

2011 DoD Environmental Monitoring and Data
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RDX Transformation In Biotic and Abiotic Systems Under Poised Redox Potentials

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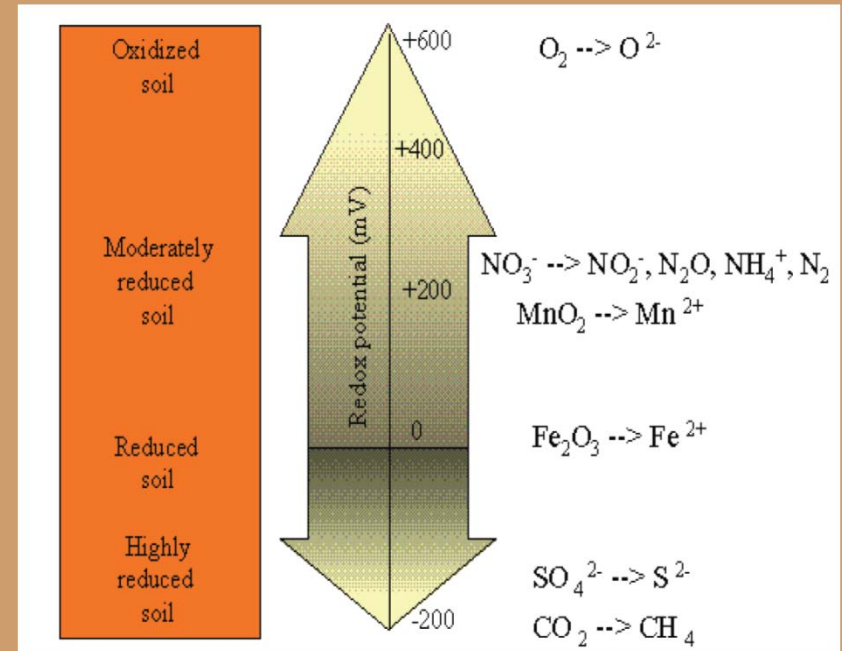


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Background

- Hexahydro-1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX) is present in soils due to training and other activities
- *In situ* techniques exist to degrade RDX
- RDX degradation could be enhanced if biogeochemical factors could be determined and/or controlled.
- Purpose was to determine the role redox potentials play in RDX degradation.



Redox potentials for common environmental electron accepting processes



Hypothesis

Biological processes of nitrate, iron, and sulfate-reducing bacteria create conditions conducive not only to direct enzymatic RDX transformations, but also to indirect abiotic RDX degradation.



Approach–3 test systems

1. **Biological:** Mixed consortium amended with terminal electron acceptor and RDX. Controls did not contain inoculum.
2. **Biologically poised (abiotic):** Biological cultures with terminal electron acceptor were grown until Eh was reduced (30 days). Cultures were autoclaved and amended with RDX. Controls did not contain inoculum.
3. **Chemically poised:** RDX solutions containing terminal electron acceptor. Eh of solutions were chemically reduced. RDX in a buffer solution was control.



Approach–continued

Mixed Culture:

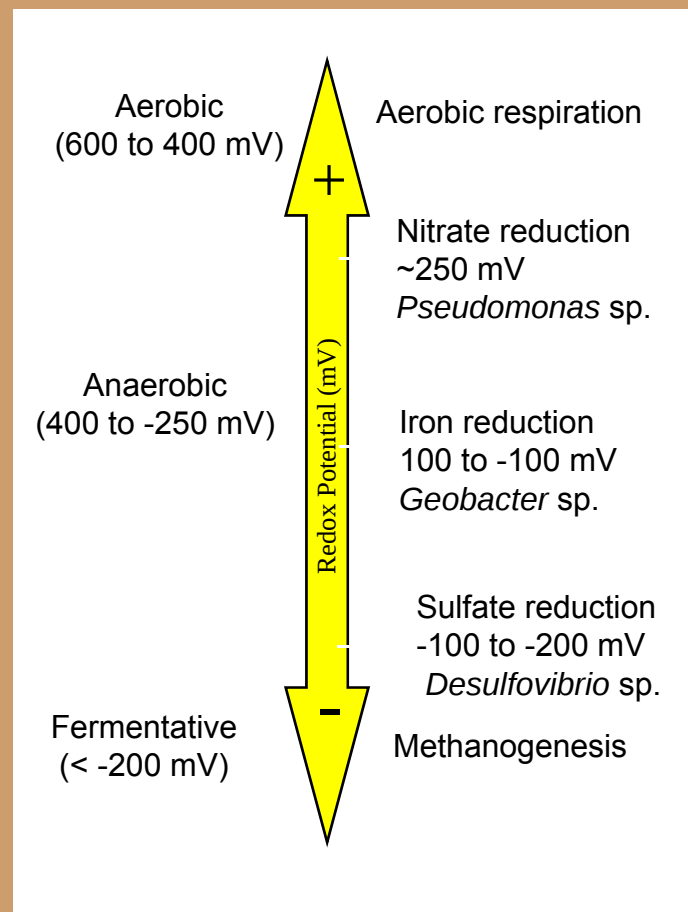
- *Pseudomonas aeruginosa* – nitrate reducer
- *Geobacter metallireducens* GS-15 – iron reducer
- *Desulfovibrio desulfuricans* G20 – sulfate reducer

