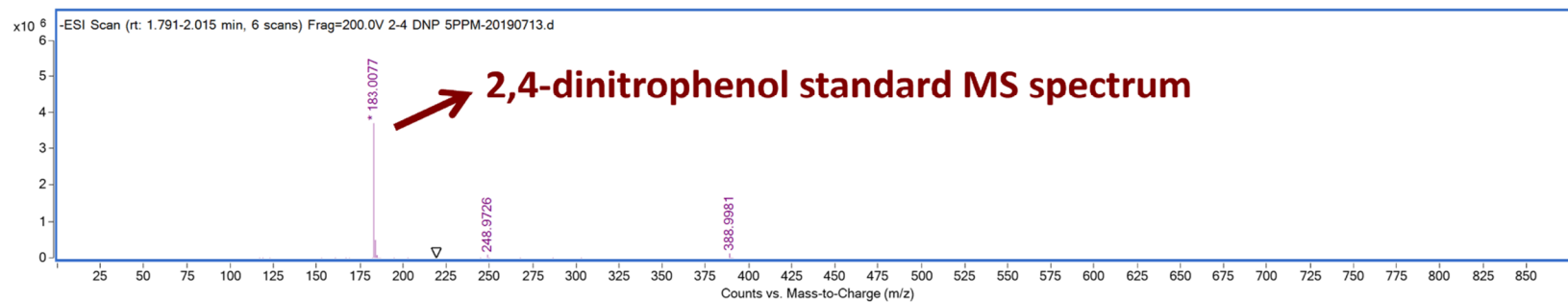
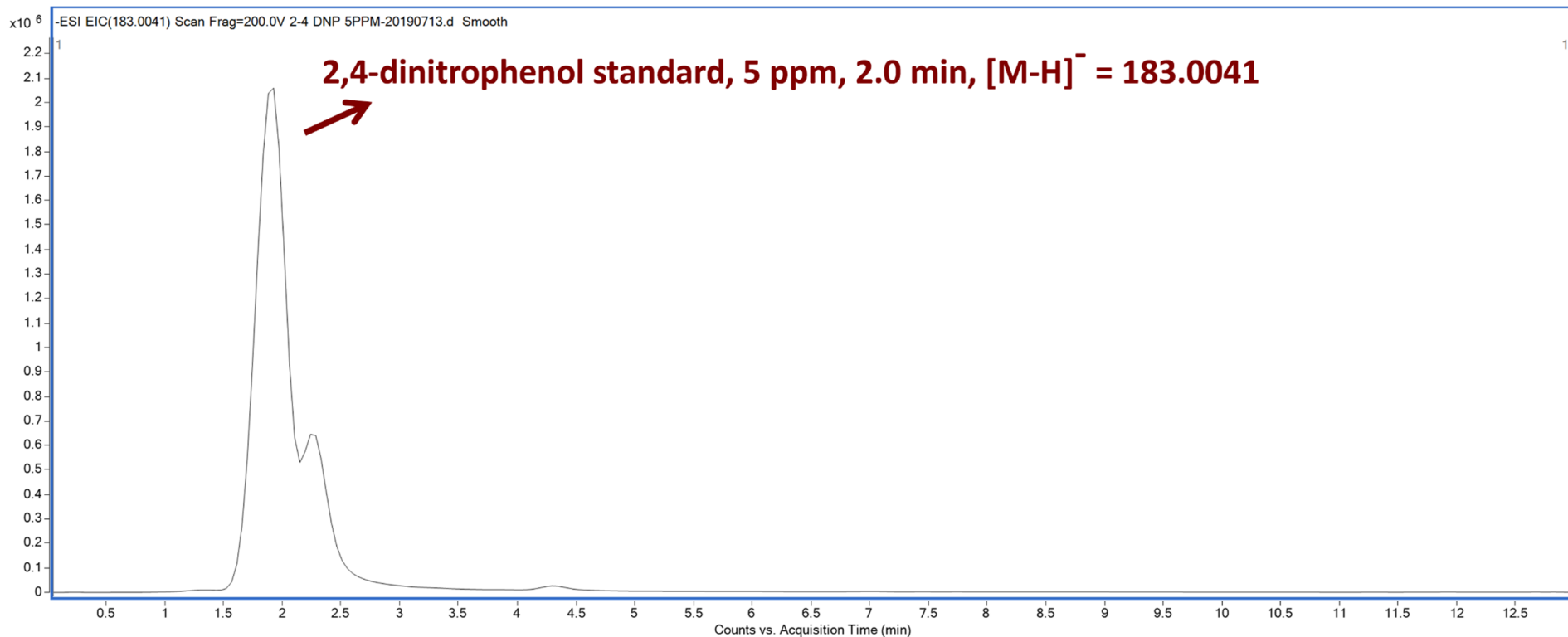


