Removal of N-Nitrosodimethylamine from Groundwater at the NASA White Sands Test Facility

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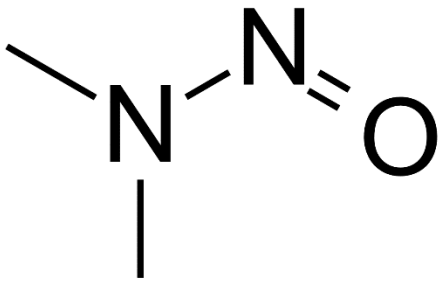
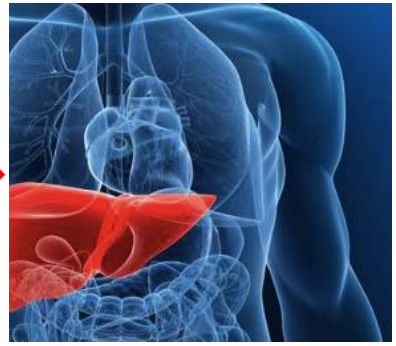
Project Background

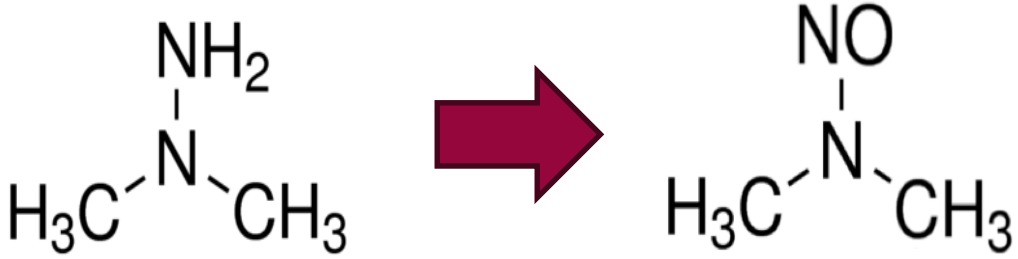
- N-Nitrosodimethylamine (NDMA)
  - U.S. EPA contaminant watch list
  - Probable human carcinogen: 1 x 10^{-6} cancer risk for 0.7 ng/L in drinking water

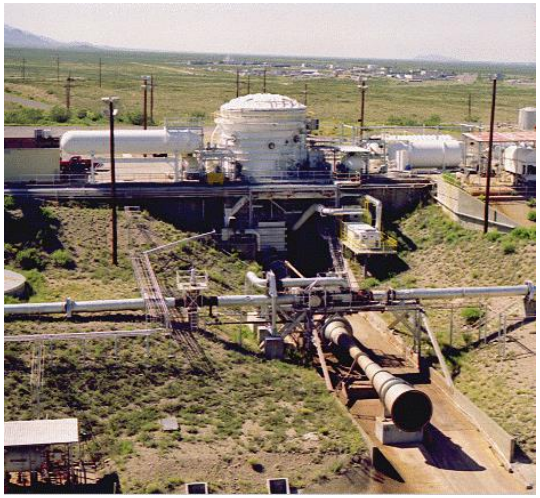




Project Background

- NDMA Source at WSTF
  - Byproduct of treating Aerozine-50 rocket fuel produced during the Apollo Program