Nutrient broth:

- Electron acceptor: Fe^{3+} , NO_3^- , or SO_4^{3-} at 10 mM
- RDX at 1 or 4 ppm (5 and 20 μM)
- Buffered to maintain pH 7.
- Initial ORP= 300mV
- N-Tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid
 - ▶ Buffer for Biotic cultures
- tris(hydroxymethyl) aminomethane
 - ▶ Buffer for chemically poised systems

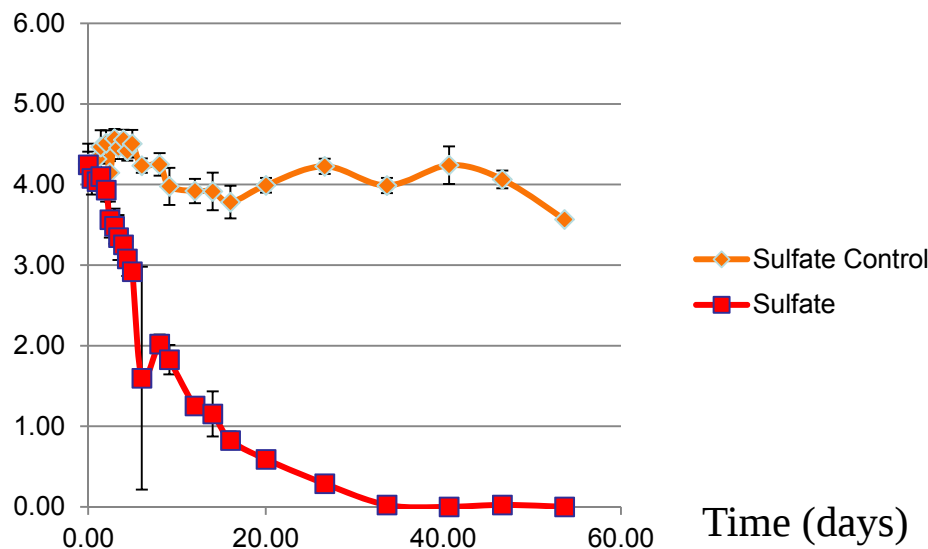
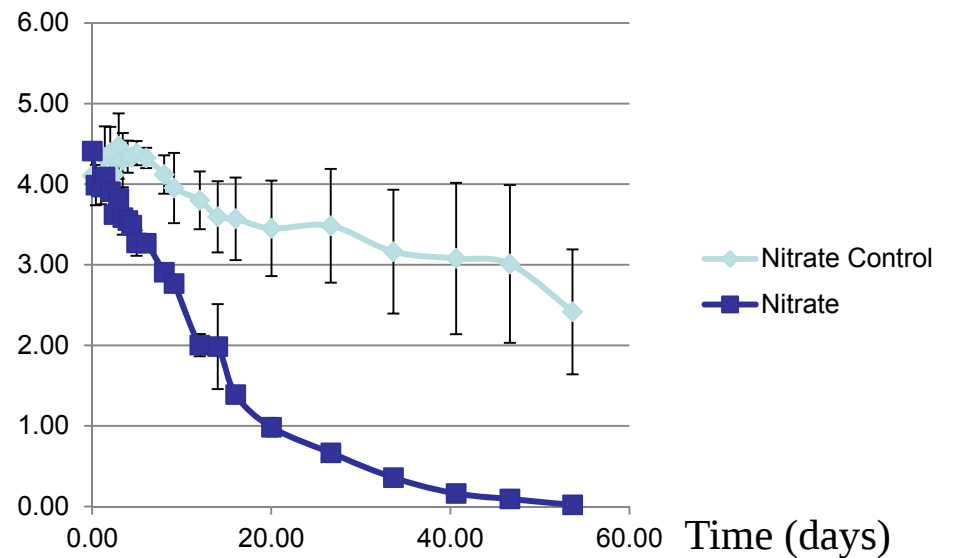
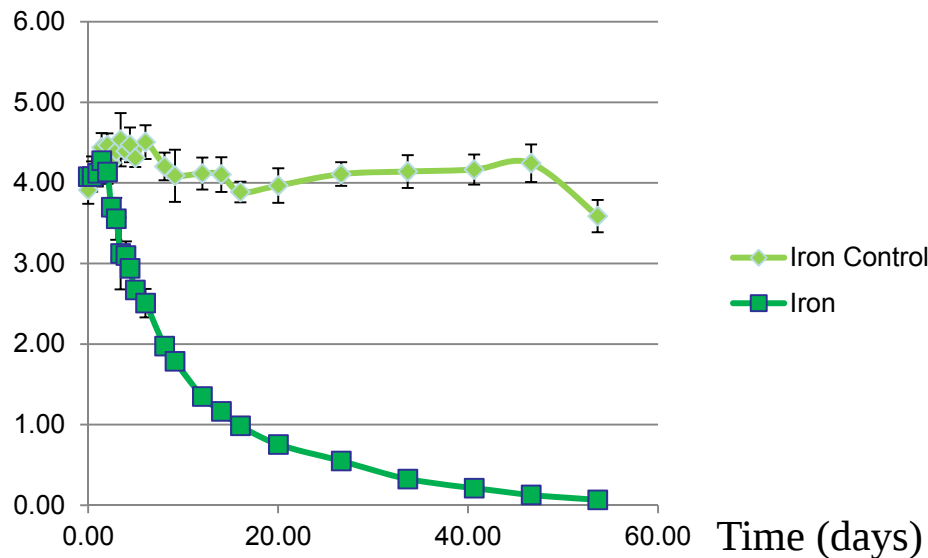
Analysis