2-methoxy-5-nitrophenol standard, 5 ppm, 3.711 min, $[M-H]^- = 168.0296$

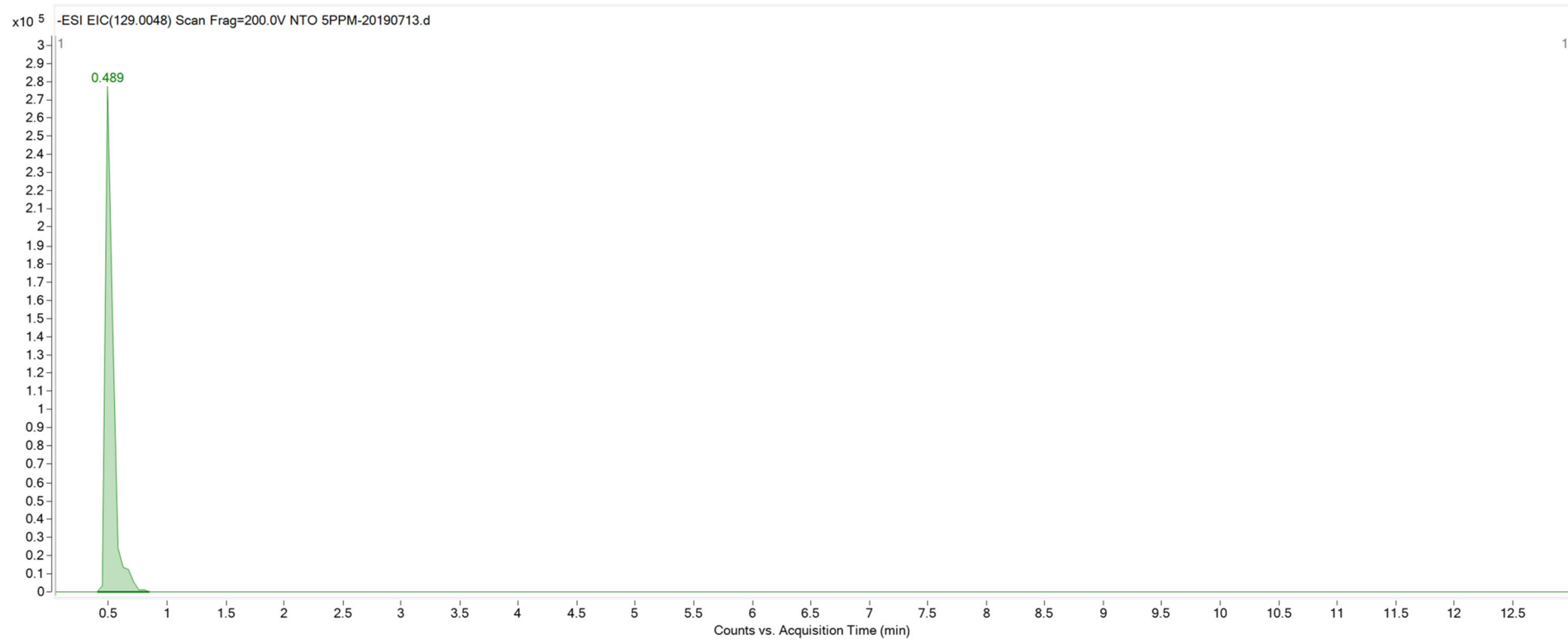


4-methoxy-3-nitrophenol standard 5 ppm, 3.578 min, $[M-H]^- = 168.0296$

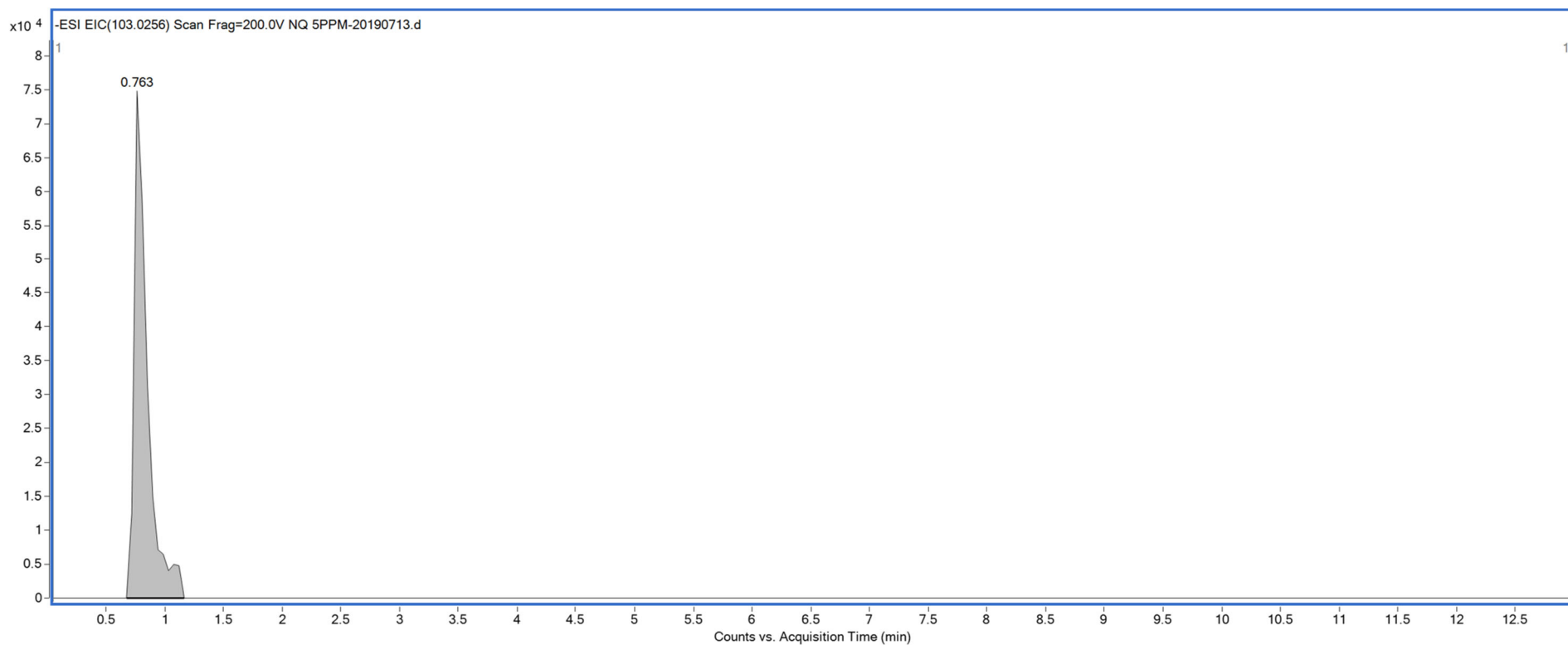




NTO standard 5 ppm, 0.489 min



NQ standard 5 ppm, 0.763 min



A2. Phototransformation data and calculations.

Table A2.1. Calculated “near-surface” specific rates of light absorption ($k_{a,\lambda}^0$) $\Delta\lambda$, s⁻¹ for Rayonet and SaniRay reactors for bulbs centered at 350 nm.

