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Biogeochemical Treatment of Organic and Inorganic Contaminants in Soil and Groundwater

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2012 remediation technologies symposium

Presentation Overview

- Brief Overview/Applications
- Case Study I – RDX in Groundwater
- Case Study II – In Situ Engineered Bioreactors for cVOCs
- Case Study III – Lead Stabilization in Soil
- Wrap-Up/Discussions/Questions

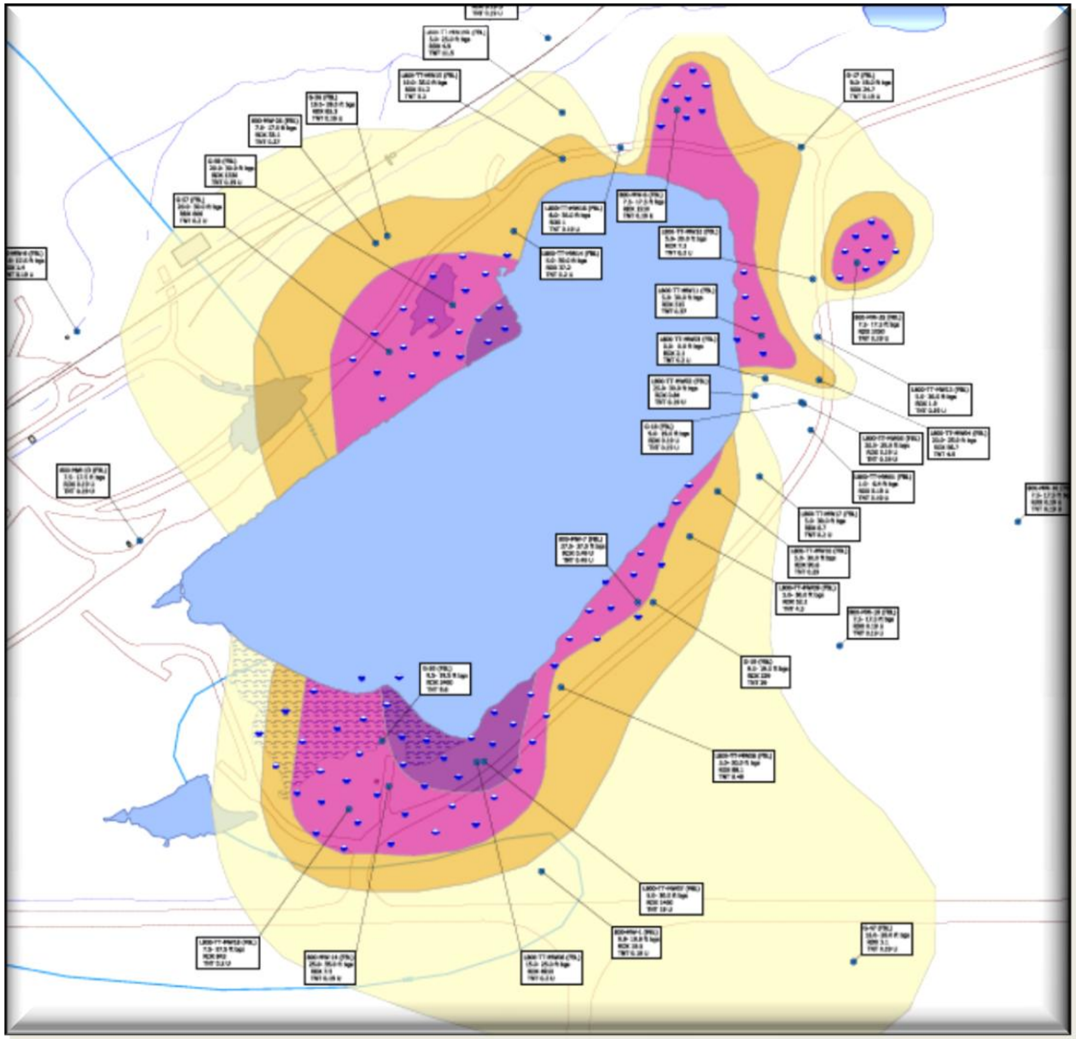
Biogeochemical Treatment

- Processes where contaminants are "degraded by abiotic reactions with minerals that are either naturally occurring or are biogenically produced in the subsurface"
- Applicable to organic contaminants such as cVOCs, organic explosives such as RDX, heavy metals such as lead
- Natural or engineered regimes
- Range of additives include different forms of dissolved iron or iron salts, sulfate, organic substrates, organo-GR (Green Rust) etc.
- Several natural and engineering factors in design and successful remediation