- Explosives (HPLC)
- pH: pH electrode
- Eh: Pt electrode and Ag Cl reference
- Amendments: IC
- Organic transformation products (HPLC-ESI-MS)



Biological RDX reduction

RDX concentration (ppm) versus time (days)

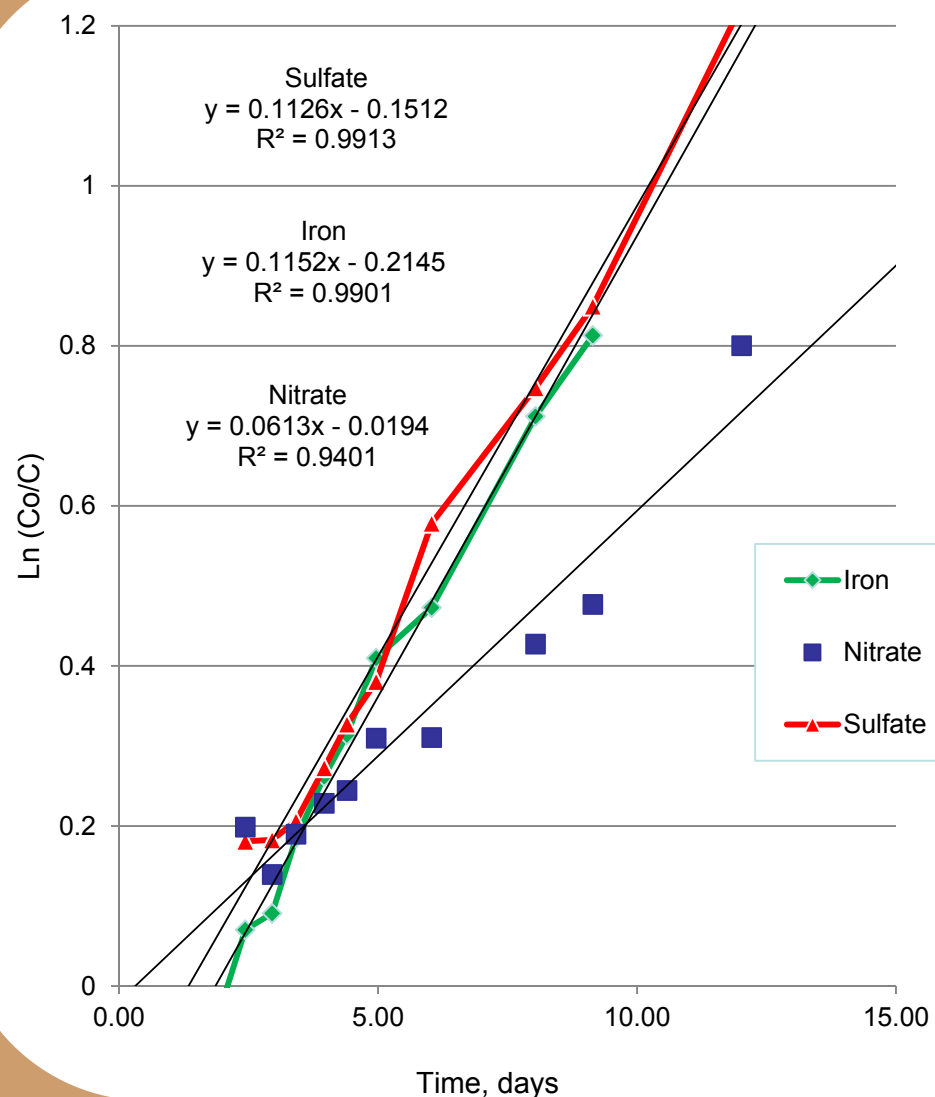


RDX was degraded under all three conditions in the biological systems.



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Kinetics of biological RDX reduction



For first-order rate kinetics
 analysis: $C = C_0 e^{-kt}$
 in which: C= concentration
 mg/L
 k=reaction rate per day
 t= time in days

Linearization yields
 $\ln (C_0/C) = kt$

	Iron	Sulfate	Nitrate
k, per day	0.1152	0.1126	0.0613
Half life, days	6.01	6.15	11.31