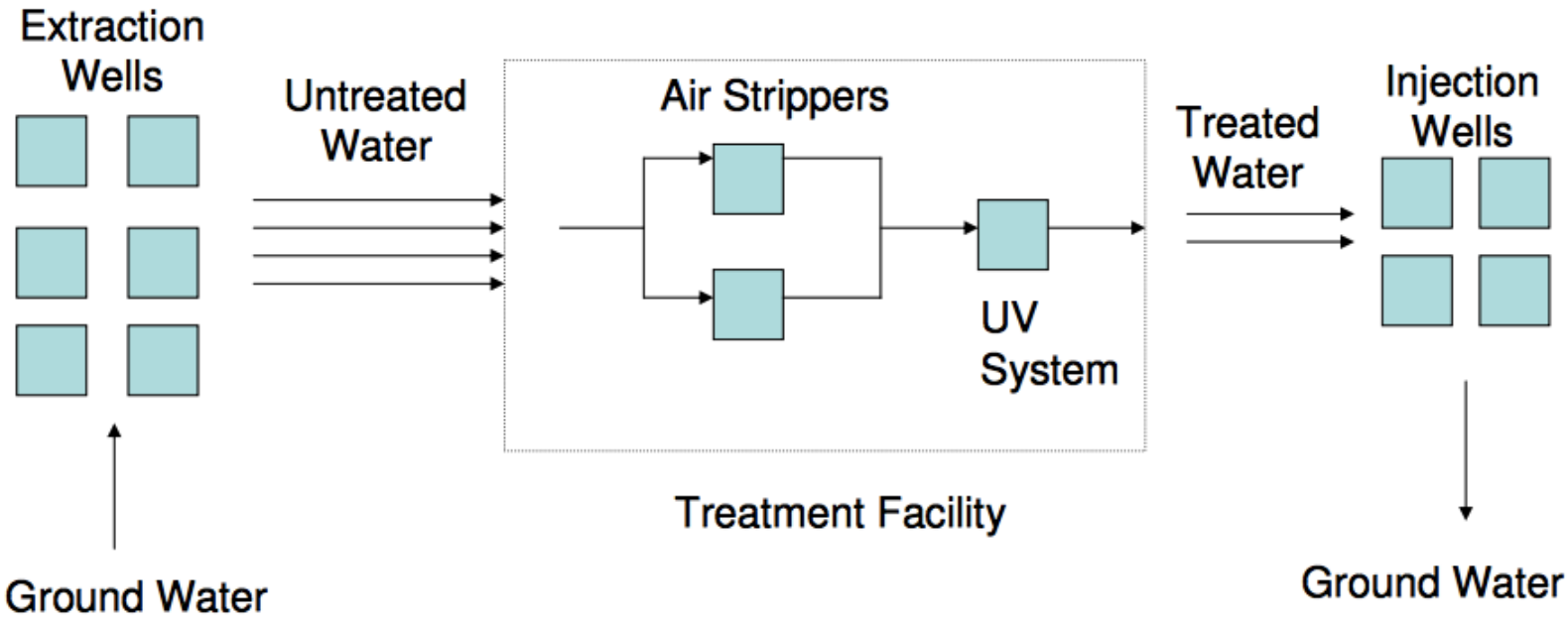
Project Background

- Other NDMA Sources
  - Beer and smoked meat
  - Water treatment systems that use chloroamines

Requirements for Removal

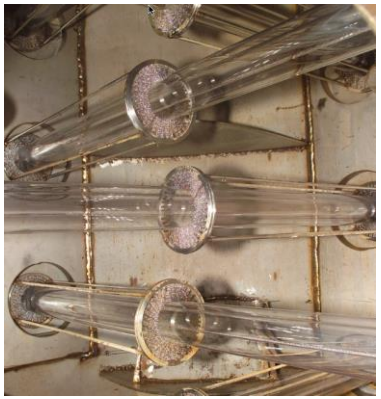
- Treated water must have an NDMA concentration of less than 10 ng/L
  - 1 ng/L = 1 part per trillion (ppt)
- Ideally, concentrations should be below detectable limits using current analytical techniques (HRGC/HRMS)
  - Less than 0.2 ppt

Current Removal System



Current Removal System

- UV photolysis
  - Band around 227 nm
  - Twelve 30-kW lamps (Hg vapor: 200-250 nm)
- Annual electrical cost
  - $112,000 (UV/Ox tower)
  - $560,000 (entire system)



Analytical Technique

- Southwest Research Institute (HRGC/HRMS)
  - Sample size of 1 L
  - Turnaround time of approximately 2-3 weeks per sample
  - Typically able to make 4-5 samples per week including blanks

New Approach

- Replace the UV system with locally-sourced activated carbons to remove NDMA
  - Pecan shells and pine bark
    - Waste from other industries as feedstock
  - More cost effective
  - Lower environmental impact

Carbon Characterization

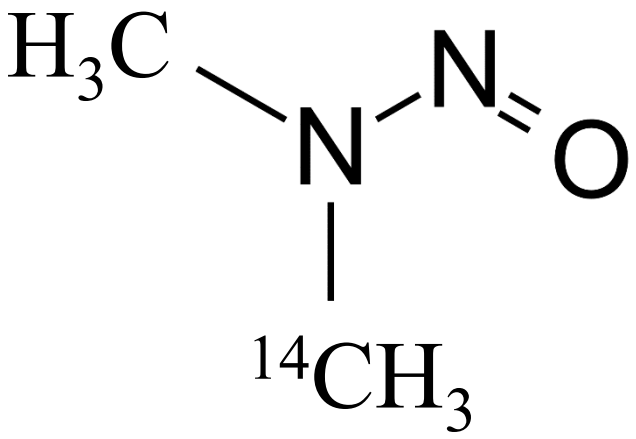
- Coconut shell
  - Commercially available
  - Common activated-carbon source
  - Used to compare results from pecan shell and pine bark chars

Carbon Characterization

- Pecan Shell and Pine Bark Chars
  - Shells were pyrolyzed at varying temperatures from 400 to 900 ºC
  - Activation methods were by heat treatment (secondary pyrolysis from 400 to 900 ºC) and K_2CO_3 (1:1:2 ratio by weight)

Different Analytical Approach

- Liquid Scintillation Counting (LSC)
  - ^{14}C-labeled NDMA
    - Commercially available
  - Detection limit of 5 ppt
  - Relatively safe