Case Study I

- Iowa Army Ammunition Plant (IAAP) located in southeastern part of Iowa near Middletown
- Currently owned by the army with plant being operated by American Ordnance
- Historic operations involved assembly (and testing) of mortars, shells, projectiles, mines, fuses, dismantling and washing activities
- Several separate areas of concern from load and pack lines, burn pad areas, landfills, impoundment areas, fire training areas, demolition areas, and trenches

Example Area of Concern – RDX in Groundwater



- >2-10 µg/L
- >10-25 µg/L
- >25-50 µg/L
- >50-100 µg/L
- >100-250 µg/L
- >250-2,500 µg/L
- >2,500 µg/L

Pilot Study Overview

- Anaerobic bioremediation using carbon substrate was the groundwater remedy of choice – pilot studies performed to test technology
- RDX concentrations were as high as 7,700 µg/L
- HFCS injections in October 2007 and October 2008
- Several effectiveness sampling events included COCs and a suite of geochemical parameters
- Biotreatment achieved substantial decreases in RDX from a high of 2,570 µg/L to ND in one well
- Analyses to examine the relationship between RDX change and geochemical response, with an emphasis on the role of iron

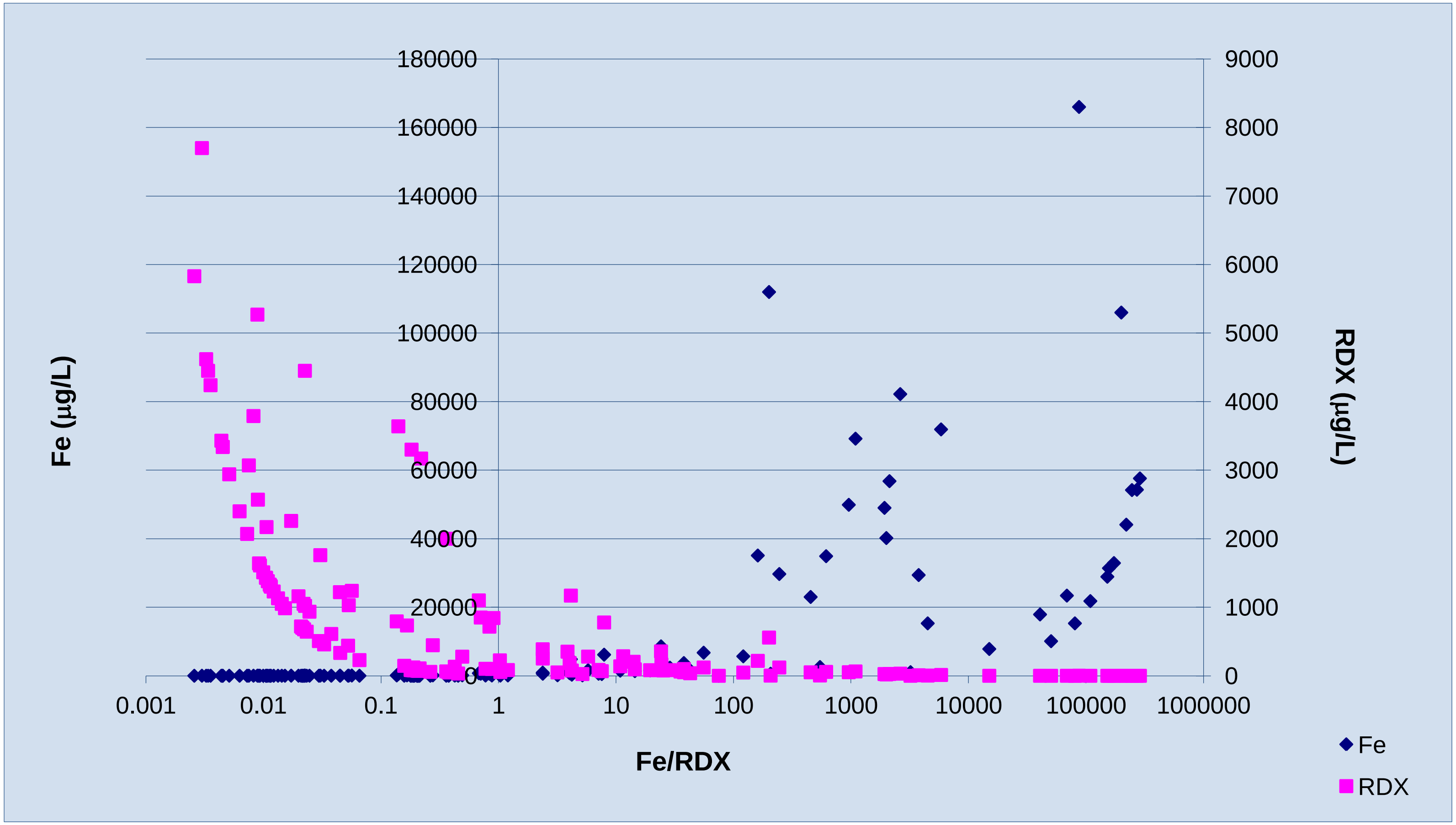
Pilot Study Findings

- Concentrations of RDX and ferrous iron were plotted against the ratio of Fe(II) to RDX; ditto for select geochemical parameters
- RDX exhibits a strongly inverse relationship with Fe(II), and, to a lesser degree, nitrate, sulfate, and DO
- No apparent relationship exists between RDX and methane, carbon dioxide, alkalinity, and total organic carbon (TOC)
- Threshold optimal ratio of Ferrous (II) to RDX appeared to be 1000:1
- RDX degradation was more efficient in slightly acidic or neutral pH's and reducing conditions (Eh < -150mV) where iron exists predominantly as soluble ferrous iron