Reactor	Rayonet						SaniRay					
IMC	DNAN		NTO		NQ		DNAN		NTO		NQ	
λ (nm)	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev
310	2.05E-03	3.09E-04	3.33E-04	5.42E-05	3.70E-04	1.45E-04	1.25E-03	3.06E-04	2.03E-04	5.13E-05	2.26E-04	9.87E-05
315	4.84E-03	7.34E-04	9.60E-04	1.57E-04	8.65E-04	3.53E-04	2.95E-03	7.24E-04	5.87E-04	1.48E-04	5.28E-04	2.39E-04
320	8.07E-03	1.23E-03	1.98E-03	3.13E-04	1.48E-03	6.68E-04	4.93E-03	1.21E-03	1.21E-03	3.01E-04	9.03E-04	4.43E-04
325	1.13E-02	1.75E-03	3.47E-03	5.36E-04	2.22E-03	1.08E-03	6.93E-03	1.71E-03	2.12E-03	5.23E-04	1.36E-03	7.10E-04
330	1.45E-02	2.26E-03	5.54E-03	8.49E-04	2.99E-03	1.51E-03	8.85E-03	2.19E-03	3.38E-03	8.32E-04	1.83E-03	9.88E-04
335	1.77E-02	2.85E-03	8.41E-03	1.27E-03	4.02E-03	2.14E-03	1.08E-02	2.71E-03	5.14E-03	1.26E-03	2.46E-03	1.39E-03
340	2.12E-02	3.52E-03	1.23E-02	1.86E-03	5.40E-03	3.01E-03	1.30E-02	3.29E-03	7.51E-03	1.84E-03	3.30E-03	1.94E-03
345	2.38E-02	4.20E-03	1.65E-02	2.52E-03	7.08E-03	4.09E-03	1.45E-02	3.80E-03	1.01E-02	2.48E-03	4.33E-03	2.63E-03
350	2.26E-02	4.19E-03	1.85E-02	2.79E-03	7.57E-03	4.36E-03	1.38E-02	3.69E-03	1.13E-02	2.76E-03	4.63E-03	2.81E-03
355	1.90E-02	3.76E-03	1.78E-02	2.70E-03	7.38E-03	4.31E-03	1.16E-02	3.20E-03	1.09E-02	2.66E-03	4.51E-03	2.77E-03
360	1.46E-02	3.10E-03	1.53E-02	2.34E-03	6.62E-03	3.98E-03	8.91E-03	2.55E-03	9.36E-03	2.30E-03	4.05E-03	2.55E-03
365	1.05E-02	2.43E-03	1.19E-02	1.83E-03	5.19E-03	3.06E-03	6.39E-03	1.92E-03	7.30E-03	1.79E-03	3.17E-03	1.97E-03
370	7.15E-03	1.86E-03	8.57E-03	1.31E-03	4.08E-03	2.44E-03	4.37E-03	1.41E-03	5.23E-03	1.29E-03	2.49E-03	1.57E-03
375	4.88E-03	1.34E-03	5.76E-03	9.05E-04	3.14E-03	1.88E-03	2.98E-03	9.98E-04	3.52E-03	8.74E-04	1.92E-03	1.20E-03
380	3.26E-03	9.46E-04	3.72E-03	5.94E-04	2.21E-03	1.34E-03	1.99E-03	6.93E-04	2.27E-03	5.68E-04	1.35E-03	8.58E-04
385	2.18E-03	6.68E-04	2.32E-03	3.79E-04	1.61E-03	9.51E-04	1.33E-03	4.81E-04	1.41E-03	3.57E-04	9.86E-04	6.11E-04
390	1.42E-03	4.60E-04	1.38E-03	2.31E-04	1.13E-03	6.42E-04	8.69E-04	3.27E-04	8.41E-04	2.15E-04	6.88E-04	4.14E-04
395	1.02E-03	3.10E-04	8.19E-04	1.43E-04	8.23E-04	4.79E-04	6.22E-04	2.24E-04	5.00E-04	1.30E-04	5.03E-04	3.08E-04
400	6.80E-04	2.13E-04	4.71E-04	8.90E-05	5.62E-04	3.30E-04	4.16E-04	1.53E-04	2.88E-04	7.76E-05	3.43E-04	2.12E-04
Sum	1.91E-01	1.01E-02	1.36E-01	6.29E-03	6.48E-02	1.05E-02	1.17E-01	8.97E-03	8.31E-02	6.19E-03	3.96E-02	6.76E-03