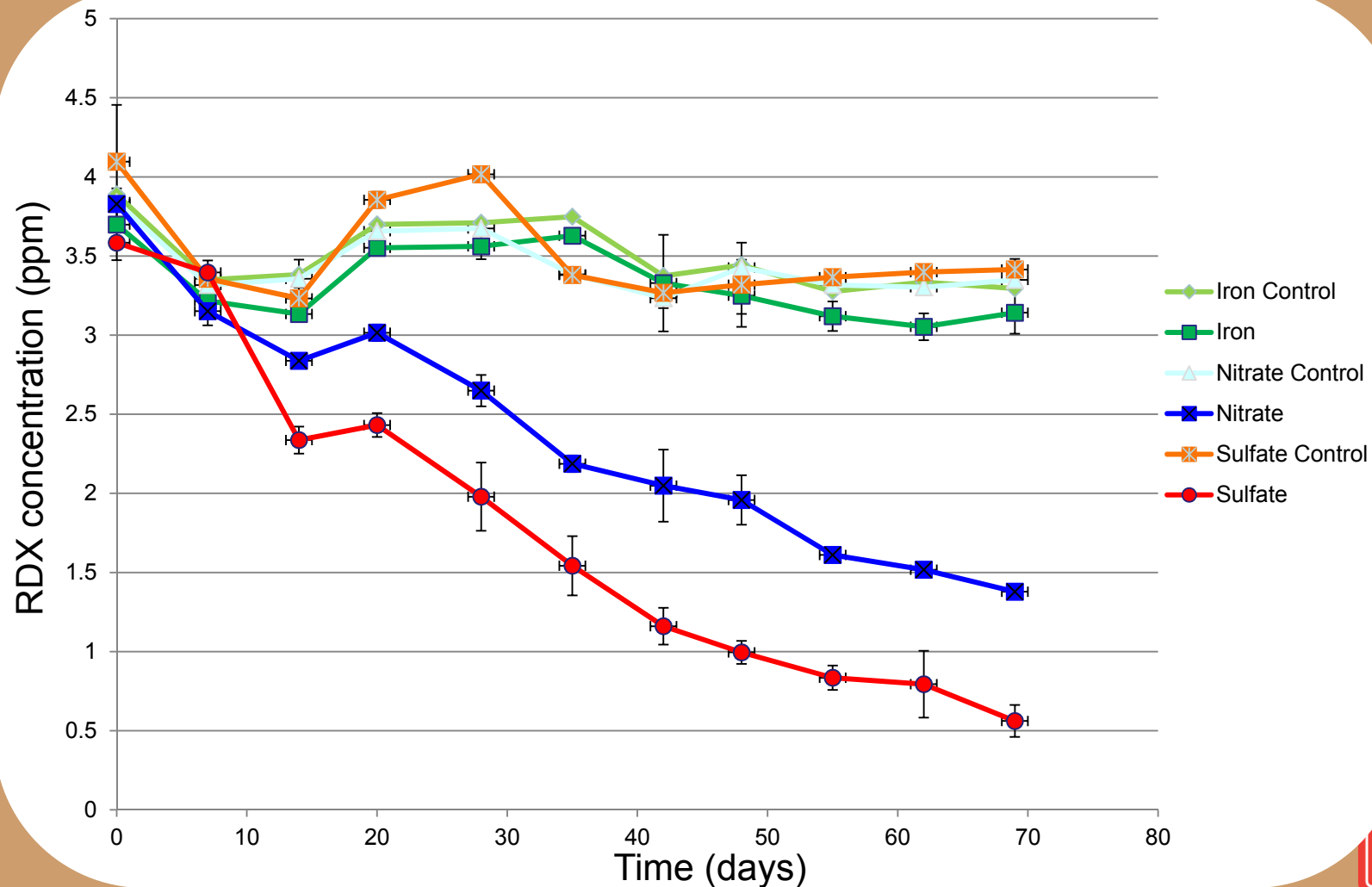
First Order Rate Kinetics