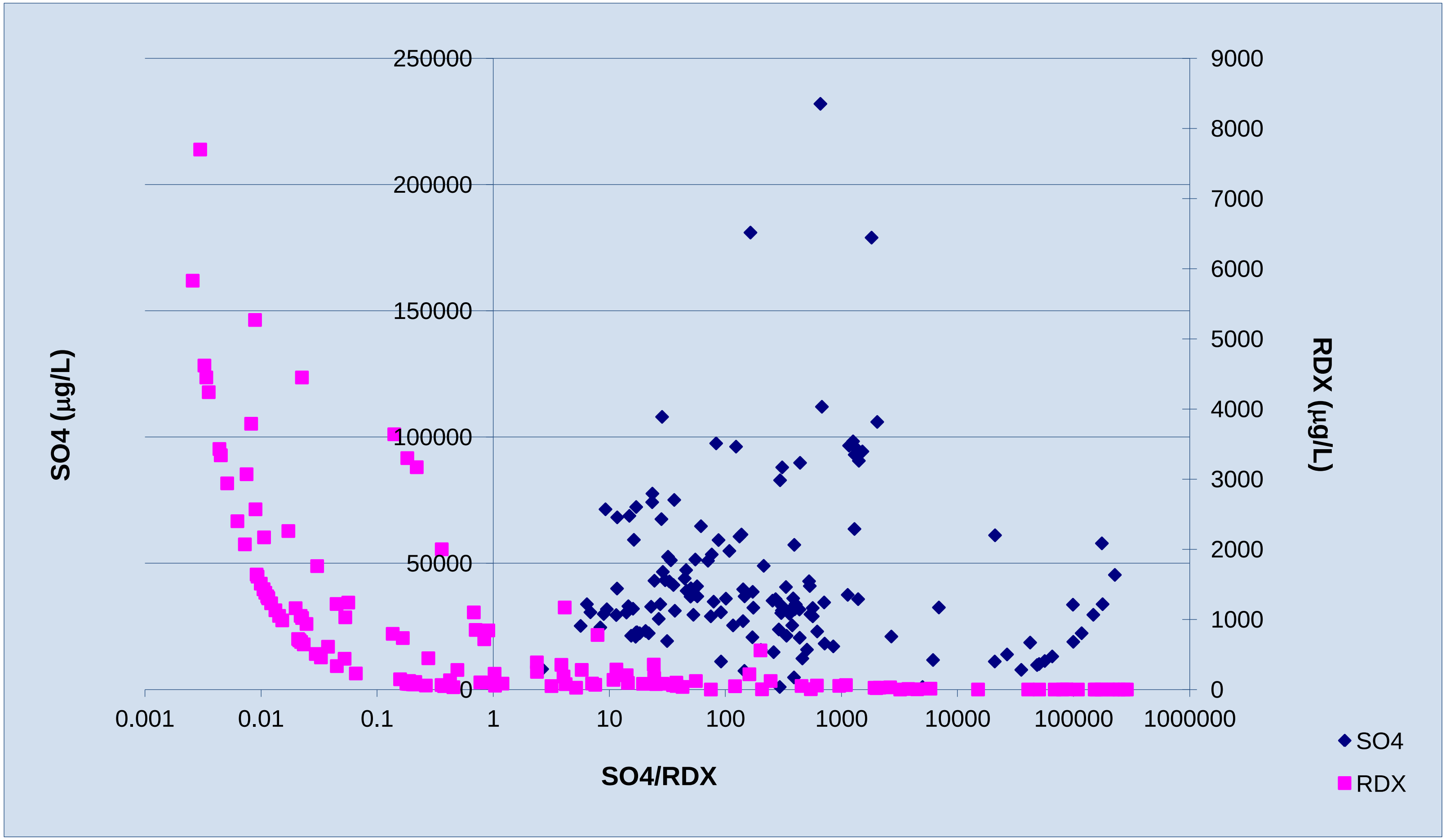
Pilot Study Data Summary

Well ID #	RDX (µg/L) change 09/08 to 03/09	ORP (mV) change	Fe (mg/L) change
MW02	2,570/0.53	42/-10	0.02/106
MW01	1,240/3.4	16.3/-79	0.07/15.3
MW26	260/78	-99/-80	0.3 to 1.9
G-56	57/2	99/38	0.057 to 166
G-57	606/0.19	91/-65	0.015 to 380
G-58	1,050/610	138/178	0.023/0.023
MW-07	5,430/4,290	83/72	0.023/0.023