Table A2.2. Calculated “near-surface” specific rates of light absorption ($k_{a,\lambda}^0$) $\Delta\lambda$, s⁻¹ for Rayonet and SaniRay reactors for bulbs centered at 300 nm.

Reactor		Rayonet						SaniRay					
IMC	DNAN		NTO		NQ		DNAN		NTO		NQ		
λ (nm)	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev	
280	1.24E-02	8.22E-04	1.08E-03	2.01E-04	9.67E-03	1.02E-03	7.38E-03	1.31E-03	6.46E-04	1.60E-04	5.77E-03	1.12E-03	
285	1.96E-02	1.25E-03	1.72E-03	2.83E-04	9.27E-03	1.42E-03	1.17E-02	2.06E-03	1.03E-03	2.38E-04	5.53E-03	1.24E-03	
290	3.40E-02	2.17E-03	3.16E-03	5.07E-04	1.03E-02	2.28E-03	2.03E-02	3.57E-03	1.88E-03	4.32E-04	6.16E-03	1.69E-03	
295	4.71E-02	2.95E-03	4.83E-03	6.50E-04	1.09E-02	3.00E-03	2.81E-02	4.93E-03	2.88E-03	6.11E-04	6.50E-03	2.08E-03	
300	5.02E-02	3.02E-03	5.85E-03	6.62E-04	1.01E-02	3.19E-03	2.99E-02	5.22E-03	3.49E-03	6.95E-04	6.01E-03	2.14E-03	
305	4.82E-02	2.93E-03	6.61E-03	6.49E-04	9.03E-03	3.06E-03	2.88E-02	5.03E-03	3.94E-03	7.53E-04	5.38E-03	2.03E-03	
310	4.27E-02	2.65E-03	6.95E-03	6.07E-04	7.72E-03	2.84E-03	2.55E-02	4.47E-03	4.15E-03	7.70E-04	4.60E-03	1.85E-03	
315	2.98E-02	1.92E-03	5.91E-03	5.20E-04	5.32E-03	2.05E-03	1.78E-02	3.13E-03	3.52E-03	6.55E-04	3.18E-03	1.33E-03	
320	1.69E-02	1.14E-03	4.16E-03	3.21E-04	3.10E-03	1.33E-03	1.01E-02	1.78E-03	2.48E-03	4.49E-04	1.85E-03	8.50E-04	
325	1.11E-02	7.69E-04	3.40E-03	2.37E-04	2.17E-03	1.01E-03	6.61E-03	1.18E-03	2.03E-03	3.61E-04	1.29E-03	6.41E-04	
330	7.36E-03	5.47E-04	2.81E-03	1.92E-04	1.52E-03	7.38E-04	4.39E-03	7.89E-04	1.68E-03	2.98E-04	9.06E-04	4.65E-04	
335	4.83E-03	3.99E-04	2.29E-03	1.44E-04	1.09E-03	5.62E-04	2.88E-03	5.28E-04	1.37E-03	2.40E-04	6.53E-04	3.52E-04	
340	3.06E-03	2.85E-04	1.78E-03	1.11E-04	7.80E-04	4.21E-04	1.83E-03	3.44E-04	1.06E-03	1.86E-04	4.65E-04	2.62E-04	
345	1.94E-03	2.15E-04	1.34E-03	8.83E-05	5.76E-04	3.23E-04	1.15E-03	2.28E-04	8.02E-04	1.41E-04	3.44E-04	2.01E-04	
350	1.21E-03	1.50E-04	9.88E-04	6.23E-05	4.05E-04	2.27E-04	7.22E-04	1.48E-04	5.89E-04	1.03E-04	2.42E-04	1.41E-04	
355	7.91E-04	1.13E-04	7.40E-04	4.83E-05	3.07E-04	1.74E-04	4.72E-04	1.03E-04	4.41E-04	7.79E-05	1.83E-04	1.08E-04	
360	5.17E-04	8.37E-05	5.43E-04	3.59E-05	2.35E-04	1.37E-04	3.08E-04	7.10E-05	3.24E-04	5.72E-05	1.40E-04	8.50E-05	
365	3.56E-04	6.64E-05	4.06E-04	2.72E-05	1.76E-04	1.01E-04	2.12E-04	5.27E-05	2.42E-04	4.29E-05	1.05E-04	6.27E-05	
370	2.51E-04	5.55E-05	3.00E-04	2.04E-05	1.43E-04	8.33E-05	1.50E-04	4.12E-05	1.79E-04	3.18E-05	8.53E-05	5.16E-05	
375	1.74E-04	4.12E-05	2.05E-04	1.56E-05	1.12E-04	6.51E-05	1.04E-04	2.99E-05	1.22E-04	2.21E-05	6.67E-05	4.03E-05	
380	1.25E-04	3.21E-05	1.43E-04	1.16E-05	8.50E-05	5.01E-05	7.47E-05	2.27E-05	8.52E-05	1.56E-05	5.07E-05	3.10E-05	
385	1.01E-04	2.77E-05	1.07E-04	9.54E-06	7.48E-05	4.28E-05	6.02E-05	1.92E-05	6.40E-05	1.19E-05	4.46E-05	2.66E-05	
390	9.46E-05	2.77E-05	9.15E-05	8.79E-06	7.49E-05	4.14E-05	5.64E-05	1.89E-05	5.46E-05	1.04E-05	4.47E-05	2.58E-05	
395	1.15E-04	3.13E-05	9.25E-05	1.00E-05	9.29E-05	5.26E-05	6.85E-05	2.18E-05	5.51E-05	1.08E-05	5.54E-05	3.27E-05	
400	1.28E-04	3.60E-05	8.89E-05	1.15E-05	1.06E-04	6.05E-05	7.66E-05	2.49E-05	5.30E-05	1.11E-05	6.33E-05	3.76E-05	
Sum	3.33E-01	6.83E-03	5.56E-02	1.59E-03	8.34E-02	7.29E-03	1.99E-01	1.14E-02	3.32E-02	1.81E-03	4.97E-02	5.05E-03	