Different Analytical Technique

- LSC
  - Available on campus
  - Smaller sample volumes (10 mL)
    - 4 replicates per sample
  - Turnaround time of approximately 1 day for analysis

Overall Process

Raw Biomass

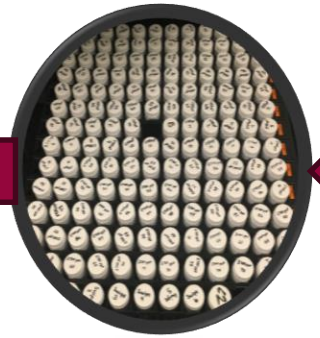
Pyrolysis at varying temperatures, with and without chemical activation

Raw and pyrolyzed biomass

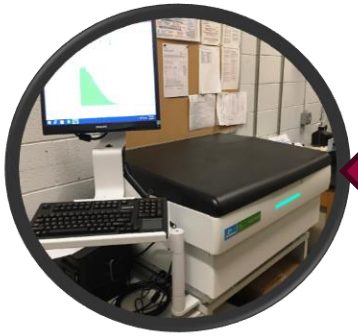
NDMA dilutions at different concentrations

Shake for 48 hours

Separate char from NDMA/water samples



Prepare samples with liquid scintillation cocktail



Analyze using liquid scintillation counting

Sample Preparation

- Isotherm Definition
  - Chars produced at one temperature and activation treatment
  - Different NDMA concentrations ranging from approximately 10 ppb to 1 ppt
  - Compared against blanks (water purified at WSTF), standards, and coconut shell char

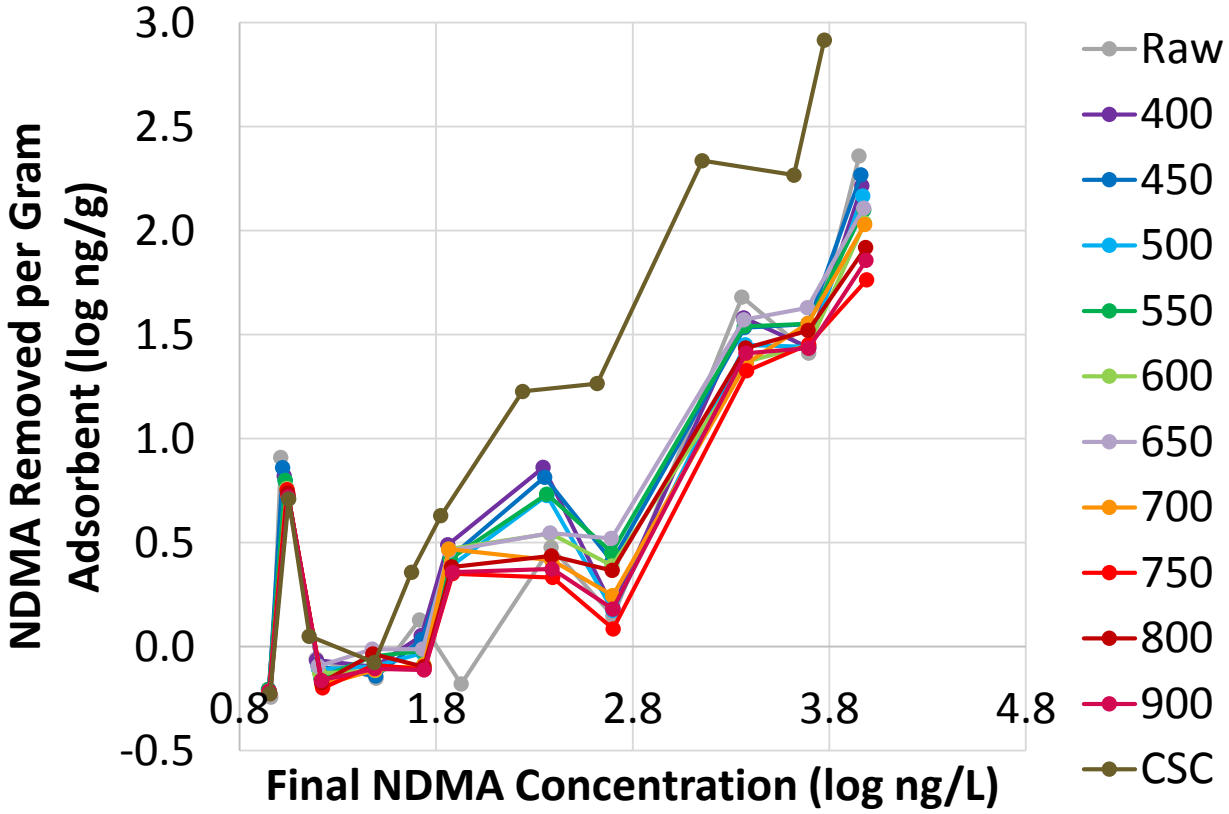
Sample Preparation

- NDMA Dilutions
  - Started from 1 mL at 30 mCi/mmol and 100 µCi/mL
  - Diluted to 100 mL for Mother Liquor
  - Individual concentrations diluted to 1 L
    - 19 samples – 50 mL each
  - 4 replicates (10 mL each) for each sample
  - Scintillation cocktail at 1:1 ratio for LSC