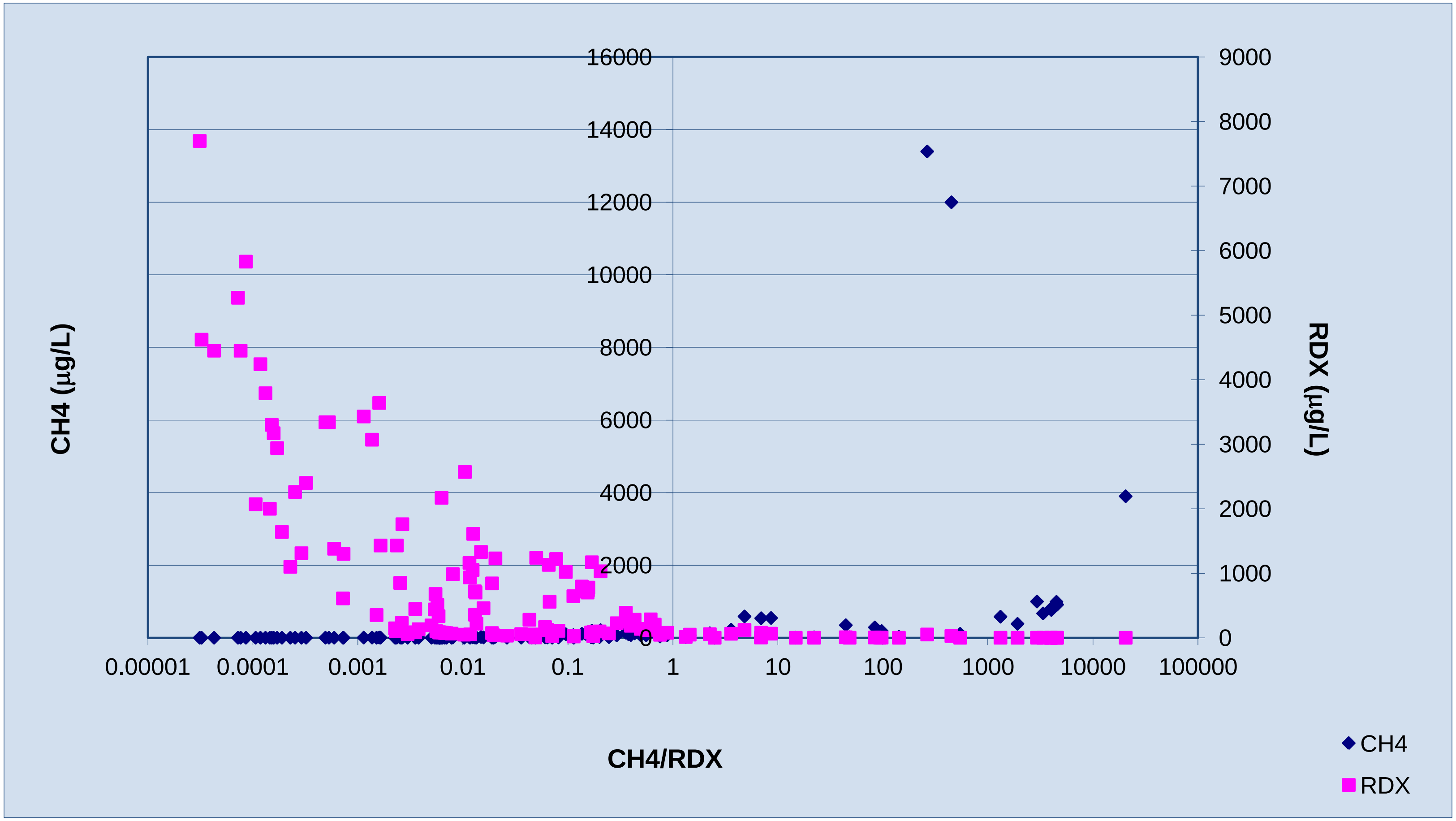
Ferrous Iron and RDX Plot



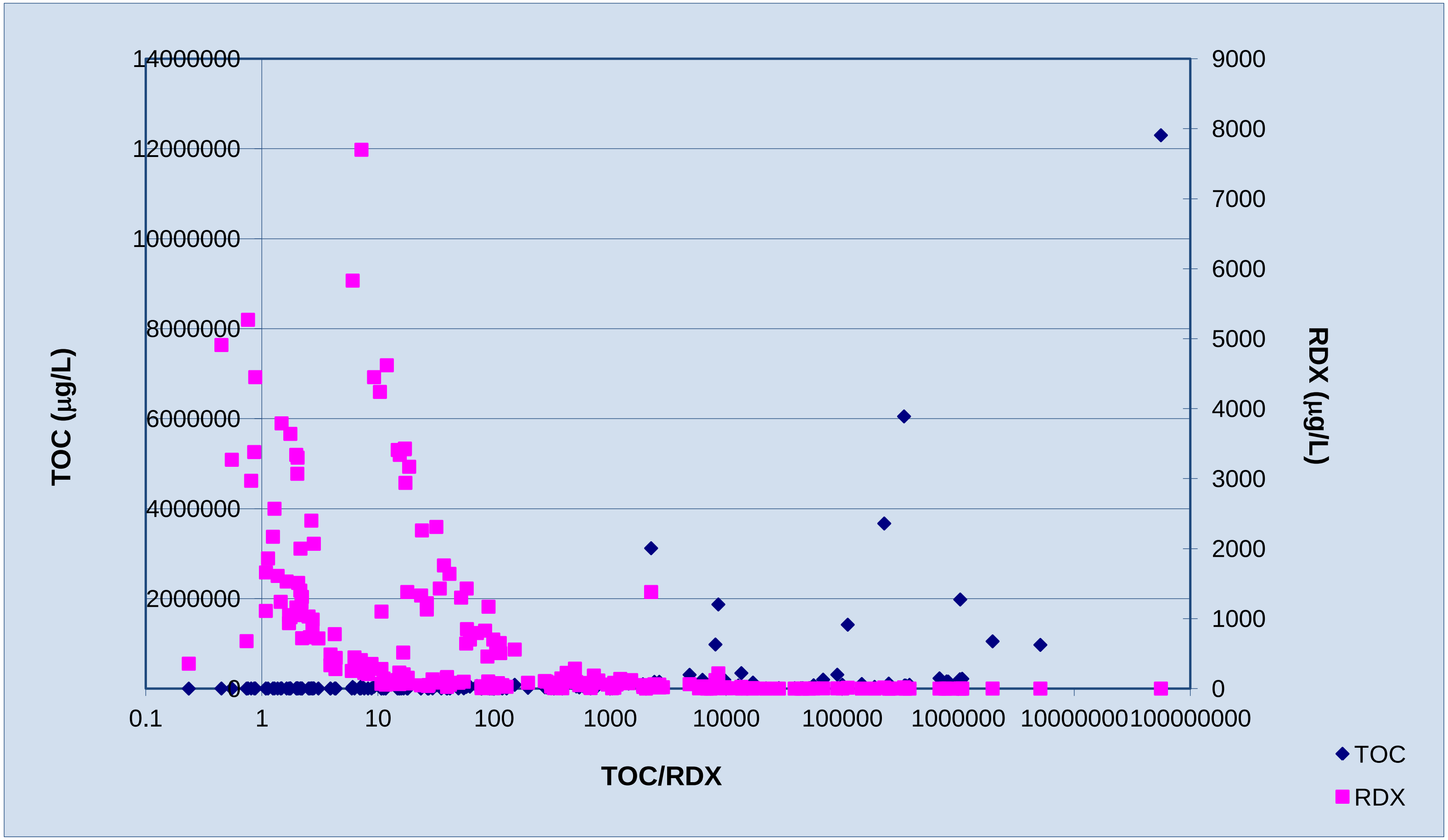
Sulfate and RDX Plot



Methane and RDX Plot



TOC and RDX Plot



RDX Literature Summary

- Summary of paper on in situ redox manipulation (ISRM) of aquifer sediments by Boparai et al (Chemosphere, 2008)
  - Employed diothionite in alkaline environment in bench-scale study
  - Abiotic Reduction resulted in the dissolution of crystalline and amorphous Fe(III) oxides to produce different Fe(II) species – structural and adsorbed Fe(II), carbonates, and sulfides
  - RDX reduction contingent upon aquifer containing sufficient iron oxides and iron-bearing clay minerals
  - Combination of (hydr)oxide surfaces, Fe(II), and alkaline pH critical for rapid degradation

RDX Literature Summary

- Summary of paper on abiotic transformation of RDX by Fe(II) bound to magnetite by Gregory et al (E, S, & T, 2004)
  - Transformation of RDX by ferrous iron associated with a mineral surface
  - RDX was transformed by Fe(II) in an aqueous suspension of magnetite (Fe_3O_4)
  - Negligible transformation when RDX was exposed to Fe(II) or magnetite alone
  - Increase in pH resulted in higher kinetic rates of degradation