Table A2.3. “Near-surface” specific rates of light absorption, $(k_{a,\lambda}^0)\Delta\lambda$, s⁻¹, for Mt. Lemmon, AZ.

IMC	DNAN		NTQ		NQ	
λ (nm)	average	stdev	average	stdev	average	stdev
280	1.36E-19	5.88E-20	1.19E-20	5.54E-21	1.06E-19	4.67E-20
285	3.66E-13	1.58E-13	3.21E-14	1.47E-14	1.73E-13	7.87E-14
290	3.67E-08	1.59E-08	3.41E-09	1.56E-09	1.12E-08	5.37E-09
295	1.40E-05	6.07E-06	1.44E-06	6.45E-07	3.24E-06	1.65E-06
300	4.26E-04	1.84E-04	4.97E-05	2.20E-05	8.56E-05	4.56E-05
305	4.75E-03	2.06E-03	6.51E-04	2.86E-04	8.89E-04	4.86E-04
310	8.63E-03	3.73E-03	1.40E-03	6.13E-04	1.56E-03	8.79E-04
315	2.29E-02	9.91E-03	4.54E-03	1.99E-03	4.09E-03	2.36E-03
320	2.91E-02	1.26E-02	7.15E-03	3.11E-03	5.33E-03	3.23E-03
325	2.94E-02	1.27E-02	8.99E-03	3.90E-03	5.74E-03	3.64E-03
330	4.50E-02	1.96E-02	1.72E-02	7.47E-03	9.30E-03	6.03E-03
335	3.43E-02	1.50E-02	1.63E-02	7.03E-03	7.77E-03	5.20E-03
340	3.62E-02	1.59E-02	2.10E-02	9.09E-03	9.22E-03	6.35E-03
345	2.87E-02	1.27E-02	2.00E-02	8.65E-03	8.56E-03	6.04E-03
350	2.77E-02	1.23E-02	2.26E-02	9.78E-03	9.26E-03	6.52E-03
355	2.63E-02	1.19E-02	2.46E-02	1.07E-02	1.02E-02	7.25E-03
360	2.41E-02	1.10E-02	2.52E-02	1.09E-02	1.09E-02	7.91E-03
365	1.87E-02	8.72E-03	2.13E-02	9.24E-03	9.25E-03	6.62E-03
370	2.28E-02	1.10E-02	2.72E-02	1.18E-02	1.30E-02	9.37E-03
375	1.36E-02	6.65E-03	1.60E-02	6.97E-03	8.74E-03	6.32E-03
380	1.63E-02	8.12E-03	1.86E-02	8.10E-03	1.11E-02	8.06E-03
385	1.61E-02	8.19E-03	1.71E-02	7.49E-03	1.19E-02	8.54E-03
390	1.79E-02	9.26E-03	1.73E-02	7.58E-03	1.41E-02	9.89E-03
395	2.00E-02	1.01E-02	1.61E-02	7.09E-03	1.61E-02	1.15E-02
400	2.51E-02	1.29E-02	1.74E-02	7.77E-03	2.07E-02	1.48E-02
Sum	4.68E-01	5.10E-02	3.21E-01	3.44E-02	1.88E-01	3.29E-02