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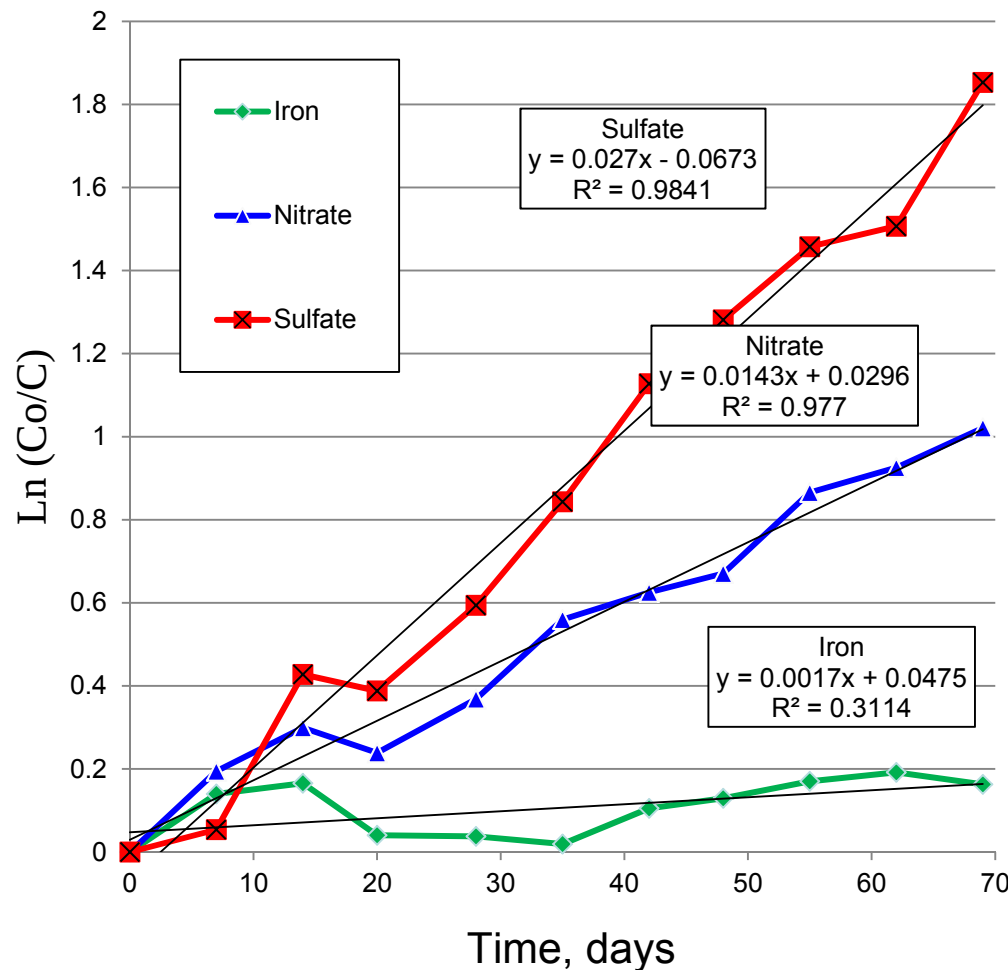
Abiotic RDX reduction