RDX Literature Summary

- Summary of paper by Kim et al (E, S, & T, 2007) who examined the role of organically complexed iron (II) species in the reductive transformation of RDX in anoxic environments
  - Complexation of Fe (II) by catechol- and thiol-containing organic ligands leads to the formation of highly reactive species that reduced RDX
  - RDX was unreactive with dissolved Fe (II) alone
  - Active reductants were Fe (II) surface complexes with hydroxyl groups associated with mineral surfaces
  - Hypothesized that hydroxyl Lewis Base donor groups preferentially stabilized Fe (III) and lowered Eh of iron couple, making Fe(II) a stronger reductant

RDX Literature Summary

- Summary of paper by Oh et al (Water Research, 2005) tested zero-valent iron pretreatment for enhancing the biodegradability of RDX
  - Hypothesis was that iron pretreatment could reductively transform RDX to products that are more amenable to biological treatment processes
  - Results of batch and column experiments showed rapid and complete reduction of RDX by Fe(0) species, *regardless of buffering capacity*
  - Transformation of RDX at pHs of 7.4 and 9.7 was substantially lower than that at neutral to acidic pHs

RDX Bench-Scale Summary Overview

- Parallel studies of biotic and abiotic degradation over a 3-week period carried out in slurry conditions
- Concentrations of RDX and total iron were established - soil material was approximately 1.28% iron by mass (58% goethite, 40% paramagnetic Fe^{3+}, and 2% Fe^{2+})
- An analyses of the relationship between RDX and dissolved Fe revealed that as the RDX concentration decreased, that of dissolved Fe decreased; similar relationship was not apparent in the biotic samples

Bench-Scale Results

- Initial testing of enhanced biodegradation revealed reduction in RDX concentrations but did not immediately meet clean-up levels
- The bench-scale for abiotic degradation using sodium sulfite with ferrous sulfate was successful at remediating RDX to below site clean-up levels within one week
- Notable results:
  - Abiotic processes reduced RDX from 657.6 μg/L to below cleanup goals of 2 μg/L in 4 of 7 trials within 1 week
  - Biotic processes reduced RDX from 640.6 μg/L to a low of only 28 μg/L

RDX Field Screening Study

- Comparison of biotic and abiotic degradation efficiencies indicates that abiotic degradation mechanism is up to 52.5% more effective at degrading aqueous RDX concentrations within the 7-day timeframe
- At groundwater RDX concentrations, biogeochemical/abiotic likely more feasible
- Site-specific iron: RDX ratio
- A pilot screening test is being performed in the DA Area to evaluate and examine the response in the field – includes comparison of biological, biogeochemical, and chemical treatment

Case Study II – In Situ Bioreactors

- Air Force facility in southeastern U.S.
- Six in-situ bioreactors within slurry wall to treat chlorinated solvent contamination with an associated metal plating shop
- Bioreactors were 10 m by 12 m and approximately 12 m below ground surface
- Biogeochemical mix consisted of a 2.5 m. thick zone consisting of 50 cu. m. of wood mulch, 200 kg of ferrous sulfate, 50 cu. m. pea gravel, and 40 cu. m. of cotton seed meal per cell
- A 5-cm perforated PVC pipe rejuvenation system for addition of substrate as required to sustain treatment

Case Study II – In Situ Bioreactors

Placing Bioreactor Material

Case Study II – In Situ Bioreactors

Adding Vegetable Oil to the Mixture

Case Study II – In Situ Bioreactors

Placing the Recharge Piping

Case Study II – In Situ Bioreactor Results

- Substantial decrease in concentrations of all cVOCs within one year
- PCE and TCE concentrations reduced from 12,000 and 2,800 μg/L, respectively, to non-detect approximately 3 months after construction was completed. Cis-1,2-DCE reduced from 12,000 μg/L to 2,700 μg/L during the same time period
- Limited geochemical data indicated conducive conditions for biological reductive dechlorination, but also indicated the likelihood of an abiotic role
- Follow-up sampling events showed very little PCE/TCE rebound, but persistent levels of cis-1,2-DCE and VC
- One recent rejuvenation event consisting of EOS (including buffer), ferrous sulfate, and sodium sulfite