Table A2.4. “Near-surface” specific rates of light absorption, $(k_{a,\lambda}^0)\Delta\lambda$, s⁻¹, for Oracle, AZ.

IMC	DNAN		NTO		NQ	
λ (nm)	average	stdev	average	stdev	average	stdev
280	7.88E-20	2.94E-20	6.90E-21	2.83E-21	6.15E-20	2.35E-20
285	2.60E-13	9.68E-14	2.28E-14	9.17E-15	1.23E-13	4.89E-14
290	2.99E-08	1.11E-08	2.78E-09	1.11E-09	9.08E-09	3.88E-09
295	1.24E-05	4.63E-06	1.28E-06	4.98E-07	2.88E-06	1.32E-06
300	3.99E-04	1.48E-04	4.64E-05	1.78E-05	8.01E-05	3.88E-05
305	4.58E-03	1.70E-03	6.27E-04	2.38E-04	8.56E-04	4.28E-04
310	8.48E-03	3.15E-03	1.38E-03	5.20E-04	1.53E-03	7.95E-04
315	2.28E-02	8.51E-03	4.54E-03	1.71E-03	4.09E-03	2.17E-03
320	2.94E-02	1.10E-02	7.24E-03	2.71E-03	5.39E-03	3.05E-03
325	3.01E-02	1.12E-02	9.22E-03	3.44E-03	5.89E-03	3.49E-03
330	4.67E-02	1.75E-02	1.78E-02	6.66E-03	9.64E-03	5.87E-03
335	3.59E-02	1.35E-02	1.70E-02	6.33E-03	8.13E-03	5.13E-03
340	3.83E-02	1.45E-02	2.22E-02	8.25E-03	9.74E-03	6.36E-03
345	3.06E-02	1.17E-02	2.13E-02	7.91E-03	9.11E-03	6.10E-03
350	2.97E-02	1.15E-02	2.42E-02	9.02E-03	9.94E-03	6.65E-03
355	2.84E-02	1.12E-02	2.66E-02	9.89E-03	1.10E-02	7.45E-03
360	2.61E-02	1.05E-02	2.74E-02	1.02E-02	1.19E-02	8.19E-03
365	2.04E-02	8.41E-03	2.33E-02	8.70E-03	1.01E-02	6.90E-03
370	2.51E-02	1.07E-02	3.00E-02	1.12E-02	1.43E-02	9.83E-03
375	1.50E-02	6.57E-03	1.78E-02	6.65E-03	9.68E-03	6.66E-03
380	1.81E-02	8.10E-03	2.07E-02	7.76E-03	1.23E-02	8.53E-03
385	1.80E-02	8.24E-03	1.91E-02	7.22E-03	1.34E-02	9.08E-03
390	2.01E-02	9.41E-03	1.94E-02	7.36E-03	1.59E-02	1.05E-02
395	2.25E-02	1.03E-02	1.81E-02	6.92E-03	1.82E-02	1.23E-02
400	2.84E-02	1.31E-02	1.97E-02	7.65E-03	2.35E-02	1.59E-02
Sum	4.99E-01	4.75E-02	3.48E-01	3.22E-02	2.05E-01	3.45E-02