Eh was reduced by biological activity, autoclaved, and amended.



Kinetics of abiotic RDX reduction

Biotic degradation was much faster—rates are at least 4X abiotic rates



For first-order rate kinetics analysis: $C = C_0 e^{-kt}$
in which:

C = concentration in mg/L

k = reaction rate per day

t = time in days

First Order Rate Kinetics

	Iron	Sulfate	Nitrate
k, per day	.0017	.027	.0143
Half life, days	407.7	25.7	48.5
Half life, biological reduction	6.01	6.15	11.31



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Chemically poised systems

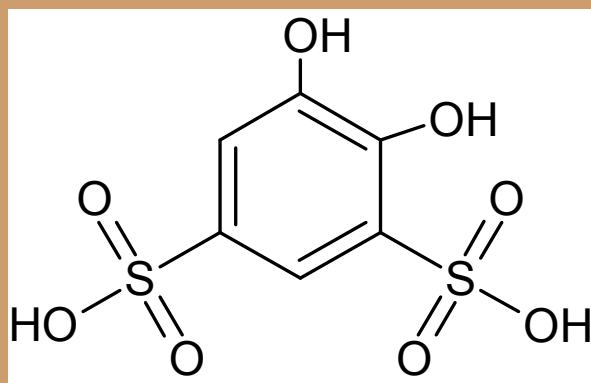
- Iron (II) as the reductant
- Sulfur/Sulfide as the reductant
- Nitrogen compounds as the reductant



Iron System

- Used 2 mM Iron (II) solutions in Tris Buffer with a Tiron ligand at pH 7.5-8
 - ▶ Ferrous Sulfate – Fe(II)
 - ▶ Ferric Sulfate – Fe(III)

Iron-facilitated abiotic degradation of RDX only occurs under anaerobic conditions.



Tiron



Iron System

Iron Species	pH	Eh	RDX Degradation
<i>Single Iron Solutions</i>			
Fe (II)	7.58	-240	Yes
Fe (II)	7.62	-268	Yes
Fe (II)	7.71	-201	Yes
Fe(III)	7.61	-220	No*
<i>Mixed Iron Solutions (50: 50):</i>			
Fe(II):Fe(III)	7.72	-223	Yes
Fe(II):Fe(III)	7.68	-255	Yes

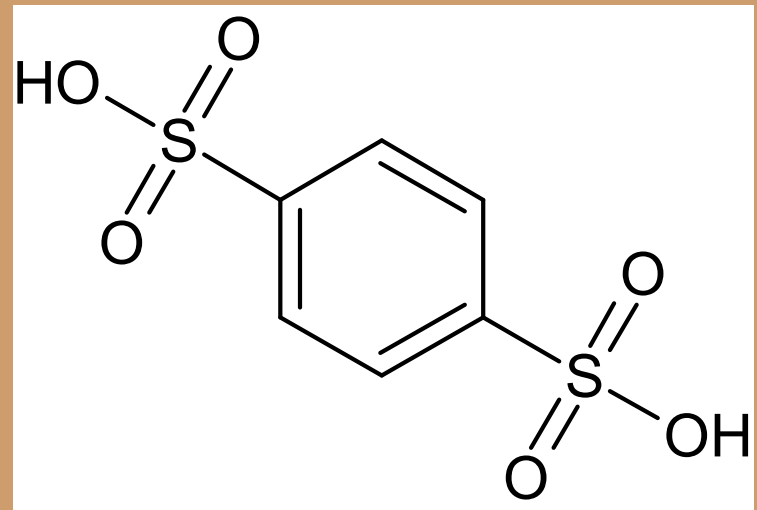
- Iron (II) was a successful reductant for RDX
 - Iron (III) exhibited minimal potential for RDX degradation
- Iron facilitated RDX degradation is most likely to occur in reducing environments (< -150 mV)