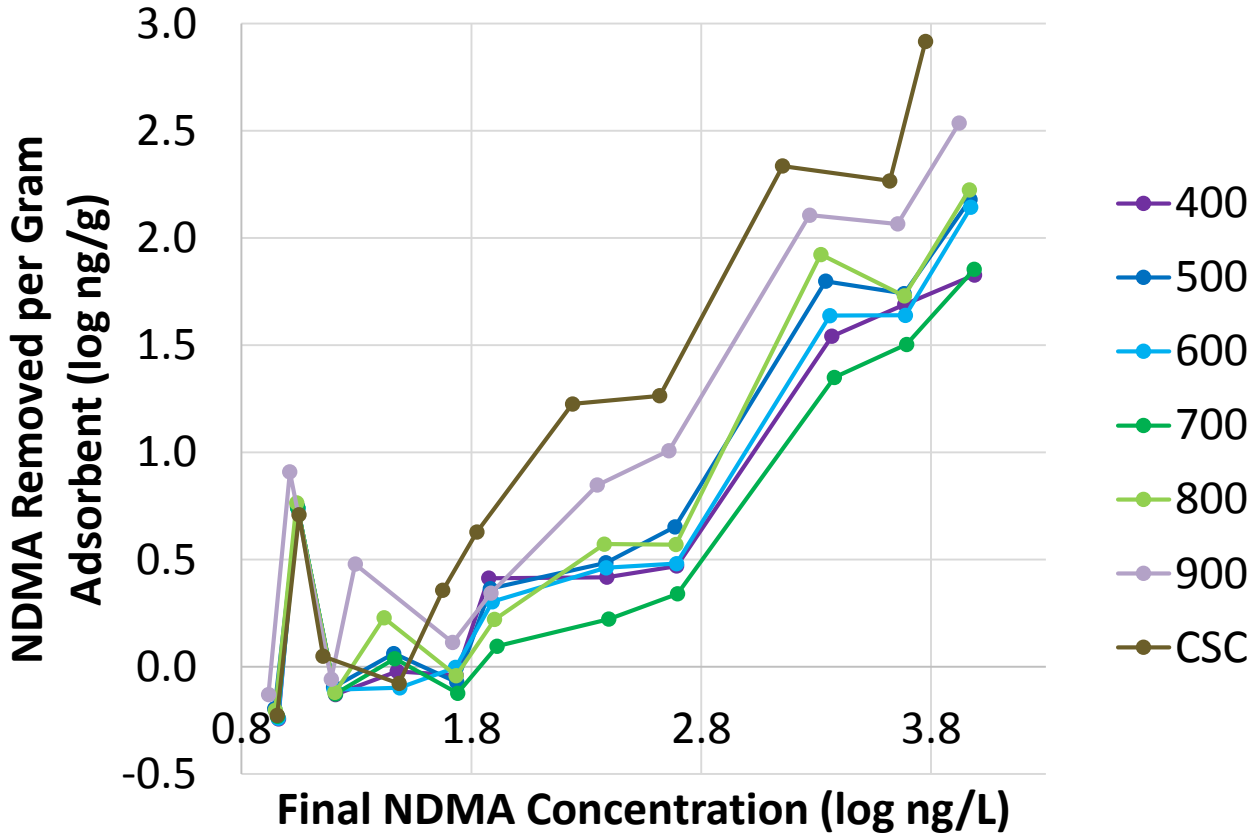
Data Analysis

- Converted NDMA activity (nCi) to mass (ng)
- Each char sample - 0.05 g per 50 mL sample
- Determined amount of NDMA removed on a mass of NDMA per mass of adsorbant

Results – Heat-Treated



Results – Activated



Conclusions

- Coconut shell had highest adsorption rates
- Best results come from chars produced at higher temperatures
- K_2CO_3-activated chars performed better than those with only heat treatment

Next Steps

- More isotherm data collection
  - Ponderosa pine (in progress)
  - Douglas fir
- Higher temperature chars
  - Pyrolysis at 1000 ºC
  - Heat-treated and K_2CO_3 activation

Next Steps

- Different activation methods
  - Steam
  - Sulfuric Acid
- Optimize activation
  - Column studies
  - Adsorption kinetics

Next Steps

- Design and Costing for WSTF
  - Feedstock of raw materials
  - Char production
  - Treatment vessels