Table A2.5. “Near-surface” specific rates of light absorption, $(k_{a,\lambda}^0)\Delta\lambda$, s⁻¹, for Tucson, AZ.

IMC	DNAN		NTQ		NQ	
λ (nm)	average	stdev	average	stdev	average	stdev
280	6.21E-20	2.21E-20	5.43E-21	2.15E-21	4.85E-20	1.77E-20
285	2.15E-13	7.64E-14	1.89E-14	7.29E-15	1.02E-13	3.88E-14
290	2.56E-08	9.09E-09	2.37E-09	9.13E-10	7.76E-09	3.21E-09
295	1.09E-05	3.86E-06	1.11E-06	4.18E-07	2.52E-06	1.12E-06
300	3.53E-04	1.25E-04	4.11E-05	1.51E-05	7.09E-05	3.34E-05
305	4.09E-03	1.45E-03	5.60E-04	2.03E-04	7.65E-04	3.73E-04
310	7.64E-03	2.71E-03	1.24E-03	4.48E-04	1.38E-03	7.00E-04
315	2.08E-02	7.38E-03	4.12E-03	1.49E-03	3.71E-03	1.93E-03
320	2.70E-02	9.61E-03	6.64E-03	2.38E-03	4.94E-03	2.74E-03
325	2.78E-02	9.91E-03	8.51E-03	3.04E-03	5.44E-03	3.17E-03
330	4.35E-02	1.55E-02	1.66E-02	5.92E-03	8.98E-03	5.37E-03
335	3.36E-02	1.21E-02	1.60E-02	5.67E-03	7.63E-03	4.74E-03
340	3.61E-02	1.31E-02	2.10E-02	7.44E-03	9.20E-03	5.92E-03
345	2.91E-02	1.07E-02	2.02E-02	7.19E-03	8.66E-03	5.72E-03
350	2.84E-02	1.05E-02	2.32E-02	8.24E-03	9.51E-03	6.27E-03
355	2.73E-02	1.03E-02	2.55E-02	9.09E-03	1.06E-02	7.07E-03
360	2.52E-02	9.72E-03	2.65E-02	9.42E-03	1.15E-02	7.80E-03
365	1.98E-02	7.87E-03	2.27E-02	8.07E-03	9.84E-03	6.61E-03
370	2.45E-02	1.01E-02	2.93E-02	1.04E-02	1.39E-02	9.47E-03
375	1.47E-02	6.23E-03	1.74E-02	6.23E-03	9.49E-03	6.44E-03
380	1.78E-02	7.71E-03	2.03E-02	7.29E-03	1.21E-02	8.28E-03
385	1.78E-02	7.90E-03	1.89E-02	6.82E-03	1.32E-02	8.85E-03
390	1.99E-02	9.06E-03	1.92E-02	6.98E-03	1.57E-02	1.03E-02
395	2.24E-02	9.92E-03	1.80E-02	6.59E-03	1.81E-02	1.20E-02
400	2.83E-02	1.27E-02	1.96E-02	7.32E-03	2.34E-02	1.57E-02
Sum	4.76E-01	4.37E-02	3.35E-01	2.98E-02	1.98E-01	3.33E-02