Sulfur/Sulfide Systems

The effectiveness of Sulfur/Sulfide as a reductant were evaluated using:

- H_2S bubbled Tris buffer solution
- Elemental Sulfur
- Dithiolbenzene (DBT)
- Sodium Sulfate
- Sodium Sulfide



dithiolbenzene



Sulfur/Sulfide Systems

DBT Experiment	pH	Eh	RDX Degradation
<i>DBT alone</i>			
	8.3	-136	Yes
	8.5	-92	Partial
<i>DBT + Iron</i>			
	8.5	-477	Yes
	8.5	-380	Yes
	9	-467	Yes
	9	-403	Yes

- Dithiolbenze is effective at abiotically degrading RDX
- It is highly effective in the presence of Iron (II)



Nitrogen Systems

The effectiveness of Nitrogen as a reductant was evaluated using:

- 1.5 mM Hydroxylamine
 - ▶ pH/Eh: 3.9/-180; 6.0/-195; 8.0/-256
- 1 mM Sodium Nitrite
 - ▶ pH/Eh: 8.0/-238
- 1 mM Sodium Nitrate
 - ▶ pH/Eh: 5.0/-246; 7.1/-261; 8.0/-266

**RDX did not degrade in the presence of these
N- compounds**



Summary of Chemically Poised tests

- We found iron to be effective at very low Eh values and under anaerobic conditions.
- Sulfur can also be an effective reductant (depending on its form). Sulfides cause degradation, while sulfates and elemental sulfur does not.
- The nitrogen compounds used did not cause RDX degradation under these experimental parameters.



Eh – pH Comparison

	Iron	Sulfate	Nitrate
Biological			
Eh	-63mV	-154 mV	-237 mV
pH	7	7	7
Abiotic			
Eh	-30 mV *	-230 mV	-215 mV
pH	7-8	7-8	7-8
Chemically Poised			
Eh	< -150 mV	-150 mV (DTB) -400 mV (DTB-Fe)	-60 mV *
pH	7.5 - 8	6 – 8.5	6 -8

* Indicates that RDX did not degrade in this system



Conclusions

- **Original hypothesis:** Biological processes of nitrate, iron, and sulfate-reducing bacteria create conditions conducive not only to direct enzymatic RDX transformations, but also to indirect abiotic RDX degradation.
- Abiotic degradation takes place under nitrate and sulfate reducing conditions that were initiated by a bacterial consortium. Abiotic iron systems did not efficiently degrade RDX.
- Abiotic degradation is much slower than biological degradation.
- RDX degraded in systems that were at neutral pH and generally at Eh values < -150 mV. Fe biological system was exception.



Project Team

- ▶ Dr. Heather Smith – ERDC-EL
- ▶ Dr. Jennifer Seiter – ERDC-EL
- ▶ Dr. Anthony Bednar – ERDC-EL
- ▶ Mr. Clint Arnett – ERDC-CERL
- ▶ Deborah Ragan – Badger Technical Services



Thanks for your attention!



Sulfur/Sulfide Systems

- Results show that elemental sulfur alone did not result in degradation of RDX at neutral pHs.
 - ▶ pH/Eh: 7.0/-280; 8.0/-285
- 10 mM Sodium Sulfate did not cause RDX degradation
 - ▶ pH/Eh: 4.8/-258; 7.1/-270; 8.0/-275
- 100 mM Sodium Sulfide effectively degraded RDX at a pH of 12, and partially degraded it at pHs 8 and 10.
 - ▶ pH/Eh: 8.0/-351; 9.9/-355; 12/-361



Lessons Learned

- ▶ RDX can degrade abiotically under anaerobic conditions that were mediated by biological processes
- ▶ Abiotic rates are slower than biological rates
- ▶ Abiotic RDX degradation rates follow sequence
$$\text{SO}_4^{-2} > \text{NO}_3^- > \text{Fe}^{+2}$$
- ▶ Eh values in effective systems were usually <-150 mV, in neutral solutions. Fe biological system was unique.
- ▶ RDX was not degraded until after nitrate was depleted – Eh value is not low enough.