Case Study III – Biogeochemical Stabilization of Lead in Soil

- Government-owned/contractor-operated ammunitions facility in southeast U.S.
- Soil lead concentrations were as high as 2,400 ppm
- Various precipitated forms include lead hydroxide, lead sulfate, lead carbonate, and lead sulfide
- Lead sulfide is stable over a wide range of pHs
- A natural form of carbon can be added to the soil to biologically convert natural or added sulfate to sulfide
- Bench-scale, pilot-scale, followed by full-scale treatment in 2009-2010 to treat over 15,000 cu m. of soil

Technology Background

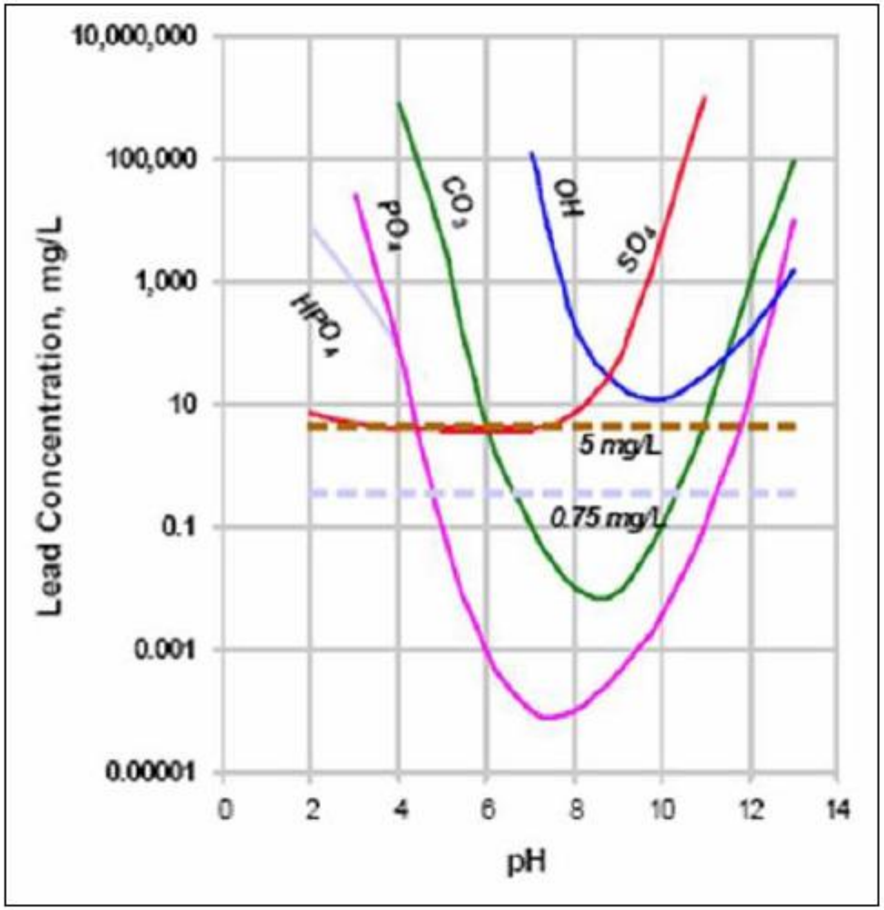


Figure 6. Solubility of common lead compounds by pH with both the TCLP and the UTS for lead indicated.

Reference – ERDC/EL TR 07-19, Evaluation of Lime and Persulfate Treatment for Mixed Contaminant Soil from Plum Brook Ordnance Works – US Army Corps of Engineers

Case Study III: Biogeochemical Stabilization of Lead in Soil

- Each 300 cu. m. batch of soil was treated with 20 % mushroom compost and blended using conventional mixing equipment
- Sulfate was added at the rate of 250 kg per 300 cu. m.
- Treatment was rapid in the span of days
- TCLP concentrations attained were consistently an order of magnitude below regulatory goals of 5 mg/L

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Questions